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Team Work

TEAM work in industry no longer means secret agreements, conspiracy in the restraint of trade, price control, and other such objectionable things. Today the much overworked word "coöperation" explains more nearly what is implied, and we do not hesitate to say that the chemical industry seems not yet to have learned its meaning and the benefits to be derived from its application.

During the last few months we have had a number of instances of the lack of team work. Several years ago the industry damaged itself through its unwillingness to work with certain government bureaus in the same whole-hearted manner as did other industries on such simple things as statistics of inventories and market. Seemingly, we are just beginning to learn the value of authoritative statistics, but there are still some groups among chemical manufacturers which are disinclined or actually refuse to supply data which would make the resulting compilations of great value to them. Complete data are valuable to all; incomplete practically worthless. It will doubtless be a long while before the units in the chemical industry are prepared to work together as do those in the mining industry. The smelter operator who finds a way to win more values from his ores is likely to be anxious to show another smelter his results and how they were obtained. Also witness the automobile industry. Perhaps that is too much to expect of chemical manufacturers, but there are plenty of fields in which team work will count heavily without calling for the disclosure of confidential technical information.

Our industry, or at least parts of it, has been guilty of a ruthless price war, from which so far as we can see there has been no advantage to those particularly concerned. True, wise purchasers have made long-term contracts and have laid in large supplies. However, in the alkali price war the industries lost perhaps ten million dollars, and we are informed that the principal aggressor in that unprofitable program emerged from the conflict with contracts at the lowest price and with the percentage of the total business enjoyed reduced by approximately 25 per cent.

Failing to learn from this demonstration, the alcohol industry has just put on a price war of its own. Rumor has it that certain officials decided that the paramount thing was to move stocks on hand regardless of costs. The low prices quoted certainly would seem to be below costs figured according to any rational accounting, and orders and contracts at such bargains must certainly have moved the surplus.

Of course the price at which a manufacturer sells his product is his own affair, but after all, no matter what the motive may be, consideration for fellow producers should dictate the fair policy of accurate cost determination and a faithful adherence to a price schedule at least not below that cost. Price wars are nearly always disastrous; if not immediately, then in the long run. Unsettled conditions are made worse, not better, and confidence is shaken by such an experience. Ultimately even the consumer is left without benefit, since the losses of today must be made up tomorrow or bankruptcy will result.

Some of the competition which has characterized still other phases of the chemical industry in the past year has been regrettable. We must not overlook the vital importance of public relations which the industry has come to have. Hearings before committees of state legislatures, attacks upon scientific work, charges and countercharges can have lasting detrimental effect upon the consuming public and, if carried to the extreme, will do far more harm than the loss of a little business.

After all, what is now known as the chemical industry is comparatively young. Maybe these experiences are a necessary accompaniment of growing pains. The further application of the scientific method with due reference to what others have endured as recorded in the literature ought to dictate the wisdom of whole-hearted team work.

Three choices present themselves. The industry might unwisely attempt to fix prices and immediately run counter to the law. It might engage in ruthless price-cutting and bring about self-destruction. The better way is to cultivate the middle ground and coöperate within the law to the benefit of all. Unfortunately this is difficult, especially in view of the customary federal attitude of suspicion toward all who endeavor to work together, even though the advantages to be gained are mutual with the public. Progress along this difficult but necessary course must be begun without delay.

Looking Ahead

THE present disturbance in industry has been characterized by frequent statements of experts that we have rounded the corner or that the bottom is being scraped, with immediate promise of an upward turn. Some business men have been misled by these over-optimistic opinions and have refrained from taking matters as seriously as they deserved, even postponing activities designed to change the course of affairs. It is well, therefore, in considering the chemical prospects of 1931 to exercise due conservatism. There seems no basis for gloomy pessimism, while here and there we find reason for at least mild optimism.

Inquiry among the representative establishments in industry indicates that, so far as the staff is concerned—the operating men and employees generally—a consistent effort is being made to maintain it as nearly intact as possible. No drastic cut in employment is contemplated, and the indications are that the men who through training, experience, and industry have made themselves valuable will continue to be retained.

While there will doubtless be fewer places for June graduates in research and control laboratories, nevertheless research is proceeding in most establishments at full tide. Concerns have finally realized that desirable work, often impossible to undertake under the pressure of boom business, can be performed to great advantage when business is quiet.

Naturally, the demand for new equipment cannot be expected to be great in such times. However, reduced production affords opportunity for replacements without disturbance, which normally is out of the question. The use of corrosion-resistant alloys in all manner of equipment, piping, valves, etc., has made available to some branches of the industry devices with which products of greater purity and more satisfactory yield can be made. Where outstanding economies and increase in efficiency can be expected, new equipment is being placed with the immediate future in mind.

As for repairs, these are going forward on a considerable scale. Buildings are being put in order or altered. Equipment not to be replaced is being put in the best of condition, and much painting is in progress. Frankly, in some cases a part of this work is being done to retain valuable men on the payroll. However, even this is an optimistic sign, indicating a belief in the need ere long for these men in their old positions.

The very large building program initiated in 1930 has naturally carried over into 1931, during which year it may be completed. It is not likely, therefore, that any considerable building will be begun later in the year to carry over into 1932. What transpires in the interim must be left to dictate those future decisions.

The favorable position of the chemical industry as compared with others can suffer from two causes. Bankers can disturb the structure if they force to be sold at any price the surplus stocks of manufacturers who become temporarily weakened. Any further price wars would be equally detrimental. The latter is more likely to be hurtful than the former. All in all the prospects seem conservatively encouraging, and the lessons being learned, if they are but remembered, will make for a stronger industry in the immediate future.

The Chemical Exposition

THE week of May 4 will find the Thirteenth National Exposition of Chemical Industries established in the Grand Central Palace in New York with as much space occupied as on former occasions and with a number of new exhibits. The exposition is more than an assembly of new and improved equipment, chemical products, raw materials of the chemical industry, and related items. Admittedly conducted as a commercial enterprise, the exposition nevertheless has become established as an important factor in the chemical life of America. Those familiar with the history of the exposition and the concurrent development of American chemical industry agree that the former has had a great influence upon the latter. It is well to recall that in those early days it was the exposition that served to emphasize the ability of our equipment manufacturers to provide the necessary devices with which to undertake seriously large-scale production of needed chemicals. It was to the earlier expositions also that manufacturers brought the first fruits of their efforts to show how successful they had been in a comparatively new and untried field. Those responsible for the advance of our chemical industry also came in numbers and found the opportunity to decide major questions after conversation with their colleagues.

The exposition is not without an enviable record of services rendered to the exhibitors. Orders approaching a quarter of a million dollars have been known to be placed with exhibitors during the exposition week, and some of the largest purchasers came from foreign lands to see and to buy. The publicity incident to the exposition's activities has been dignified and constructive, thereby adding its bit to our success in winning the sympathy of the general public.

There has been the educational side. Students, accompanied by instructors, have attended, but far more should make the most of the opportunity. However, those who have come—and the number has increased as we have gone along—have been able to see in the compass of a week more pertaining to their work than would be possible in weeks of travel to the various plants and warehouses. The students' courses have called forth the coöperation of well-trained specialists, who have been glad to present discussions on topics chosen by the director of the students' courses to produce a well-rounded program and leave the lasting impression which comes from the receipt of valuable information.

The event is important from many points of view. That section of the public which comes in the evening cannot fail to go away impressed with the fact that this industry, so little known prior to 1914, is now fundamental to public well-being and is conducted on a scale comparable with other commercial enterprises. There will be stockholders interested in more intimate details of the products of various concerns. There are sure to be bankers and financiers, executives and economists, journalists and teachers, among the crowds of plant operatives, technical men, and students. All are a part of the great army of ultimate consumers whom we seek to serve.

The exposition is an occasion of moment. It is a biennial opportunity to get abreast of new developments. It is one of the yardsticks by which we can measure our progress.

Taxes

IN SCHEDULES of costs an item for taxes may frequently be found toward the end of the column, and we view it more as an indication of the completeness of the estimate than as a matter of serious consequence. We know taxes are necessary. We know they must be paid, but we pay altogether too little heed to current trends in taxation and their direct bearing upon industry and the cost of doing business.

Because of the publicity given to the federal budget and expenditures, when the subject of taxes is broached we are inclined to think of the income tax, or of customs, or some other federal levy and leave out of consideration state, county, and municipal taxes. Of late the only encouraging sign in taxation has been the decrease, until 1930, in the federal budget, and consequently in federal taxation. During the 1925–28 period the interest payments by the Federal Government decreased 5.7 per cent, 5.2 per cent, and 7.1 per cent over each preceding year. There was a decrease in total federal expenditures, aside from public debt requirement, up to 1930, but the commitments made by an overgenerous Congress indicate a considerable increase from that time through 1932, for which estimates have been made. The actual expenditures, after setting aside something over 100 million dollars to meet the soldiers' bonus, "adjusted compensation," maturities in 1944, are $3,994,152,487.09 for 1930, $4,014-941,900 for 1931, and $4,054,519,200 for 1932. The item for soldiers' relief, which appears as veterans' administration in the budget, will be almost one billion dollars in 1932. And the end is not yet.

Substantial sums raised by taxation are distributed by appropriations under the heading "loans." The 500 million dollars originally authorized for the Farm Board, all of which and more will doubtless be used, are listed as loans. The Shipping Board advances with a total authorization of 225 million dollars are loans. The 60 million dollars to relieve drought sufferers are loans, and there are many more loans, totaling nearly a billion dollars. Whether or not any serious-minded person really expects any of these loans ever to be repaid, so far as the current taxpayer is concerned they are just as expensive as if known by any other name. In 1932 the Post Office Department is expected to incur expenses in operation in excess of income by 114 million, and the franking privileges continue.

Recent figures showing where the tax dollar goes may be illuminating, the following estimates being from the *National Sphere* of January, 1931:

	1929–30 Actual	1931–32 Estimated
	Cents	*Cents*
Public debt (war cost)	30.7	26.3
Veterans Bureau (war cost)	13.0	15.1
Navy Department (war cost)	9.4	8.8
War Department (war cost)	8.2	8.4
Pensions (war cost)	5.5	6.1
Highways, federal aid	2.1	3.1
Rivers, harbors, and flood control	2.6	2.7
Public buildings	1.5	2.2
Postal deficit	2.3	2.9
Federal Farm Board	3.8	2.6
Prohibition Bureau	0.4	0.3
Coast Guard	0.7	0.8
Tax refunds	3.2	2.4
Administration, executive, and general	16.6	18.3
TOTAL	$1.00	$1.00

It is interesting to note the source of federal revenue. It is estimated that, in 1932, $2,250,000,000 will be raised by taxation, divided between individual and corporation taxes; $700,000,000 from miscellaneous taxes, largely upon tobacco; and $600,000,000 through custom levies. It is in the $2,250,000,000 that we are most interested, for of that part paid by individuals 97 per cent comes from somewhat fewer than 300,000 people who have incomes of $10,000 or more, while of the part paid by corporations more than 50 per cent of the sum is paid by approximately 1000 corporations. These statistics are interesting as explaining a certain apathy on the part of our people toward mounting taxes. "Let the Government pay," "appropriated from the treasury," and similar expressions are made by those who feel that they have little share in the expenditure, but who in the long run suffer directly or indirectly from an unreasonable outlay of public funds. If more people paid federal taxes, there would be a wider interest in what is done by Congress and a decreasing opportunity to curry political favor at the direct expense of a comparatively small fraction of our population.

The mounting expense of doing business because of taxation unfortunately is not confined to what Congress may regard as wise and expedient. Whereas the Federal Government has seemingly made an effort to curtail expenses, and certainly our executives have, though their vetoes have been overridden, the states in large part seem to have spent out of all reason. During the four-year period when the Federal Government was steadily decreasing its interest payments, the 48 states showed a very different trend. There were constant increases by 13.6 per cent, 2.4 per cent, and 10.4 per cent over each preceding year. Only half the states in 1928 had revenues to meet their expenditures with a balance available for debt-paying. The other half were adding to their indebtedness. Most of these excessive expenditures went into improved highways, into education, and similar programs, often in compliance with popular demand, but evidently without much thought of what it would mean in the future. That, of course, is a favorite trick in the expenditure of public money. The funds are raised by bond issues or other contrivances and spent today, leaving posterity to pay. Sir Ernest Benn states that in England the total liability per capita, including national and local debts, in 1900 was $90, whereas in 1930 it had reached $2500. While war debt is largely responsible for this enormous increase, other considerable factors are involved. The figures are something of a warning to us concerning possible burdens in the near future, if all of us as individuals do not take a deeper interest in public appropriations.

Now, when states and communities find themselves spending so much more than they earn that bankruptcy seems just around the corner, all manner of devices are brought out for increasing tax revenues. At the same time many individuals are allowed to escape, with the result that business and non-business license taxes in many states have taken the lead over the general property tax as a method of obtaining funds. Corporations not only must pay a variety of taxes unknown to the average individual, but of late in some states there have been plans to tax natural resources removed as raw material for industry, particularly the chemical industry, and this may be followed by still other means of requiring business to carry a load which is rapidly becoming disproportionate.

As individuals we are interested more directly than we often realize in the success of organized commerce. Enthusiasm for an expensive local program, to be paid from taxes and too frequently undertaken because of pride rather than necessity, should be tempered by careful consideration of what it eventually will mean. Whole industries have been compelled to leave communities and take up their work elsewhere because of unreasonable taxation. You can legislate and tax an industry out of existence. It is almost impossible to create one by the same means.

We repeat that we all pay taxes. The majority pay indirectly—so indirectly that they have no interest in ever-increasing expenditures. The basis for correction of this dangerous trend is in a wider distribution of the tax burden.

Institutes of Industry

THERE is much that is encouraging in the growing tendency of the older established industries to turn to science as a foundation for the future. Several have set up institutes or have research laboratories supported by associations. Among these are leather, baking, laundering, dry cleaning, meat packing, and the numerous associations that have maintained fellowships in institutes and universities.

A newcomer is the Institute of Paper Chemistry organized by the pulp and paper industry and established at Lawrence College, Appleton, Wis. This institute takes graduate students only. There were three students in February, 1930, and the number has grown to the capacity of temporary quarters. The institute is supported by a levy on the contributing mills per ton of daily output. Its purpose is to train men, to build up and maintain the best possible library for the industry, so that an informational service may be made valuable to the supporters, and to conduct research. At present there are ten fellowships and more are in prospect. Fifteen graduate students are to be admitted annually, so that the maximum, exclusive of staff, at any one time will be sixty. The course leads to the master of science degree in paper technology, and ultimately to the degree of doctor of philosophy. A new institute building is to be ready in the autumn of 1931.

Institutes somewhat similar in organization and scope are in operation in other parts of the world. This is the first of the kind in the United States. There is no dearth of work for it to do and there is great need in the industry for the technically trained men who presently will come from its doors, equipped to serve in such a manner as to repay adequately for the support it has given to make the institute possible. Which industry will be the next?

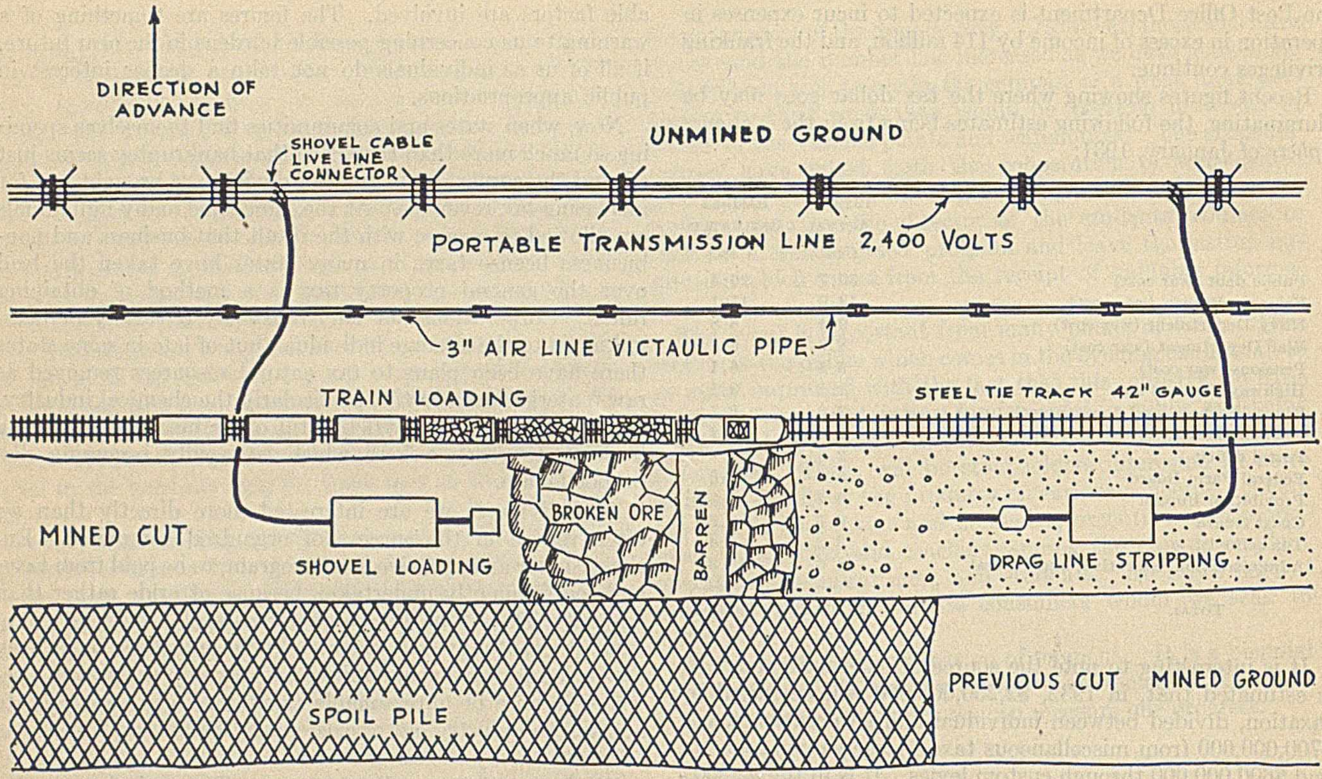

Figure 1—Method of Mining Nitrate Ores with Power Shovels

Technology of the Chilean Nitrate Industry[1]

Location and Nature of Nitrate Ore Deposits

THE coastal range in northern Chile rises abruptly from the ocean floor. Between this range and the lower slopes of the Andes lies a desert, or *pampa*, varying in elevation from 4000 to 9000 feet above sea level. The nitrate-bearing lands lie mainly along the western side of this desert on the eastern slopes of the coastal range, not in a continuous strip, but intermittently over an irregular belt some 400 miles long from north to south, and 5 to 40 miles wide. The deposits actually worked are at elevations between 4000 and 7500 feet and are grouped in five main fields inland from the ports of Iquique, Tocopilla, Antofagasta, and Taltal.

The sodium nitrate, along with other soluble salts, occurs for the most part as a cementing material in the outwash sands and gravels which form the eastern slopes of the coastal range. At the lower edges of the slopes the nitrate deposits in some places extend and merge with ordinary salt deposits lying in shallow undrained basins.

The physical occurrence of the deposits is such as would be expected from a surface deposition in mixed gravels, sands, and clays, showing every variety of aggregate, hardness of cementing, and grade of salt. Close study has shown some degree of conformity of occurrence with surface features, such as local drainage systems and severity of washing by the infrequent rainstorms, but on a smaller scale deposits are quite erratic. Regardless of the primary origin, it appears probable that the nitrate was collected in an inland sea. Later, owing to tectonic movements and changes in climate, this sea evidently deposited part of its nitrate along the shore lines. Eventually the sea was probably drained into the Pacific Ocean. But few deposits would be laid down on the eastern shore because the drainage from the Andes would redissolve the nitrate, or cover it with a thick coating of alluvial débris. During the deposition of the nitrate, and continuing until today, the nitrate ore bodies have been leached, transported, and concentrated or lost by the occasional rainstorms or cloudbursts that fall on the nitrate pampas.

In general the harder cemented material in the deposits is overlaid by barren overburden of loose aggregate, which varies in thickness from a few inches to several feet. The thickness of overburden shows a general conformity with surface features. The harder cemented material itself varies in thickness within the same range as the overburden. Its grade of sodium nitrate varies from almost nothing to almost pure nitrate. It is usually slightly stratified or slabby. The higher grade hard material (above 14 per cent) is not easily distinguished from material of somewhat lower grade, as the considerable quantities of other salts present much the same appearance as nitrate. The higher grade hard material is called "caliche;" the lower grade, "costra."

There is usually a fairly sharp separation between the deepest hard material of commercial grade and a loose underburden, though occasionally the ore of commercial grade shades off into both overlying and underlying hard, barren material with no plane of separation.

The soluble salts which cement together the sands, clay, and stones, in the mixture known as caliche are the nitrates,

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[1] Received January 22, 1931.

EDITOR'S NOTE—The text of this article will appear as a part of a chapter on "The Chilean Nitrate Industry" in a forthcoming American Chemical Society Monograph written by members of the Fixed Nitrogen Research Laboratory and edited by Harry A. Curtis. The discussion of the technology of the industry and description of the Guggenheim process as applied at the Maria Elena plant have been supplied by the Anglo-Chilean Consolidated Nitrate Corporation, of New York.

chlorides, sulfates, iodates, borates, and perchlorates of sodium, potassium, calcium, and magnesium. The chemical analysis of the salts of a typical caliche is as follows:

	%		%
Sodium nitrate	17.6	Calcium sulfate	5.5
Potassium nitrate	1.3	Sodium iodate	0.11
Sodium chloride	16.1	Sodium borate	0.94
Sodium sulfate	6.5	Potassium perchlorate	0.23
Magnesium sulfate	3.9		

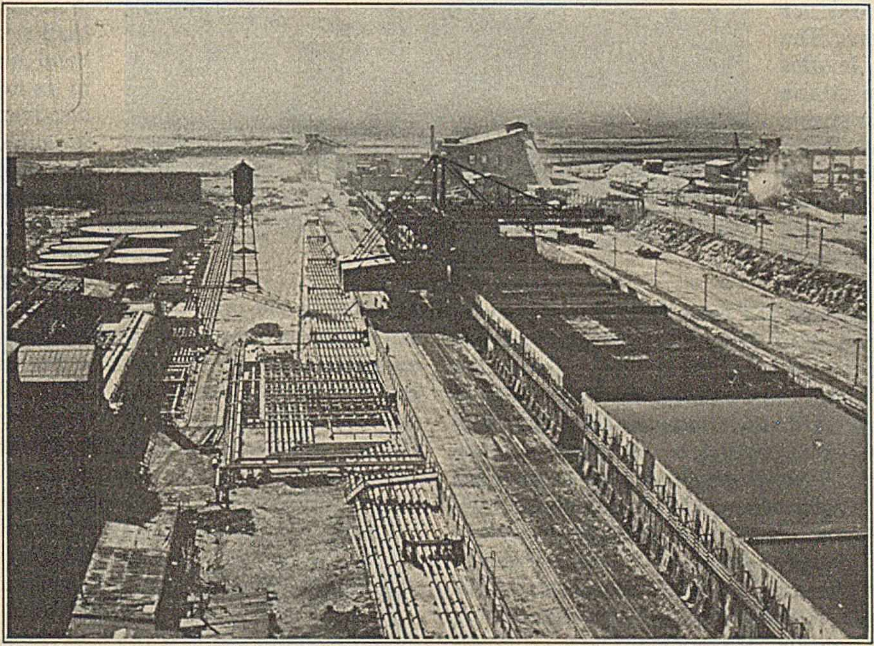
Depending upon the relative proportions of the sulfates present, their double salts may occur as darapskite ($NaNO_3.Na_2SO_4.H_2O$), glauberite ($CaSO_4.Na_2SO_4$), bloedite ($MgSO_4.Na_2SO_4.4H_2O$), or polyhalite ($K_2SO_4.MgSO_4.2CaSO_4.2H_2O$). The occurrence of darapskite is rare, sodium nitrate usually being present in caliche as a simple salt.

Proving of Ore Bodies

In a preliminary reconnaissance, test pits are sunk at widespread intervals for a rough confirmation that the area is commercially exploitable. In the more detailed examination, on the results of which the purchase price is based, the area is covered with a sampling screen of test pits at 100-meter intervals.

This part of the technology of Chilean nitrate has until recently been in a very unsatisfactory state of advancement. The older method consisted of sampling through a very small pit, 8 to 12 inches in diameter, too small to allow either an adequate sample or a record of the nature of the ore to be made. The prime sample was then subject to sorting by the sampler, who rejected pieces with the intention of making it conform with his judgment of the ore that would be hand-sorted from that mined from the area. Finally, the analytical method in ordinary use was inaccurate.

The great amount of both reconnaissance and control sampling work done by the Anglo-Chilean Consolidated Nitrate Corporation in the past few years has put nitrate ground sampling on a sound engineering basis. The accuracy of the present method for prediction of tonnage and grade has been proved by the normal mine scheduling sampling at the Maria Elena plant covering the more than 20 million tons of ore that have been mined to date for that plant.



Partial View of Maria Elena Plant, Anglo-Chilean Consolidated Nitrate Corporation

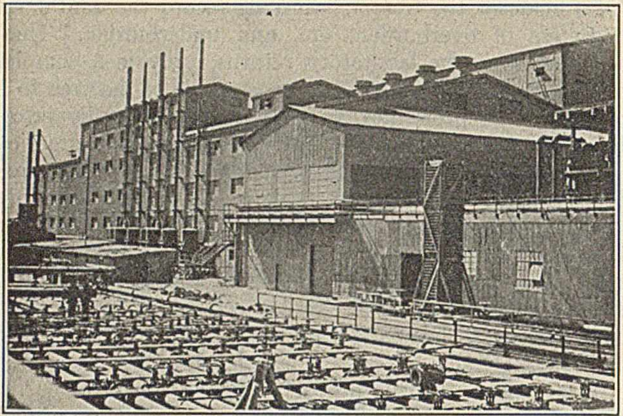
The present method, briefly, is the opening of regularly spaced pits through the ore large enough for a man to work in, and with vertical walls. The sampler cuts an even groove about 2 by 4 inches and sectionalizes his samples according to visually apparent changes in the character of the ore, with no sample section greater than 50 cm. in depth. Each sample is ground entire, before reducing in amount; the reduction of the sample is properly done, and the old inaccurate analytical method has been replaced by a rapid accurate method. Notes made at the time of sampling record the depths and characters of overburden, ore, and underburden. These, combined with the laboratory returns, provide a complete working picture of the test pit as a sample of the area to be worked. This procedure, in spite of the generally erratic character of the ore, has proved very accurate and practical.

For estimating the contents of a large area, a sample screen of test pits at 100-meter intervals is fine enough for a high degree of accuracy, as is indicated by probability considerations and proved by actual mining operations over a large area. Mechanical mining, however, as does every operation of this nature, requires day-to-day scheduling of ore for as much as a week ahead and a prediction of tonnage and grade over relatively small areas. A supplementary sample screen on a 20-meter interval thrown somewhat ahead of current ore excavation is sufficiently fine to allow prediction of daily tonnages and grades well within the limits of variation obtained in any other operation in open-pit shovel mining in spite of the notoriously erratic occurrence of nitrate ore.

Mining Methods

Until the development of the Guggenheim process, the mining of nitrate ores had received very little expert attention, and a survey of current mining operations showed all sorts of policies in mining, ranging from very poorly supervised, promiscuous high-grading of properties to careful, well-supervised operations obtaining the best recoveries consistent with the grade limit imposed by the extraction process in use. Even in the last-mentioned cases, however, the possibilities for development of improved mining methods were not very great because of the restriction imposed by the economical grade of ore.

HAND MINING—The method then in use, and still in use for all plants except the Maria Elena plant, is one of hand mining and sorting. In only a very few instances among Shanks process operations is there a preliminary stripping of overburden. The usual first operation is the sinking of a 6-inch hole through the ore into the underburden by means of a hand drill, small charges of explosives, and spoons, followed by the springing of a cavity in the underburden large enough to hold the charge of black powder. This large charge lifts the ore from the underburden and leaves it broken into large blocks. There is then a secondary blasting with dynamite, and a final breaking with heavy sledges to about 8-inch pieces, the size shipped to the plant. The broken ore is sorted and that judged of suitable grade stacked for shipment. The stacked ore is loaded by hand into mule carts, trucks, or rail cars, according to the equipment available and the accessibility of the body being mined.

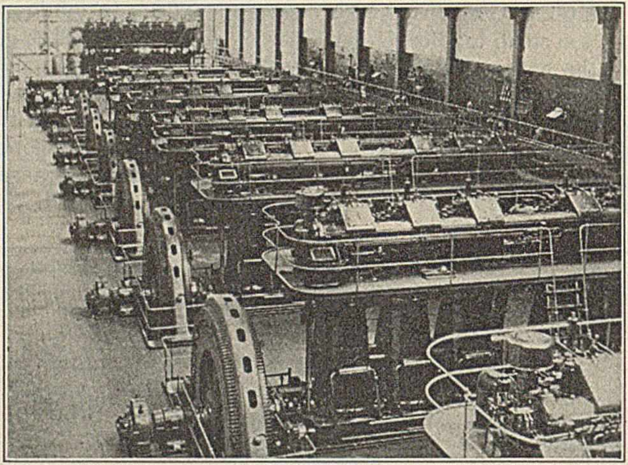


Power House

The work is done by two sorts of labor: drillers, who sink the holes and do the primary blasting; and miners or sorters, who do the secondary breaking, sorting, and stacking.

In the more careful and conservative hand mining, operations are usually arranged along a transportation line, resulting in a sort of working trench face that advances across the nitrate field. In the less conservative operations the "eyes" are picked from a field, resulting in no regularity of development of the field.

The method of hand mining briefly described above is very crude and wasteful, but recent developments in mining practice make it entirely out of date and it need not be discussed further. The modern operations in this line, initiated at the Maria Elena plant, are now being incorporated in the Pedro de Valdivia plant, which will start production around the middle of 1931, and will soon be extended to a third plant.



Power Plant

Guggenheim Process—As has been pointed out, Shanks operators are prevented from attempting any radical departures from the older method of hand mining, since the minimum economical grade of ore that they can process is around 15 per cent, and with their remaining reserves it is requiring increasingly severe sorting to maintain a grade better than this. With the development of the Guggenheim process for treatment of nitrate ore, and the ability to process low-grade ore profitably, it becomes possible to develop and use mechanical methods of mining. After preliminary tests made in the field late in 1925, the Anglo-Chilean Consolidated Nitrate Corporation introduced mechanical mining methods into its operation and has since developed and expanded them so that the ore supply of its Maria Elena plant is now entirely mechanically mined ore. This operation ranks in size probably among the first five, and certainly among the first ten, shovel mining operations in the world.

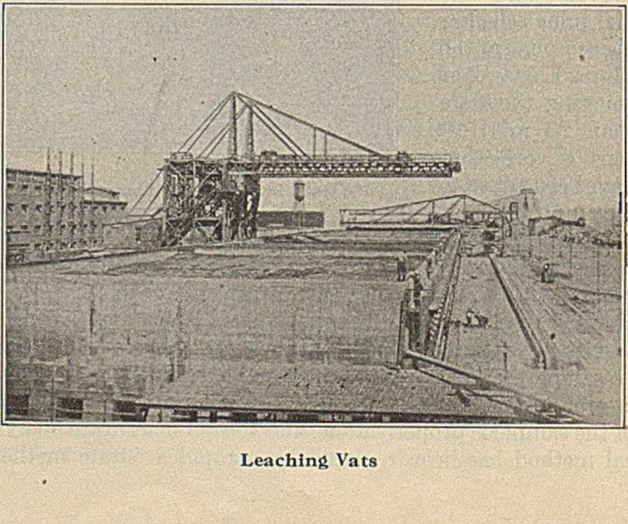
Mining practice as developed for the Maria Elena plant may be briefly described as follows: The nitrate field being exploited is developed in a regular manner through a system of semi-permanent main haulage lines, and supplementary temporary movable haulage lines along the working face, with their corresponding electric and air-supply lines for traction, shovel, and dragline power and air drills. A unit for each working face consists of two electrically driven excavating machines especially constructed to meet the problems peculiar to nitrate mining; one a dragline for stripping the overburden, the other a shovel for loading out the ore. The breaking of the ore is done by a drilling and blasting crew; the supplying of empty cars and taking away of loaded cars, by the general mine transportation system.

The first operation is the drilling and blasting of all hard overburden, followed by the stripping of overburden by the dragline, which backcasts the overburden onto the ground already exhausted. Other drilling and blasting crews then go into the stripped area and break the ore. The shovel follows and loads out the broken ore into 30-ton ore cars for shipment to the plant. Operations proceed in this sequence for the whole length of a working face, covering a strip about 13 meters wide and of the order of 1.5 to 2 km. in length. Upon the completion of such a cut, the ore-car track is shifted the width of a strip by the dragline and a new cycle begins. These operations are shown schematically in Figure 1.

Power for shovel and dragline operation and for the electrified transportation system is supplied from the central Diesel power plant; air for drilling, from a central compressor station. Mine explosives are now manufactured almost entirely at the explosive plant operated as an adjunct to the mine. This plant includes the largest black-powder plant in the world.

The general trend in all mining practice has been toward the mining of larger tonnages of lower grades of ore because, though large-scale equipment is necessarily less selective than small-scale equipment or hand methods, the economies in its use more than offset the disadvantage of the decrease in grade. This is the direction that the Chilean mining developments have taken, the average grade of run-of-mine ore mined by shovel being 8 to 9 per cent. The inclusion of lower grade ores that are not mined in ordinary hand-mining operations and the avoidance of large losses of fines so produced more than double the amount of nitrate that is recovered from an area.

A major economy resulting from shovel mining is the reduction in labor per ton of nitrate produced to less than a



Leaching Vats

sixth of that required for hand mining. The corresponding reduction in capital expenditure for housing of labor more than offsets the expenditures required for mechanical mining and transport equipment.

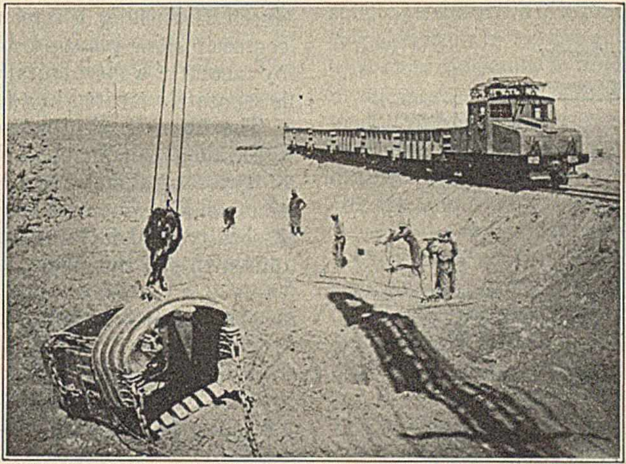
Methods of Manufacture

Shanks Process—The Shanks process for manufacture of nitrate has been in use with only minor modifications for about fifty years. Although a large part of Chilean nitrate is still manufactured by the Shanks process it is inherently an inefficient and expensive process and, since it is being supplanted by a newer process, it will be described only briefly.

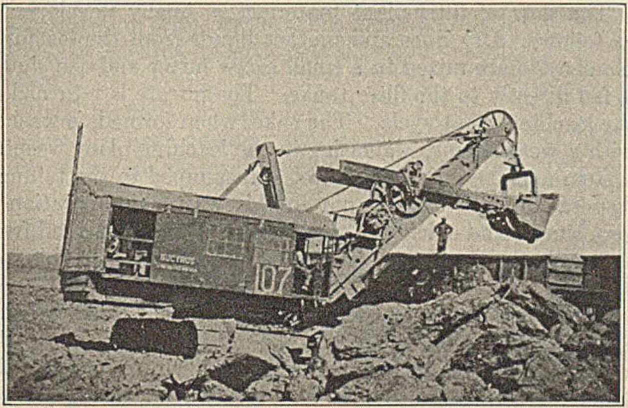
In Shanks practice the run-of-mine ore is in 8- or 10-inch pieces. This is commonly reduced in a single stage in small jaw crushers to about $1^{1}/_{2}$ or 2 inches. The fine material, minus $^{1}/_{8}$ inch, is screened out, but in only two or three instances is it processed in a filter plant, the usual procedure being either to discard it entirely or to load it into the boiling tanks on top of the coarse ore. The loading of the ore into the boiling tanks is usually done from slam, bottom-dumping, hand-push cars, though sometimes from belts.

Shanks leaching is carried out in steel boiling tanks set up on columns about 10 feet high to allow the tailings to be removed from below. The usual sized tank holds 75 tons of ore, is fitted with steam-heating coils, a false perforated bottom to aid in leach liquor circulation, and two or three ports at the bottom of the tank for discharge of tailings. The extraction is countercurrent with cross-downward percolation, the temperature and nitrate content of the leach liquor increasing from tank to tank in the series.

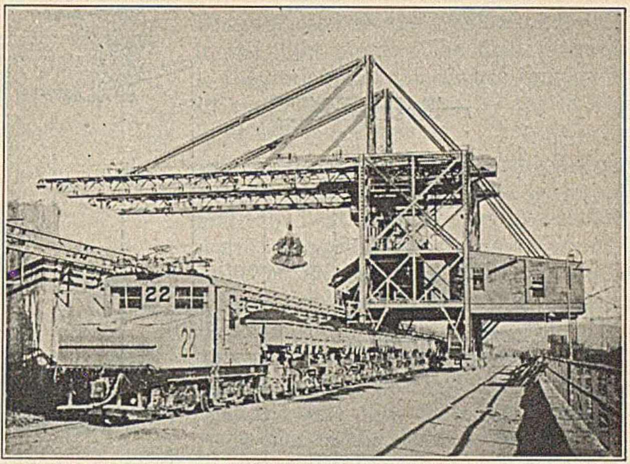
After loading with ore, a tank is filled with the depleted leach solution returned from the crystallizers. This solution is boiled for 8 or 9 hours and at the end of this time the tank is made the head of a series of three other tanks and hot saturated liquor is drawn off to the crystallizing pans. The saturated liquor is displaced by hot, less saturated liquor from the preceding tank in the series. The tank then passes through the succeeding three stages of leaching, is subjected to one or two washes circulated on the tail-end tank only, and then to a water wash.



Drilling Caliche for Blasting



Shovel



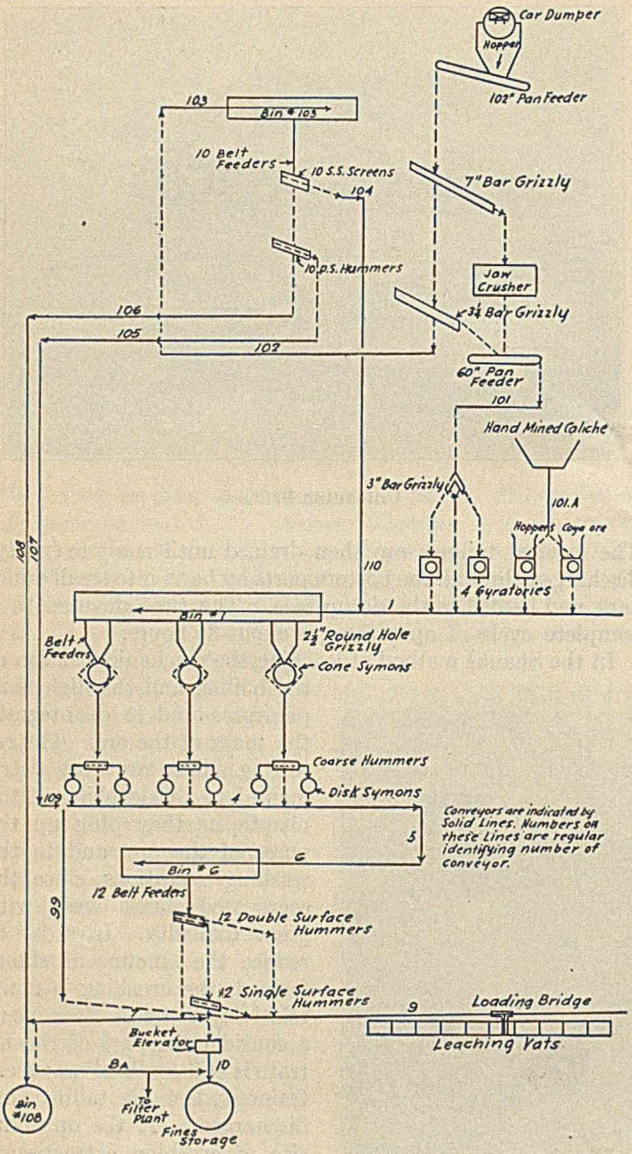
Unloading Bridges

The leached tailings are then drained until ready to empty, discharged through the bottom ports by hand into small dump cars, and hauled to the dump face. The time devoted to a complete cycle of operations is about 36 hours.

In the Shanks method of leaching the mechanical action of the boiling and the high temperatures tend to disintegrate the mass of the ore. The resulting slimes are very detrimental to the leaching of the nitrate, as they plug up the pores of the ore, and to the washing operations, since the segregated slimes wash with great difficulty. In order to reduce the amount of slimes formed, the crushing is made relatively coarse. As a result a considerable part of the nitrate is still undissolved or entrained when the tailings are discharged. At the optimum size of crushing extraction is poor, even though the factors of sliming and size of particles are balanced as well as they can be.

In addition, the circulation of the leach liquors is unfavorable for good extraction, since in effect a closed cycle is maintained only on the one head-end tank of the series, all the weakest current liquor—that returned from the crystallizers—being put on the fresh charge of ore. The remaining tanks in the series theoretically amount to a washing cycle on which the functions of a leaching cycle have been forced. Further, it is universal practice to demand a heavy duty of the leaching-tank volume; 50 tons of nitrate per year per cubic meter of leaching volume being demanded in Shanks practice, whereas the usual duty in the Guggenheim process is only 8 to 10 tons per year per cubic meter, even though using much lower grade ore. These are the main factors responsible for the poor extractions obtained in spite of the high temperatures used and the large amount of wash-water advance allowed by the boiling and other rapid evaporation.

The high cost of Shanks leaching is caused by the great amount of fuel required, the poor extractions, and the small-scale hand methods employed. The hot, nearly saturated liquor is first run into a settling tank, where it is allowed to cool a few degrees to its saturation temperature with respect



Conveyors are indicated by Solid Lines. Numbers on these Lines are regular identifying number of conveyor.

Figure 2—Crushing Operations

to nitrate. In this cooling a small amount of chloride is crystallized out. At the same time a coagulant, usually flour, is added to aid in settling out the slimes suspended in the liquor. When clear and cooled to the saturation point, the liquor is run into shallow cooling pans and cooled to atmospheric temperature. The mother liquor is drained off and the cake of crystals allowed to drain for a day or two, then shoveled over in the pan and allowed to drain some more. While still carrying 7 or 8 per cent moisture, it is loaded out of the cooling pans and piled on a drying floor, where it drains and dries to its shipping moisture content of 2 to 3 per cent. When ready to ship it is broken up, having hardened during the drying period, the bags filled and sewed, and loaded into railroad cars for shipment. All of these operations are done by hand.

GUGGENHEIM PROCESS—The Shanks process is a high-temperature process resulting in unavoidably high fuel costs. The new process, usually called the Guggenheim process, is a low-temperature leaching process. It is based on an investigation of nitrate ore-salt systems carried out several years ago by the firm of Guggenheim Brothers. The process was developed through the semi-commercial stage in a small plant built for the purpose near Oficina Cecilia in Chile, and finally incorporated in the Anglo-Chilean Consolidated Nitrate Corporation's plant inland from Tocopilla, originally called the Coya Norte, now the Maria Elena, plant. This plant began production early in 1927, and has gradually been developed to a demonstrated capacity of 600,000 tons of nitrate per year. A similar plant with somewhat greater capacity is now under construction. In view of these recent developments the new process is of great interest as an important part in the technology of the industry.

In mechanical mining it is impracticable to ship completely clean ore to the plant; some of the mixed burden or waste is excavated and loaded with the ore. The ore of this barren material, generally in the form of fines, is cleaned at the plant as the first operation before crushing by passing it over a grizzly, and subsequently cleaning the undersize of the barren material by finer screening. The material rejected in this way averages about 15 per cent of the tonnage shipped to the plant. The ore itself varies in size up to blocks of about 5 feet in maximum dimension.

The sequence of crushing operations is shown in Figure 2, and is largely that of standard large-scale crushing practice. The run-of-mine ore is dumped by a rotary tipple into a hopper from which a large pan feeder draws. The feeder discharges over the cleaning grizzly into an 84 by 66 inch Blake type jaw crusher, which does the primary breaking. This is followed by secondary breaking in 30-inch gyratories, cone and disk crushers in order. The final product is about $^5/_8$ inch size. The fine material, minus about 30 mesh, produced in crushing, is screened out by vibrating screens. The coarse crushing-plant product is loaded into the leaching tanks by means of a mechanical loading bridge. The fine product is separately treated in a filter plant.

The filtering of nitrate-ore slimes has gone through considerable development at the Maria Elena plant. A number of types of slime filters have been put through large-scale tests, and the outcome has been the installation of a modified Moore type of filter as best conforming to the peculiar requirements of this work.

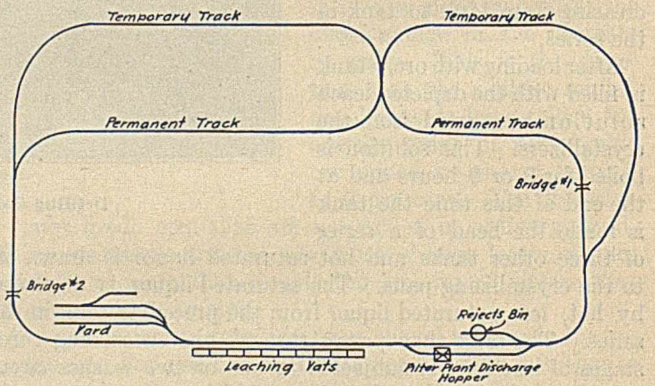


Figure 3—Tailings Disposal System

The flow of filter-plant materials as finally developed is as follows: Dry fines and mother liquor from the leaching-plant cycle are mixed in a small screw mixer and the sludge is fed directly to the filter tanks. The filtrate is returned to the leaching-plant cycle. The cake, when formed, is washed with a weak liquor originating in the leaching-plant washing system and then discharged wet and pumped to the tailings-disposal dump. Carried out in this way, this operation is very simple and efficient. A very high duty is obtained from the equipment and costs are better than is usual in this sort of work.

The coarse ore is leached in large concrete tanks holding about 7500 tons of ore each. The filling of the ore into the leaching tanks is done by a mechanical loading bridge; the emptying of the leached tailings by two unloading bridges that empty a vat in 8 hours. The tailings feed by gravity

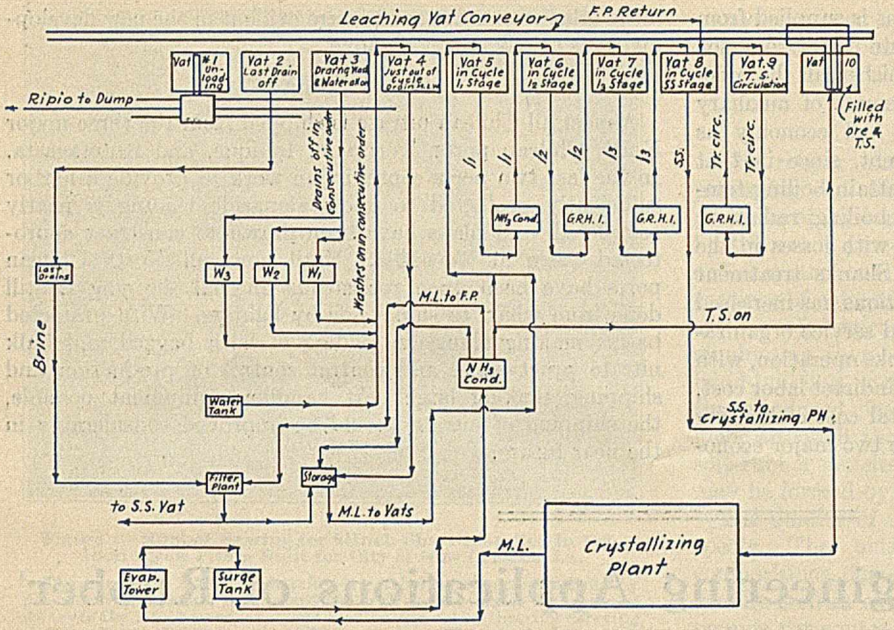


Figure 4—Leaching Operations

from the unloading-bridge hopper into the dump cars of tailings-disposal convoys and are hauled electrically to the tailings-disposal dump, which is a loop dumping face. In this way tailings disposal is made a smooth cycle. The general arrangement of the tailings-disposal system is shown in Figure 3.

When a leaching tank is completely loaded with dry ore, it is filled from below with a strong mother liquor originating from the filter-plant filtrate, mother liquor drains from the last tank in the series, and liquors bled from near the head of the series. The liquor is then circulated downward on the tank full of ore in circuit with heat interchangers in which the liquor recovers heat from Diesel engine exhaust gas and cooling water. When the temperature of the tankful of ore and liquor has reached about 40° C., the circulation is stopped and the tank is made the head of a series of four tanks. From the head tank of this series a liquor nearly saturated at 40° C. is pumped off and sent to the crystallizing plant, which returns a depleted mother liquor at 35° C. This depleted mother liquor is pumped over an evaporating tower, then through the ammonia condensers, where it is reheated, and finally onto the tail-end tank of the series. From the bottom of this tank it is pumped over another section of ammonia condensers and back onto the second vat in the series, then through heat interchangers countercurrent with the Diesel engine cooling water, back into the third tank in the series, and so on to the completion of the cycle. The general scheme of leaching operations is shown in Figure 4.

When leaching of the final tank is complete, a fresh tank of ore is cut in and the completely leached tank dropped out of the cycle. The tail-end tank is subjected to a series of displacement washes to remove the mother liquor contained in the tank when cut out of cycle, the final displacement wash being salt river water of an amount equivalent to the water content of the final drained tailings plus a quantity advanced into the washing and leaching liquors to make up for atmospheric evaporation and the quantity used as the displacement wash in the filter plant. The final operation is the draining of the leached tailings until ready for excavation by the unloading-bridge buckets.

The crystallizing plant in the Guggenheim process consists of a series of shell and tube heat interchangers in which the warm, strong liquor is pumped countercurrent to the cold, depleted mother liquor, in this way refrigerating the strong liquor and allowing the mother liquor to be heated. The final refrigeration needed by the strong liquor is done in a series of shell and tube ammonia refrigerators. The remainder of the plant consists of an ammonia-compressor plant with condensers, and Dorr thickeners for thickening the sludge of nitrate crystals.

The warm, strong liquor is cooled in the series of interchangers or recuperator tanks from about 40° C. to around 15° C., dropping some of the crystallized nitrate into the cone bottoms of the tanks from where it can be tapped off, but carrying much of it in suspension. In the series of ammonia refrigerators the strong liquor is cooled from 15° to about 5° C., at which temperature it goes to a Dorr thickener in order to settle out nitrate crystals held in suspension. The clarified, cold mother liquor is pumped back through the recuperator tanks, in which it is warmed to about 35° C. At this temperature it is pumped over an evaporating tower, then over a section of the ammonia condensers, and finally returning to the leaching cycle. A flow sheet of the crystallizing plant is shown in Figure 5.

The thick sludge from the recuperator and refrigerator tank cone bottoms and from the Dorr thickener is centrifuged, and the crystalline nitrate thus dried is ready for the final stages of graining and packaging.

The crystalline centrifuge product is briquetted and melted in a direct-fired combination reverberatory and shaft furnace. The molten nitrate is pumped directly to spray nozzles which are specially designed to deliver an evenly sized pellet. The chilled grained nitrate is conveyed to storage bins feeding either directly to cars for bulk shipment or to automatic bagging machines delivering an evenly weighted package. The purity of the final product is 98.8 per cent, that of the ordinary Shanks product around 95.5 per cent.

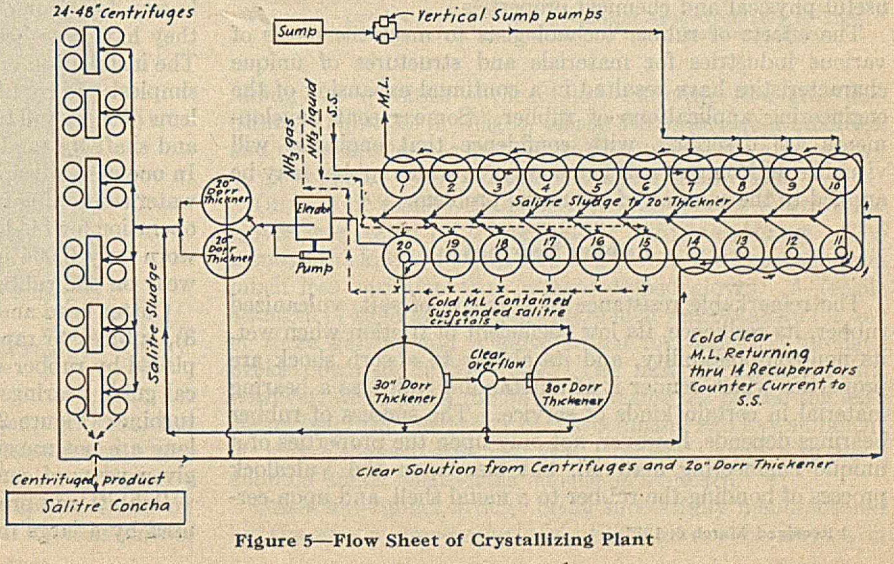


Figure 5—Flow Sheet of Crystallizing Plant

Power for all mining and plant operations is supplied from a central Diesel engine plant. The waste heat from the Diesels and from the graining plant furnishes all the process heat with the exception of a small amount of auxiliary heat for the granulating process. The fuel economy as compared with Shanks operation is evident, since in that process direct steam heat is employed to attain boiling temperatures and the heat dissipated through boiling, radiation, and from the crystallizing pans, together with losses in the hot tailings, results in half the cost of Shanks treatment being a fuel cost. Mechanization of operations has increased the output per man employed in plant and service organizations over three times that obtained in Shanks operation, with resultant economies in direct labor cost, in indirect labor cost, such as welfare expense, etc., and in capital cost of housing and public buildings. In addition to these two major economies, other important savings are evident in the new developments as briefly outlined above.

Shipping

Almost all Chilean nitrate is shipped from the three major North Chilean ports, Tocopilla, Iquique, and Antofagasta. In the last two ports construction work to provide a harbor sufficiently protected to allow alongside loading is nearly completed, and plans have been drawn to construct a protected basin at Tocopilla. Until now, all North Chilean ports have been open roadsteads and all shipping is still done from wharf to ship's side by lighters. With protected basins making alongside loading of both bagged and bulk nitrate practicable, and central control of production and shipping, making large port handling equipment possible, the shipping of nitrate should be improved considerably in the near future.

Some Recent Engineering Applications of Rubber[1]

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THE wide variety of demands made upon rubber as a material of commerce seem paradoxical unless it is fully realized that the term "rubber" as used in industry connotes, not a single substance, but a vast range of compositions, each designed to meet the engineering requirements of some particular service, and each representing careful development on the part of the rubber technologist in order to secure the desired physical and chemical characteristics.

The rubber manufacturer has facilities for selecting and blending with the basic material a variety of materials other than rubber, for processing and vulcanizing rubber compounds to meet specific requirements, and for combining rubber in commercial articles with almost every other type of structural material. These facilities, together with the rapid strides being made continually in rubber technology through research, are resulting in new applications of rubber and rubber structures to the needs of industry. Engineers are constantly bringing more of their problems to the rubber technologist, recognizing in rubber an engineering material of fundamental importance, capable of being widely varied in useful physical and chemical properties.

The efforts of rubber technologists to meet the needs of various industries for materials and structures of unique characteristics have resulted in a continual expansion of the engineering applications of rubber. Some recent developments are described, with confidence that engineers will visualize and suggest other new ways in which rubber may be applied to the solution of industrial problems.

Rubber Bearings

The remarkable resistance to abrasion of soft, vulcanized rubber, its resilience, its low coefficient of friction when wet, its non-compressibility, and its ability to absorb shock are properties which render it of outstanding value as a bearing material in certain kinds of service. The success of rubber bearings depends, however, not only upon the properties of a unique engineering material, but also upon the Vulcalock process of bonding the rubber to a metal shell, and upon certain fundamental features of design. The fluted construction shown in Figure 1 and the spirally grooved construction used in vertical guide bearings (Figure 2) both provide waterways essential to continuous lubrication of the bearing and the washing away of abrasive material.

Years of continuous use have proved beyond all question that rubber is better fitted for certain types of installation than any other bearing material. Where lubrication by oil is difficult or impossible, and where other bearings cut out owing to sand or other abrasives, rubber bearings endure. There are cases on record where they have outworn other bearing materials, such as *lignum vitae* and babbitt, by as much as ten times.

The highest operating temperature ordinarily recommended for rubber bearings is 150° F. Special bearings have been designed, however, for use at higher temperatures, in places where loads are not excessive and where it is possible to work out a satisfactory holding device for the special type bearing required. Another limitation necessarily imposed is that rubber bearings are not serviceable in contact with oils.

While water-lubricated soft-rubber bearings are most widely known for their outstanding performance in marine service, they have also been applied economically to industrial uses. The installation of rubber bearings, for example, provides the simplest and by far the most effective solution of three problems of deep-well turbine-pump operation—cutting of bearings and shaft by sand and grit, shaft vibration, and lubrication. In one case a deep-well turbine pump was required to handle water containing 25 per cent of sharp sand. After continuous operation for 144 hours at a speed of 1150 r. p. m., the shaft had worn only 0.004 inch and there was no trace whatsoever of wear on the rubber bearing.

Cutter head and ladder bearings on suction dredges (Figure 3), subject to rapid wear and heavy strains, have been replaced by rubber without increasing the bearing size. Vertical guide bearings of tremendous sizes are used in hydraulic turbines (Figure 2). Bearings 2 feet in diameter and 6 feet long are not unusual. Rubber bearings in this service have given years of continuous operation.

Babbitt and bronze bearings in the centrifugal sand pumps used by a large mining company required replacement after

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[1] Received March 6, 1931.

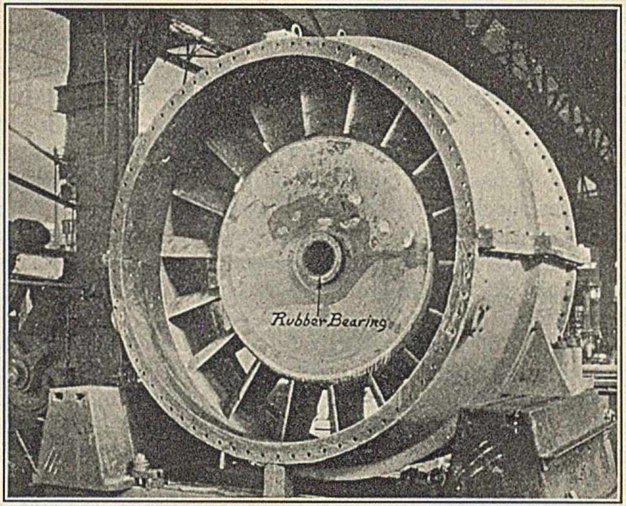

Figure 1—Rubber Bearing for 9-Inch Shaft Installed in 110-Inch Screw Pump Built for City of New Orleans, La.

The housing in which the bearing is carried is supported radially by diffusion vanes, which also retard the whirling motion of the water as it leaves the 9-foot impeller. The load on the rubber bearing carrying the impeller shaft is approximately four tons. The speed of the shaft is 83 r. p. m. View from suction side of pump.

an average of 4000 tons of fine sand (under 20 mesh) had been handled, whereas rubber bearings, after 14,000 tons of the same material had been pumped, were in perfect condition, and the shaft showed very slight scoring.

Other applications of rubber bearings to the service of industry include brine agitators, dredging pumps, various horizontal and vertical centrifugal pumps, some of which handle abrasives, cement slurry agitators, chemical tanks, elevator boot shafts, mine tailing pumps, flotation agitators, sand and gravel washers (where rubber bearings have outworn metal 4 to 1), paper-stock agitators, wood-pulp grinders, and other machinery where shaft scoring is a problem and where water lubrication is available.

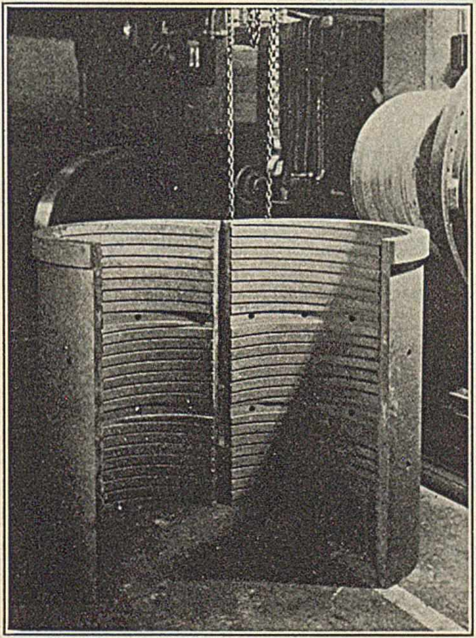

Figure 2—Spirally Grooved Rubber Guide Bearing for 31$^{1}/_{2}$-Inch Diameter Vertical Shaft of a 32,000 Horsepower Hydraulic Turbine

The rubber casing guard recently developed for use on rotary-drill pipe in the petroleum industry is another form of water-lubricated bearing, the principal difference in this case being that the bearing is attached to the shaft.

The Anode Process

The rubber manufacturer has recently acquired a new processing tool which enables him to fabricate high-quality products of intricate shape at reasonable cost. It is possible by the anode process (electrodeposition of rubber from latex or other aqueous rubber dispersions) to lay down uniform coatings of soft, semi-hard, or hard rubber compositions upon articles of intricate shape by a single, simple operation; eliminating thereby numerous sheeting, cutting, and costly hand-building operations. The thickness of the coatings thus produced may be readily varied between 0.008 and 0.125 inch, although these are not the absolute limits. Likewise soft-rubber articles of shapes difficult or impossible to mold may be formed by this process with comparative ease.

The quality of anode rubber is outstanding in certain respects. The tensile strength of vulcanized soft-rubber compositions deposited from latex by the anode process is usually well in excess of 4500 pounds per square inch, 5200 pounds per square inch being not uncommon, with ultimate elongations in the neighborhood of 900 per cent. The aging properties of such compositions, as measured by the Bierer bomb, indicate considerable advantage over mill-mixed compounds of similar composition, and this has been well substantiated by the exceptional durability in actual service of electricians' gloves made by the anode process. In combining the qualities of flexibility, dielectric strength, uniformity, lightness in weight, tensile strength, aging qualities, and resistance to tear and abrasion, anode gloves are superior to gloves made by any previous commercial process.

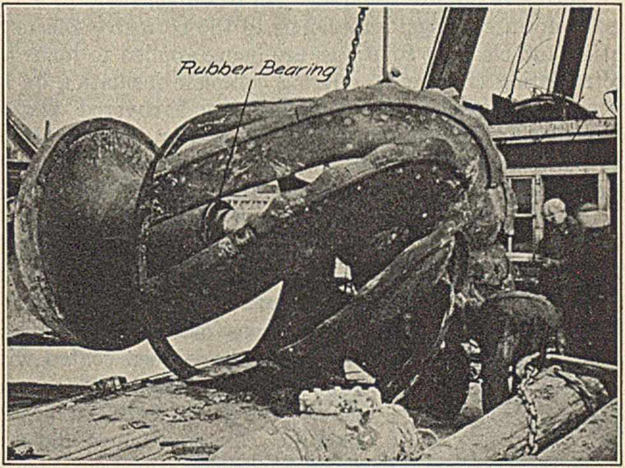

Figure 3—Dredge Cutter Head, Weighing Approximately 10 Tons, on 14$^{1}/_{2}$-Inch Shaft Supported by Fluted Rubber Bearing

One lot of twenty-six pairs of anode-process electricians' gloves was tested by a large public utilities company. The average thickness of the sides and between the fingers showed much less variation than cement-dipped gloves. A tensile strength of 5143 pounds per square inch was obtained for one of these gloves, and a glove tested for dielectric strength broke down at 26,200 volts. The most significant point, however, was that of the 52 gloves tested, 52 passed the test. Never before in the history of this company had any shipment of gloves passed 100 per cent. Several companies have adopted anode electricians' gloves as standard.

Other soft-rubber articles being successfully manufactured by the anode process include utility gloves for service in

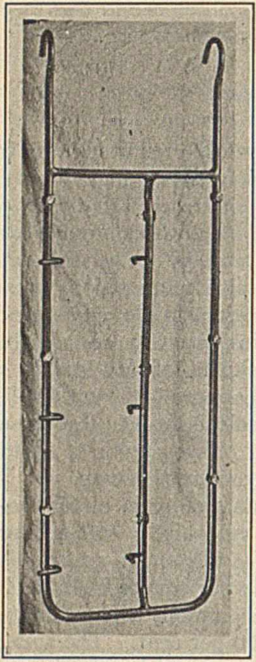

Figure 4—Electroplating Rack Covered with Rubber by Anode Process

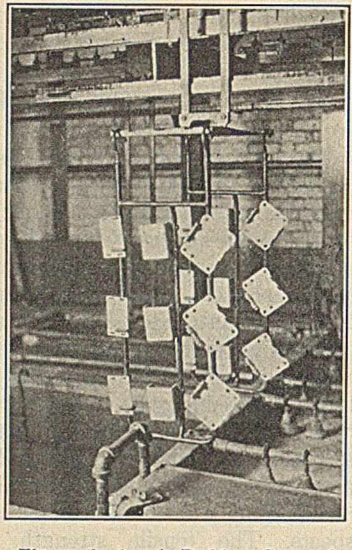

Figure 5—Anode Rubber-Covered Electroplating Rack in Service

contact with acids and other corrosives, surgeons' gloves, colored branding labels, and various types of tubing.

Probably of greatest interest to chemical engineers is the value of the anode process in laying down a uniform protective coating of rubber upon articles designed to serve in contact with corrosive liquids or gases. For example, smooth, seamless, uniform coatings, impervious to the corrosive effects of plating and cleaning solutions, are being applied to racks for electroplating (Figure 4), offering complete insulation on all parts except the contact points. Anode-covered plating racks, forming racks, plating-barrel hanger arms, washing trays, and dipping baskets are being used successfully in gold, silver, copper, brass, nickel, cadmium, and zinc plating (Figure 5). Owing to the flexibility of the anode process, it is possible to rubber-cover almost any design of plating rack or other metal part.

Numerous other types of metal equipment have been coated with rubber by the anode process, including fan blades, conoidal fans for handling corrosive fumes and suspended abrasive matter, spineret tubes for the rayon industry, lamp guards, rubber-covered metal parts for airplanes, perforated metal and screen for wet screening or for screening corrosive materials, acid-dipping and rinsing baskets (Figure 6). Other applications will suggest themselves to engineers confronted by problems of corrosion, abrasion, or insulation (Figure 7).

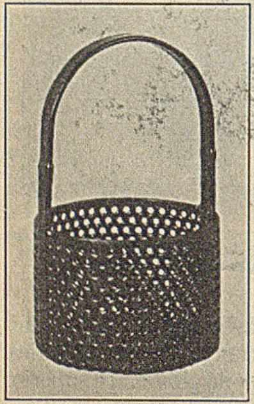

Figure 6—Perforated Metal Acid-Dipping or Rinsing Basket, Covered with Rubber by the Anode Process

Absorption of Vibration and Noise

Rubber is destined to find wide application as a vibration insulator and shock absorber. Uses of rubber by automobile manufacturers already afford a background of experience which gives rubber technologists confidence in projecting their material into any other engineering problems where the elimination of noise, shock, and vibration is important both from the standpoint of human fatigue and the fatigue of metals and machines. Delicate instruments have been devised for recording the fatigue of occupants of automobiles. There is every reason to believe that this work will be enlarged and extended to other fields.

Engineers are studying how rubber may be applied to machines to increase the life of parts subject to vibration fatigue. It has been definitely proved that the application of rubber shock insulators to the ends of springs (Figure 8) on automotive trucks and busses appreciably reduces the cost of maintenance on these vehicles. In this service rubber absorbs shocks imposed upon the vehicles in striking road obstructions.

The range of uses to which rubber shock absorbers may be applied has been greatly extended by recent developments in the technic of bonding rubber to metal. Bonds of rubber to steel of 200 to 600 pounds per square inch or more are obtainable. Rubber is thus adhered to two or more steel plates in the form of a mounting to suspend motors or other vibrating machinery (Figure 9). The great advantage of such a suspension is that the rubber may be used in shear rather than under direct compression. It has been found that the shear type mountings are more effective in dampening vibration than mountings loaded in compression or pulled apart in tension. About a dozen automobile manufacturers now support their motors at the frame by either two- or three-plate rubber-to-steel mountings, the rubber being used in shear rather than in compression or tension.

A recent application of the shear-type rubber mounting to the base of a vibrating screen greatly reduced the vibration transmitted to the floor of the building.

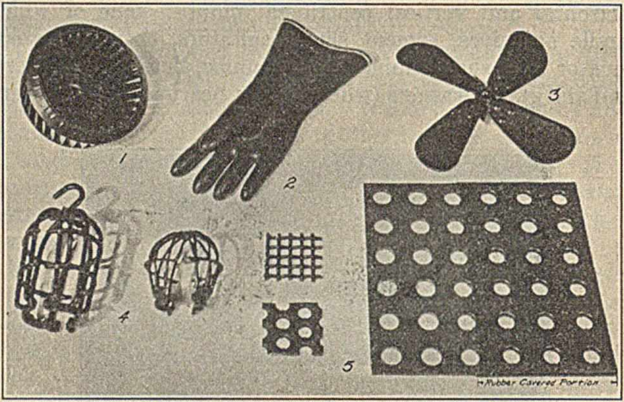

Figure 7—Some Products Covered with or Made from Anode Rubber

(1) Anode-rubber-covered conoidal fan for handling corrosive fumes and suspended abrasive matter
(2) Electricians' glove by the anode process
(3) Fan blades covered with anode rubber
(4) Anode-rubber-covered lamp guards
(5) Screen and perforated metal, rubber-covered by the anode process

Rubber-to-metal plates are also being used as crankshaft-vibration dampeners to reduce torsional vibration, replacing the old-type frictional dampeners. It has been found that the rubber dampener maintains its characteristics much longer without adjustment than the other type, in its function of decreasing variations in the angular velocity of the crankshaft.

Rubber is seeking a wider field of usefulness in eliminating the necessity for lubrication between two mechanical parts in relative rotatory movement. Pressed between two steel sleeves, rubber has now replaced lubricated spring shackles on some makes of automobiles. The mass of the rubber in this application takes up the whole rotary motion produced by the deflection of the spring (Figure 10).

The same principle is being applied to the treads of caterpillar tractors in an effort to eliminate bearing pins, which are very difficult to lubricate properly on account of the severe abrasive service to which they are subjected. The field of application of such a torsional bushing may be very wide indeed. The rubber compound used must have exceptionally low permanent set, good aging qualities, and stress-strain characteristics suited to each particular application.

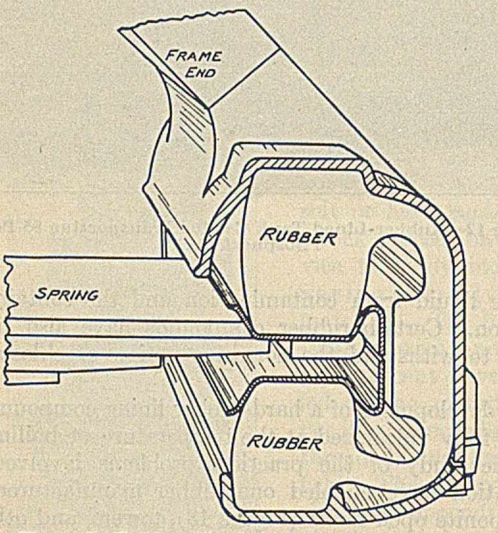

Figure 8—Rubber Shock Absorber as Installed on Rear End of Automobile Rear Spring, Replacing the Customary Type of Spring Shackle

Rubber is fast replacing fabric webbings for automobile body shims and hood cushion strips. The latter, in addition to their function as noise eliminators, must incorporate a high degree of resistance to heat and oil.

It has been demonstrated that a coating of rubber on the blades of an automobile fan reduces the noise produced by high air velocities. This undoubtedly will lead to other similar applications.

The railroads are now applying rubber at the ends of elliptical springs, at the tops and bottoms of coil springs, over equalizer bars and journals, and at the center plates of the trucks. A definite saving in maintenance cost has been established, in addition to increased passenger comfort.

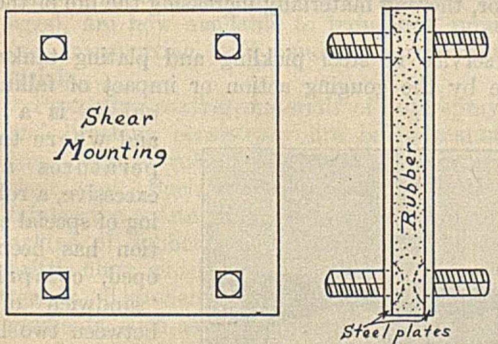

Figure 9—Rubber Vibration Dampener between Two Steel Plates, for Shear Mounting of Vibrating Machinery

Transportation commissions in our large cities are turning their attention to the elimination of street and subway noises and the vibration of adjoining buildings. Rubber is a logical material to use in the solution of such problems, for by proper compounding and vulcanizing it is possible to provide rubber slabs of the proper hardness to absorb vibrations of considerable amplitude and various frequencies, while maintaining their physical properties with very little change over a long period of years.

The shock- and vibration-absorbing properties of sponge rubber, as well as its value as a heat insulator, are being constantly utilized in new ways. Sponge rubber finds extensive engineering application in the automotive, aircraft, radio, and refrigerator industries, and there are numerous general industrial uses. A novel and potentially important field for sponge rubber is in expansion and contraction joints for concrete highways.

Rubber in Contact with Heat and Oil

Although it is proverbial that heat and oil deteriorate rubber quickly and seriously, the technologist has not been deterred from seeking to produce a paradox. In recent years outstanding advances have been made in the development and application of accelerators, age resistors, and other compounding materials. With this new knowledge at hand, products embodying improved rubber compounds have been designed to withstand heat and contact with oils, greases, and organic solvents, thus rendering available to industry the unique properties of rubber in uses heretofore considered too severe.

Technological development has produced air hose for pneumatic tools which withstands the action of hot lubricating oil under high pulsating air pressure, and hose for handling live steam under pressure. Improvements in gasoline and distillate hose, car-washing hose, paint-spray hose, oil-suction and discharge hose, gaskets, and packing are being made continually, resulting in a steady increase in the durability of these articles.

The thousands of miles of modern high-pressure natural-gas lines illustrate the value in an industrial product of rubber designed to resist oil. Each pipe joint is sealed with the aid of rubber packing rings which successfully resist the deteriorating action of condensates.

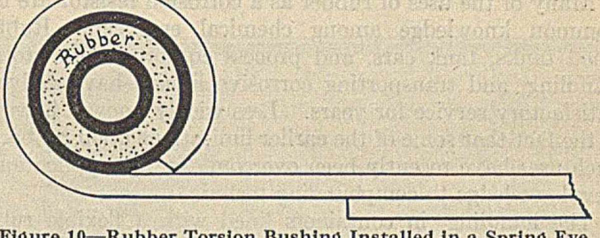

Figure 10—Rubber Torsion Bushing Installed in a Spring Eye

In the printing industry oil-resistant rubber inking rollers, rubber surface engraving plates, newspaper blankets, and blankets for offset printing find wide usage.

Molded oil-resistant rubber, reënforced by fabric, is being used in covers for automobile springs and universal joints, serving to retain the lubricant and to exclude dirt, as well as having a dampening effect upon vibration.

Braided metal jacket grease-gun hose, embodying the flexibility of an oil-resistant rubber compound, has a bursting strength of 10,000 to 12,000 pounds per square inch and operates under working pressures in the neighborhood of 6000 pounds per square inch.

The rubber compounds used in conveyor belts have been immensely improved in regard to heat resistance. Rubber-covered conveyor belts are successfully handling hot cement, sand, limestone, and coke.

Despite such improvements in the resistance of rubber to service in contact with its natural enemies, heat and oil, there is a great deal yet to be desired. Rubber manufacturers and their technologists are keenly competing for leadership in this field, a condition which assures further advances.

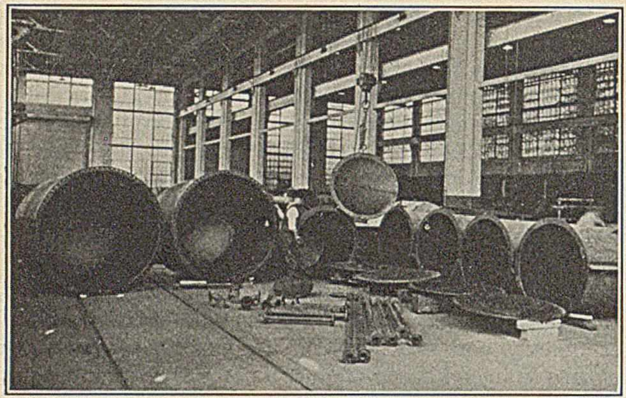

Figure 11—Rubber-Lined Tanks, Pipe, and Fittings for Handling Glacial Acetic Acid

Figure 12—Rubber-Lined Tank Car for Transporting 85 Per Cent Phosphoric Acid

Rubber as Chemically Resistant Engineering Material

The value of rubber-covered and rubber-lined equipment in the chemical industry, and in other industries handling corrosive and abrasive substances, lies in the reduction of maintenance costs. Various structural and plastic materials, such as wood, brick, glass, asphalt, and various alloys, have been used in the attempt to meet this fundamental problem of chemical engineering.

Recognizing the potentialities of his basic material, the rubber manufacturer began several years ago to develop special resistant compounds and methods for adhering rubber to other structural materials, until at the present time it is a well-established fact that rubber is the outstanding practical material for resisting corrosion and abrasion in industrial processes. Rubber, with its resistant properties and ease of installation, has made possible the profitable manufacture of certain chemical products which formerly could not be produced on an economic basis.

Many of the uses of rubber as a corrosion resistor are thus common knowledge among chemical engineers. Rubber-lined tanks, tank cars, and process equipment for storing, handling, and transporting corrosive liquids have delivered satisfactory service for years. Less widely known, however, is the fact that some of the earlier limitations upon rubber for such uses have recently been overcome by the application of new knowledge to compounding technic.

The handling, in containers lined with a flexible rubber compound, of glacial acetic acid, without appreciable discoloration of the acid or damage to the rubber, is an achievement worthy of note (Figure 11). Similarly, 85 per cent water-white phosphoric acid is being stored and transported in tanks and tank cars (Figure 12) lined with a new soft-rubber composition designed especially to meet this particular service.

The problem of handling perishable food products, such as vinegar and milk, in rubber-lined containers is progressing rapidly, the rubber serving the purpose of a heat insulator as well as protecting the liquid from contamination and the container from corrosion. Certain rubber compounds have also been designed to withstand the corrosive action of chlorine solutions.

The development of a hard-rubber lining compound which can be fully vulcanized at the temperature of boiling water and the study of the practical problems involved in its application have enabled one rubber manufacturer to line with ebonite open tanks (Figure 13), towers, and other storage and process equipment too large for railroad transportation or structurally unsuited to withstand steam pressures of 50 to 75 pounds per square inch formerly necessary to vulcanize hard-rubber linings. In many cases this process will render economical the lining with hard rubber of equipment which would otherwise have to be less effectively protected.

Similarly, the development of soft-rubber linings which vulcanize well in boiling water represents a technological achievement, and renders rubber more widely available to chemical engineers in the solution of their maintenance problems.

Large pickling tanks are being successfully lined with rubber. Such tanks usually contain sulfuric or hydrochloric acid in 5 to 15 per cent concentration, and operate at temperatures as high as 220° F. A brick inner lining protects the rubber from the impact of heavy blows and serves as a heat insulator, thereby materially increasing the life of the rubber lining.

For service in steel pickling and plating tanks, where damage by the gouging action or impact of falling metal objects is a problem and where the temperatures are not excessive, a rubber lining of special construction has been developed, comprising a "sandwich" of ebonite between two layers of resilient soft rubber. The soft-rubber layer, bonded to the tank structure, absorbs the stresses caused by the difference in expansion coefficients between metal and ebonite, whereas the outer soft-rubber layer absorbs the shock of accidental blows from within the

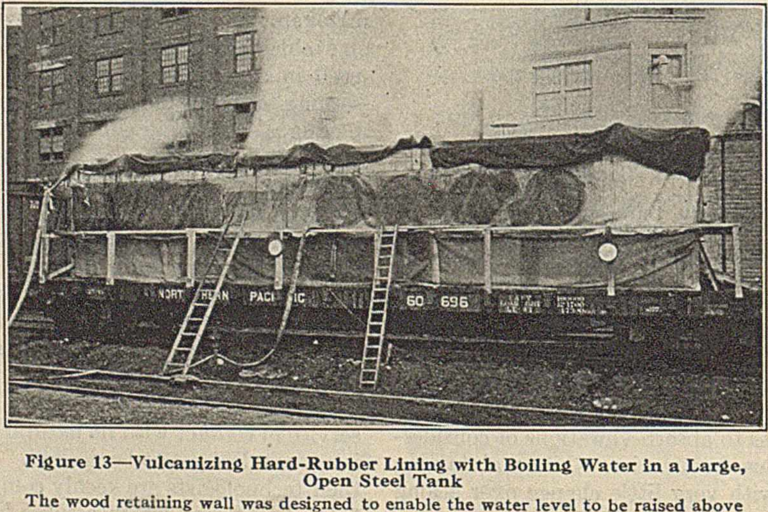

Figure 13—Vulcanizing Hard-Rubber Lining with Boiling Water in a Large, Open Steel Tank

The wood retaining wall was designed to enable the water level to be raised above the top of the tank.

tank. This construction can be applied in the field by vulcanizing in boiling water, and is more easily repaired than ordinary hard-rubber linings.

Ebonite finds a comparatively little known application as a corrosion resistor in the polished coverings for bleach rods and dye sticks which support delicate skeins of rayon fiber during various processing operations. This rubber must withstand immersion in sodium sulfide solutions at temperatures up to 200° F., sodium hypochlorite bleaching baths, and acetic acid sours, without etching or cracking of the polished surface.

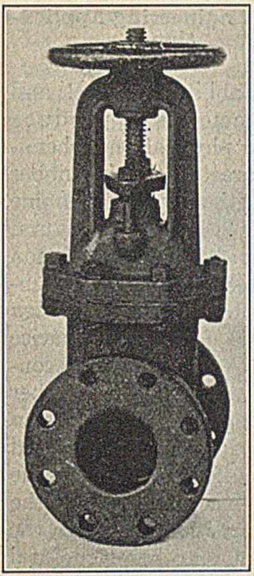

Figure 14—Rubber-Lined Gate Valve for Handling Corrosive Liquids

Pipe and fittings lined with soft or hard rubber by the Vulcalock process have been of service to many industries in conveying corrosive and abrasive materials. The first rubber pipe linings were applied to flanged pipe; recent developments have led to the manufacture of rubber-lined pipe which can be cut, threaded, and assembled in the field. The success of this construction depends upon the use of a special rubber-covered metal washer inserted between threaded metal flanges which are screwed upon the ends of the pipe.

Rubber-lined relinable valves operating on the principle of the laboratory screw clamp are resulting in considerable saving to the chemical industry, both in initial cost and maintenance. The soft-rubber liner, replaceable by a simple, rapid, and inexpensive operation, is so shaped that a minimum of distortion occurs at the point of compression. Since the liner is completely surrounded by the reënforcing casting, pressures up to 100 pounds per square inch may be safely used. Rubber-lined gate valves (Figure 14) have also been developed to fit pipe sizes from 2- to 12-inch. Centrifugal and pulsating pumps completely lined with rubber, as well as rubber-lined air lifts (acid eggs), are now available to industries producing, transporting, and handling corrosive materials.

Protective coating materials of both spraying and brushing consistency are being manufactured with a rubber isomer (thermoprene) as their base. Such coatings, in addition to retaining the outstanding chemical-resistant properties of rubber, yield tough, durable, nonbrittle films, which adhere tenaciously to most structural materials. The thermoprene base is compounded with other ingredients, such as graphite or aluminum powder, to meet the requirements of various types of service. The uses to which such coatings are applied include the protection against corrosion of structural steel, interior walls and ceilings, pipe lines and machinery in chemical plants, rayon plants, dye houses, laundries, coke plants, and around pickling tanks, where acid or alkali fumes or direct spillage are a problem. The protection of magnesium alloys during shipment and of magnesium-alloy parts in aircraft; the coating of metal parts in refrigerators; priming coats for lacquer films and for "metal-to-metal contacts;" the coating of wood, steel, and concrete tanks and boxes; the protection of metal sheets subjected to flexing; and the protection of machinery to be shipped overseas (the film being readily removable by the use of gasoline or benzene) illustrate further uses for these coatings.

Certain limitations are necessarily imposed. Thermoprene coatings, for example, are not exceptionally resistant to oil or to severe abrasive service, nor are they recommended for use at temperatures in excess of 180° F. The character of corrosives to which they are resistant is in general the same as for soft rubber, except that the coating films, being much thinner than sheet rubber, are not intended to replace rubber linings or coverings for immersion in corrosive liquids.

A significant development is in progress on a hard-rubber baking enamel designed primarily for industrial use in places where exceptional corrosion resistance and a very hard, durable film are required.

Removing the Aviation Ice Hazard

A novel and important development in rubber is the part it plays in a new device for removing the ice which forms under certain conditions on the leading edges of airplanes in flight. Ice formation presents a grave menace to safety in flying and to the maintenance of scheduled trips, as well as to the widespread future use of commercial aircraft.

The most common meteorological condition under which ice forms on a plane is that within a region containing minute water droplets in the form of fog, mist, or cloud, when such a region is at a temperature below the freezing point of water. Over the New York-Cleveland airway dangerous ice accumulations are encountered in fog, mist, or cloud, when the humidity is 90 per cent or more, and within the temperature range 0° to −20° C. (*2*). A plane flying in such an ice-forming region may be thrown completely out of control in less than 30 minutes by the vibrations set up, the additional weight imposed, and the effects of the ice deposit upon the aerodynamics of the wings, struts, and wires.

It was with a view to preventing this hazard that the Daniel Guggenheim Fund for the Promotion of Aeronautics supported the fundamental work of Geer and Scott (*1*), which has been followed by intensive development under the sponsorship of one of the larger rubber companies, working in coöperation with a leading commercial air transport company. This program of research, at first conducted by the use of miniature struts, wires, and wing sections suspended in a small refrigerated wind tunnel; later using full-sized sections in the largest tunnel of its kind in the world (Figure 15); and finally on an actual plane in flight, has resulted in defining the conditions governing ice formation on airplanes and in a simple method for removal of the ice deposit. The latter device embodies a "pneumatic leading edge," consisting of a thin rubber overshoe, with fabric reënforcement, containing flat rubber tubes connected to an air pump.

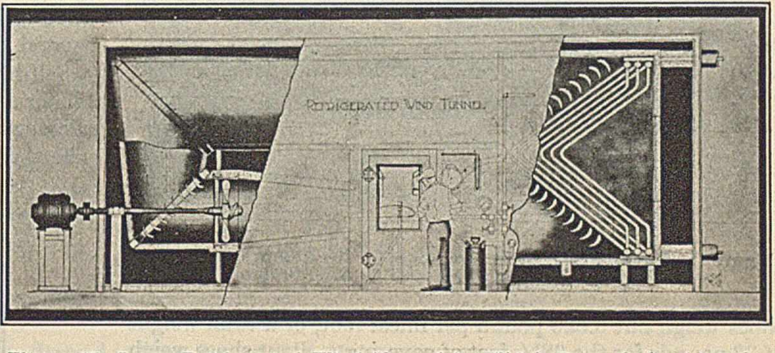

Figure 15—Large Refrigerated Wind Tunnel in Which Part of the Aircraft Research Dealing with the Formation and Removal of Ice Is Being Conducted

Several forces tend to hold the ice, once it has formed, upon the leading edge—the adhesion between the ice and the surface upon which it freezes, the pressure of the atmosphere, and the aerodynamic pressure due to the flight speed of the plane. By expanding or contracting the surface of the new overshoes, the ice deposit, being comparatively inflexible, is cracked and its adhesion for the surface destroyed. The wind stream then lifts the broken ice away from the surface, completing the removal process (Figure 16).

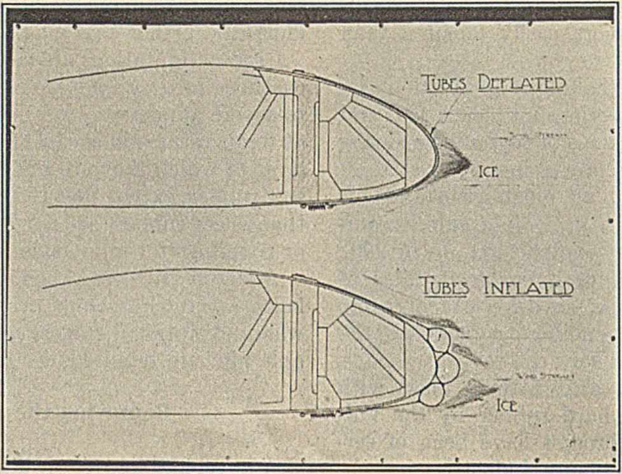

Figure 16—Sketch Illustrating Principle of Pneumatic Rubber Leading Edge for Removal of Ice from Airplane Wings

This device, although still in the stage of development, with many of the practical details, such as standardizing the equipment for various types of planes, details of valves and compressor equipment, methods of attachment of the overshoes, remaining to be perfected, has already proved its worth on the leading edges of wings in actual air trials under ice-forming conditions.

The weight of the rubber overshoes will not materially affect the pay load of the protected plane. On the biplane now used in tests, for example (Figure 17), the wing overshoes weigh but 0.526 pound per lineal foot, or a total weight of 36 pounds for the $68^{1}/_{2}$ feet of covering. Strut shoes weigh about 0.36 pound per foot, or a total of $12^{1}/_{4}$ pounds for the 34 feet to be covered. The weight of the wire coverings is almost negligible (0.03 pound per foot, or a total weight of less than 5 pounds). Thus the total weight of the pneumatic overshoes for this plane is less than 53 pounds (not including the air compressor), as compared with a pay load of 1000 pounds. On the newer type monomail plane the overshoe weight will be reduced by 25 to 30 per cent, with the pay load increased to 2500 pounds.

Figure 17—Pneumatic Rubber Overshoes for Ice Removal, Installed for Test on the Wings of No. 33 N. A. T. Biplane

Flight tests have already demonstrated that the aerodynamics of the plane are not noticeably affected by the weight, shape, or movement of the rubber overshoes. The inflation and deflation of the tubes will be entirely automatic, with a cycle of approximately one minute, rendering it necessary for the pilot, upon entering an ice-forming region, merely to start the device functioning.

Thus it is expected that rubber will make an important contribution to the safety and dependability of commercial flying, paving the way toward increasing development of our air-transportation facilities.

Other Engineering Applications

The ability to select and blend materials to produce definite physical and chemical characteristics in rubber compositions, and to combine rubber with other structural materials, such as cotton and steel, has enabled rubber technologists to design products for useful service under extremely varied conditions. It is now possible to mold and vulcanize rubber to automobile running boards, securing excellent adhesion which eliminates the creeping tendency inherent in cemented mats. Improvements in the field of adhesion, notably the Vulcalock bond, have made it possible to secure, not only the outstanding advantages of rubber compositions, but also the added mechanical strength or rigidity of other structural materials.

Rubber is now replacing steel and Silex linings for ball mills used in the wet grinding of clays, enamels, ores, and Portland cement. Figure 18 shows the interior of a 7 by 18 foot ball mill, lined with 1-inch thick slabs of rubber with a stiff backing of fiber and fabric, held to the mill shell by special grooved manganese-steel retainer bars. This mill is used in the finish grinding of Portland cement and is the result of a systematic five-year development program on the part of a large rubber manufacturer. The chief advantages of rubber over steel linings are ease of installation, quietness of mill operation, and increased mill capacity, the usual steel or Silex lining being several times thicker than a rubber lining.

Self-healing cutting blocks embodying thermoprene as a binder are successfully replacing the maple blocks used under clicking machines for cutting out leather shoe and glove parts. The thermoprene blocks have a longer useful life than wood

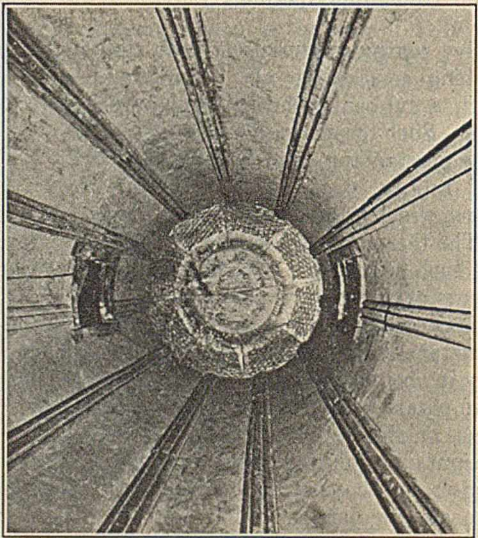

Figure 18—Interior of a 7 by 18 Foot Ball Mill Lined with 1-Inch Thick Slabs of Rubber Held in Place by Grooved Manganese-Steel Retainer Bars

blocks and show less tendency to chip. Worn blocks can readily be reworked, since the binder is thermoplastic.

Rubber serves the oil industry in many ways. Of special interest are recent improvements in high-pressure rotary-drill hose to meet the grueling conditions of deep-well drilling service. Such hose, although of fairly large inside diameter ($2^1/_2$ to 3 inches), will stand pressures of 6000 pounds per square inch under test, and normally operates at pressures of 1000 pounds per square inch or more in deep drilling. One hose served in the drilling of a 9000-foot California well (one of the deepest on record), and remained in good enough condition for further service.

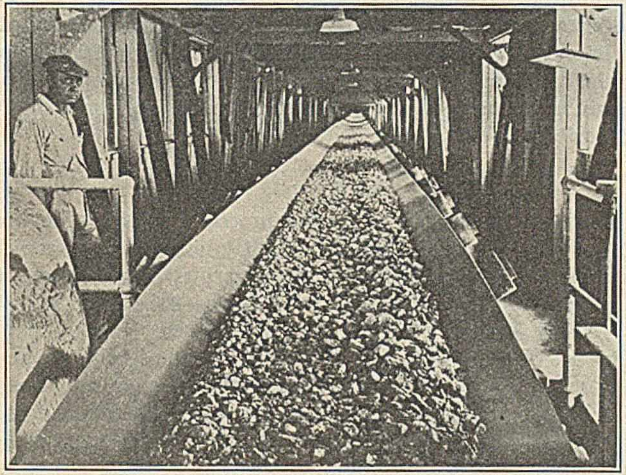

Figure 19—A Rubber-Covered Belt Conveying Crushed Ore, Illustrating a Type of Abrasive Service in Which Rubber Is Outstanding

Rubber-metal pack-off rings of two kinds are utilized in a new type of high-pressure, deep-well rotary-drill pipe joint which is thus more effectively sealed against hydraulic leakage.

Improvements in oil-tanker suction and discharge hose to prevent leakage at the nipples have reduced the fire hazard in the vicinity of docks. The advances in adhesion bonds between rubber and metal made this development possible.

In the printing industry hand-engraved rubber plates comprising a metal backing adhered to frictioned fabric, a layer of cushion rubber, a second fabric layer, and finally a uniform surface layer of oil-resistant "engraving gum" have contributed a new process for printing in brilliant colors, both with water color and oil inks.

The comparatively recent seamless, laminated, flat belt construction, in which folded edges are eliminated, and which utilizes in the rubber the latest advances in compounding technic, enabling the use of a close-woven hard duck without danger of ply separation, has resulted in greater flexibility and longer belt life in power transmission and conveyor service. Transmission belts delivering greater horsepower with less slip and practically no stretch are thus produced. Conveyor belts made with this construction embody also a new method for securing the rubber cover at the edges of the belt. A striking example of the type of service in which such belts are performing is the case of a high-speed loading belt used to distribute coal in the hold of a vessel. Coal from an inclined conveyor drops vertically 60 feet, striking this horizontal loading belt, which travels at a speed of 4500 feet per minute and handles up to 2260 tons of coal per hour.

There are innumerable examples of the outstanding performance of rubber belts in service. One installation 565 feet long handled more than 39,000,000 tons of crushed copper ore over a period of ten years of useful life, at a total belt cost of less than 10 cents per 1000 tons (Figure 19). High-speed projector belts are used to throw dolomite into blast furnaces.

Flat power-transmission belting of the new type, with its improved flexibility, permits closer hook-ups and greater driving efficiency than the older constructions containing folded edges and longitudinal seams.

The combination of rubber with fabric in a unique way has resulted in the development of multiple-drive V-belts, which are coming into very wide usage, owing to their exceptional efficiency and durability, for power transmission on both horizontal and vertical short-center drives.

Conclusion

The wide range of new uses to which rubber is continually being applied in the solution of industrial problems renders it of fundamental importance as an engineering material. Let engineers, confronted with problems of corrosion, abrasion, noise, vibration, insulation, flexibility, resilience, or the storing of resilient energy, point out the needs. New tools are at the command of rubber technologists—a wider knowledge of compounding, new processing methods, and new ways of combining rubber with other structural materials, enabling them more effectively to apply their unique material to the varied requirements of industry.

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(1) Geer and Scott, Natl. Advisory Comm. Aeronautics, *Tech. Note* **345.**
(2) Scott, *J. Franklin Inst.*, **210,** 554 (1930).

Liquefied Helium Produced after Lengthy Experiment

Liquid helium was produced for the first time in the United States in the Bureau of Standards' low-temperature laboratory on April 3. It is the most difficult of all gases to liquefy, the boiling point of the liquid being −452° F., or only 7.4 degrees above absolute zero. The extremely low temperature which this represents will be realized when one considers that it is approximately 142 degrees below the temperature of liquid air.

The process used in the production of liquid helium is an extremely complex and difficult one. It involves the progressive production of lowered temperatures by brine, carbon dioxide, liquid air, liquid hydrogen, and finally by expansion of the hydrogen to produce liquid helium. By "boiling" the helium under a high vacuum a temperature of −456° F. was obtained.

The establishment of fixed points on the temperature scale from the lowest to the highest attainable temperatures is one of the basic functions of the National Bureau of Standards. Naturally, the greatest difficulty is experienced in setting up standards at the two ends of the scale.

Such fixed points as the freezing and boiling points of water and the freezing point of gold no longer present any particular difficulties. But in only three other places in the world—Leiden, Toronto, and Berlin—has helium ever been liquefied. The successful production of liquid helium at the Bureau of Standards will aid in the accurate establishment of another low fixed point for the further extension of the international temperature scale.

The success attending the experiment comes as the result of many months of effort on the part of H. C. Dickinson, chief of the heat and power division; F. C. Brickwedde, chief of the low-temperature section; J. W. Cook; and R. B. Scott. These men have worked far into the night on many occasions to overcome the many obstacles caused by traces of impurities in the gases and the necessarily limited information available on the best method of carrying out the process.

The full significance of this accomplishment cannot, of course, be predicted at the present time, but there is no question that it is of the highest scientific importance. Many of the phenomena of modern physics, such as some of the postulates of Einstein and others, can be studied only at these extremely low temperatures.

Trisodium Phosphate—Its Manufacture and Use[1]

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In the manufacture of trisodium phosphate, phosphoric acid is added to a solution of soda ash to form disodium phosphate, with evolution of carbon dioxide. The solution is diluted and extraneous matter removed by filtration. Sodium hydroxide, added to the filtrate, converts it to trisodium phosphate. This solution is diluted, filtered hot, and crystallized. The crystals of trisodium phosphate are separated from the filtrate, dried, meshed, and aged. A spray-congealed product may also be prepared from the clear trisodium phosphate solution.

Caking of the crystals may be avoided either by formation of double salts in the product or by spray-congealing.

The value of trisodium phosphate as a detergent is due to its high pH value in solution, its ability to lower interfacial tension against oils or solids, and its marked power of emulsifying oils. Trisodium phosphate is used as a detergent in households, laundries, factories, hotels, dairies, and garages. It is used as a water softener and boiler compound because of its ability to precipitate calcium and magnesium phosphates. It has many other miscellaneous uses.

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THE tertiary sodium salt of phosphoric acid finds use in industry because of various applications of two properties. The salt in water hydrolyzes to give a solution of reasonably high pH value, well buffered at that level against neutralization. This pH value is higher than that of soda ash and modified soda, the principal competitive alkalies. The salt forms insoluble phosphates under conditions which permit its use for removal of heavy metal ions from solution.

The manufacture of trisodium phosphate is essentially the neutralization of phosphoric acid and subsequent crystallization. For economic reasons it is desirable to neutralize in two stages as follows:

$$Na_2CO_3 + H_3PO_4 = Na_2HPO_4 + H_2O + CO_2$$
$$Na_2HPO_4 + NaOH = Na_3PO_4 + H_2O$$

The phosphoric acid may be of variable purity and concentration. The process described in this paper is one used with electric furnace acid by the Swann Chemical Company. An outstanding feature of the process is the absence of concentration or evaporation steps. With some modification it is applicable to acid made by the Dorr process.

MANUFACTURE

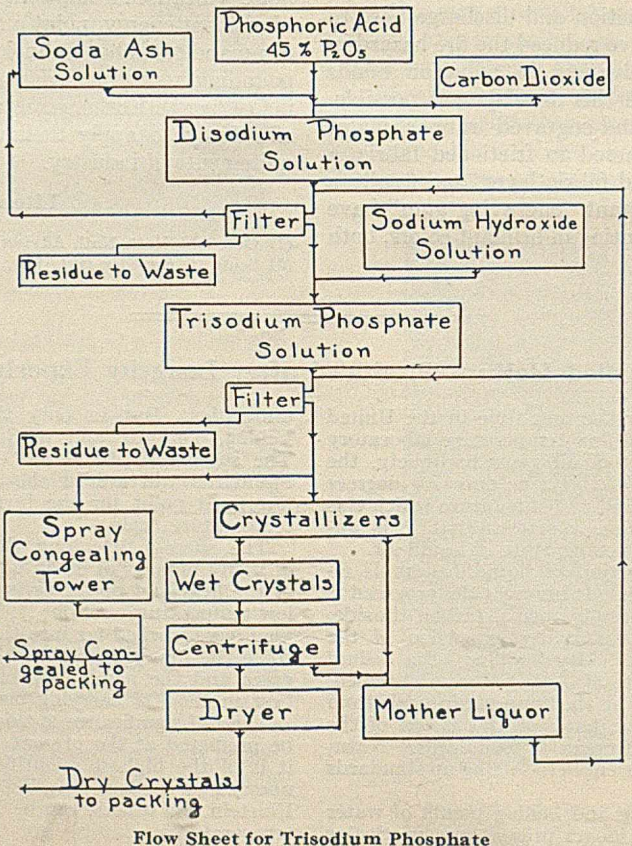
Production of Disodium Phosphate Liquor

In a 4000-gallon tank (right, Figure 1) equipped with an agitator, 7000 pounds of 58 per cent soda ash are suspended in 900 gallons of hot liquid. This liquid may be water, but is more commonly wash liquor from filtration of previous batches of disodium phosphate or mother liquor from disodium phosphate manufacture. Phosphoric acid containing approximately 45 per cent P_2O_5 is added at the surface of the tank so that the carbon dioxide evolved can be more readily liberated. As the neutralization proceeds, steam is used for heating the batch to boiling. Slightly more phosphoric acid is added than that required to convert all the soda ash to disodium phosphate. The solution is then boiled until all the carbon dioxide has been eliminated. Since the pH level at which the third hydrogen of phosphoric acid is neutralized is higher than that at which the second hydrogen of carbonic acid is converted to form sodium carbonate, it is not to be expected that phosphoric acid can be neutralized further than to the disodium stage with sodium carbonate. Plant experience confirms this since, if just sufficient phosphoric acid is added theoretically to convert all the soda ash to disodium phosphate, some remains unconverted in the mix.

The practically complete elimination of carbon dioxide by boiling is insured by laboratory control. At suitable intervals the batch is sampled. One portion of the sample is further boiled in the laboratory; another is not. Both are then titrated. Agreement shows complete removal of carbon dioxide in the plant.

By addition of mother liquor from a previous crystallization of trisodium phosphate the specific gravity of the mix is suitably lowered. This gives a solution of disodium phosphate, the excess alkalinity of the trisodium phosphate crystallizing liquor having neutralized any deficiency in the batch below the disodium phosphate stage. This solution of disodium phosphate carries in suspension any solid impurities from the phosphoric acid, as well as iron, aluminum, and calcium which were in the phosphoric acid and soda ash solutions.

The diluted disodium phosphate solution is filtered through a deeply recessed plate-and-frame filter press (left, Figure 1) and the filtrate pumped directly to storage tanks. This filtration is carried out at 85–100° C. The



Flow Sheet for Trisodium Phosphate

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[1] Received December 9, 1930.

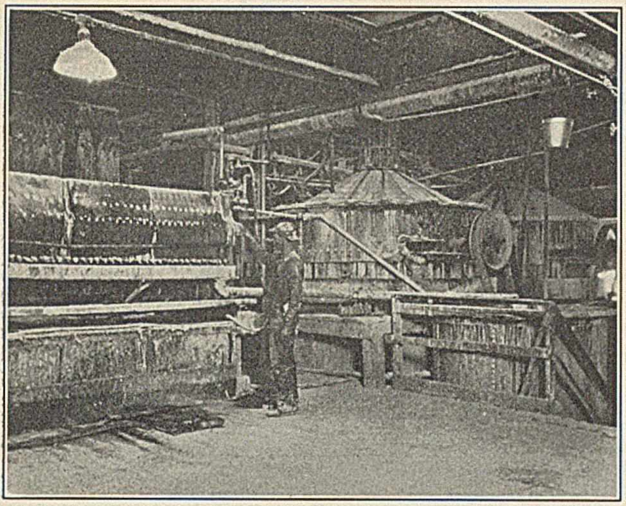

Figure 1—Tanks and Filter Press Used in Manufacture of Disodium Phosphate

Figure 2—Caustic Pots

resulting clear solution of disodium phosphate contains 14.5 per cent P_2O_5 and 13 per cent Na_2O. The press cake is washed with water and the dilute disodium phosphate solution so obtained used as make-up water for the first stage of the process. The cake from the press is waste.

Conversion to Trisodium Phosphate

In order to convert disodium phosphate to trisodium phosphate it is necessary to use sodium hydroxide. For this causticizing operation 1500 gallons of disodium phosphate solution are pumped into a 4000-gallon iron tank. To this are added approximately 2800 pounds of sodium hydroxide in 300 gallons of water at 90° C. (Figure 2). An additional 1000-gallon quantity of disodium phosphate solution is then added. The evolution of heat by reaction of disodium phosphate and sodium hydroxide necessitates venting these tanks through the roof of the building to carry off caustic spray. The boiling point of this liquor is about 112° C.

As a control on the solution a sample is titrated to phenolphthalein and methyl orange end points. At this stage an excess of sodium hydroxide over that for exact neutralization is desirable. The ratio of the reading using phenolphthalein to the total reading should lie between 0.51 and 0.54.

The solution of trisodium phosphate is next diluted with mother liquor from the crystallizers to a specific gravity of 1.34–1.40 at 90° C. At that stage it contains 10.5 per cent P_2O_5 and 15 per cent Na_2O. It is then filtered through a press which is efficiently heat-lagged. This filtration removes any precipitate introduced with the sodium hydroxide. The trisodium phosphate solution must be kept hot through this operation or it will freeze in the press.

Crystallization

The trisodium phosphate solution is then pumped to a common feed tank, where the temperature is adjusted to produce uniform crystals in the crystallizing units. The solution goes to the crystallizers through steam-jacketed pipes at an average temperature of 70° C. with a ratio of phenolphthalein to methyl orange end points of 0.527. By analysis it shows 9.25 per cent P_2O_5 and 13.2 per cent Na_2O. The crystallizers are of the Swenson-Walker type (Figure 3), water-cooled, and are installed in banks of three, each 24 feet long. Four such banks in parallel produce 175,000 pounds of trisodium phosphate per 24 hours. The liquor is fed to the crystallizers through a visible-feed Wier box at the head of the machine to give volume control. In the crystallizers the temperature is reduced from 60° C. to 30° C. at a uniform rate.

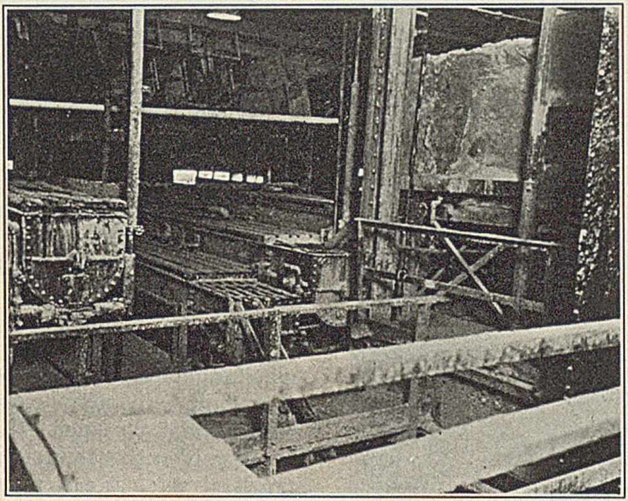

Figure 3—Swenson-Walker Crystallizer

The crystals discharge to a separating pan and are dried in a centrifuge (Figure 4). The discharge liquor at 30° C. has a specific gravity of 1.235 and contains 5 per cent P_2O_5 and 7.1 per cent Na_2O. In the crystallizers 70 per cent of the trisodium phosphate has been separated as crystals and only 30 per cent left in the mother liquor. This liquor is stored in a submerged sump for use in subsequent batches.

The crystals pass from the centrifuge to a rotary drier (Figure 5). Warm crystals from the drier pass into a rotary cooler and thence to a screen (Figure 6), where they are screened and distributed to storage bins in four sizes—coarse, medium, fine, and powdered. When screened the crystals have cooled nearly to room temperature. After screening they are aged 3 or 4 days by storage in piles.

The product then goes to packing and is placed in 125-pound kegs, 200-pound bags, or 325-pound barrels.

Spray-Congealing

A spray-congealed grade is also produced. The clear, filtered solution of trisodium phosphate is adjusted to a concentration approximating $Na_3PO_4.12H_2O$, which will congeal to a solid at room temperature. This liquid trisodium phosphate is pumped into the top of a spray chamber. A motor-driven atomizer discharges it and during a free fall of 70 feet the liquid particles assume a spherical form and congeal. Various sizes are produced by variation of temperature and concentration of the liquid. The product collected on conveyor belts is screened to give a close classification as to size.

This globular form sells without premium as a competitive grade for the package-goods trade.

Physical Properties

As with all crystalline products, one problem is that of caking. In general, coarse crystals are produced because the caking tendencies are less. Government specifications require that at least 50 per cent of the product pass 10 mesh and be retained on 100 mesh (*5*).

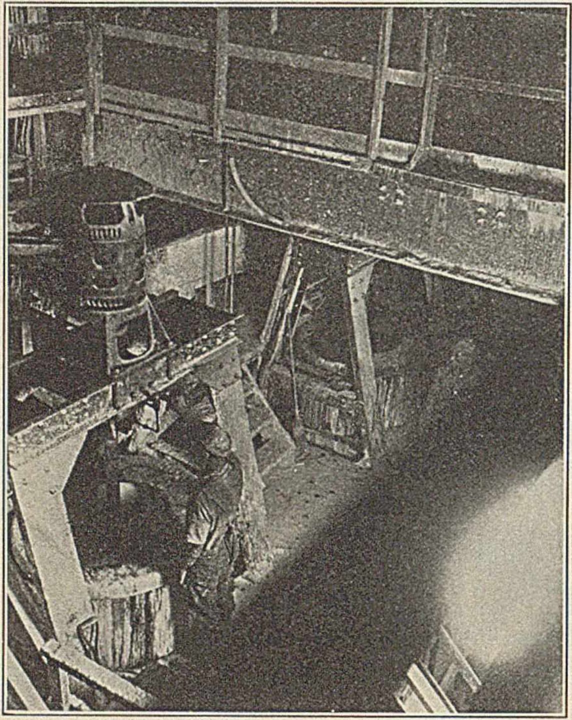

Figure 4—Centrifugal Drier for Trisodium Phosphate Crystals

The introduction of other salts to form double salts with trisodium phosphate tends to reduce this caking. At least one manufacturer's product contains sodium fluoride for that purpose. Other double salts with sodium chloride, sodium borate, sodium hypochlorite, etc., have been produced, a typical one having approximately the formula $5(Na_3PO_4,12H_2O)$, NaCl (*1*). As might be predicted, the electrometric titration curve of this saline trisodium phosphate falls uniformly below that of normal trisodium phosphate.

It is highly desirable that the crystals have sharp, even surfaces. Caking can be predicted when crystal surfaces are rough and uneven. Moisture absorption by trisodium phosphate does not start at room temperature until the relative humidity is 60 to 65 per cent. At 100 per cent relative humidity it is rapid, but in all cases is lower than with anhydrous sodium carbonate.

Another method of obtaining desirable physical properties has been to spray-congeal the product. This gives a smooth, globular product with few points of contact, which is correspondingly free-flowing. An offsetting disadvantage is that a lower ratio of surface to mass causes it to dissolve in water more slowly than the crystalline form.

Production and Consumption

The most recent production figures available are given in Table I.

Table I—Production Figures for Trisodium Phosphate

Year	Production	Value	Average Value per Ton
	Tons		
1927	63,531	$4,524,595	$71
1929	82,045	5,008,815	61

A decline in average value in a period of generally advancing prices is indicated. The distribution of consumption in 1927 is shown in Table II.

Table II—Consumption of Trisodium Phosphate in 1927

	Pounds	*% of Total*
New England	3,411,339	3.11
Middle Atlantic	34,253,088	31.21
East North Central	37,475,365	34.11
West North Central	11,336,824	10.32
South Atlantic and East South Central	10,712,654	9.75
West South Central	464,890	0.42
Mountain	8,829,578	8.04
Pacific	3,349,751	3.04
Total	109,833,489	100.00

Imports in 1926 totaled only 664 tons as compared with exports of 1000 tons, mainly to Canada.

USES

Detergents

A material may be valuable as a detergent if it possesses one or more of the following properties: high pH value, well buffered in fairly dilute solution; marked lowering of interfacial tension against oils and solids; marked emulsifying power.

The relative pH values of solutions of several common alkaline detergents are given in Table III. It is evident that a higher pH value may be obtained with a reasonable amount of trisodium phosphate than with any detergent available to the public other than sodium hydroxide. The comparative practical value is not so clearly shown in terms of pH, a logarithmic function, as in terms of C_{OH}.

Table III—Comparative pH and C_{OH} Values of Alkaline Detergents

Detergent	0.033% Solution		0.66% Solution	
	pH	C_{OH}	pH	C_{OH}
Sodium hydroxide	11.85	0.0071	12.90	0.0794
Trisodium phosphate	10.80	0.0006	11.45	0.0028
Sodium carbonate	10.65	0.0005	11.20	0.0016
Sodium oleate	10.20	0.0002	10.20	0.0002
Modified soda	10.00	0.0001	10.00	0.0001

As a detergent the concentration used in practice does not ordinarily exceed 1 per cent, a common figure being 1 ounce per gallon of water.

The lowering of interfacial tension against oils or solids by trisodium phosphate is not marked as compared with other detergent alkalies. It is not sufficiently poorer, however, to react against its use.

For the emulsification of oils it has repeatedly been stated that trisodium phosphate has remarkable properties. Experimental work to be published in detail later has shown that it approaches in emulsifying power the properties of a colloidal emulsifying agent. No satisfactory explanation of this emulsifying power is available.

Trisodium phosphate has almost entirely displaced borax as a household detergent and is definitely displacing sodium carbonate for that purpose. It is probably impossible to estimate the number of manufacturers of household detergent products having trisodium phosphate as a base. One large manufacturer packs it without admixture and advertises on a national scale. Another product sold similarly differs only in the addition of a fraction of a per cent of perborate. Others are admixtures in almost any imaginable proportion with high and low titer soaps, soda ash, and even with modified soda. It is used in dish washing for everything from the finest glassware and silver to greasy or burnt pots and pans. In the proper concentration it is useful for cleaning painted woodwork or walls, furniture, marble, tile, cement, linoleum, rubber, wood floors, and shelving. When used in cleaning woodwork it removes the oil film which gives the polished effect. The wood must therefore be given an oil polish after cleaning.

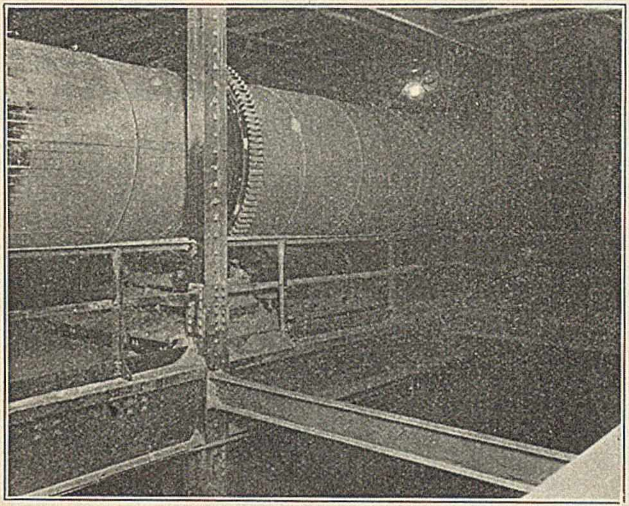

Figure 5—Jacketed Trisodium Phosphate Drier

As a laundry soap builder the use of trisodium phosphate has been limited by its price. For this purpose the total alkalinity available is utilized to a much greater extent than in most uses of alkaline salts. The amount of trisodium phosphate required is therefore relatively high. Despite that fact at least two widely distributed soap builders are composed largely of trisodium phosphate. It has also been recommended for fine laundering in the home.

It is sold directly in large quantities for use in factories to remove oil and grease and other stains both from clothing and from machinery. One peculiar detergent use of trisodium phosphate is in the laundering of greasy overalls. The basis of its unusual efficiency is believed to be the fact that calcium soap is often used for bodying grease. The calcium soap reacts with trisodium phosphate to form calcium phosphate and sodium soap and the latter then acts as a detergent.

A large use is in institutions such as hotels and restaurants where an antiseptic cleaner is necessary. Trisodium phosphate is superior to soap for antiseptic cleaning because it thoroughly removes grease whereas soap often leaves a film in which bacteria may grow. The cleaning of milk tanks, pipe lines, pasteurizers, etc., with soap tends to leave a deposit containing traces of milk. This antiseptic property of trisodium phosphate is especially important in such places where the presence of bacteria must be eliminated (*10*). For germicidal purposes neither the pH nor the concentration of the alkaline salt alone is the determining factor (*7*, *8*, *9*).

The cleaning of metals, particularly prior to electroplating, furnishes an important market. Any film of grease or fatty acids is distinctly objectionable in this work. Unlike household and laundry detergency, the use of sodium hydroxide is not necessarily objectionable. In this field, nevertheless, trisodium phosphate has found extensive use. It is sold either alone or admixed with caustic soda, soda ash, and soaps.

As a cleaner in garages it is used on metal work and running gear. It is often recommended for use on car bodies, but such use is not advisable. A nationally distributed radiator cleaner is perfumed trisodium phosphate.

The effect of trisodium phosphate on the hands is one limitation on its detergent use. To some it is non-objectionable, while others find that it is harmful to the skin. Comparative tests by measurement of the rate of hydrolysis of standard hide powder do not indicate that its effect is much more serious than that of other household alkalies and, as would be expected, its action is not at all comparable to that of sodium hydroxide.

Many users of detergents lack confidence in trisodium phosphate because it produces no suds. That probably hinders its sale, particularly for household use, more than any limitation in the efficiency of the product.

Water Softeners and Boiler Compounds

The hardness of water varies throughout the United States, so that requirements for water softening are widely different in different parts of the country. In general water is soft around the margin of the country and becomes increasingly harder as one goes inland. This hardness is due mainly to calcium and magnesium carbonates and sulfates which form insoluble compounds on reaction with soap. Chemical water softeners react to precipitate these so that the full value of the soap may be utilized. The efficiency of alkaline phosphates in precipitating calcium and magnesium phosphates is high.

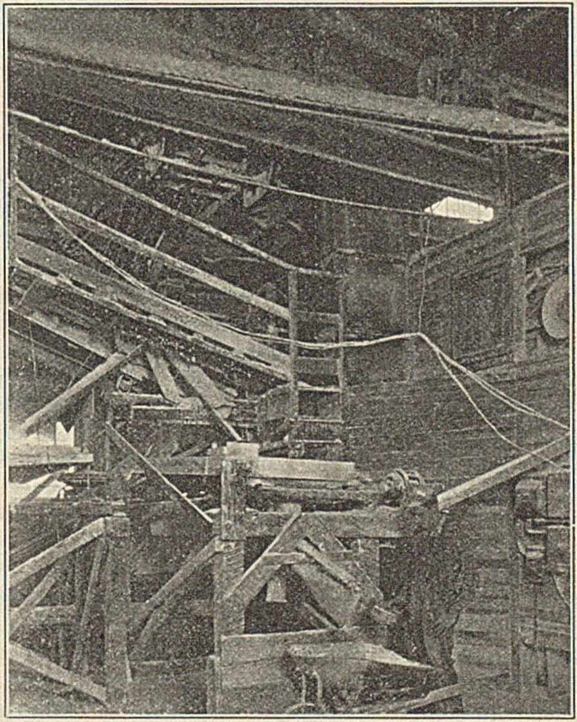

Figure 6—Screening and Classification

In practice it is desirable to use a mixture of phosphate and carbonate to get the maximum precipitation of calcium, magnesium, and iron salts. If sodium carbonate is used alone in a boiler operating at high pressures, an objectionable concentration of sodium hydroxide may be built up (*11*).

The amount of trisodium phosphate required to soften 1000 gallons of any water may be estimated by multiplying the number of parts per million of calcium carbonate hardness by 0.021, except that a minimum of 4 pounds is usually specified. One company furnishes a test solution, phenolphthalein, to be sure that sufficient trisodium phosphate is present to maintain the alkalinity above pH 8.0.

The use of trisodium phosphate as a boiler compound is closely related to its use as a water softener. Its function in boiler-water treatment is to precipitate salts which cause scale formation. The conditions to be overcome in a boiler are scale formation, corrosion, and foaming. Trisodium phosphate will have no effect in preventing foaming or corrosion, but properly used in a boiler compound will prevent scale formation. Where this problem is the only one to be met, treatment with trisodium phosphate may be sufficient.

Either as a water softener or in boiler compounds trisodium phosphate is effective, but its use is justified only when intelligently prescribed. It is no more a wonder worker than are other materials similarly recommended.

Miscellaneous Uses

As a paint remover, trisodium phosphate is used at about 1 pound to the gallon, in contrast with the use of 1 ounce per gallon in cleaning. So applied it softens the paint readily so that it can be removed with a scraper. It does not raise the grain as caustic soda would. A closely related package-goods business is its sale as paint-brush cleaner.

Another use of large crystals of trisodium phosphate is as bath salts, although it is probably used less for this purpose than sodium chloride and sal soda.

Trisodium phosphate is recommended as a cleaner for the face and hands and as a shampoo, although the justification for these uses is subject to question.

Other uses include soaking of hides, stripping of color from leather, clarification of sugar, and photographic applications. It is used to inhibit corrosion of steel (*4*). It has been used for control of pH during perborate bleaching (*6*). When added to chlorine bleach liquor, it increases its efficiency as an ink eradicator against an iron tannate ink (*2*). Added to loaf cheeses it is an alternate for trisodium citrate, serves as an emulsifying agent, and does not give such a salty taste to the cheese (*3*).

The claims for its virtues are so broad and numerous that one manufacturer states, "Trisodium phosphate is the universal cleaner."

An enterprising advertiser offers a formula for a marvelous cleaner which will sell itself. The information available on payment of five dollars is a list of manufacturers of trisodium phosphate. Perhaps this is the last word in using trisodium phosphate to "clean up."

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Cheaper Power for the Chemical Industry[1]

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THE chemical industry probably uses as much steam and electricity per ton of finished product as any industry in this country. Many of the manufacturing units are small and widely scattered geographically, but others are very large owing either to their own natural growth or the amalgamation of a number of smaller ones. In any case the expense of production reflects the cost of the steam and electric services required. In the smaller and less modern establishments the steam necessary for process is generated locally in part of the manufacturing plant and the electricity needed for driving the machinery is purchased from the public utility serving that section.

The costs of both these services are doubtlessly much higher than they might be under more favorable circumstances. The boiler plant which makes the steam is probably of such poor efficiency that were it actually known the plant would be immediately and thoroughly renovated and modernized. Owing to the characteristics of the electric load, the monthly power bills are much higher than they should be. All of which is directly attributable to the fact that the methods of manufacture of the product and the machinery required have been foremost in the mind of the management and have received greater attention in the effort to decrease manufacturing costs to meet the keen competition of rival concerns.

The United States, if not the entire world, is in the midst of an era of falling commodity prices. The downward trend will probably continue for another decade, maybe longer, provided world peace obtains. Upon the return of commerce and industry to normal volumes, the world consumption of goods will probably increase in proportion to the growth of population, with no abnormal ratio of demand to supply. Hence, in general, the price one obtains for one's product is likely to be less in the future than it has been in the past. Those manufacturers that were hard-pressed to show a profit heretofore will be facing a deficit unless production costs are rigorously pared by using only the most modern facilities in their establishments. With this thought in mind there will be outlined some of the methods used by leading chemical plants to effect savings by changing the method of developing steam and electric services.

Efficient Steam and Electric Energy in Chemical Plant

Ten years or so ago a concern making a well-known and widely distributed commercial fertilizer built a chemical plant along conservative lines, but owing to the success of their particular brand additional plant facilities were repeatedly needed. Over two years ago the establishment found itself greatly handicapped in meeting price competition by expensive steam costs to which had to be added the power company's charge for electrical energy. Steam was being generated at 120 to 130 pounds in a number of small boiler units, none of which was modern and efficient or suitable for the increasing demands of the manufacturing departments. At this pressure it was delivered to the autoclaves used for digesting the chemical fertilizer and at lower pressures to other manufacturing processes. At the same time electricity

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[1] Received January 24, 1931.

[2] Mechanical engineer.

was needed throughout the plant for the mechanical operations of conveying, agitating, etc.

The management, with keen appreciation of the advantages of high-pressure steam and the possibilities of by-product power generation, besought the advice and assistance of experienced power-plant engineers. An analysis of the manufacturing processes indicated that the autoclaves could profitably use steam at a pressure of 250 pounds. Other processes needed steam at 125 pounds and still others at as low as 40 pounds. The annual quantities of steam required at each pressure were determined, as was also the yearly electrical power consumption. From these data were computed the hourly quantities for the expected future rate of production.

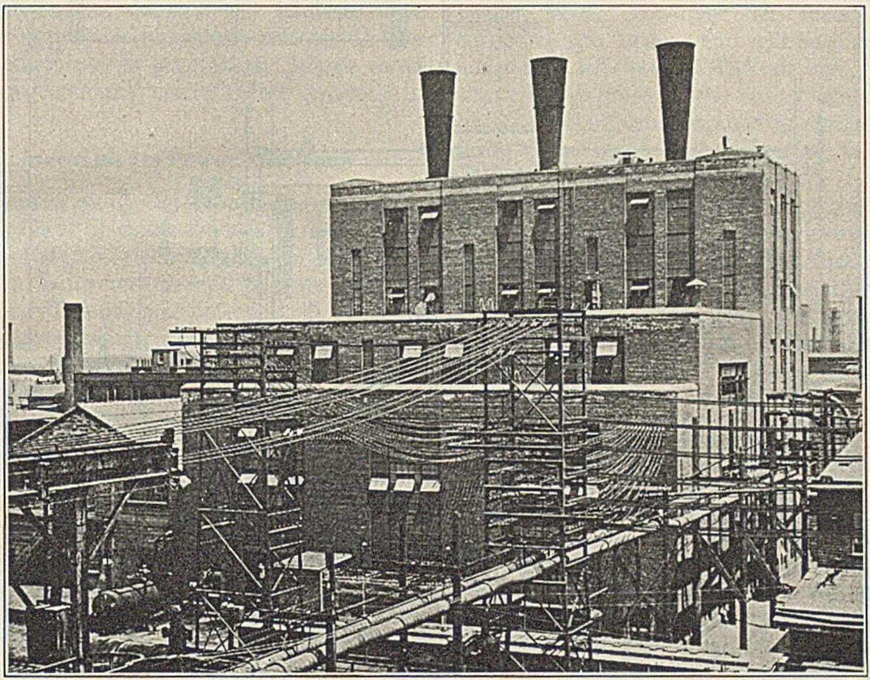

Figure 1—Electric and Steam Lines Supplying Energy from a Modern Power Plant

A study of the commercial steam turbines available on the market revealed that all the electrical energy required could be generated at the plant if the boilers were designed for 250 pounds pressure. At the same time it was found that the turbines could be so built that the desired quantities of 40- and 125-pound steam might be drawn off from their casings and delivered to process without interfering with the required electrical output. There were purchased then three boilers designed to develop a total of 260,000 pounds of steam per hour at 250 pounds pressure and two 3000-kilowatt turbine generators. One boiler and one turbine were considered as spare equipment to provide for normal outages of the regular units and future growth of the demand for service.

Owing to its location on tidewater, bunker oil delivered by barge presented the most economical fuel at the existing prices. As a provision against the loss of the price advantage of oil, the plant and boiler units were designed for a quick change-over to pulverized coal. More than 75 per cent of the steam output of the boilers is delivered to process and represents a loss from the power plant's water system, which has to be replaced. Water is purchased from two local water companies, softened by the zeolite process, and thoroughly de-aerated in a closed heater to remove all dissolved oxygen.

To conserve heat and secure maximum efficiency from the boilers, two devices are employed. De-aeration of all the boiler feed water requires it to be heated theoretically to 212° F.; actually it is necessary to carry the temperature around 218–220° F. The heat in the exhaust steam from the boiler-feed-pump turbines is used for this purpose, any deficiency being made up by steam from the 40-pound extraction point on the turbine in service and reduced in pressure by passing through a valve. The de-aerated water is then further heated in the 40- and 125-pound heaters. The latter are the conventional tubular heat exchangers and take the steam they require for the respective extraction points on the turbines. Thus, water is fed the boilers at 345° F., while the saturated temperature for 250-pound steam pressure is 406° F. This recirculation of heat, taken out of the boiler in the steam it produces, passed through part of the turbine to transform some of its energy into electricity, and returned to the boiler in the feed water, is known as the regenerative cycle. It is generally an effective means of saving fuel.

Since the water is fed the boilers at such a high temperature to secure greater thermal efficiency in the turbine room, there is no opportunity to add economizers to the boiler units to lower the temperatures of the exit gas. For this purpose the designers used air heaters, another form of heat exchanger wherein the gases resulting from combustion give up part of their sensible heat to raise the temperature of the air required for combustion of the fuel. When it is recalled that each pound of fuel requires about 16 pounds of air and 17 pounds of gases are produced, some conception may be gained of the mass flows obtaining and the quantity of heat units recirculated within the boiler units themselves.

Through the combined use of the regenerative cycle and preheated air, it was calculated that about a 9 per cent saving in fuel was effected at the annual output of steam and electricity for which the plant was designed. Like economy may be secured at other plants in a similar manner.

As to the operation of the power house in conjunction with the manufacturing plant, the use of 250-pound steam in the battery of autoclaves cuts down the time cycle required for digesting. Steam at both 40 and 125 pounds is extracted from the turbines, after performing some useful work in generating electrical energy, and delivered through the piping system to the various departments. Electricity is distributed over a number of feeders at the generator voltage to all points on the property. Any two of the three boilers will supply all the steam required up to the maximum output for which they are designed, but not much more because the maximum is already pretty high. The turbine generators, however, have carried continuously more than 3500 kilowatts each. Apparently the manufacturer designed them with ample margin of capacity.

This chemical manufacturing establishment has at its disposal a power plant designed precisely like a public utility's central station, with the same inherent high degree of economy of operation and reliability for continuity of service. In fact, the power-plant services are less likely to be interrupted through outages of its machinery than are the manufacturing departments by reason of the failure of the process

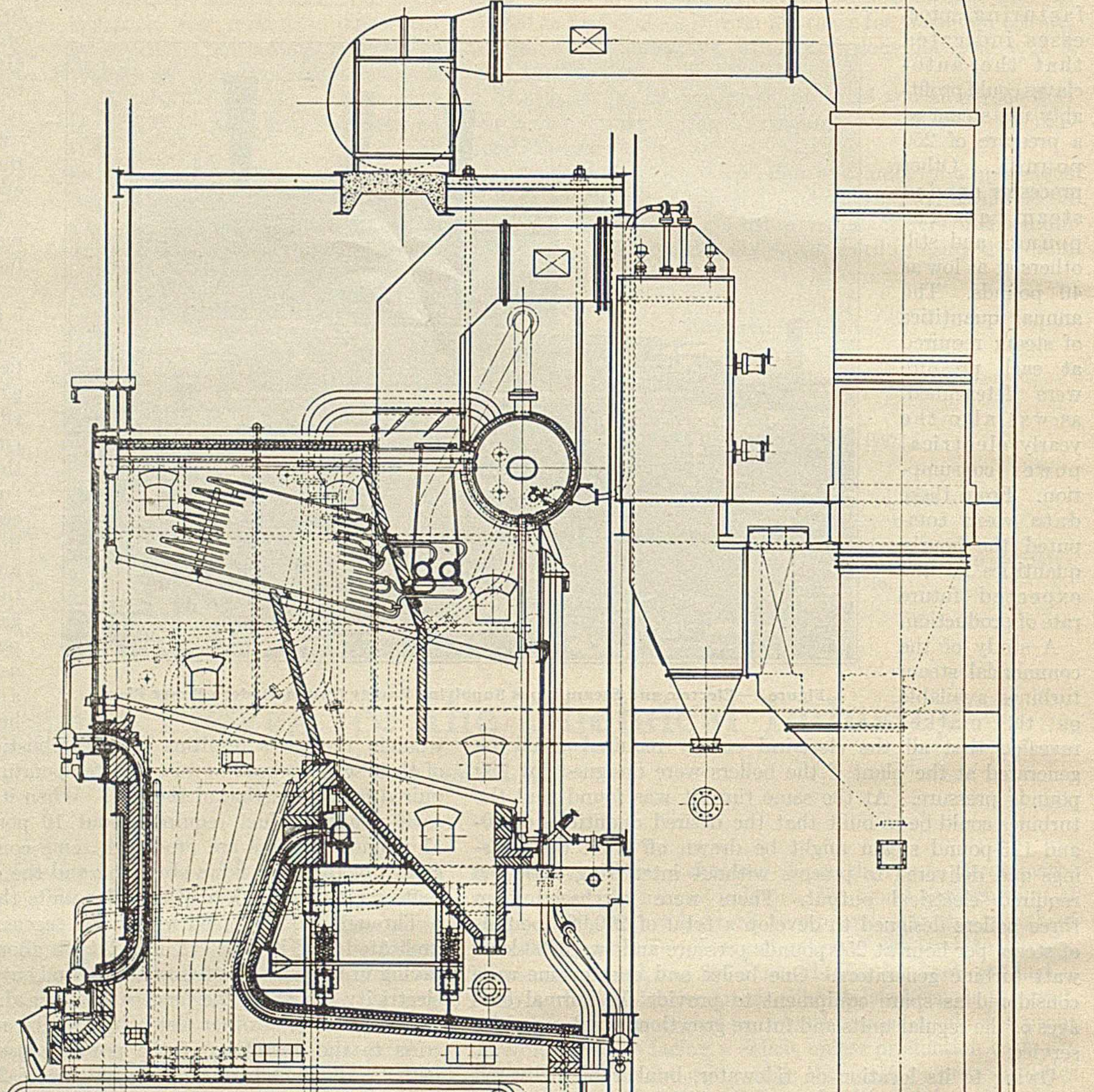

Figure 2—Sectional Side Elevation of Boiler Unit in Dyestuffs Plant

equipment. The use of an automatic combustion-control system coördinates fuel and water feed to the boilers with the steam demand. Changes in the electrical load are taken care of automatically. Thus the human factor is eliminated as much as possible to avoid errors and decrease the expense of operating personnel.

The power plant is now supplying the manufacturing departments with services costing about 20 per cent less than formerly. The saving is practically entirely due to modern equipment and by-product power generation, though some is attributable to more economic use of these services in process work.

Dyestuffs Plant Increases Its Power Efficiency

Another establishment making intermediates, dyestuffs, and finished chemicals found it difficult to carry the winter load, with its increase of steam for heating and of electricity for lighting, in addition to its normal load of these services for manufacturing only. The original power plant was well laid out, but its burden became greater than it could carry. The boilers were fired with buckwheat No. 3 anthracite from overhead bunkers through a traveling weigh hopper and scale upon hand-operated stokers. This method required a fireman for each of the four boilers, who had to work hard to keep up steam under heavy loads in barring the fires and shaking the grates. The two turbine generators, each of 300 kilowatt capacity, were carrying full load and the remaining power requirements were purchased from a public utility.

After an analysis of the situation, the engineers retained determined that an addition could be built to the existing power-plant building to house a large high-pressure boiler unit and a turbine generator could be set in an available space in the turbine room. Thus, the cost of the new structure required for modern equipment was minimized.

Similar analysis of the load indicated that the boiler unit should develop a maximum of 100,000 pounds of steam per hour, while at least 1500 kilowatts of electrical capacity would make some provision for future growth. An examination of manufacturing requirements revealed that steam was used at 125 and 400 pounds pressure for process work. It was then decided to purchase a boiler of the 400-pound class with a superheater to give steam at a total temperature of 725° F. and a high-back-pressure turbine generator taking steam of the above characteristics at the throttle end and exhausting at 125 pounds pressure while developing up to 1500 kilowatts at full load. The boiler purchased is actually good for 488 pounds working steam pressure, as it was found that a boiler built for this pressure costs but little more than one for 400 pounds.

As the buckwheat size of anthracite had been successfully used as fuel by this plant for many years and it had a certain price advantage over other available fuels, it was decided to continue its use and equip the boiler unit with a mechanically driven stoker especially designed to burn it economically at high combustion rates. The stoker selected permitted the use of preheated air delivered under forced draft.

A sectional side elevation of the entire boiler unit is shown in Figure 2. Attention is directed particularly to all the latest features contributing to high efficiency. The front and rear arches are designed to assure the complete combustion of the fuel at minimum maintenance cost, being water-cooled tubes carrying refractory blocks. The side walls are similarly water-cooled, with bare tubes above the throat of the furnace to absorb the radiant heat of the fuel bed. The temperature of the waste gases of combustion is reduced to the lowest permissible point by passing them through both an economizer and air preheater, thus returning large quantities of heat to the boiler proper in the feedwater and the air required for combustion.

The forced draft under the stoker was expected to blow some of the smaller particles of fuel into the gases and they would be carried out the stack with resultant loss of combustible. To permit these small particles to drop out of the gases at convenient points, a hopper was built under the third pass of the boiler, another under the economizer, and a cinder catcher interposed between the latter and the preheater. The "blow-over" or "fines" thus captured are returned to the furnace and will account for about 1 per cent additional efficiency. The siftings of fine fuel dropping through the grate of the stoker are collected and, if found high in carbon, are disposed of similarly. The heating surfaces of the boiler and economizer are kept clean by hand-operated steam soot blowers.

The efficiency of such a compact boiler unit is unquestioned. Every known device has been incorporated in it to utilize the available heat in the fuel fired. The ash discharged at the rear end of the stoker is very low in combustibles. Daily operating efficiencies of 85 per cent are customary, with but a normal amount of work, care, and supervision.

The turbine generator is also a very efficient unit. Except for a small portion delivered to one of the manufacturing departments at 400 pounds pressure, the boiler steam is taken by the turbine and its pressure is reduced to 125 pounds while generating electrical energy. Thus the latter is a by-product of the process of supplying the manufacturing plant with 125-pound steam. If the demand for steam at this pressure is greater than the amount of the exhaust from the turbine because of the limitations imposed by the electrical load, any deficiency can be made up by passing steam directly from the boiler through an automatic reducing-pressure valve to the 125-pound system. This procedure does not make for better efficiency, but provides flexibility to meet load conditions. If the temperature of the lower pressure steam is too high for process purposes, it is decreased by desuperheaters.

It is evident from the foregoing that the boiler feed water is all make-up except for the exhaust steam from a couple of air compressors supplied from the 125-pound system and any drips that may be returned. The exhaust steam is condensed in a de-aerating heater and any deficiency of steam for de-aeration is made up by passing 125-pound steam through a reducing-pressure valve decreasing it to a pound or two. Although the use of the reducing valve does not add to the plant efficiency, it is an expedient to secure complete removal of all dissolved oxygen in the feed water and thus avoid internal corrosion of the boiler and economizer parts.

River water polluted by manufacturing wastes from establishments upstream is the source of the boiler feed. With an hourly demand of possibly 85,000 pounds of water, it was not considered practical or economical to install evaporators. The water is pumped quite a distance from the river to a large pond on the property. Alum is used for coagulation. Pressure filters remove the solid particles. Then the water is passed through zeolite softeners before being heated in the de-aerator. The operation of the water-treating and heating equipment is closely watched to prevent any lapses in the functioning of the system with possible disastrous results in the boiler and furnace water wall tubes.

Now as to results at this establishment. There is ample and sufficient steam at several pressures for all normal requirements in the manufacturing departments and for heating buildings in general. The maximum electrical load at present is about two-thirds of the capacity of the turbine generator. The older generators have been retained as stand-by units. The original boilers will be remodeled and furnaces modernized to provide for spare low-pressure steam capacity in the future as it may be required.

The new boiler unit has effected a 15 per cent reduction in the annual fuel costs. The non-condensing turbine generator is supplying electric energy at a fraction of the former costs, because it is developed as a by-product of the steam supply service and is very much cheaper than purchased power.

Conclusion

There have been described above the most modern facilities for the generation of steam and electric services possessed by two chemical manufacturing plants. They are ready now to meet any production schedule imposed by the management within their capacities. The cost of production per unit of finished product cannot but reflect the savings effected by making their own steam and electricity at the minimum expense. It is hoped other companies in the industry may find herein an incentive to do likewise and reap similar benefits.

California Desert Soda[1]

Plant of the Natural Soda Products Company at Keeler, Calif., on Owens Lake

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MANKIND, in quest of sodium carbonate, usually has to wrest it from common salt. California, preferring to be unusual, snatches hers from the desert. And there is plenty to be snatched. Folks in humid regions may thank Ernest Solvay for their soda; the golden state thanks Providence, freak geography, and a blazing sun.

About 200 miles north of Los Angeles, and far inland, lies the arid county of Inyo. This desolate area seems to have been a playground in past ages for extreme geological uprisings and earthly contortions. As a result, Inyo County boasts the highest eminence in the United States, Mt. Whitney, 14,500 feet above sea level; and the lowest and hottest hole in the United States, Death Valley, 300 feet below sea level.

When Nature twisted up Inyo County, she made several errors from the drainage engineer's standpoint, and left a few sinks without outlet to the sea. From the chemist's standpoint this was an excellent idea. A hundred million tons or more of sodium and potassium salts were trapped before they could escape to the ocean.

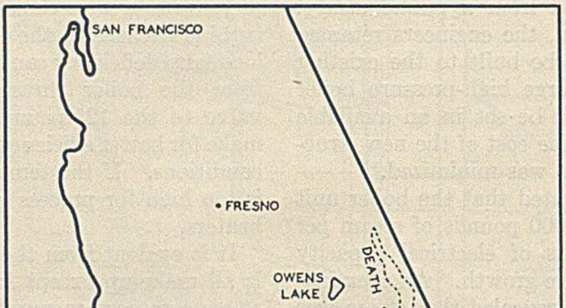

Figure 1

Desert Lakes

Owens Lake (Figure 1), almost at the foot of Mt. Whitney and 11,000 feet below that snowy peak, is the storehouse where sodium carbonate in particular was collected. To the south and east are Searles Lake and its great potash industry; Panamint Basin, unused; and finally Death Valley, once an important source of borax, now a tourist stamping ground during certain well-chosen months of the year.

Twenty years ago Owens Lake covered 100 square miles, and received a large part of its water supply from the east watershed of the high Sierra Nevada. More recently the city of Los Angeles, in need of water, diverted the Owens River into its famous Mulholland aqueduct. Owens Lake, robbed of a normal supply, shrank greatly, and deposited vast amounts of commercially valuable salts. In the burning inland desert, shut off completely from sea breezes by the towering barrier of the Sierra, the normal evaporation from a lake is about 4 feet annually, while the rainfall is but 2 inches. Quite obviously the lake lost the race.

Salt Accumulations

During the several thousand years in which Owens Lake received water without drainage to the outside, minerals predominating in sodium and potassium must have delivered an abnormally alkaline charge to the streams. Owens and Searles lakes, accordingly, are practically devoid of the alkaline earth metals common to salt seas. The sodium and potassium components, attracting carbon dioxide from the air, undoubtedly assisted in the elimination of calcium and magnesium ions from the streams which eventually were concentrated to form Owens Lake brine.

Rough estimates of recent date indicate possibly 35 million tons of sodium carbonate available in Owens Lake. This ought to take care even of industrial Los Angeles for quite a spell. There are perhaps 2 million tons of potential borax and 4 million tons of available potassium chloride. Or, if somebody can juggle the phase rule cleverly, let us say nearly 5 million tons of potassium sulfate, which is better yet. The borax-potash reserves only mildly interest the Owens Lake producers, since their rivals down at Searles Lake have a brine somewhat richer in the valued components. Sodium sulfate and chloride, totaling over 50 million tons, do not arouse even a ripple of commercial enthusiasm.

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[1] Received February 10, 1931.

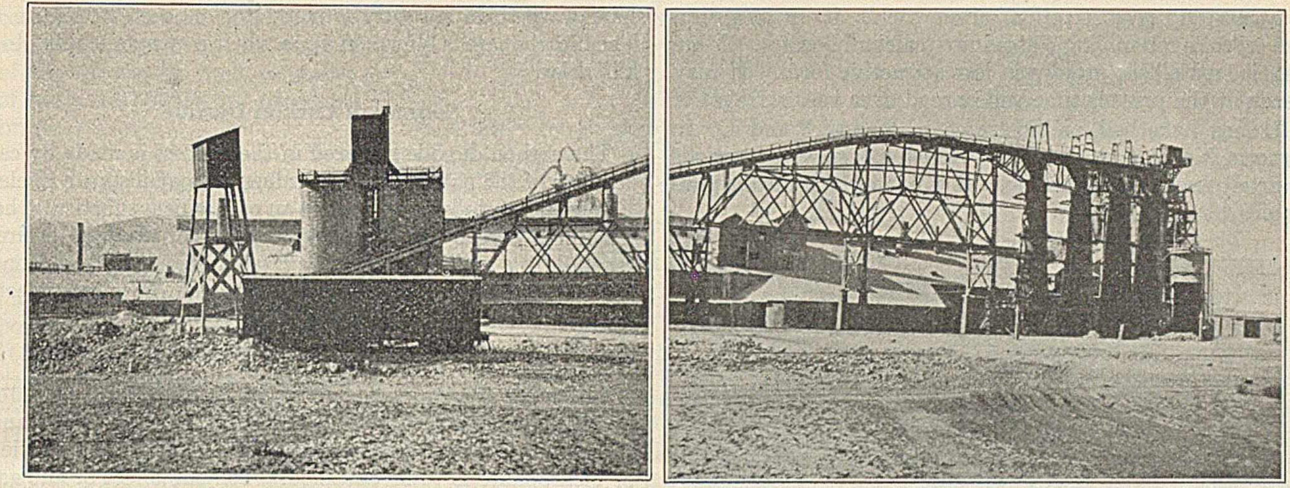

Figure 2—Plant of the Natural Soda Products Company, Showing Carbon Dioxide Kilns to the Right

These colossal tonnages lead to the estimate that Owens Lake is the second largest soda reserve in the world. First place seems to be conceded to the Magadi deposit of British East Africa.

Several corporations have leased rights on Owens Lake, and have developed plants of somewhat similar type, principally for the manufacture of soda ash and closely allied carbonate products. At least three of these plants are in active operation, and one, located at Keeler, Calif., on the northeast shore, has had a long term of successful development. The technic described herewith applies principally to the Keeler plant.

Life in the Desert

Keeler is a nice place to live if you like that kind of a climate. The mid-day temperature in July and August occasionally falls a trifle under 95° F. in the shade. Normally it varies between 100° and 110° F., with occasional spurts to 114° F. To be sure, the altitude is nearly 3700 feet, but that doesn't seem to do any good. The company physician says the climate is healthful, but when he gets a case of pneumonia he must get the patient out of the district promptly.

Life for the townspeople is somewhat drab and plain. If there is a tree, a rosebush, or a lawn in town, the writer confesses that he missed it. A few desert shrubs of sorry appearance hang on for dear life, proving that the region is not totally anhydrous. The magnificent Owens Valley highway not far to the west leads easily to the oranges and rose bushes. Accordingly, Keeler is said to have one of the highest ratings on concentration of automobiles in the United States.

Rain is just a rare nuisance to which nobody feels accustomed. The visitor notices a thousand tons of sodium bicarbonate stored out under the open sky. A board fence surrounds it, probably so that it will not blow away; but the scant rainfall does not warrant the expense of a roof.

Changes in Lake Brine

The extraction of sodium carbonate from Owens Lake brine, like that of potash from Searles Lake, is beset with complications due to the number of constituents present. Furthermore, the tactics of the Los Angeles water department have added still more to the complexity of things by causing changes both in concentration and relative proportion of the ionic constituents due to crystallization in the lake bed. Two analyses, one of April, 1918, the other of 1930, lead one to sympathize with the chief chemist in his desire to standardize his process:

	1918 *% by wt.*	1930 *% by wt.*
Na_2CO_3	4.16	9
$NaHCO_3$	0.88	1.2
$Na_2B_4O_7$	0.27	1
Na_2SO_4	1.76	3
NaCl	4.27	16
KCl	0.51	1.5

The 1930 column shows only rounded-off values, there being no uniformity in analyses taken from different parts of the lake, nor at different seasons from any one location. Moreover, the expression of composition as complete salts does not represent conditions strictly as they are. For example, pending a study of pH values, one might guess that the borate exists largely as metaborate ion, BO_2^-, rather than the tetraborate, $B_4O_7^{--}$. If such be true, one would then have to adjust the tabular values for carbonate and bicarbonate to suit.

In view of the fact that the plants are taking out carbonates from the lake and returning the undesired sulfate and chloride, one might wonder if the analytical changes from decade to decade might not be thus accounted for. Desert experts do not feel, however, that the industry has had an appreciable effect; rather the shifts in proportions have been due to irregular crystallization from more or less natural causes.

At Keeler both solid and solution are used as raw material. The solid is "trona," or native sodium sesquicarbonate, $Na_2CO_3.NaHCO_3.2H_2O$.

Ancient Soda

Trona, though little known in common technology, is by no means new in the chemical world. Probably the ancient "nitrum," "natrum," and "natron" soda preparations of early civilizations consisted largely of this substance. Such crude natural soda was known at Fezzan, Egypt, and in various locations in India, Persia, and Hindustan.

The word "trona" is but another of the various corruptions of the original word. After further vicissitudes of language, it has finally landed in the atomic weight table as "natrium" and is tagged "Na." To add to the rhetorical complication, the potash interests of Searles Lake have named their bustling little desert town "Trona." This is interesting in view of the fact that sodium carbonate is one of the principal things the potash people throw away in their process.

The Mineral Trona

Trona seems to be the solid phase which is produced naturally from many desert-lake brines upon solar evaporation.

Slow natural crystallization often yields it in beautiful large crystals resembling colemanite (calcium borate). More often it crystallizes rapidly in less attractive form. It may be seen at the present time widespread over vast acreages of the Owens Lake bed, as illustrated in Figures 3 and 4. In this form it resembles dirty snow which has survived periods of partial thaw and refreezing. It is not by any means pure sesquicarbonate.

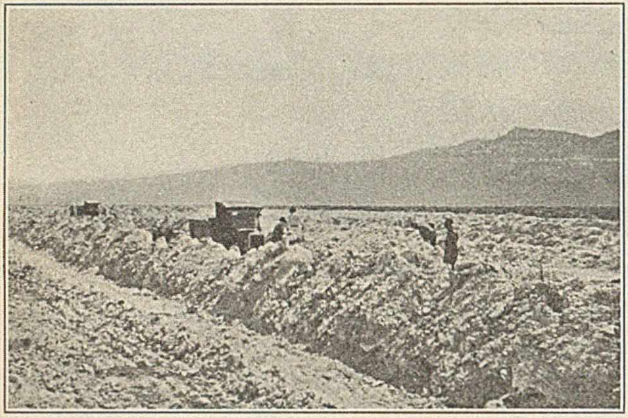

Figure 3—Shoveling Trona on Owens Lake

This material is calcined at Keeler, and then shows a variable purity value, ranging around 70 per cent. Hundreds of tons of the product are shipped monthly to the San Francisco industrial district, where it is converted into crude caustic soda. Apparently the economy in buying crude trona outweighs the advantage of higher purity available in the purified product, particularly where the ultimate product of caustic soda goes into the oil-refining trade.

Plant Operations

Both natural trona and brine are employed. First the lake brine is allowed to evaporate in solar ponds, or "vats," until its concentration attains a value favorable for blending with trona (Figure 5). The trona, which by this time has been shoveled up into windrows and hauled in with narrow-gage dump cars, is dissolved in fresh water to a suitable concentration, and is mixed with brine in proportions dictated by the season and temperature.

Although Keeler is torrid in July, it is frost-bitten in winter. It is thus frequently necessary to heat the brine before it runs the gauntlet of the plant. By the partial use of natural crystallized carbonate, the alkali content is run up high enough to render the isolation of bicarbonate efficient. On account of the scant water supply, it would hardly be feasible to attempt purification of the trona alone without recourse to the large supply of brine. Furthermore, the process of crystallization of bicarbonate is favored in the presence of foreign salts.

The obvious advantage gained by blending is found in a uniform brine composition for plant use. A standardized plant technic is thus attained. The dilution of the lake brine with the second component also reduces the silicate content, which is otherwise difficult to keep out of the final product.

A quantity of blended brine is kept on hand at all times in emergency storage, ready to enter the carbonation towers. These towers are merely very tall, open wooden tanks. Carbon dioxide bubbles through the brine until so large a fraction of carbonate ion has been converted into bicarbonate that further passage of gas is not rewarded with a corresponding value in precipitated product. Sodium bicarbonate is produced in its familiar form as a fine granular mass.

The thin sludge of bicarbonate in brine is filtered and the solid washed on a rotary Oliver filter, as seen in Figure 6. The bicarbonate is blown off upon a belt conveyer leading to a kiln drier.

Sources of Carbon Dioxide

The carbon dioxide required in the process is made by calcination of the native dolomite mined in the hills near Keeler. Flue gas, naturally suggested as an economical substitute, has too low a percentage of carbon dioxide to drive the desired reaction to a sufficient extent. Examination of the carbonation equilibrium shows a critical dependence upon gaseous concentration:

$$H_2O + CO_2 + CO_3^{--} \rightleftarrows 2HCO_3^-$$

Inasmuch as carbon dioxide is but slightly soluble in water, and perhaps less soluble in brine, it is of great importance to keep its concentration at maximum value if a high yield of bicarbonate is to be obtained. Ten cubic feet of flue gas, carrying about 10 per cent of carbon dioxide, would hardly replace 1 cubic foot of pure carbon dioxide. There is not entire agreement, however, among the rival producers in this matter.

The Keeler plant, therefore, continues to use dolomite. Thousands of tons of an equimolal mixture of CaO and MgO—or their weathered products—are piled up on the desert landscape. This material awaits somebody with a bright idea of what to do with it.

Carbonation Efficiency

Theoretically the plant needs no supply of carbon dioxide beyond the capital stock, as long as it markets carbonate rather than bicarbonate. The carbon dioxide which is absorbed in the bicarbonate intermediate is shortly expelled and returned to the start of the process again. Losses are inevitably serious, however, in the absorption and expulsion of so inert a reagent as carbon dioxide. In practice the plant during one cycle wastes about half of the gas which in theory would be the constant stock-in-trade of the process.

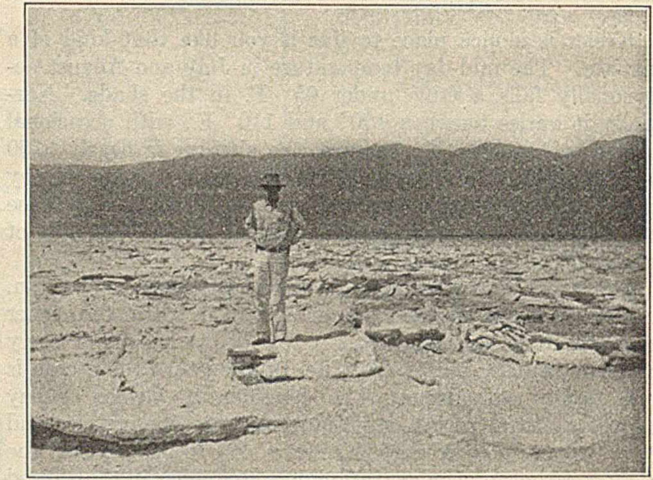

Figure 4—Natural Trona Bed, Ready to Harvest

Semi-Carbonation

Certain other experts in the desert soda industry, objecting to the excessive waste of carbon dioxide in the bicarbonate process, prefer Nature's method—viz., carbonation to the sesqui stage only—at high brine concentration and not too high temperature. Thus they are enabled to prepare artificial trona itself in the plant. Since the liquor is not heavily carbonated in this scheme, it is possible that flue gas would carry the reaction far enough, with obvious economy. This plan is not favored at Keeler, however, on account of the relatively high solubility of sesquicarbonate in processed brines.

Light Soda Ash

The sodium bicarbonate at Keeler is partially dried, care being taken not to expel any important amount of carbon dioxide. It is preferably stored in this form during times when production of soda ash would outrun shipments. The bicarbonate is now calcined in a large rotary kiln and the carbon dioxide recovered. The residue is "light soda ash," a product acceptable to some industries, and thus ready for shipment. Analysis of one of the Owens Lake commercial products gave the following typical analysis:

	%
Na_2CO_3	98.16
$NaHCO_3$	0.90
$Na_2B_4O_7$	0.33
$NaCl$	0.05
Na_2SO_4	0.33
SiO_2	0.25
Al, Fe oxides	0.02
$CaCO_3$	Trace
$MgCO_3$	Trace

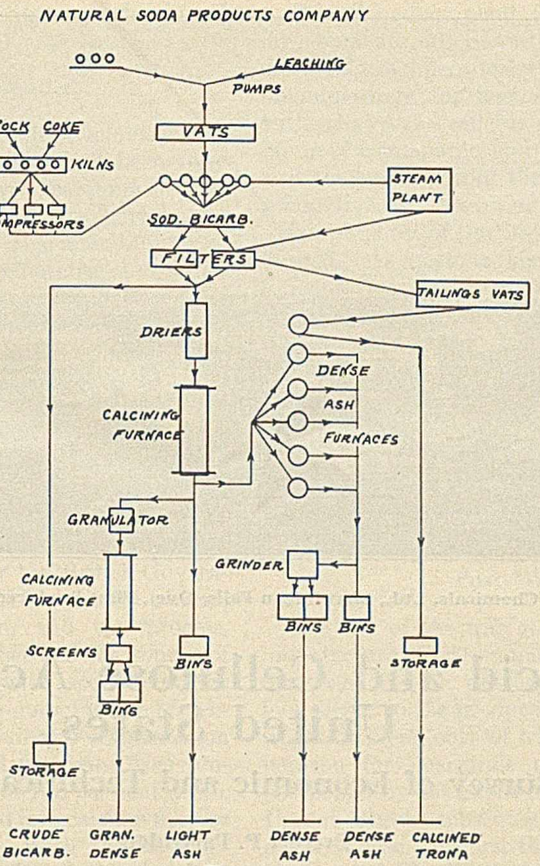

Figure 5

Since the desert soda does not figure in food or medicinal products, the above impurities raise no question. In fact, the borate content makes the desert ash just so much more valuable to the glass manufacturer, a principal consumer.

Dense Soda Ash

The expulsion of steam and carbon dioxide from the bicarbonate in the standard process leaves the alkali in a fluffy, dusty condition. It is of low density, not readily compressed, and objectionable to people who have to shovel and dump the product. These mechanical difficulties lead to the conversion of the Keeler product largely into a more condensed form, known as "globular dense ash." This novel product emerges in pellet form, suggestive of the finely granulated grade of quick-cooking tapioca.

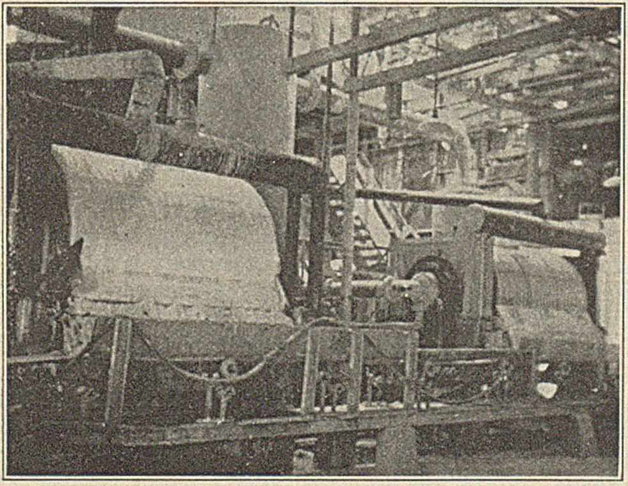

Figure 6—Oliver Filter Handling Sodium Bicarbonate

The light ash is melted at about 850° C., and the fused liquid poured in a small stream into a blast of compressed air. The atomized product is blown out from 10 to 20 feet in a room well lined with fire-proof material. An attendant stands on a balcony above this holocaust. He was asked what the place was like in summer, with the thermometer at 112° F. in the shade outside. The expected answer was obtained.

The globular sodium carbonate is ground, yielding a dense powder which is favored particularly in the glass industry. In fact, ground globular ash is the densest carbonate obtainable in the market.

Part of the soda ash is rendered dense by the water process, in the manner familiar in the East. The light soda ash is hydrated slightly, perhaps to the monohydrate. Calcination of the hydrated cake, with resultant expulsion of water vapor only, yields a somewhat granular ash that is popular with some consumers. The Keeler plant offers no less than ten grades of soda ash, differing principally in form or state of division.

Marketing Problems

Carbonate products from Owens Lake are consumed largely in the Los Angeles and San Francisco industrial districts. On account of the long, high barrier of the Sierra Nevada Mountains, it is necessary to haul the product down into southern California before there is access to the coastwise rail service to San Francisco. Fortunately there is a narrow-gage railway with terminus at Keeler, built long ago to serve mining interests of eastern California and Nevada. This connects with the newer broad-gage Southern Pacific line which was built in the Owens Valley to handle the aqueduct job.

The distribution of soda ash on the Pacific coast runs approximately on the following schedule:

	%
Glass industry	55
Soap	25
General chemical manufactures	10
Miscellaneous, including household	10

A detailed report on saline waters and deposits of the California deserts has been given by Gale (*1*). References to other papers are given more recently (*2*).

Acknowledgment

The writer wishes to thank David B. Scott and John E. Skelton for assistance in the preparation of this manuscript.

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(2) Robertson, Ind. Eng. Chem., **21**, 520 (1929).

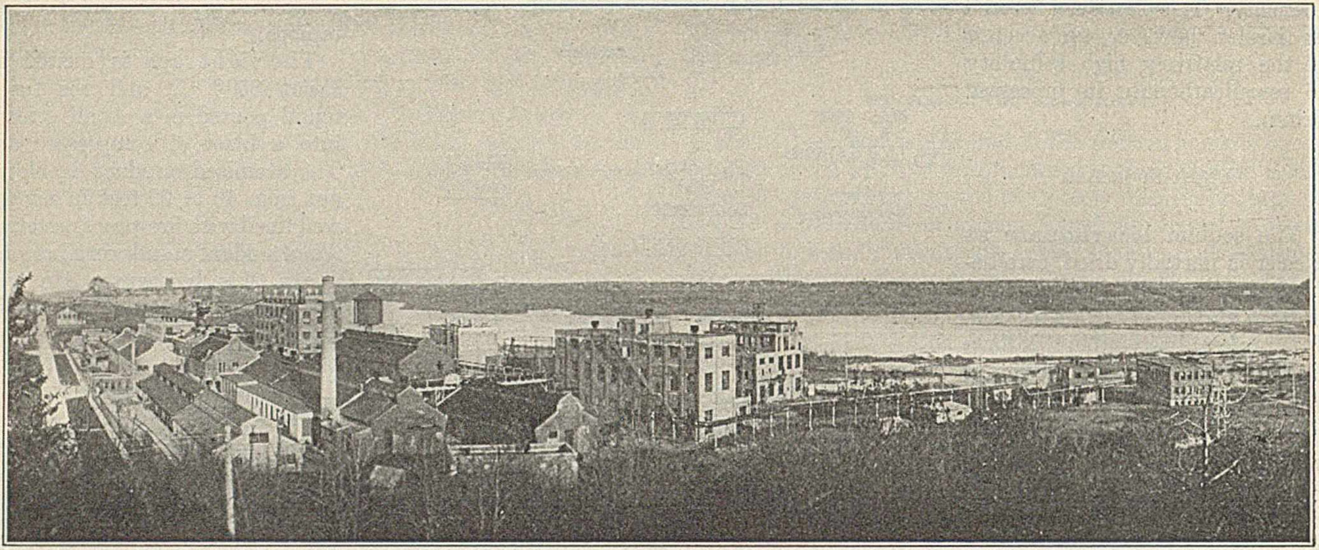

Figure 1—Plant of Shawinigan Chemicals, Ltd., Shawinigan Falls, Que., First Producers of Synthetic Acetic Acid in America

Acetic Acid and Cellulose Acetate in the United States[1]

A General Survey of Economic and Technical Developments

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This survey is an attempt at a general view of the acetic acid industry in the United States and of the cellulose acetate industry as it affects the consumption of acetic acid. The survey is divided into five parts dealing, respectively, with (1) the general developments affecting the manufacture of acetic acid since 1914; (2) the general technology of the various processes used or proposed for the manufacture of acetic acid; (3) the production of acetic acid and its consumption in various industries during 1929; (4) the general development of the cellulose acetate industry in the United States; and (5) the manufacture of cellulose acetate as it affects the consumption of acetic acid and acetic anhydride.

While this survey cannot pretend to be a comprehensive record of all technical developments or a complete economic study of the wide ramifications of acetic acid in industry, it is hoped that it will prove valuable both as a general summary for the person acquainted with the industry and as an introduction for the person without previous information on the subject.

MOST people are acquainted with acetic acid in the form of vinegar. Probably few of them realize that acetic acid is also an industrial chemical produced in a variety of ways from the most dissimilar materials, and vitally necessary for the production of such apparently unrelated commodities as lacquer solvents, white lead, and one type of regenerated fiber.

Acetic acid is closely related both chemically and economically to wood and molasses, which are its chief ultimate parent substances today. For its immediate ancestors it has acetate of lime, alcohol, and acetaldehyde, which may eventually be joined by methane, methanol, carbon monoxide, carbon dioxide, or what not, as the organic chemist and the chemical engineer join forces to extend the domain of chemical synthesis. The other family relationships are badly scrambled, for while acetic acid may be the son of acetate of lime, he is the father of sodium acetate, who in turn begets acetic anhydride, who has only to take up water in the production of cellulose acetate to reproduce acetic acid. And nobody ever could certify whether the egg or the hen came first in the ethylidene diacetate cycle.

The story of acetic acid, its source materials and its derivatives in the United States in the past ten years, is a story involving the most diverse aspects of our civilization. Physical chemistry thumbing its nose at Prohibition, overproduction riding on the back of supersalesmanship to a most discomforting fall, deadly competition between the principles of chemical decomposition and of chemical synthesis in the production of materials, with chemical engineering and "ordinary practice" in continuous combat along the whole front, all contribute their very serious or equally comic portions to the composite picture, which is sketched rapidly in the following survey.

GENERAL DEVELOPMENTS SINCE 1914

Before the World War the world's supply of acetic acid and of acetone was derived almost entirely from acetate of lime. Approximately half of this material came from the United States and Canada (*20*), while a large part of the other half was produced within what is now Czechoslovakia. Approximately 40 per cent of the American production was exported (*15*), largely to Belgium (*11*). Most of this went from Antwerp up the Rhine into Germany. The total capacity of wood-distillation plants in the United States and Canada in 1914 was estimated at 5274 cords per day (*11*), but records from a private source set the figure about 500 cords

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[1] Received March 12, 1931.

lower; as shown in Table I, the United States production of acetate of lime for that year was 166 million pounds.

War Emergency Developments

Within a year after the start of the war, the available stocks and current production of acetate of lime had been fully utilized, and the British Government was searching desperately for other sources of acetic acid and acetone, particularly the latter, which was indispensable in the manufacture of cordite. This emergency was father to a number of developments, such as the fermentation of kelp on the Pacific Coast by the Hercules Powder Company to produce calcium acetate for acetone manufacture (*1*), the fermentation of corn by the Fernbach and Weizmann processes to produce acetone and butanol, a large increase in the production of acetic acid from alcohol by the quick vinegar fermentation process, and the production of acetic acid by synthesis from acetylene.

Both the Weizmann process and the fermentation of alcohol were to figure prominently in the post-war development of solvents. The distilleries at Terre Haute, Ind., in which the Weizmann process was operated for the British Government during the latter part of the war, subsequently became the Commercial Solvents Corporation, and the process, originally intended to supply acetone, became the source of butanol and hence of butyl acetate, with acetone in the role of by-product severely limiting the manufacture of acetone from acetate of lime. The quick-vinegar fermentation plant of the U. S. Industrial Chemical Company was producing the equivalent of 70,000 pounds of 100 per cent acetic acid per day in 1918, which was converted into calcium acetate for the manufacture of acetone (*20*). With the development of nitrocellulose lacquers after the war, this plant found a new outlet in the production of ethyl acetate.

SYNTHETIC ACETIC ACID—The synthesis of acetic acid from acetylene was perhaps more significant than any of the wartime developments previously mentioned. It was first worked out in Germany, and is described in the Wunderlich patents of the Consortium für elektrochemische Industrie from 1907 on. Considerable conflict between these patents and those of Grünstein, dating from 1910, enlivened the technical press in Germany during and after the war. The fundamental process in each case was the conversion of acetylene to acetaldehyde in the presence of a catalyst of mercuric oxide. The acetaldehyde was subsequently purified and oxidized to acetic acid. A German plant is said to have been in operation two or three years before the outbreak of the war (*20*), although Marshall (*25*) claims that the plant of the Canadian Electro Products Company, which was built during 1916 and started production in January, 1917, was the first venture on a commercial scale.

Table I—Statistics for Calcium Acetate

YEAR	U. S. PRODUCTION[a]			IMPORTS[b]	EXPORTS[b]	APPROX. TOTAL PRODUCTION + IMPORTS − EXPORTS	AVERAGE VALUE PER POUND		
	Total	Made and consumed	For sale				Production	Imports	Exports
	1000 lbs.	*1000 lbs.*	*1000 lbs.*	*1000 lbs.*	*1000 lbs.*	*1000 lbs.*			
1909			141,478				$0.015		
1914	166,084	2,562	163,522				0.013		
1919	168,956	15,046	153,910				0.017		
1921	61,316	5,868	55,448				0.013		
1922					27,596				$0.021
1923	161,556	16,988	144,588		21,952		0.033		0.037
1924					23,166				0.032
1925	163,446	18,142	145,304		22,038		0.024		0.031
1926	157,078[b]			4,934	18,588	143,400		$0.031	0.034
1927	156,280	18,248	138,032	6,894	11,634	151,600	0.029	0.033	0.035
1928	132,098[b]			9,006	11,172	130,000		0.035	0.033
1929	140,518[b]	24,374[d]	116,144[c]	24,584	102	165,000	0.040	0.041	0.064

[a] From Census of Manufactures, except as otherwise noted.
[b] From Bureau of Foreign and Domestic Commerce.
[c] Preliminary report, Census of Manufactures.
[d] Estimated by difference.

This Canadian plant located at the power and carbide developments at Shawinigan Falls, Que. (Figure 1) was intended to supply the desperate need of the British munitions manufacturers for acetone. Starting in December, 1915, with what was available in the German patent literature, a group of Canadian chemists headed by H. W. Matheson carried the process from the laboratory to the first carload of production in fourteen months.

During most of the first year acetone was the final product desired. As acetone became available from plants using fermentation processes, and as the demand for cellulose acetate dope for airplane wings increased, the Canadian plant was switched late in 1917 to the production of acetic acid. When the United States entered the war in 1918, the capacity of the Canadian plant was 800 tons of 99.8 per cent acetic acid per month. A second plant to double this capacity was at once built for the United States. At the close of the war the production at Shawinigan Falls was equal to half of the United States production of acetic acid from calcium acetate (*27*).

Post-War Developments

The end of the war meant an immediate decrease in the manufacture of war supplies. This, coupled with the general deflation of 1921, did not offer a particularly cheerful outlook either to the producers of synthetic acetic acid or to the wood distillers, both of whom recognized the inevitable competition for peacetime markets. Severe competition was postponed by the rapid increase in industrial activity in the United States subsequent to 1921. The development of nitrocellulose lacquers, the start of cellulose acetate production, and the application of chemical engineering to the problems of supplying bootleg liquor, all created new markets for acetic acid in addition to the general expansion of old markets on the advancing wave of prosperity. This period lasted well into 1929, when the wave at last collapsed into foam.

In the meantime the Shawinigan interests had pooled their experience with the resources of the Carbide and Carbon Chemicals Corporation and the du Pont organization in establishing the jointly owned plant of the Niacet Chemicals Corporation at Niagara Falls, N. Y., for the synthetic production of acetic acid in the United States. This plant went into production in 1927 with a capacity estimated at 3000 tons of acid per year, and is said to have commenced expansion of its facilities in 1929 to give a production capacity of 15,000 tons per year. As business gradually improves in the coming months it is probable that Niacet will make a determined effort to operate at capacity and the severest competition may be anticipated between synthetic acetic acid and that derived from calcium acetate. Since the 1930 tariff revision raised the duty on acetic acid of less than 65 per cent strength from 0.75 to 1.37 cents per pound and retained the duty of 2 cents per pound on acid above this strength, the importations from Canada will probably be supplanted to a considerable extent by domestic production.

PRODUCTION OF ACETIC ACID

The rapid development of cellulose acetate in the United States in recent years and the great interest in the special properties of this material have led to much speculation concerning its future. As a necessary corollary there has been an equal amount of discussion concerning acetic acid and acetic anhydride. A survey of the methods of production and an estimate of the economic situation with respect to acetic acid is accordingly presented here. Additional details and patent abstracts on acetic acid manufacture are given in a series of articles by Mullin and Hunter (*31*).

Commercial Methods of Producing Acetic Acid

Three general primary methods of producing acetic acid are in use today. The oldest is the fermentation method, well known to anyone who has had a cherished jug of cider go to vinegar. The next method is the destructive distillation of wood, which may also be applied to other cellulosic materials such as corncobs, straw, kelp, or peach pits. The newest method is chemical synthesis, in which acetylene and ethylene are at present the most important building blocks.

ACETIC ACID BY FERMENTATION—The production of vinegar as such lies outside of the scope of this discussion. A considerable amount of acetic acid is, however, produced for industrial use by the quick-vinegar fermentation process. Tall vats filled with beechwood shavings as a contact surface and a support for the ferment are used in series. A dilute mixture of alcohol and vinegar is introduced at the top of the first vat and trickles down over the shavings countercurrent to the natural convection of air sent up by the heat of the oxidation reaction. The air enters through a perforated false bottom and passes from the top to a scrubber, which removes alcohol and acetic acid. The liquor leaving the bottom of the tank is richer in acetic acid than the entering liquor, and is introduced at the top of the next vat. The temperature is maintained at approximately 30° C. by controlling the rate of air flow. The maximum concentration of acetic acid obtained is limited by its effect on the ferment which cannot live in a concentration of more than 13 or 14 per cent. Acetic acid and alcohol are distilled from the final liquor, and used with additional alcohol in the manufacture of ethyl acetate.

WOOD-DISTILLATION INDUSTRY—Descriptions of the usual type of wood-distillation plant have been given by Hawley (*18, 19*) and a rather complete article on the operation of the Stafford process has been published by Nelson (*33*). Further description of the technology prior to the recovery of acetic acid will not be given here, since the developments have been largely in the mechanical equipment. The recent chemical engineering developments in the recovery of acetic acid will be mentioned, since they appear to offer definite advantages in cost reduction and improvement of product.

Until very recently none of the wood distillers produced acetic acid directly. The calcium acetate obtained by neutralization of pyroligneous liquors was recovered and was largely sold to other concerns, which converted it into acetone or acetic acid. Increasing competition encouraged the search for more economical and more efficient methods, and various processes for obtaining acetic acid directly from the pyroligneous liquors were proposed. Of these the Brewster, the modified Brewster, and the Suida processes are now in commercial operation in the United States.

Brewster Processes. The original Brewster process (*3*) depends upon the extraction of acetic acid from the pyroligneous liquors by means of ethyl ether, which has a boiling point well below that of acetic acid. A recovery of 98 or 99 per cent is claimed for a countercurrent extractor without agitation, but with a type of packing designed to give intimate contact. By distillation of the ethyl ether solution acetic acid of 65 to 70 per cent strength is obtained. Somewhat more concentrated acid may be recovered by adding various hydrocarbons to the ethyl ether used for extraction in order to decrease the solubility of water in the ether, but more solvent is required in this case. The availability of isopropyl ether in commercial quantities as a result of the developments of the Carbon and Carbide Chemicals Corporation made possible an improved modification of the Brewster process. The same degree of recovery is obtainable, but practically water-free acid is produced, owing to the fact that isopropyl ether dissolves but very little water and with the addition of certain other substances forms a constant-boiling mixture with this water. The steam consumption for the modified Brewster process is approximately half that for the original Brewster process, because no fractionation is necessary. The poorer partition coefficient with isopropyl ether is a slight disadvantage, but the higher boiling point of this substance materially reduces solvent loss, particularly in warm climates where difficulty used to be encountered in condensing ethyl ether with the water supply available.

The original Brewster process is reported to have been in use at one 220-cord wood distillation plant in New York, at two plants totaling 184 cords capacity in Pennsylvania, and on approximately 110 cords capacity at a plant in Tennessee. The Brewster process has been used in England, and it is to be included in a large plant now being built in U. S. S. R. The process has also been used for the recovery of acetic acid from the carbonization of peach and apricot pits on the West Coast. The modified process has been applied to the reconcentration of the dilute acid obtained in the production of cellulose acetate, an installation having been made recently at the Tubize-Chatillon plant at Rome, Ga. The modified process may be applied abroad as well as in the United States, but at present this will require the exportation of the requisite isopropyl ether from the United States.

Suida Process. The Suida process is also an extraction process, but a solvent with a boiling point well above that of acetic acid is used. The extraction may be carried out with the acetic acid in either the liquid or the vapor phase, associated with water, methanol, and other impurities (*40*).

The first plant to adopt the Suida process in this country was the Forest Products Chemical Company, at Memphis, Tenn., which uses high-boiling wood oils from its own operations as the solvent, and carries out the extraction from a superheated vapor phase. The acetic acid is subsequently separated from the solvent by vacuum distillation with an over-all recovery of 95 or 96 per cent. Steam consumption during a test run was found to be 0.565 pound per pound of feed (*23*).

While the Suida process is theoretically capable of producing glacial acetic acid, up until early 1930 the Forest Products Chemical Company was marketing acid of about 80 per cent strength. This material had a yellow color, but was not contaminated with oil as rumored by various interested parties. Changing market conditions following the depression late in 1929 necessitated rearrangement of the process to produce a practically water-white product of higher concentration.

The present arrangement of the Suida process is indicated in the flow sheet of Figure 2. The chief changes from the previous set-up described by Krase (*23*) are the replacement of the 10-plate upper vacuum column by one with 29 plates

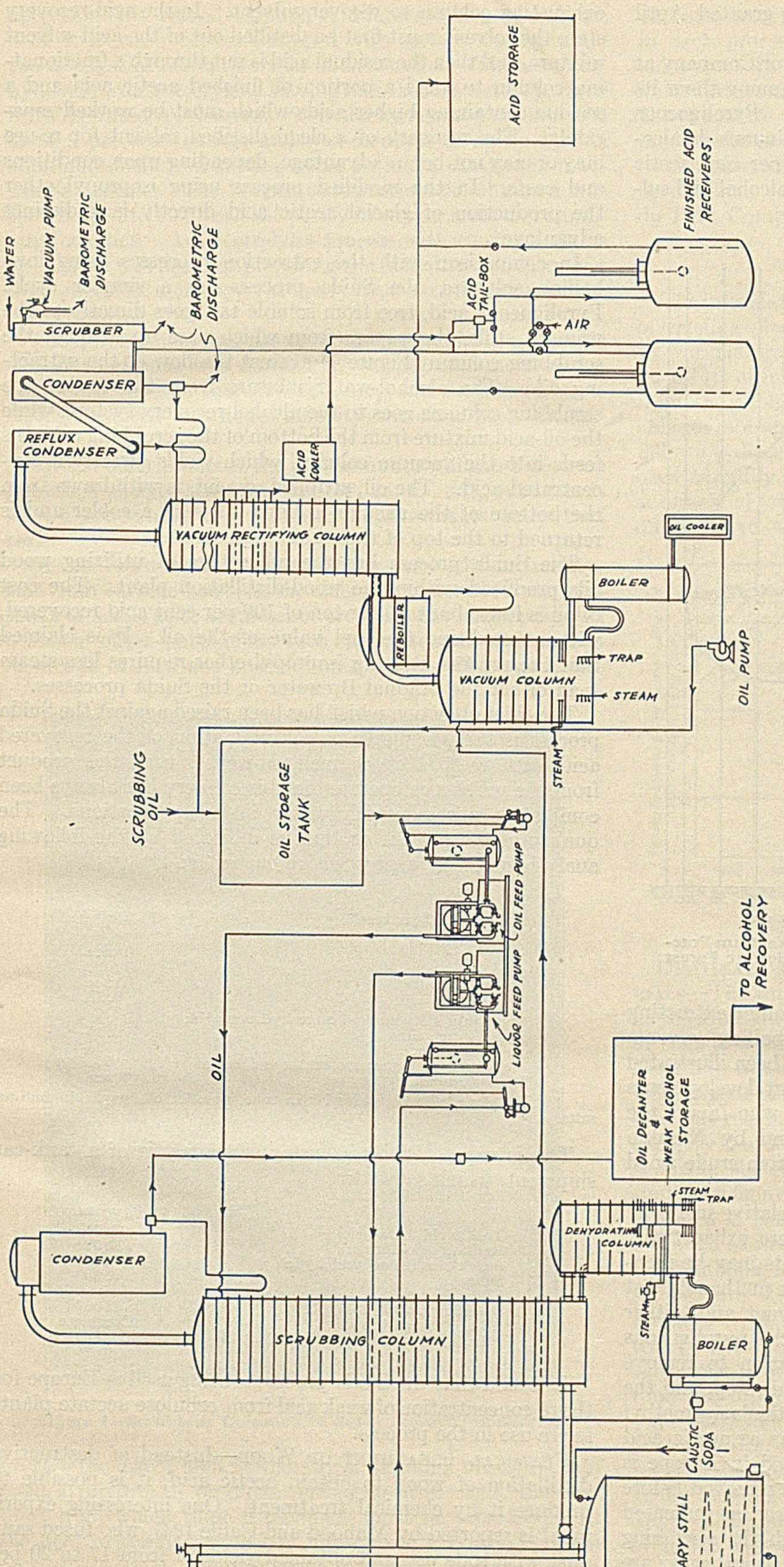

Figure 2—Flow Sheet of Acid Department of American Installation of the Suida Process
Note that the settled pyroligneous acid is extracted before fractionating off methanol

and the insertion of a reboiler between the upper and lower vacuum columns. The original 10-plate upper column gave very little rectification. The product was drawn from the condenser at the top and only enough reflux was carried to hold back the oil. The product contained any water that was not removed from the oil in the dehydrating column below the scrubbing column.

The new 29-plate upper vacuum column is equipped with condensers of large enough capacity to carry a fairly heavy reflux. The temperature in the reboiler between the upper and lower columns is maintained by a Foxboro controller at a high enough level to revaporize most of the reflux from the upper column, so that only high-boiling material is allowed to pass back to the lower column.

The small amount of condensate from the top of the upper column carries about 15 per cent acid and is returned to the pyroligneous storage tanks for return through the process. The product, practically water-white and containing 90 to 95 per cent acetic acid by weight, is usually taken off from about plate 12 of the upper column. A manifold connection allows withdrawal of product from plates above and below this point. The concentration of acid and temperature on each plate in the upper column are shown in Figure 3, which represents regular production conditions.

The steam consumption of the process was changed very little by increasing the height of the column, since the oil-acid mixture from the scrubbing columns is superheated with respect to the vacuum column and the acid vapor is flashed off in the latter.

Considerable development work is still being done in this country on the Suida process. It is being installed in the new plant of the Crossett Chemical Company at Crossett, Ark., affiliated with the Forest Products Chemical Company, and some existing wood-distillation plants are said to be considering its adoption in the near future.

Other Processes. In addition to the processes described, mention should be made of the systems employed at the wood-distillation plants of the Tennessee Eastman Corporation and the Ford Motor Company. At Tennessee Eastman the pyroligneous acid is neutralized with soda ash instead of lime, and sodium acetate is recovered for the production of the acetic anhydride used in their manufacture of cellulose acetate. The weak acid from the cellulose acetate plant is concentrated by an azeotropic process, probably involving the use of ethylene dichloride, as specified in their British Patent 327,444, granted April 3, 1930.

The wood-distillation plant of the Ford Motor Company at Iron Mountain is unique in many respects, among them its production of ethyl acetate by a direct process. Pyroligneous acid liquors freed from tars are fed to a continuous de-alcoholizing still from the bottom of which a 15 per cent acetic acid is obtained. This is treated with ethyl alcohol and sulfuric acid to produce ethyl acetate (*33*).

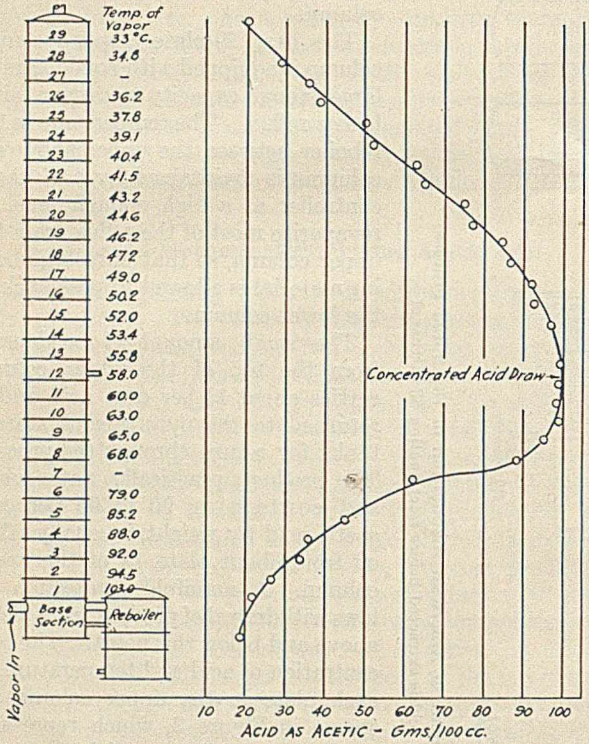

Figure 3—Composition of Liquid on Plates of Vacuum Fractionating Column in Suida Process Installation at Forest Products Chemical Company

Brewster's scheme of using relatively low-boiling extracting solvents and Suida's system of using high-boiling solvents represent two general viewpoints which have been illustrated by many patents on various materials. Recent developments along these lines are given by Guinot (*16*), who favors the use of amyl, butyl, and ethyl acetates, and by Nasakin (*32*), who describes a new solvent prepared from crude wood alcohol and coal tar.

Comparison of Various Processes. The relative merits of the various systems cannot be discussed here exhaustively for lack of specific information. A few points may be mentioned, however. In the Brewster process the methanol must be removed before extraction with the solvent and, either before or after the removal of methanol, the pyroligneous acid must pass through a primary distillation to remove soluble tar. There is some loss of acid in this step, and the recovered methanol is higher in esters, particularly methyl acetate, which represents another loss as far as acetic acid is concerned. The Suida process as operated in Europe is subject to this same loss, as the methanol is removed before the extraction step. In this country, however, as indicated in Figure 1, the methanol is carried through the scrubbing columns, and the vapors, practically free from acid, are condensed and fed to the crude-alcohol column. The percentage of esters in the crude methanol is approximately half that obtained when the methanol is removed preceding extraction.

In the Brewster and similar processes using extracting liquids soluble in water, the water must be put through an exhausting column to recover solvent. In the acid-recovery step, the solvent must first be distilled out of the acid-solvent mixture, and then the residual acid is put through a fractionating column to yield a portion of finished acetic acid and a residue containing higher acids which must be worked separately. The recovery of a clean distilled solvent for re-use may or may not be an advantage, depending upon conditions and costs. In the modified process using isopropyl ether the production of glacial acetic acid directly is a distinct advantage.

In comparison with the extraction processes using low-boiling solvents, the Suida process has a simpler cycle. Pyroligneous acid, free from soluble tar, goes directly to the primary stills, the vapors from which pass up through the scrubbing column (Figure 4) against the flow of the extracting oils. The alcohol-water mixture from the top of the scrubbing columns goes to the alcohol-recovery system, while the oil-acid mixture from the bottom of the scrubbing columns feeds into the vacuum column, which yields directly a concentrated acid. The oil, stripped of acid, is withdrawn from the bottom of the vacuum column through a cooler and is returned to the top of the scrubbing column.

The Suida process has the advantage of utilizing wood oils produced within the wood-distillation plant. The cost of oil is low, about $4 per ton of 100 per cent acid recovered, without crediting the fuel value of the oil. It is claimed that the process utilizing isopropyl ether requires less steam than either the original Brewster or the Suida processes.

The chief objection which has been raised against the Suida process is the possibility of contamination of the recovered acid with oil. It is claimed, however, that the product from the process as operated in this country has always been completely miscible with water in all proportions. The quality of the present product is indicated by the following analysis made by a prospective customer:

	% by wt.
Total acid (as acetic)	91.9
Impurities:	
HCl	Trace
SO_3	Trace
SO_2	Trace
Formic acid	0.78
Sodium salts method on anhydrous acid:	
Acetic acid	99.15
Formic acid	0.85
Acids of higher molecular weight (as propionic)	Trace

Sample clear, slightly yellowish in tone, no odor of butyric in sodium salts.

This is supported by a customer's analysis of a tank-car shipment, which showed:

	% by wt.
Total acid (as acetic)	93.95
Reducers (as formic)	1.02
Aldehydes (as acetaldehyde)	0.039
Sulfates	0.000
Chlorides	0.000
Specific gravity, 15.5° C.	1.067
Miscibility with water	Complete
Miscibility with benzene (1:1)	Complete

It is said that the Suida process is being used in Europe for the re-concentration of weak acid from cellulose acetate plants for re-use in the process.

CHEMICAL TREATMENT OF WOOD—Instead of destructive distillation of wood to obtain acetic acid, it is possible to produce it by chemical treatment. One interesting experiment is reported by Mahood and Cable (*24*), who fused sawdust with soda ash and obtained yields of from 17 to 20 per cent of acetic acid. Little has been done along this line on an engineering scale, however.

SYNTHESIS FROM ACETYLENE—The process developed at Shawinigan Falls involved several steps for the production of glacial acetic acid. Acetylene was produced from calcium carbide by reaction with water in large generators. This acetylene was passed through a dilute solution of sulfuric acid in Duriron kettles equipped with agitators to maintain the catalyst of mercuric oxide in suspension. The acetaldehyde and excess acetylene leaving these kettles were separated in refrigerated condensers. The aldehyde was then rectified to 99.9 per cent purity, and was oxidized to acetic acid in aluminum-lined iron kettles, using air and a catalyst of manganese acetate. The 98 per cent acetic acid obtained was then refined to 99.8 per cent purity in copper stills and aluminum columns. An electrolytic process with caustic soda as electrolyte was used for preparing the mercuric oxide catalyst from metallic mercury. Mercury was recovered from the spent catalyst.

The development and use of the process under the pressure of war conditions was marked by several explosions and a number of cases of mercury poisoning, but the hazards were rapidly reduced and little difficulty has since been encountered.

Several descriptions of the process at Shawinigan Falls were published shortly after the war (*20*, *25*, *27*, *36*), but little is known concerning the technical improvements since that time.

Other Possible Synthetic Processes—Although acetylene from carbide has been the chief raw material for the synthesis of acetic acid, a number of processes have been proposed utilizing other substances such as methanol and carbon monoxide or methane and carbon dioxide. These processes involve the use of high temperatures and high pressures, and yield a mixture of products, including acetic acid and acetone, from which these compounds must be separated. In the light of recent progress in high-pressure synthesis, these processes cannot be dismissed carelessly, particularly in view of the low cost of the raw materials in comparison with acetylene from carbide. There is also the possibility of deriving acetylene from methane for use in the existing process for acetic acid.

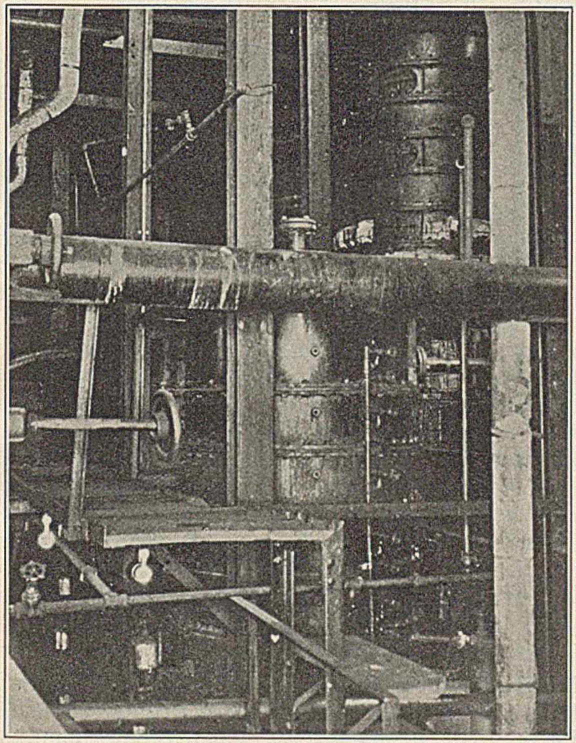

Figure 4—Scrubbing Columns in Suida Process Installation

The Hale and Haldeman (*17*) and the Zeisberg processes (*44*) are of specific interest in this country from the standpoint of both industrial alcohol and acetic acid. The first step in each process is the dehydrogenation of ethanol to acetaldehyde. In the Hale and Haldeman process there is an immediate oxidation of the acetaldehyde to acetic acid. Ethyl acetate is obtained as a by-product. In the Zeisberg process the acetaldehyde is converted to ethyl acetate by a Cannizzaro condensation. Butyl alcohol is obtained as a by-product. This process is now being operated by the du Pont Company.

Economic Considerations

The information generally available concerning the capacity of existing plants and the cost of production of acetic acid by various processes is sketchy, as such data generally are. Such bits of information as the writer has been able to glean from the published articles and such estimates as he has been able to obtain from reputable sources are included in the following discussion. Personal guesswork by the writer has been carefully suppressed, but he is not responsible for the accuracy of other persons' estimates. Wherever possible, sources have been indicated.

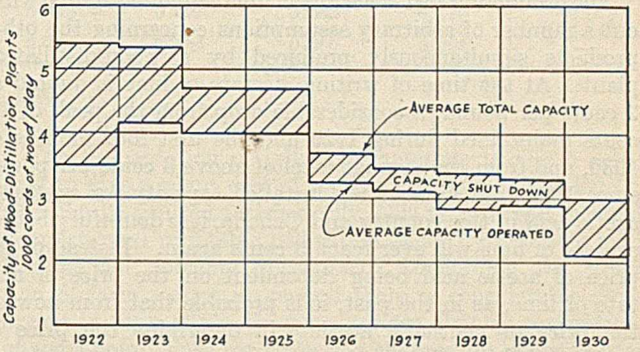

Figure 5—Average Capacity of the Wood-Distillation Industry in the United States, 1922–1930

From statistics of Department of Commerce

Distillation of Wood and Other Cellulosic Materials—The total capacity of all the wood-distillation plants in the United States has descreased from 5400 cords per day in 1922 to 3000[2] cords per day in 1930, as shown in Figure 5, according to annual averages of the monthly reports of the Department of Commerce. Since 1925 the decrease has been slow but regular. For the years 1926 to 1929, inclusive, the capacity shutdown averaged 440 cords per day. The general slump in business is reflected in the increase of the average shutdown figure to 900 cords per day in 1930. Of the capacity operated in 1929 and 1930, between 16 and 17 per cent used millwood as raw material and the remainder cordwood.

Production, import, and export statistics from government sources are shown in Table I for calcium acetate. The production in the United States shows a slight irregular trend downward since 1914. Imports have been increasing since 1926, with a big jump in 1929, when exports simultaneously dropped practically to zero. In Table II are shown some statistics obtained from a private source on the production, sales, and exports for the United States and Canada together, as well as separate figures for Canada since 1925. While these figures do not agree in some cases with those in Table I, the discrepancies are generally small and tend to even out over successive years. The last column of Table II is an estimate at the amount of calcium acetate consumed directly in the production of acetate solvents, particularly ethyl acetate. The rapid increase in recent years has been attributed both to the growing demand for nitrocellulose

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[2] The Department of Commerce reports do not include a few plants. An estimate from a private source places the 1930 capacity of wood distillation plants at 3700 cords per day.

lacquers and to the use of ethyl acetate as a raw material for the large-scale production of illicit alcohol.

Table II—Statistics for Calcium Acetate

Year	Production		Sales		U. S. Exports	Estd. Approx. Amt. Used for Production Ethyl Acetate and Other Solvents in U. S.
	U. S. and Canada	Canada	U. S. and Canada	Canada		
	1000 lbs.	*1000 lbs.*	*1000 lbs.*	*1000 lbs.*	*1000 lbs.*	*1000 lbs.*
1914	156,000		146,100		54,400	1,985
1915	153,950		193,100		23,000	2,475
1916	147,200		137,700		16,700	6,700
1917	167,100		176,500		14,930	7,530
1918	166,900		154,700		12,900	5,580
1919	122,750		105,500		22,000	5,075
1920	139,000		88,900		16,140	6,400
1921	61,600		59,850		10,200	3,455
1922	106,900		146,100		22,220	9,850
1923	141,800		134,000		17,100	5,750
1924	118,000		106,500		20,450	11,750
1925	98,300	3,230	97,950	4,450	24,750	19,420
1926	104,200	5,800	103,100	5,275	19,600	20,780
1927	150,600	8,940	143,500	7,855	14,500	31,500
1928	141,200	9,110	166,550	10,740	16,180	45,250
1929	148,750	10,170	141,500	9,245	1,540	39,000
1930		6,890		4,865		10,575

The production cost of acetate of lime cannot be figured without a number of arbitrary assumptions concerning the other products simultaneously produced by a wood-distillation plant. At the time of writing, acetate of lime is quoted at 2 cents per pound, a considerable drop from the peak of 4.5 cents maintained during 1929 and the first four months of 1930, and from the average level of above 3 cents per pound since 1922. In view of the installed capacity for synthetic acetic acid in this country and Canada, it is doubtful whether acetate of lime will ever reach 3 cents again. Instead of the price of acetic acid being dependent on the price of acetate of lime, as in the past, it is probable that from now on the price of synthetic acetic will determine the price of acetate of lime.

Methanol has been the second stand-by of the wood distillers, but this, as well as acetate of lime, is being attacked by synthetic chemistry. The production of synthetic methanol in 1927 was half a million gallons against nearly 6 million gallons of "refined" methanol from wood distillation; in 1930 synthetic methanol had climbed to 10 million gallons while "refined" methanol was 5.5 million gallons (*6*). Furthermore, the one use for which the product from wood was preferred, the denaturing of industrial alcohol, has been nearly wiped out by the recent official adoption of alcotate as a denaturant. Methanol from wood must compete on a price basis in the remaining fields, and it is probable that the steady price decline of the last ten years will be continued as a result of the rapidly increasing production of the synthetic product, which is now quoted at somewhat under 40 cents per gallon in tank-car lots at the works.

The way out for the wood distiller may lie in the adoption of extraction processes for the direct production of acetic acid from pyroligneous liquor, in the intensive cultivation of the domestic market for charcoal, and in the fuller exploitation of uses for wood oils. One of the most progressive firms in the country, the Forest Products Chemical Company, of Memphis, Tenn., has done all three things with such success that an affiliated plant is now being built in spite of the unattractive prospects generally facing the industry. It has been said that, if the wood distiller could sell his charcoal as a package product for domestic use, he could afford to give away his methanol and acetate of lime. Although the last two products probably never will be given away, the wood distiller probably must face a diminishing revenue from them from now on.

Synthetic Processes—The manufacture of acetic acid by synthetic processes has been established in Germany, Switzerland, France, Great Britain, Canada, and the United States, and the total capacity has increased markedly in recent years. The Niacet Chemical Corporation at Niagara Falls, N. Y., and the Shawinigan Chemicals, Ltd., at Shawinigan Falls, Que., are the only concerns at present affecting conditions in the United States. The capacity of the latter is unknown, possibly 40 million pounds per year. During 1929 the carbide plant at Shawinigan Falls was enlarged, probably as a forerunner to an increase in the acetic acid plant. The present capacity of the Niacet plant has been estimated as 30 million pounds per year. Both Shawinigan and Niacet produce acetic acid from calcium carbide by way of acetylene and acetaldehyde.

Since the American Cyanamid Company probably has the largest production of carbide at the lowest cost of any concern on this continent, the production of acetic acid by this method must have been considered by this organization. The Union Carbide and Carbon Corporation, the other important producer of carbide, through the Carbide and Carbon Chemicals Corporation, has an interest in Niacet and supplies the acetylene used by the latter. In the South the Federal Carbide plant of the Swann Corporation might be a base for the possible future production of acetic acid for southern cellulose acetate plants. It seems probable, however, that any further development of synthetic acetic acid in the United States will be postponed for several years, for two reasons: first, the probability of only a slow acceleration of general industrial activity, and second, the certainty of very persistent competition from the wood distillation industry.

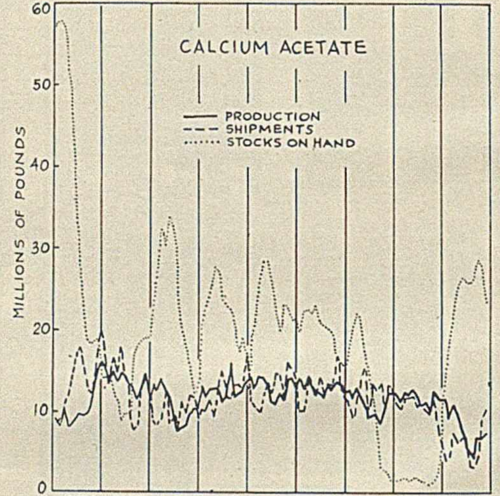

Figure 6—Production, Shipments, and Stocks on Hand for Acetate of Lime, 1922–1930

From statistics of Department of Commerce

The plant cost of production for acetic acid at Niagara Falls including plant overhead but excluding containers and sales and administrative expenses, is estimated to be from 5 to 5.25 cents per pound. The cost at Shawinigan Falls is probably about the same. Since, with acetate of lime at its present level of 2 cents per pound, the converters can sell glacial acid at 6.25 to 7 cents, importation of Canadian synthetic acid is practically barred by the import duty of 2 cents per pound on acid above 65 per cent strength, and profit at Niagara Falls is reduced to a narrow margin.

Both the wood distiller and the producer of synthetic acetic acid from carbide are open to the danger of competition from newer and cheaper synthetic processes. One of the possibilities is the oxidation of ethanol to acetic acid. The ethanol may be derived from fermentation, or by synthesis from ethylene. The conversion of ethylene directly to acetic acid has not yet been made commercial. The production of ethanol as the intermediate compound is, however, now in operation.

The cost of ethanol made from ethylene may be taken roughly as 16 to 18 cents per gallon—that is, 3 cents per pound. The oxidation of this ethanol to acetic acid has little if any cost, as the increase in weight of product over alcohol consumed is sufficient to bear all manufacturing charges, so that we can assume 3 cents as the cost per pound of acetic acid. In this connection should be cited the Hale and Haldeman patents (*17*) and the alcohol oxidation process of the Holzverkohlungsindustrie as carried out in the new plant of British Industrial Solvents, recently completed in Great Britain as a subsidiary of the Distillers Company (*2*). This plant is to produce acetone and butanol as well as acetic acid. Since all three of these commodities have previously been imported into Great Britain in large quantities, the new plant capacity of 6 million pounds of acetone, 3 million pounds of butanol, and 20 million pounds of acetic acid per year will have a significant effect upon international trade.

Table III—Statistics for Acetic Acid

Year	Imports[a]			Exports[b]	Av. Value per Pound				
					Production		Imports		Exports
	Total	Less than 65%	More than 65%		Dilute	Glacial	Less than 65%	More than 65%	
	1000 lbs.	*1000 lbs.*	*1000 lbs.*	*1000 lbs.*					
1923	701	37	664		$0.031	$0.111	$0.129	$0.120	
1924	1,575	372	1,203				0.073	0.120	
1925	2,421	362	2,059		0.027	0.099	0.080	0.113	
1926	8,023	6,027	1,996				0.048	0.117	
1927	10,552	6,767	3,785		0.115	0.097	0.052	0.120	
1928	18,221	12,163	6,058	298			0.053	0.120	$0.140
1929	29,235	21,410	7,825		0.104	0.105	0.060	0.093	

[a] From Bureau of Foreign and Domestic Commerce.
[b] Less than 1,000,000 lbs. annually exported since 1922. Export negligible in 1929.

In the United States acetic acid from alcohol may possibly threaten that from carbide if ethanol from fermentation is forced to seek new outlets as the result of competition from synthetic methanol. Since the production cost of the latter has been estimated at 20 cents per gallon with water gas at 25 cents per 1000 cubic feet (*12*), and since the actual present cost is probably 18 cents or less, such competition seems inevitable; in fact, it may be said to have arrived last year, when the price of methanol dropped to the level of denatured alcohol and began to make large inroads on its use as an antifreeze (*6*). The recent entrance of the U. S. Industrial Alcohol Company into the manufacture of cellulose acetate may indicate future diversion of their alcohol production to the manufacture of acetic anhydride, through acetic acid or acetates, for use in their new process for cellulose acetate. It may be said here that industrial alcohol by fermentation does not face a very rosy future in its customary markets, as synthetic methanol has definitely arrived, and synthetic ethanol is an accomplished fact, 5,000,000 gallons having been produced in 1930. The entrance of U. S. I. into new fields of activity is evidence that this concern has been planning for the future.

Fermentation Processes for Acetic Acid—As mentioned previously, U. S. Industrial Chemical Company was making large quantities of acetic acid by the quick-vinegar fermentation process at the end of the World War. This plant has lately been producing approximately 10 million pounds of acetic acid per year, all of which was utilized in the manufacture of ester solvents.

Recently announcement was made that the Commercial Solvents Corporation expected to produce acetic acid for their own use in the manufacture of butyl acetate (*13*). While this development has been retarded by the general industrial depression, and may be postponed in view of the probable excess of acetic acid production for several years to come, it remains a possibility for the future. The Commercial Solvents plan was to utilize distillery slop from their butanol-acetone production for fermentation to acetic acid. Farm wastes, such as corncobs, might also be used, as indicated by the work of Fred and Peterson (*10*), who found that they could obtain acetic and lactic acids by fermentation of a sirup produced by the hydrolysis of corncobs with dilute sulfuric acid. On the basis of laboratory results, they calculated a yield of 300 pounds of acetic and 320 pounds of lactic acid per ton of corncobs.

The fermentation of cellulosic materials to acetic acid is said to give a plant cost of 4 cents per pound. If distillery slop can be utilized satisfactorily, this process will mean the complete and profitable utilization of all by-products in the Commercial Solvents operations. Concerning the utilization of farm wastes in general there is considerable doubt, except in cases where these wastes are already concentrated at some point, since the collection charges are likely to prove rather high.

The fermentation of sugar to produce a mixture of one-third acetic and two-thirds propionic acid has been proposed. According to W. A. Bridgeman, of the Wilbur White Chemical Company, Owego, N. Y., the mixed acids can be produced at a cost not to exceed the present market price for acetic acid. Production on a commercial scale is to be tried in the near future.

There is also always the possibility that a ferment may sometime be discovered which will take molasses to acetic acid in one step and give good yields under the limitations imposed by industrial conditions.

Prospects for Future Development

It is highly improbable that the wood-distillation industry will disappear before the attack of synthetic chemistry, at least for a good many years. Certain large concerns in which the distillation of wood is tied in with lumber operations seem likely to persist without too severe difficulties. It is probable, however, that the smaller operators will gradually drop out as the increasing cost of wood and the restricted return from methanol and acetate of lime gradually squeeze their margin of profit.

As a result of the increased capacity for synthetic acetic acid, it seems probable that the price of this commodity will fix the price of acetate of lime, rather than the reverse, which has heretofore been true. The much greater flexibility of the synthetic process will enable its users to follow fluctuations in demand more rapidly than the wood distillers.

The possibility of synthetic production of acetic acid from other materials than carbide must be kept in sight. It is not likely, however, that high-pressure syntheses will invade this field on a commercial scale until there is a greatly in-

Table IV—Production Statistics for Acetic Acid and Acetic Anhydride
(From Census of Manufactures)

Year	U. S. Production			Av. Value of Material for Sale per lb.	U. S. Production			Av. Value of Material for Sale per lb.
	Total	Made and consumed	For sale		Total	Made and consumed	For sale	
	1000 lbs.	*1000 lbs.*	*1000 lbs.*		*1000 lbs.*	*1000 lbs.*	*1000 lbs.*	
	DILUTE, AS VARIOUS STRENGTHS				GLACIAL AND ANHYDRIDE			
1909				$0.023				
1914				0.018				
1919	42,249	9,191	33,058	0.041	21,927[c]	1,468	20,459[c]	$0.142[c]
1921	23,530	1,081	22,449	0.031	15,544	3,448	12,096	0.090
1923	29,470	1,438	28,032	0.031	32,663	3,043	29,620	0.111
1925	29,825	1,103	28,722	0.027	37,109[d]	240	36,869[d]	0.099[d]
1927	56,990	10,762	46,228	0.050	38,944	8,740	30,204	0.106
	DILUTE, AS 100 PER CENT ACID				GLACIAL ONLY			
1927[a]	41,400	10,918	30,481	0.116			15,815	0.097
1929[b]	72,431	19,526	52,905	0.104			13,349	0.105

[a] Revised values published in preliminary report for Census of Manufactures for 1929.
[b] Preliminary report for 1929.
[c] Separate figures for acetic anhydride in 1919 show a total production of 1,794,985 lbs., of which 1,213,861 lbs. were produced for sale with an average value of $0.47 per lb.
[d] Separate figures for acetic anhydride in 1925 show a production for sale of 2,088,567 lbs., with an average value of $0.28 per lb.

creased potential market for acetic acid. The oxidation of alcohol seems to offer the most promising development for the immediate future. This process has already been applied on a large scale in England and supplies a large part of the acetic acid consumed in that country.

While fermentation may be used by certain concerns under special conditions, it is not likely that there will be any general trend toward the production of acetic acid by this method.

As the cost of ethanol by fermentation may be considered at present as practically the equivalent of the cost by synthesis from ethylene—that is, 18 to 20 cents per gallon—we can consider 3 cents per pound as the manufacturing cost of acetic acid on the basis of present prices; hence, a selling price of 5 cents per pound for glacial acetic acid is perfectly within reason. As the cost of ethanol drops this price of acetic acid will likewise follow.

PRODUCTION AND CONSUMPTION OF ACETIC ACID DURING 1929

Industrial activity and general prosperity in the United States increased rather steadily from 1922 to 1929 and then collapsed suddenly. The year of 1929 was decidedly above the average, but since it is the last year for which anything like complete information is available, it will be used here for analysis of the production and consumption of acetic acid.

Acetic Acid Available for Use

In calculating the amount of acetic acid available for use during 1929, the writer has considered the production and imports of calcium acetate and of acetic acid for the last quarter of 1928 and the first three quarters of 1929. During this period the demand for acetic acid was intense and the conversion of acetate of lime to acetic acid or directly to ethyl acetate was following close on the production of acetate of lime, the stocks of which were almost negligible, as indicated in Figure 6. Imports of acetate of lime and of acetic acid rose sharply in 1929, as indicated in Tables I and III, and in Figure 7, while exports of both of these commodities were practically zero.

The writer has weighted the figures for the two years in the ratio of 25 per cent for 1928 and 75 per cent for 1929 in calculating the amount available for consumption during the latter year. On this basis the United States production of acetate of lime was 138 million pounds, which is equivalent to approximately 69 million pounds of acetic acid. The imported acetate of lime on the same basis amounted to somewhat over 20 million pounds, equivalent to 10 million pounds of acetic acid. The writer has estimated that the imports of acetic acid shown in Table III amounted to approximately 18 million pounds on the 100 per cent basis. The production of synthetic acetic acid in the United States was probably at the estimated capacity of 6 million pounds. The amount produced by fermentation processes for industrial use was approximately 10 million pounds. The total amount of acetic acid, as such, or in the form of calcium acetate, available for consumption in the United States during 1929 thus is estimated at 113 million pounds on the 100 per cent basis.

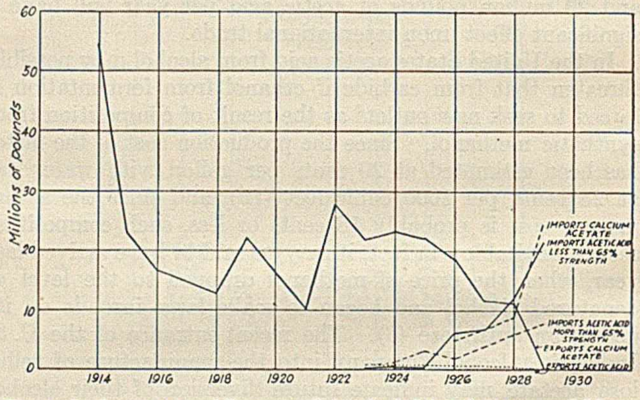

Figure 7—Imports and Exports of Acetic Acid and Acetate of Lime, 1914–1929
From statistics of Department of Commerce

In comparison with these figures, the Census data for 1929, given in Table IV, show a dilute acid production, calculated to the 100 per cent basis, of somewhat more than 72 million pounds and a glacial acid production for sale of more than 13 million pounds. The amount of glacial acid made and consumed in the same establishments is not given, but aside from the reclamation of glacial acid in cellulose acetate plants this figure is probably small, and the operations in connection with cellulose acetate should not be considered since they form a cyclical process in which acid is diluted and reconcentrated continuously. The difference between the nearly 86 million pounds of acid shown in the Census data and the 95 million pounds previously estimated for the synthetic and fermentation products and the production from domestic and imported acetate of lime may be attributed to the direct use of considerable amounts of the latter material in the manufacture of ethyl acetate.

Consumption of Acetic Acid in Various Industries

The consumption of acetic acid during 1929 in various industries is estimated in Table V.

Table V—Consumption of Acetic Acid in the United States during 1929

Industry	Production of Specified Commodity	Equivalent Consumption of Acetic Acid or Calcium Acetate
	1000 lbs.	*1000 lbs. 100% acid*
Solvents:		
Amyl acetate	1,900	870[a]
Butyl acetate	44,100	22,800[a]
Ethyl acetate	83,000	41,000[b]
Cellulose acetate	7,000	7,600[c]
Textile dyeing		15,000
Chemicals and dyes:		
Lead acetate	8,000	3,000
Sodium acetate	592	430
Acetic anhydride		4,000
Other substances		500
White lead	320,000	1,400
Leather tanning		2,000
Miscellaneous uses and unused production		14,400

[a] Theoretical equivalent.
[b] Theoretical equivalent 48 million lbs. See text.
[c] Combined in cellulose diacetate, 3.4 million lbs.; lost during recovery from dilute acetic acid liquors, 4.2 million lbs., based on 10 per cent loss on 41.5 million lbs. Approximately half of this entered the process as acetic anhydride.

SOLVENTS—It is evident that the manufacture of solvents comprised the largest market, and that ethyl acetate alone accounted for twice as much acetic acid as any other commodity. The item for acetic acid used in the production of ethyl acetate is uncertain, owing to the enthusiastic use of this substance for conversion to bootleg alcohol, and to its manufacture by processes not involving the intermediate production of acetate of lime or acetic acid. The figure of 41 million pounds is, however, believed to be conservative. The annual production of ethyl acetate has increased tremendously since 1929, as shown in Table VI and Figure 8, reaching a value of 83 million pounds for 1929. This has been due largely to two influences very prominent in American life—the development of nitrocellulose lacquers and the well-known but not very well-respected Eighteenth Amendment. It has been estimated by persons connected with the industry that when the Government clamped the lid on the diversion of ethyl acetate late in 1929, as high as 50 per cent of the production was being expeditiously converted into alcohol by bootleggers who remembered their chemistry. There is

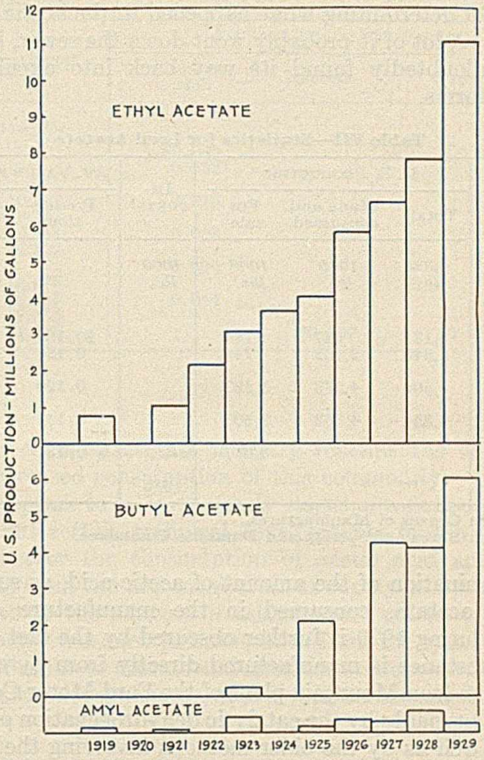

Figure 8—Production of Solvent Acetates in the United States, 1919–1929
From statistics of Department of Commerce

Table VI—Statistics for Solvent Acetates

Year	U. S. Production[a]			Imports[b]	Exports[c]	Approx. Total Production + Imports − Exports	Av. Value per Gallon	
	Total	Made and consumed	For sale				Production[a]	Import[b]
	Gal.	*Gal.*	*Gal.*	*Gal.*	*Gal.*	*Gal.*		
	AMYL ACETATE							
1909			204,000				$2.17	
1914			180,200				2.58	
1919	125,692	29,589	96,103			125,000	3.65	
1921	88,688	23,334	65,354			88,000	2.29	
1923	440,976	191,083	249,893	3,660		444,000	3.98	$2.62
1925	168,251	30,768	137,483	2,850		171,000	3.02	2.52
1926	375,000[b]		260,000[b]	750		375,000	2.09[b]	3.42
1927	316,578	97,702	218,876	42		316,000	1.98	3.50
1928	594,000[b]			75	50,000		1.77[b]	2.74
1929	262,825	81,631	181,194	42	80,000	180,000	1.75	1.91
	BUTYL ACETATE[d]							
1923	252,706	188,908	64,608				3.00	
1925	2,078,926	1,208,436	870,463				1.81	
1927	4,220,490	1,878,479	2,342,011				1.54	
1928	4,085,000[b]		2,825,000[b]	727,500			1.34[b]	0.97
1929	6,006,081	1,618,313	4,378,768	1,065,000		7,000,000	1.28	0.92
	ETHYL ACETATE							
1919	770,739	416,346	354,393				0.96	
1921	1,016,677	496,292	520,385	4			0.61	2.00
1922	2,150,000[b]		1,573,000[b]	27			0.64	
1923	3,091,024	561,236	2,529,788	3,630			0.87	3.22
1924	3,630,000[b]		2,575,000[b]	34			0.93[b]	1.16
1925	4,021,653	1,114,441	2,907,212	1,700			0.83	1.26
1926	5,820,000[b]		4,290,000[b]	115			0.69[b]	0.78
1927	6,638,147	2,031,245	4,606,902	500			0.80	0.78
1928	7,810,000[b]		5,850,000[b]	15	65,000		0.81[b]	2.25
1929	11,065,326	488,941	10,576,385	10	15,000	11,000,000	0.82	7.40

[a] From Census of Manufactures, except as otherwise noted.
[b] From Bureau of Foreign and Domestic Commerce.
[c] Estimated from combined totals for amyl, butyl, and ethyl acetates on assumption that exports of butyl acetate were negligible. In 1928, 841,564 lbs. of amyl, butyl, and ethyl acetates, valued at $141,240, were exported; in 1929, the total was 698,367 lbs., valued at $156,241.
[d] No separate data prior to 1923.

no way of determining what happened to the acetic acid left behind. A lot of it probably went down the sewer, but some of it undoubtedly found its way back into circulation in various forms.

Table VII—Statistics for Lead Acetate

Year	U. S. Production[a]			Imports[b]	Av. Value per Pound	
	Total	Made and consumed	For sale		Production	Imports
	1000 lbs.	*1000 lbs.*	*1000 lbs.*	*1000 lbs.*		
1909						
1914						
1919	5,131	947	4,184		$0.132	
1921	2,846	2,102	744		0.121	
1922						
1923	5,506	4,273	1,233		0.120	
1924						
1925	6,864	4,363	2,501		0.144	
1926						
1927			3,017		0.131	
1928						
1929				385		$0.079

[a] From Census of Manufactures.
[b] From Bureau of Foreign and Domestic Commerce.

Determination of the amount of acetic acid, as such or as calcium acetate, consumed in the manufacture of ethyl acetate during 1929 is further obscured by the fact that the latter substance is manufactured directly from pyroligneous acid at the Iron Mountain plant of the Ford Motor Company, and also probably by the catalytic dehydrogenation of alcohol (*44*), as well as by the older methods involving the reaction of acetate of lime or acetic acid with alcohol. The writer has estimated from data on the published description of the Iron Mountain operations (*33*) that ethyl acetate equivalent to 7 million pounds of acetic acid was produced in this plant during 1929, and has neglected the amounts of acetic acid recovered from ethyl acetate or produced by the catalytic dehydrogenation of alcohol during 1929. By subtracting 7 million pounds from the 48 million pounds of acetic acid equivalent to the total 1929 production of 83 million pounds of 85 per cent ethyl acetate, an estimated consumption of 41 million pounds of acetic acid is obtained for the ethyl acetate industry during this year.

The amounts of acetic acid consumed in the manufacture of amyl acetate and butyl acetate during 1929 are shown in Table V as the theoretical equivalents of the production of these substances.

CELLULOSE ACETATE—The estimated production of cellulose acetate during 1929 was 7 million pounds (*43*). According to Mullin (*29*), an average of 350 parts of glacial acetic acid and 400 parts of acetic anhydride are used to produce 150 parts of primary triacetate, which is subsequently hydrolyzed to approximately the acetyl content of diacetate. To produce 7 million pounds of celanese 19.2 million pounds of glacial acetic acid and 21.9 million pounds of acetic anhydride were required. These figures are greatly in excess of actual consumption, however, as but 3.4 million pounds of acetic acid actually were contained in the product, and 41.5 million pounds of acetic acid in the form of a dilute solution of approximately 25 per cent concentration were sent to recovery processes for conversion back into glacial acid, anhydride, or acetates. Even if as high as 10 per cent loss during recovery is assumed, the actual consumption due to loss was only 4.2 million pounds, and the total consumption of acetic acid and anhydride by the cellulose acetate industry during 1929 was equivalent to 7.6 million pounds of acetic acid.

The recovery processes used and the economic significance of the acetic acid recovery problem in the cellulose acetate industry are discussed in another section of this survey.

TEXTILE DYEING—The writer has been unable to obtain any estimates from authoritative sources concerning the quantity of acetic acid used in dyeing and printing textiles during 1929, although it is generally known that this industry is one of the major markets for dilute acid. A guess of 15 million pounds has been made, but this should not be used as a basis for further calculations.

CHEMICALS AND DYES—Estimation of the consumption of acetic acid in the chemical and dye industry is complicated by the lack of data and by the complex inter-relationships of the products which may be the raw materials for the production of other substances. Incomplete data from the Census of Manufactures are available for the production of lead acetate, sodium acetate, and acetic anhydride in recent years. These have been used with several assumptions.

From the incomplete information concerning lead acetate in Table VII, it has been assumed that the total production of this substance during 1929 approximated 8 million pounds, which is approximately equivalent to 3 million pounds of acetic acid.

The data for sodium acetate in Table VIII give little basis for an estimate of the production during 1929. Sodium acetate is used extensively in the manufacture of acetic anhydride, and is derived in large quantities from the dilute acetic acid obtained in the manufacture of cellulose acetate. It has been assumed that the 592,000 pounds produced for sale during 1929 represent the use of sodium acetate for all purposes other than the production of acetic anhydride, which has been listed separately. The amount of acetic acid equivalent to this amount of sodium acetate is approximately 430,000 pounds.

The only Census figure for acetic anhydride in recent years is a production for sale of 2 million pounds during 1925, given in footnote *d* of Table IV. Since the consumption of acetic anhydride in the manufacture of cellulose acetate has already been included under the estimate for this industry, an estimate of the amount of anhydride used for all other purposes is needed. This has been placed as equivalent to 4 million pounds of acetic acid. A further item of 500,000 pounds of acetic acid has been included for other chemical uses not involving acetic anhydride.

Table VIII—Statistics for Sodium Acetate

Year	U. S. Production[a]			Imports[b]	Av. Value per lb.	
	Total	Made and consumed	For sale		Production	Imports
	1000 lbs.	*1000 lbs.*	*1000 lbs.*	*1000 lbs.*		
1919	2,260	64	2,196		$0.075	
1921	312	0	312		0.052	
1922				342		$0.049
1923	2,472	1,366	906	620	0.066	0.051
1924				103		0.055
1925	860	46	814	495	0.059	0.038
1926				753		0.057
1927			1,855	1,113	0.043	0.054
1928				1,401		0.046
1929			592	875	0.056	0.048

[a] From Census of Manufactures.
[b] From Bureau of Foreign and Domestic Commerce.
[c] No statistics available for exports, amount exported probably small.

WHITE LEAD—The production of white lead in the United States has been rather steady for a number of years, as indicated in Table IX. At the time of writing the 1929 figure was not available, but it has been estimated as 320 million pounds. Approximately 0.0044 pound of acetic acid on the 100 per cent basis is used per pound of white lead produced, according to one large manufacturer; hence the consumption of acetic acid in the industry during 1929 has been calculated as 1.4 million pounds. It is estimated that on the average 0.004 pound of acetic acid on the 100 per cent basis is consumed per pound of white lead produced by the Old Dutch process, while the quick processes show a higher consumption of 0.006 to 0.0064 pound of acid per pound of white lead.

Table IX—Statistics for White Lead

YEAR	U. S. PRODUCTION[a]			IMPORTS	EXPORTS[b]	AVERAGE VALUE PER POUND		
	Total	Made and consumed	For sale			Production	Imports	Exports
	1000 lbs.	*1000 lbs.*	*1000 lbs.*	*1000 lbs.*	*1000 lbs.*			
1909	247,972	162,703	85,269			$0.046		
1914	279,270	207,626	71,644			0.052		
1919								
1921	334,949	211,081	123,868		10,321	0.073		
1922					9,722			
1923	301,083	160,956	140,127		10,344	0.088		
1924					10,109			
1925	342,132	199,202	142,930			0.099		
1926					12,478			
1927	331,617	188,312	143,305		12,095	0.084		
1928					12,953			
1929	320,000[c]			196	11,815		$0.097	$0.078

[a] From Census of Manufactures, except as otherwise noted.
[b] Statistical Abstract of United States, white and sublimed lead.
[c] Estimated.

LEATHER TANNING—No specific information concerning the amounts of acetic acid used in leather tanning could be obtained from inquiries. The use of acetic acid in this industry appears to be decreasing, however. A figure of 2 million pounds for the consumption during 1929 is probably adequate.

MISCELLANEOUS USES AND UNUSED PRODUCTION—Under this item have been included the 14.4 million pounds difference between the sum of the preceding amounts and the 113 million pounds total production of acetic acid available for consumption during 1929. Since there was a strong demand for acetic acid during 1929, it is probable that very little of the production was unused. The amount exported was negligible.

Probable Trend of Consumption

The great demand for acetic acid during 1929 has been interpreted in some quarters as indicating a rapidly expanding market for this commodity. Particular attention has been called to the rapid increase in the production of acetate solvents and of cellulose acetate as indicating the need for greater production of acetic acid. Before analyzing the situation in these two industries, the remaining ones listed in Table V may be briefly noted. The use of acetic acid and of acetic anhydride derived in one way or another from acetic acid in the production of chemicals and dyes will probably increase more or less steadily, but slowly. The consumption of acetic acid in the production of white lead and in the dyeing and printing of textiles will be practically stationary, while the use in leather tanning seems to be on the decrease. Some of the small miscellaneous uses may show sudden activity, but it is improbable that any new large outlet for acetic acid will be developed among them. Altogether, there will probably be a slightly expanding market due to activity in the production of organic chemicals and dyes.

The acetate solvents accounted for something like 64.7 million pounds of acetic acid or 57 per cent of the total amount available during 1929. When the data for 1930 are in, however, there will be a sad shrinkage both in the total amount and the percentage. If it is true that large amounts of ethyl acetate were diverted into bootleg channels during 1928 and 1929 and that this diversion was effectively plugged late in 1929, the market for acetic acid has been decreased very severely by this one effect. In addition, the decrease in business activity has been particularly marked in the automotive industry, the greatest single market for lacquers using acetate solvents. It is now expected that recovery from the depression will be slow. It seems certain, therefore, that the consumption of acetic acid in the production of acetate solvents for several years will be well below the peak established in 1929.

With the acetate solvent industry rather definitely out of the picture for a few years as an expanding market for acetic acid, the cellulose acetate industry remains the only hope for an increased consumption of this commodity. Cellulose acetate appears to be in the early stages of a period of rapid growth, but certain technical developments raise a question as to whether the consumption of acetic acid and acetic anhydride from the present sources of supply will increase in proportion to the amount of celanese and plastic produced. The industry has such promise, both from the standpoint of the use of cellulose acetate and from the standpoint of radical technological developments, that it will be discussed more at length.

GENERAL DEVELOPMENT OF CELLULOSE ACETATE INDUSTRY IN UNITED STATES

The first commercial production of acetate fiber is credited to the Lustron Company, which operated a small plant in South Boston for a number of years on the basis of the investigations of H. S. Mork and A. D. Little. This plant, which had a capacity under 500,000 pounds per year, was subsequently absorbed by the Celanese organization. The latter concern, established during the war as the American Cellulose and Chemical Manufacturing Company and now the Celanese Corporation of America, started production of acetate fiber in its plant at Amcelle, near Cumberland, Md., in 1925. During the middle of 1929 the plant of the American Chatillon Corporation at Rome, Ga., began operation, followed closely by the acetate fiber plant of the Du Pont Rayon Company at Waynesboro, Va., in December, 1929. The acetate fiber plant of the Viscose Company at Meadville, Pa., began to produce during 1930. During this same year a radically new process was announced by the U. S. Industrial Alcohol Company. At the same time the Tennessee Eastman Corporation was planning to build a new acetate fiber plant which is expected to start production in the fall of 1931. With the inclusion of the capacity of this first Eastman unit, the 1931 capacity for the production of acetate fiber in the United States is estimated to be at least 30 tons per day. This figure represents the capacity for spinning yarn. The capacity for the manufacture of cellulose acetate undoubtedly is somewhat greater, owing to the use of this material as a plastic, the amount so used during 1929 having been estimated at between 0.5 and 1 million pounds.

There is no doubt concerning the rapid development which has taken place in the manufacture of cellulose acetate. The United States production has risen from less than 0.5 million pounds in 1924 to somewhat more than 7 million pounds in 1929. In spite of the industrial depression, the increase in production continued during 1930, the amount for this year being estimated at more than 10 million pounds. The important question of the future trend of this industry has been discussed in countless Pullman symposia during the past two years without being settled even tentatively; at the present time, however, it seems to be definitely going somewhere.

Properties of Cellulose Acetate

Cellulose acetate has certain properties which make it desirable as a synthetic fiber and also as a plastic. Its advantages have, however, been somewhat overworked by its enthusiastic admirers. It is probably not the ultimate paragon of synthetic fibers, even though it does lose a smaller percentage of its strength when wetted than viscose.

Cellulose acetate was first brought to general attention during the World War by its use as a varnish for airplane wings. The chief properties which led to its extensive application in this field were its low hygroscopicity and its slow rate of burning. Other properties which have been exploited to advantage are its greater stability against light and heat than nitrocellulose, its low specific gravity, its high dielectric strength, and its elasticity. Certain of these properties are especially important from the viewpoint of synthetic fiber, while others affect the use of cellulose acetate as a lacquer or a molding plastic.

Properties as a Synthetic Fiber—One of the chief objections to rayon has been its low strength when wet. Owing to its small tendency to absorb water, acetate silk shows a much smaller percentage decrease in strength on wetting than any other type of synthetic fiber. The actual wet strength of average commercial acetate yarn is, however, very close to that of average commercial viscose yarn, while the latter shows an appreciably greater dry strength. Both the Viscose Company and the Du Pont Rayon Company have produced and sold as a standard brand millions of pounds of viscose yarn with wet strengths from 15 to 30 per cent higher than the wet strength of any acetate yarn at present on the market. More than 60 per cent of the yarn produced by the Viscose Company during 1930 fell in this class. In addition, there are on the market standard Tubize yarns of nitrocellulose origin and standard Bemberg yarns of cuprammonium origin with wet strengths greatly exceeding the highest wet strength yet obtained with cellulose acetate. In view of these facts, the argument that acetate fiber loses a smaller percentage of its strength on wetting has relatively little significance.

Acetate fiber takes up approximately one-half as much moisture as other types under given conditions of temperature and humidity, the actual amount of water being a function of the degree of esterification. While the change in specific volume of synthetic fibers on wetting is not of primary importance, the fact that acetate fiber swells less than other types gives it some advantage.

The extensibility of acetate fibers is definitely greater than that of other types. This is an advantage in fabrics subjected to irregular stresses, since it prevents or largely reduces bagging and wrinkling. It also makes acetate silk easier to handle in dyeing.

The difficulty encountered from the first in dyeing celanese has been overcome by the development of special dyes, and what was once its greatest handicap now bids fair to be its most valuable property. While a large part of the early trouble was due to the difficulty in obtaining even wetting, it was not until 1922 that the first new dyes especially developed for use on celanese were available. Since that time there has been a rapid increase in the quality and quantity of dyes for celanese. Since, in general, the dyes for other fibers do not affect celanese, and many of those developed for celanese have no effect on other fibers, a great field for cross-dyeing has been opened up and is being exploited more and more extensively. The ability to cross-dye mixtures of acetate fibers with other materials has probably been the chief factor up to the present time in maintaining the price level of acetate. The ability to cross-dye one woven design in such a fabric in a practically infinite number of color combinations has made it possible for the textile mills to reduce their inventories materially.

It has been the opinion in some quarters that the use of celanese would be limited largely to those cases in which cross-dyeing was desired. It seems probable, however, that the ability to spin a fine-denier product rapidly will give celanese a much broader field of use. The trend appears to be toward finer filaments, since these result in softer fabrics, with better appearance and feel and better covering power. In the fine-denier range, celanese can compete more nearly on a price basis with viscose than in the range of coarser filaments, since with decrease in filament size the rate of spinning for viscose must be materially decreased. Mullin (*30*) has even stated his opinion that celanese yarn can now be produced at a lower total cost than any other synthetic fiber. While this is doubtful, it is certain that costs are being reduced in the production of celanese, while in the manufacture of viscose, owing to the longer period of commercial operation, costs have already been pared close to the minimum. As acetic acid becomes cheaper any difference in production cost between acetate fiber and other synthetic fibers will tend to disappear.

Properties as a Film or Plastic—While cellulose acetate has gone a long way since its wartime use as an airplane-wing dope, its use as a lacquer or a molding plastic is still young. Its property of non-inflammability has led to one important field of use, the manufacture of 16-mm. safety film for home movies. Cellulose acetate film has not yet been able to obtain a foothold in the commercial movie field. Its higher cost and the alleged warping of the wider commercial film have more than offset the safety considerations involved.

The stability of cellulose acetate to sunlight and heat have led to attempts to use it in place of celluloid in safety glass. Thus far, however, this application has been limited by the poorer adhesion and greater brittleness of the acetate sheets available. Since the value of safety glass depends upon perfect adhesion between the glass sheets and the film of plastic between them, acetate will have no extensive use in this field until the problem of obtaining such adhesion is solved. It is reported, however, that in Europe considerable quantities of Usines du Rhône acetate are used in the manufacture of safety glass. Furthermore, whereas nitrocellulose gradually discolors in sunlight, the acetate sheets obtainable up to the present show a slight haziness. There is a good field open for industrial use where the ability of glass made with acetate to stand up continuously at 100° C. would far overbalance the very minor disadvantage of the haze. Cellulose acetate sheet will stand a temperature of 100° C. for several hundred hours with no decrease in flexibility. One limited but rather interesting utilization of the heat resistance of cellulose acetate has been in the manufacture of art shades for electric lights.

The relatively small tendency of cellulose acetate to absorb water gives it a high dielectric strength under ordinary humidity conditions. The work of A. C. Walker at the Bell Laboratories indicates that at the same moisture content a number of cellulose esters have the same dielectric strength as pure cotton, so that it is incorrect to speak of high dielectric strength as an inherent property of cellulose acetate. From the practical standpoint, however, the greater insulating ability of cellulose acetate under service conditions is causing its use not only as thread for the woven fabric covering the rubber insulation on electric wiring, but also as an insulating lacquer and as a molding plastic for parts of electrical equipment.

As a molding material, cellulose acetate has certain advantageous properties. It may be extruded with extremely thin walls, thus reducing cost. It is tough, water-resistant, and light-proof. Owing to its translucence, a small amount of pigment gives a good depth of color, while its ability to

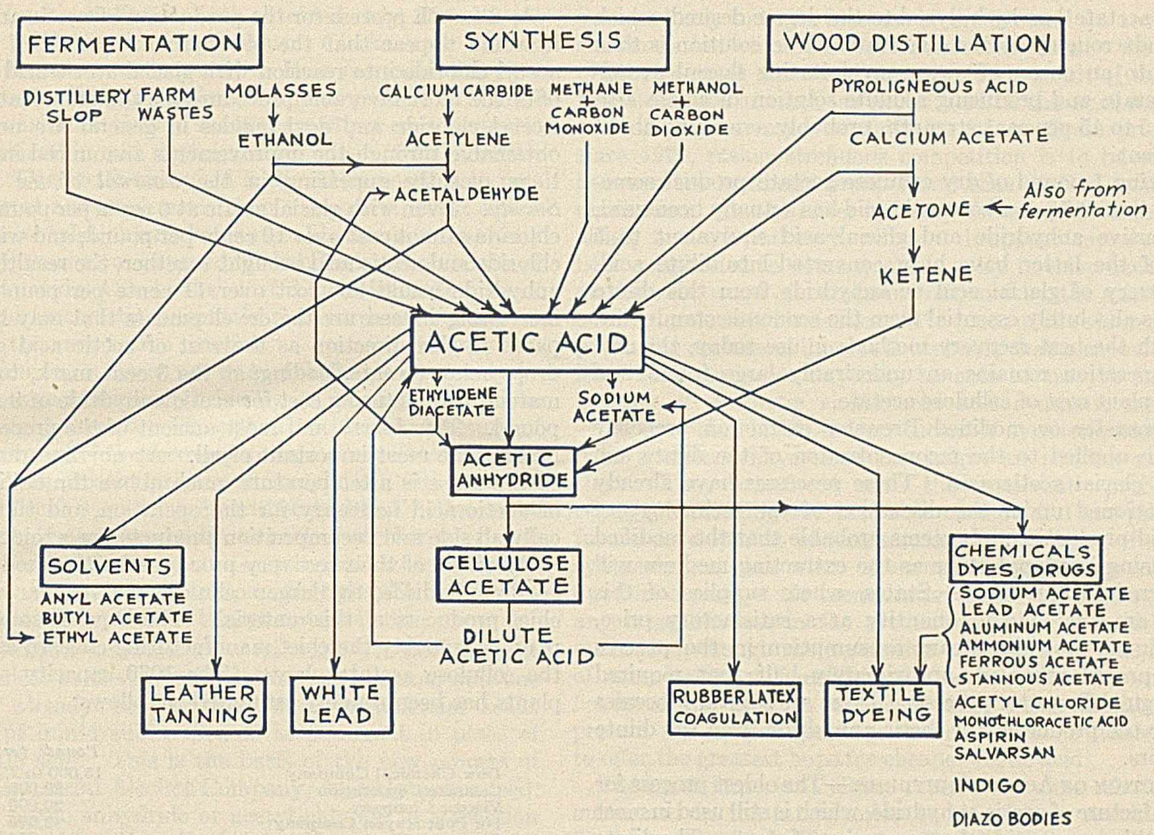

Figure 9—Chemical Relationships in the Production and Use of Acetic Acid

stand heat again serves it well. In fact, its chief claim to a place in the strenuous commodity competition of the plastics field is its easy thermoplastic production of a mottled, translucent, or nearly transparent product which is resistant to ordinary heat and is not attacked by water, as are the casein plastics. Acetate plastic is more susceptible to attack by acid and alkali than nitrocellulose, but it is not affected by alcohol, while both stand hydrocarbons quite well.

No single plasticizer for cellulose acetate comparable to camphor in the case of nitrocellulose has yet been found, and several combinations of varied materials have been used (*39*). The development of acetate lacquer has been hindered by the problem of finding compatible plasticizers and solvents which were at the same time desirable from both the technical and economic standpoints. While acetone appears to be the ideal solvent for cellulose acetate, it absorbs water readily, causing blushing, and it is highly inflammable.

Uses of Cellulose Acetate

The single quantity use of cellulose acetate at present is in celanese, while the production of safety film probably ranks first among the other applications. Lacquers for airplane surfaces have been in use since the war, but represent only a small outlet for the material, which seems bound to decrease with the trend toward all-metal planes. Cellulose acetate lacquers for insulating purposes probably have more of a future. Molding powder for the production of anything from phonograph records to cups and saucers has recently been placed on the market, and thin, transparent cellulose acetate wrapping which can be sealed by heat is just about to arrive. There is a tentative market of some importance in safety glass. New applications in molded articles present the most probable line of development, although there is a large possible market in commercial movie film which may some day be tapped.

MANUFACTURE OF CELLULOSE ACETATE

It is not the purpose of this survey to go into the technical details of cellulose acetate production. In the first place, little significant information is available outside of the patent literature which is sufficiently extensive, cryptic, and contradictory to render it meaningless to anyone not having direct contact with the industry. Since this survey is interested primarily in the possible future markets for acetic acid and acetic anhydride, attention will be confined to the present practice and future possibilities in acetylation and in the recovery of acetic acid or anhydride.

Present General Practice

Acetylation of cellulose is generally carried out at present by the use of acetic anhydride with sulfuric acid as a catalyst and glacial acetic acid as a solvent for the triacetate produced. A rather large excess of acetic anhydride is required in acetylation, since each mol of anhydride reacting with a hydroxyl group produces a mol of acetic acid as well as introducing an acetyl group into the cellulose, and since the moisture in the cotton, amounting generally to 5 per cent, reacts with an equivalent amount of anhydride to produce acetic acid. Mullin (*29*) has estimated, probably from the patent literature, that 350 parts of glacial acetic acid and 400 parts of acetic anhydride are used on the average to produce 150 parts of primary triacetate from 100 parts of cotton cellulose. The cotton cellulose, as customarily used, contains about 5 per cent moisture, since thoroughly dried cotton does not acetylate readily or evenly.

To produce acetone-soluble secondary acetates, the solution of primary triacetate in glacial acetic acid containing excess anhydride is diluted gradually with water until the glacial acid and anhydride have been converted to acetic acid of 90 to 95 per cent strength. This solution is allowed to ripen for 10 to 12 hours, or until control tests indicate that the cellulose acetate has hydrolyzed to the degree desired, which corresponds roughly to the diacetate. The solution is then poured into an excess of water, precipitating flocculent cellulose acetate and producing a dilute solution of acetic acid of from 15 to 45 per cent strength, probably averaging about 25 per cent.

In making 1 pound of dry cellulose acetate product somewhat less than 0.5 pound of acetic acid has actually been used, but expensive anhydride and glacial acid equivalent to 5 pounds of the latter have been converted into dilute acid. The recovery of glacial acid or anhydride from this dilute solution is absolutely essential from the economic standpoint. Even with the best recovery methods in use today, the cost of this operation remains an undesirably large fraction of the total plant cost of cellulose acetate.

The Brewster or modified Brewster extraction processes have been applied to the reconcentration of the dilute end liquor to glacial acetic acid. These processes have already been mentioned under the discussion of the technology of acetic acid production. It seems probable that the modified process using isopropyl ether as the extracting medium will be preferred in the United States, where supplies of this material are available in quantity at a satisfactory price. It is claimed that the steam consumption in the process using isopropyl ether is approximately half that required in the original Brewster process. There are several processes in use for the production of acetic anhydride from the dilute end liquors.

PRODUCTION OF ACETIC ANHYDRIDE—The oldest process for the manufacture of acetic anhydride, which is still used in most plants in this country, involves a number of steps. The dilute acid is first concentrated to approximately 60 per cent strength with the simultaneous removal of cellulosic impurities. It is then neutralized with soda ash and evaporated to dryness, producing anhydrous sodium acetate. This is either sold to a chemical manufacturer in return for anhydride or is used in the manufacture of anhydride directly at the plant. The latter course is followed where the volume of operations will justify the investment in equipment. A plant to recover 20,000 pounds of anhydride per day will, however, require an investment of about $400,000. The operating cost on this scale is said to be nearly 75 per cent of the cost of acetic anhydride.

The manufacture of anhydride from sodium acetate involves the use of sulfuryl chloride, sulfur dichloride, or a mixture of sulfur dichloride and liquid chlorine. These chlorine products are cheap at present, which somewhat balances the expense of the extensive plant required.

The second process for the production of anhydride requires the preliminary manufacture of glacial acetic acid. This is vaporized and passed over a catalyst such as sodium metaphosphate at from 400° to 800° C. Acetic anhydride and water are produced, and separation is effected either by refrigeration or fractional distillation under reduced pressure (*28*, *8*). This process is said to be in operation in Germany on a commercial scale, and is reputed to be very good when it is good, but somewhat inclined to be temperamental. The cost of plant is only about 60 per cent of that for the process using sodium acetate, but under present conditions it is believed that the over-all cost of anhydride by the old process is less than that of anhydride obtained by the catalytic decomposition of acetic acid.

The third process involves the intermediate production of ethylidene diacetate from acetic acid vapor and acetylene. The ethylidene diacetate is then decomposed into acetic anhydride and acetaldehyde (*22*, *37*). It is understood that this process has been in operation on a commercial scale at the Waynesboro, Va., acetate plant of the Du Pont Rayon Company.

As a fourth process for the production of acetic anhydride, it would appear that the old German method of bringing acetyl chloride into reaction with glacial acetic acid may yet offer the most favorable procedure for the immediate future. Acetyl chloride and acyl halides in general are now easily obtainable through the improvements announced in publications recently appearing in the *Journal of the Chemical Society*. Even with glacial acetic at 6 cents per pound, acetyl chloride cannot cost over 10 cents per pound, and with acetyl chloride and acetic acid brought together, the resulting acetic anhydride would not cost over 11 cents per pound. Most interesting indeed are the developments that may be anticipated in this direction as the cost of acetic acid gradually drops below 6 cents, leading, at the 3 cent mark, to an estimated manufacturing cost for acetic anhydride of 8 cents per pound. This fourth and most ancient of the processes may become the most important of all. At no time during any of the steps is a temperature much above the boiling point of acetic acid necessary for the operation, and thus practically all side and decomposition products are avoided.

By virtue of their recovery processes for the production of acetic anhydride, the larger cellulose acetate plants are the chief producers of this material. The Dow Chemical Company is probably the chief manufacturing concern aside from the cellulose acetate plants. The 1930 capacity of several plants has been roughly estimated as follows:

	Pounds per day
Dow Chemical Company	15,000 to 25,000
Celanese Corporation	20,000
Viscose Company	20,000
Du Pont Rayon Company	10,000
Tennessee Eastman Corporation	8,000

If the dilute end liquors from a cellulose acetate plant are converted entirely into glacial acetic acid, more of this material will be produced than can be consumed in acetylation. Similarly, if the dilute acid is converted entirely into anhydride, an excess of this material will be obtained. A recovery plant to produce glacial acetic by the modified Brewster process, with subsequent catalytic conversion of part of this into anhydride, is one solution to this situation. The ethylidene diacetate process is another, since the aldehyde produced simultaneously with the anhydride may be readily converted into glacial acetic acid.

Proposed Processes

The necessity for reclamation of large amounts of dilute acetic acid in the present processes for the manufacture of cellulose acetate has led to many attempts at modification of the acetylation step. Among these have been the use of non-aqueous precipitants for cellulose acetate, such as benzene, carbon tetrachloride, and ethyl ether. The recent availability of ethyl ether in increased quantities has received interest in its use as a precipitant. Attempts at direct partial acetylation, using only acetic acid and no anhydride, have been made since the early days, but thus far have not proved satisfactory.

ACETYLATION WITH KETENE—One of the radical changes proposed is the use of ketene for acetylation. According to the Nightingale patent (*34*), cellulose is acetylated by treatment with ketene dissolved in a neutral solvent such as ether, benzene, or gasoline, in the presence of zinc chloride or other catalysts. Ketene adds on directly to a hydroxyl group forming an acetyl group. If this process can be made to work on a commercial scale, there is a definite prospect for it in this country. Ketene is produced by the pyrolysis of acetone (*35*, *5*), which is available at less than half the cost of acetic anhydride. According to Nightingale (*35*), approximately quantitative yields of ketene may be obtained, although Hurd and Fallyn (*21*) obtained only 35 to 40 per cent yield in laboratory apparatus. Clarke and Waring (*5*) used a negative catalyst said to have increased the yield to 80 per cent. It is probably not safe at present to assume an actual maximum yield of more than 55 per cent, owing to the polymerization and decomposition inherent in pyrolytic processes. Even with this yield it should be possible to produce ketene at not much more than the cost of acetic anhydride, while acetylation with ketene would eliminate the costly recovery systems now required to handle large amounts of dilute acetic acid. One of the chief difficulties in the use of ketene as an acetylating agent is the extreme difficulty in controlling the very active reaction.

In addition to its direct use in acetylation, ketene may be used to produce acetic anhydride by its reaction with acetic acid. It might therefore be applied to the manufacture of anhydride as part of the recovery system of a cellulose acetate plant using the present process of acetylation, although the economics of such a system seem rather doubtful. Also, since the pyrolysis of acetone yields one mol of methane for each mol of ketene, and since methane may be cracked to acetylene for the production of acetic acid, another possible tie-in with existing processes is possible, though not probable.

LIQUID SULFUR DIOXIDE AS A SOLVENT—A development fully as radical as that of acetylation with ketene, and one which has already been applied on a commercial scale, is the use of liquid sulfur dioxide as a solvent in place of glacial acetic acid. This is the basis of the new process of the U. S. Industrial Alcohol Company, recently announced. The use of acetic anhydride or acetyl chloride in a reaction medium of liquid sulfur dioxide, with or without glacial acetic acid, and in the presence of the customary catalysts, such as zinc chloride or sulfuric acid, is described in the patent (*4*).

This new process has been called the greatest development in cellulose acetate since Cross and Bevan. It is difficult to estimate its possibilities, but it is now in commercial production on a small scale. Definite information concerning it probably will not be available for some time, but the replacement of glacial acetic acid by liquid sulfur dioxide should reduce production costs materially.

Summary

The development of processes for acetylation which may render unnecessary the present expensive recovery of large quantities of acetic acid from dilute solutions has considerable significance for both the acetic acid industry and the manufacturers of acetic anhydride. These processes have been developed in an attempt to cut the production cost of cellulose acetate. If successful, they will simultaneously tend to reduce the market for acetic acid and acetic anhydride. The only possible way of postponing the eventual successful introduction of these new methods of acetylation is to lower the production cost of acetic acid and acetic anhydride for use in the present methods. Whether the efforts along this line will manage to keep ahead of the use of ketene as an acetylating agent or of sulfur dioxide as a solvent during acetylation is a matter for conjecture.

GENERAL CONCLUSIONS

The preparation of this survey has led the writer to the conclusion that it will be at least three years before the consumption of acetic acid in the United States reaches or materially surpasses the high value established in 1929. This conclusion is based on the expectation that general industrial activity will increase slowly from the low level during 1930, and on the belief that neither in the acetate solvents industry nor in the manufacture of cellulose acetate is there likely to be an increase in the demand for acetic acid similar to that which was created in recent years by the growth of ethyl acetate and butyl acetate. As a result of the probable decreased market for acetic acid in the next few years and of the increased capacity for its synthetic production since 1929, rather strenuous competition is to be expected between the synthetic product and that derived from wood distillation. In the latter industry there will be some casualties, but the industry will not disappear rapidly as has been prophesied in some quarters. By development of the markets for wood oils and charcoal, and by the substitution of direct processes for acetic acid in place of the old method of producing acetate of lime, it is probable that a capacity of at least 2000 cords per day may be able to survive the competition of synthetic acetic acid and synthetic methanol.

On the other hand, the producers of synthetic acetic acid from acetylene have none too bright an outlook ahead of them. They are faced with the immediate problem of capacity exceeding the probable market and the threat of future development of fermentation processes or of cheaper synthetic processes when consumption catches up with production capacity. It seems improbable that there will be any large increase in the production of acetic acid by fermentation, though the possibility of recourse to this method of manufacture will undoubtedly be held as a club over the heads of the present producers using other methods. At present the dehydrogenation and oxidation of ethanol seem to offer the greatest hope for cheaper acetic acid.

The most important of the diverse chemical relationships mentioned in the introduction to this survey are indicated diagrammatically in Figure 9. These, however, include only processes in actual commercial operation, or rather definitely in prospect for such operation. The place of acetic acid in the chemical industry of the future is a subject for prophets only.

Acknowledgments

Some thirty individuals, representing a wide range of business affiliations and fields of technical experience, have assisted to varying degrees in the preparation of this survey. It is impossible to acknowledge separately the debt to these persons who have contributed information and criticized the manuscript. The survey itself is a synthesis from the frequently incompatible bits of raw material which they have supplied. The writer hopes that his interpretation, based upon conflicting viewpoints will be, in the main, as accurate an estimate of present conditions and future trends as is possible in such a piece of work.

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Burning Characteristics of Smokeless Powder

I—Burning Temperature[1]

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Among the causes of erosion in small-arms barrels are several which are functions of the kind of powder used. Whether or not a change from one powder to another will tend to increase or decrease the amount of erosion in a gun barrel may be estimated from a comparison of the powders with respect to burning temperature, composition of gases evolved, and rate of burning. A powder with a high burning temperature should produce more erosion than one with a low burning temperature, because it should heat the inner surface of the barrel to a higher temperature, especially in rapid firing such as occurs in machine-gun operation. At the higher temperature the metal is softer and consequently can be worn away more rapidly by the friction of projectiles and by jets of hot high-pressure gas escaping around the projectiles; it is also more subject to chemical reaction with the combustion gases.

The effect of the composition of the combustion gases is shown in their chemical reactions with the metal of the barrel, especially with a thin skin at the surface of the bore. Oxidizing gases should tend to oxidize metals that are subject to oxidation, and reducing gases should tend to carburize metals subject to carburization. The question of smoke is also related to the composition of the products of combustion.

The rate of burning has at least three effects. A "fast" powder (one that burns rapidly) will develop a higher maximum pressure, because it will be changed to gaseous products before the projectile gets as far as in the case of a "slow" powder; hence it burns in a smaller volume. A fast powder will come closer to developing its burning temperature, because the cooling effect of the metal about it will be felt for a shorter time during the burning. A fast powder will permit more gas to escape around the projectile, especially when a streamline or boat-tail projectile is used, because the pressure behind the projectile will be much higher in the time before the projectile takes the rifling, thereby tending to seal the bore. The gases from a fast powder will emerge at the muzzle cooler than from a slow one, because much of the work on the projectile is done by expanding gases after the powder is all burned. If the powder is fast enough, the gases are cooled below the ignition point of their combustible constituents before they reach the air, and the blast is flashless. The erosion of a fast powder will be greater near the breach and less near the muzzle, so that the accuracy of the barrel should remain high for a greater part of the life of the barrel, although the total life of the barrel may be shorter.

This paper is concerned with the calculation of burning temperatures and the composition of the gases evolved.

From the literature (*1*) we find that attempts have been made to arrive at the burning temperature in the following ways:

Experimentally: (1) By measuring the throw of a ballistic galvanometer connected with a platinum, platinum-rhodium thermocouple placed in a constant-volume bomb.

(2) By dilution of an explosive until the temperature of the explosion is just enough to melt a thin platinum wire, the burning temperature of the diluted explosive being fixed at just above the melting point of platinum.

By calculation: (3) From the heat of burning of the powder and the specific heats of the gases.

(4) From the pressure measured in bomb experiments and the specific volume, by Abel's equation of state

$$P = \frac{fL}{V - \alpha L}$$

in which L is the weight of charge and $f = \frac{P_0 V_0}{273} \times T_0$. T_0 is the burning temperature. This equation can be written

$$P(V - \alpha L) = nRT_0$$

Method of Calculation

Most calculations have been made by the third method, which combines convenience and reliability to the greatest extent of the four methods. In outline, the process is to determine the heat developed by burning the powder in some sort of calorimetric device, analyze the gaseous products, and correct the gas composition and the heat of burning to the figures obtained in an ideal burning, where the powder burns in a constant volume with no heat losses, by means of known heat data and the water-gas equilibrium. The corrected heat of burning is equal to the integrated specific heats of the gases up to the burning temperature. Calculations based on the heat of formation of the powder are but a special case of this method, because the heat of formation is originally calculated from a calorimetric value. Such

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[1] Received January 23, 1931.

a calculation of burning temperature contains all the assumptions of a direct calculation from the calorimetric value, and in addition there is a greater risk of computational error on account of the greater length of the calculation.

When powder burns in a closed container, there are formed gases at the burning temperature which satisfy the water-gas equilibrium at that temperature. That is, the composition and temperature of the gases are related by Equations 1 and 2 below. The cooling process starts immediately. During the first part of this process the gases give off heat to the walls of the container and react to satisfy the water-gas equilibrium, and later also the methane equilibrium. There comes a time, however, when the rate of reaction becomes so slow that it cannot keep up with the cooling. After this the gases are not in equilibrium proportions with respect to their temperature, and the reaction is said to be frozen. During this second part of the cooling, heat continues to be given off by the gases, but their composition does not change much.

For the purpose of calculation, we shall assume that the cooling process follows a different course. Consider that the powder burns as before, but that the reaction freezes at the burning temperature, so that the gases first cool to the original temperature of the powder and then react at that temperature to form the gases found in the analysis. As the initial and final states of the actual and the assumed courses of cooling are the same, the heat effect is also the same by the principle of conservation of energy. Diagrammatically:

ACTUAL	ASSUMED
Powder at atmospheric temperature	Powder at atmospheric temperature
Step 1. Gases at burning temperature satisfying water-gas equilibrium	*Step 1.* Gases at burning temperature satisfying water-gas equilibrium
Step 2. Heat Q_1 and gases at intermediate temperature where reaction freezes and in equilibrium at final composition	*Step 4.* Heat Q_3 and gases at original powder temperature and composition same as after step 1
Step 3. Heat Q_2 and gases in final state, water condensed	*Step 5.* Heat Q_4 and gases in final state, water condensed

$$Q = Q_1 + Q_2 = Q_3 + Q_4$$

is the heat measured in the calorimeter; the gases in the final state have the composition ascertained in a gas analysis made on the cooled gases. The corrected heat of burning is Q_3.

The gases formed when powder burns are hydrogen, water vapor, carbon monoxide, carbon dioxide, and nitrogen. The nitrogen is assumed to be inert. The other four gases react according to the equation:

$$H_2 + CO_2 = H_2O + CO$$

This is the water-gas reaction. Its equilibrium constant

$$K = \frac{(CO)\ (H_2O)}{(H_2)\ (CO_2)} \qquad (1)$$

is related to the temperature:

$$\log K = f\ (t) \qquad (2)$$

In Equation 1 the expression (CO) means "the concentration of carbon monoxide;" but as the total number of molecules is unchanged when the gases react, we can use in place of concentration the number of molecules of carbon monoxide produced by one unit weight of powder, or the partial pressure of carbon monoxide, provided that we do it consistently throughout the calculation. We have chosen to let the parenthesis represent the number of gram-molecules per gram of powder for our calculation:

A carbon balance gives us:

$$(CO) + (CO_2) = (CO') + (CO_2') + (CH_4') \qquad (3)$$

where the primed quantities are those found in the gas analysis and the unprimed refer to products first formed in the burning. Similarly a hydrogen balance gives:

$$2\ (H_2O) + 2\ (H_2) = 2\ (H_2O') + 2\ (H_2') + 4\ (CH_4') \qquad (4)$$

and an oxygen balance:

$$(CO) + 2\ (CO_2) + (H_2O) = (CO') + 2\ (CO_2') + (H_2O') \qquad (5)$$

Step 4 gives us:

$$\Sigma \int C_v\, dt = Q_3 \qquad (6)$$

where C_v is the specific heat of a gas at constant volume. The integration is performed between the original powder temperature and the burning temperature:

$$Q - Q_3 = Q_4 = 97\ [(CO_2') - (CO_2)] + 57.5\ [(H_2O') - (H_2O)] + 29\ [(CO') - (CO)] + 18.9\ (CH_4') + 10.5\ (H_2O') \qquad (7)$$

where 97 is the heat of formation of carbon dioxide, 57.5 is that of gaseous water, 29 is that of carbon monoxide, 18.9 is that of methane, and 10.5 is the heat of vaporization of water—all in large calories per gram-molecule at constant volume and temperature 20° C.

For the determination of Q we may work in a vacuum, in air, in inert gas, or in an excess of oxygen. The last method is simplest because no hydrogen, carbon monoxide, or methane is formed, and gas analysis can be eliminated if the composition of the powder is known. The nitrogen, instead of forming nitrogen gas, becomes liquid nitric acid. To cover this the equations are changed as follows:

$$(CO) + (CO_2) = (CO_2') = \text{atoms C in 1 gram powder} \qquad (3a)$$

$$(H_2O) + (H_2) = (H_2O') + {}^1/_2\ (HNO_3') = {}^1/_2 \text{ atom H in 1 gram powder} \qquad (4a)$$

$$(CO) + 2\ (CO_2) + (H_2O) = \text{atoms O in 1 gram powder} \qquad (5a)$$

$$Q - Q_3 = 68\ (CO) + 68\ [(H_2) - (N_2)] + 40.2\ (HNO_3')$$

$$(HNO_3') = \text{atoms N in 1 gram powder} \qquad (7a)$$

Where the constituents of the powder are known, Q can easily be calculated from the heats of combustion of the constituents; otherwise it may be determined experimentally by the use of a good oxygen-bomb calorimeter, such as the Emerson or the Parr.

Table I—Heat Data for Various Constituents of Powders

CONSTITUENT	CARBON	HYDROGEN	NITROGEN	OXYGEN	HEAT OF COMBUSTION
	Atom/gram	*Atom/gram*	*Atom/gram*	*Atom/gram*	*Atom/gram*
Nitrocellulose:					
13.28% N	0.0212	0.0259	0.0095	0.0366	2.332
12.97% N	0.0216	0.0268	0.0093	0.0365	2.370
12.58% N	0.0221	0.0278	0.0090	0.0363	2.418
12.14% N	0.0226	0.0289	0.0086	0.0361	2.474
11.29% N	0.0246	0.0312	0.0080	0.0357	2.576
Nitroglycerin	0.0132	0.0220	0.0132	0.0396	1.698
Dinitrobenzene	0.0357	0.0238	0.0118	0.0328	3.94
Starch	0.0370	0.0618	....	0.0309	3.96
Dinitrotoluene	0.0385	0.0330	0.0110	0.0220	4.46
Diethyl phthalate	0.0529	0.0616	....	0.0176	6.54
Vaseline, C_nH_{2n}	0.0714	0.1428	....	....	11.04
sym-Diethyldiphenylurea	0.0635	0.0746	0.0074	0.0037	8.48
Diphenylamine	0.0710	0.0650	0.0060	....	9.10

In Table I the heat data for dinitrobenzene, starch, dinitrotoluene, and diphenylamine are taken from International Critical Tables and recalculated to Calories per gram at constant volume. The value for nitroglycerin in the Critical Tables is correct, but the units are wrong. Comparison with other sources shows that the value given there is the heat of formation in calories per gram, but it is labeled "heat of combustion in calories per gram-molecule." Our figure is calculated from the Critical Tables value. The remaining heats of combustion were determined in the Hercules Experimental Station laboratory with an Emerson calorimeter, using 300 pounds (20 atm.) of oxygen. In each case, the bomb was filled three times with oxygen at 80 pounds (5.4 atm.) and released before finally filling to 300 pounds (20 atm.), in order to eliminate the correction for nitrogen in the air originally filling the calorimeter. The other data are calculated from the formulas of the substances.

A number of samples of powder have been made up and run in the calorimeter to determine whether their heats of combustion are the same as the sum of the heats of combustion of the constituents; in other words, whether there is an appreciable heat effect of manufacture of the powders. These samples showed that it is justifiable to neglect the heat effect of manufacture. Therefore, in these calculations the heat of combustion of a powder is taken as the sum of the heats of combustion of the constituents.

Typical Calculation

A burning-temperature calculation is given here on a powder containing nitroglycerin, diphenylamine, and nitrocellulose of 13.28 per cent nitrogen content.

CONSTITUENT	%	HEAT OF COMBUSTION	CARBON	HYDROGEN	OXYGEN	NITROGEN
		Cal./gram	*Atom/gram*	*Atom/gram*	*Atom/gram*	*Atom/gram*
Nitrocellulose	79.50	1.858	0.0169	0.0206	0.0291	0.0076
Nitroglycerin	20.00	0.340	0.0026	0.0044	0.0079	0.0026
Diphenylamine	0.50	0.046	0.0004	0.0003	....	....
	100.00	2.244	0.0199	0.0253	0.0370	0.0102

To facilitate calculation we tabulate the values of K and the $\int C_v dt$ figures for the various gases in Table II. The values of K are computed from Saunder's equation (*3*):

$$\log K = \frac{-2290}{T} + 0.11 \log T - 0.000639T + 10.14 \times 10^{-8} T^2 + 2.3$$

The $\int C_v dt$ values are calculated from Eastman's equations (*2*):

$$\begin{aligned} H_2{:}C_p &= 6.85 + 0.00028\,T + 22 \times 10^{-8}\,T^2 \\ N_2,\ CO{:}C_p &= 6.76 + 0.000606\,T + 13 \times 10^{-8}\,T^2 \\ CO_2{:}C_p &= 7.70 + 0.0053\,T - 83 \times 10^{-8}\,T^2 \\ H_2O{:}C_p &= 8.22 + 0.00015\,T + 134 \times 10^{-8}\,T^2 \end{aligned}$$

The T in these equations is Kelvin temperature and, where t is Centigrade temperature, is related to Centigrade by the equation $t + 273 = T$.

Table II—Values of $\int C_v\,dt$ and K

t	H_2	CO, N_2	CO_2	H_2O	K
° C.	*Cal.*	*Cal.*	*Cal.*	*Cal.*	
2000	11.21	11.52	21.53	17.97	5.4
2200	12.56	12.91	24.27	20.80	6.1
2400	13.97	14.34	27.04	23.91	6.9
2600	15.43	15.83	29.84	27.29	7.6
2800	16.97	17.38	32.66	31.01	8.6
3000	18.56	18.97	35.52	35.05	9.6
3200	20.22	20.64	38.35	39.42	10.8
3400	21.95	22.35	41.21	44.18	12.4
3600	23.76	24.14	43.91	49.39	14.3
3800	25.66	25.99	46.67	55.03	16.6
4000	27.64	27.92	49.36	61.08	19.4

We write down immediately:

$$(CO) + (CO_2) = 0.0199 \qquad (3a)$$

$$(CO) + 2\,(CO_2) + (H_2O) = 0.0370 \qquad (5a)$$

From this we get (H_2O) in terms of (CO):

$$(H_2O) = 0.0370 - (CO) - 2\,[0.0199 - (CO)] = (CO) - 0.0028$$

(H_2O) is obtained similarly in terms of (CO):

$$(H_2) + (H_2O) = 0.0127 \qquad (4a)$$

$$(H_2) = 0.0127 - [(CO) - 0.0028] = 0.0155 - (CO)$$

$$Q - Q_3 = 68\,(CO) + 68\,[0.0155 - (CO) - 0.0051] + 40 \times 0.0102 \qquad (7a)$$

$$Q_3 = 1.129 = \Sigma \int C_v\,dt$$

Assume a burning temperature of 3300° C. Let X = (CO). By Equation 1 and Table II:

$$11.6 = \frac{X\,(X - 0.0028)}{(0.0199 - X)\,(0.0155 - X)}$$

$$\begin{aligned} (CO) = X &= 0.0135 \\ (CO_2) &= 0.0064 \\ (H_2O) &= 0.0107 \\ (H_2) &= 0.0020 \\ (N_2) &= 0.0051 \end{aligned}$$

Multiplying these numbers of mols by the integrated specific heats from table we have, for two temperatures:

	t = 3300° C.	t = 3200° C.
CO	$0.0135 \times 21.45 = 0.290$	$\times 20.64 = 0.278$
CO_2	$0.0064 \times 39.78 = 0.254$	$\times 38.35 = 0.246$
H_2O	$0.0107 \times 41.80 = 0.447$	$\times 39.42 = 0.422$
H_2	$0.0020 \times 21.09 = 0.042$	$\times 20.22 = 0.040$
N_2	$0.0051 \times 21.45 = 0.109$	$\times 20.64 = 0.105$
	$\Sigma \int C_v\,dt = 1.142$	1.091

To the nearest 50° C., therefore, the burning temperature of this powder is 3300° C.

The total number of mols of gas formed per gram of powder is 0.0377. Consequently, the percentage of carbon monoxide in the gases as formed from the burning powder is $\frac{0.0153}{0.0377}$ or 35.8 per cent, etc.

In the same way calculations have been made for a number of powders as shown in Table III.

Discussion of Data

It must be borne in mind that these specific-heat data and the water-gas equilibrium constants were determined at lower temperatures (to 2500° K.) and have been extrapolated about 1000 degrees. Other calculations have been made using different heat data and with correspondingly different burning temperatures. The value of such calculations is, therefore, in giving not so much the actual burning temperatures as the differences in burning temperature due to differences in composition. The actual burning temperatures are no better than the heat data from which they are derived, but the difference between two burning temperatures calculated from the same heat data is much better, as is shown by the fact that different writers give almost the same values of the differences. We cannot say with certainty that the burning temperature of a single-base powder made with nitrocellulose of 13.28 per cent nitrogen content is 3000° C., but we can say with a fair degree of certainty that the inclusion of 20 per cent nitroglycerin in the powder raises the burning temperature 300 degrees, and that 5.50 per cent starch added to the powder lowers the burning temperature 200 degrees.

Table III shows that a 20 per cent nitroglycerin powder is only 10 per cent hotter than a single-base powder of the same nitrogen content. If the nitroglycerin powder is made of lower nitration nitrocellulose, this difference decreases until a single-base powder of 13.28 per cent nitrogen nitrocellulose has actually a higher burning temperature than a 20 per cent nitroglycerin powder containing nitrocellulose of 12.00 per cent nitrogen. The burning temperature of a nitroglycerin powder can be decreased also by the addition of deterrent materials, or fuels, which are low in oxygen content and high in carbon and hydrogen. Such substances nearly always will produce powders having a larger gas volume when used in quantity sufficient to bring the temperature down to the level of the single-base powder. This is demonstrated by powder No. 16, a 30 per cent nitroglycerin powder which has 0.0418 mol of gas as contrasted with 0.0392 for

Table III—Burning Temperatures and Composition of Various Powders

No.	Q	Q_3	t	Gas	Composition of Powder Gas as Burned					Composition of Powders					
					CO	CO_2	H_2O	H_2	N_2	Nitrocellulose	Nitrogen in nitrocellulose	Nitroglycerin	Diphenylamine	Deterrent	
			° C.	Mol/gram	%	%	%	%	%	%	%	%	%		%
1	2.366	0.966	3000	0.0392	41.4	13.2	24.7	8.7	12.0	99.50	13.28	...	0.50	....	
2	2.304	1.047	3150	0.0384	38.8	15.1	26.8	6.5	12.8	89.50	13.28	10.00	0.50	....	
3	2.242	1.127	3300	0.0376	35.8	17.0	28.4	5.3	13.5	79.50	13.28	20.00	0.50	....	
4	2.177	1.209	3450	0.0368	32.4	19.3	30.2	3.7	14.4	69.50	13.28	30.00	0.50	....	
5	2.113	1.283	3550	0.0359	28.1	22.5	31.1	2.8	15.3	59.50	13.28	40.00	0.50	....	
6	2.271	1.089	3200	0.0382	37.2	15.7	28.0	6.0	13.1	79.50	13.00	20.00	0.50	....	
7	2.308	1.040	3100	0.0389	38.6	14.4	27.2	7.2	12.6	79.50	12.60	20.00	0.50	....	
8	2.344	0.990	3000	0.0394	39.9	13.2	26.4	8.6	11.9	79.50	12.14	20.00	0.50	....	
9	2.434	0.952	2850	0.0410	41.0	12.2	25.6	10.2	11.0	79.50	11.29	20.00	0.50	....	
10	2.418	1.084	3200	0.0392	40.9	13.8	25.1	6.9	13.3	68.50	13.28	20.00	0.50	Dinitrobenzene	11.00
11	2.331	1.029	3100	0.0392	39.2	13.8	27.0	7.7	12.3	74.00	13.28	20.00	0.50	Starch	5.50
12	2.400	1.013	3100	0.0392	41.5	12.5	24.9	8.1	13.0	72.00	13.28	20.00	0.50	Dinitrotoluene	7.50
13	2.376	1.086	3200	0.0392	39.1	13.6	27.3	7.2	12.8	77.96	13.28	20.00	0.50	Vaseline	1.54
14	2.392	1.042	3150	0.0392	40.6	13.0	26.0	7.9	12.5	75.90	13.28	20.00	0.50	Diethylphthalate	3.60
15	2.390	1.055	3150	0.0392	40.1	13.0	26.4	7.7	12.8	76.90	13.28	20.00	..	Centralite I	3.00
16	2.577	0.999	2950	0.0418	41.9	9.3	25.1	11.5	12.2	65.00	13.28	30.00	..	Vaseline	5.00

powder No. 1. Consequently, nitroglycerin powders, even when brought to the same temperature level as single-base powders, should shoot on a lower charge than the single-base powders. This is, indeed, found to be the case.

Sometimes a deterrent is placed in the outer layers of the powder grains. In this way the effective burning temperature is lowered just as much as though the deterrent were distributed uniformly through the grain. In addition, the layers of the powder grains containing the deterrent burn comparatively slowly, so that while they are burning the projectile has opportunity to move into the bore and take the rifling. As soon as the deterrent is all burned off, the powder burns as rapidly as if no deterrent had been used. As the projectile is at that time in the barrel, the volume in which the powder burns is greater, the pressure in the gun being correspondingly lower. That is the explanation of the behavior of the so-called progressive burning powders.

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Organic Bases for Gas Purification[1]

R. R. Bottoms

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THE problem of removing objectionable impurities from fuel gas and from industrial gases has existed from the very beginning of the gas industry. The two principal impurities occurring in industrial gases are carbon dioxide and hydrogen sulfide, with smaller quantities of carbon monoxide, sulfur dioxide, hydrocyanic acid, carbon disulfide, and mercaptans. Since hydrogen sulfide is especially objectionable owing to its toxicity for both animal and vegetable life, its corrosive action on structures, gas lines, meters, holders, and household and other equipment, it is advisable to remove this impurity completely, no matter for what use the gas is intended. Carbon dioxide is not objectionable in fuel gases except as a diluent, and then only when the percentage is relatively high. But in gases intended for use in chemical processes or in gases to be liquefied, as in the production of helium, or when fractional distillation is used for the separation of gases, the complete removal of carbon dioxide becomes necessary.

Existing Methods for Removal of Carbon Dioxide and Hydrogen Sulfide

Both carbon dioxide and hydrogen sulfide are acidic, are active chemically, and are highly soluble in water. Such characteristics have made it a relatively simple matter to remove these compounds from other gases. Hydrogen sulfide reacts quantitatively with iron oxide and by this means can be eliminated. This reaction forms the basis of the so-called dry process for eliminating hydrogen sulfide from manufactured gas.

Both carbon dioxide and hydrogen sulfide are soluble in water and can be removed from other gases by countercurrent scrubbing with water under pressure, but the large volume of water required, the large, and therefore expensive, equipment, and the expense of circulation make it uneconomical. Both compounds react with alkalies and also with neutral alkaline carbonates to form pyrolytically unstable compounds. This fact forms the basis of the usual method of liquid purification of gases. In the case of carbon dioxide this reaction with an alkaline carbonate produces an unstable bicarbonate:

$$Na_2CO_3 + CO_2 + H_2O \rightleftharpoons 2NaHCO_3$$

This reaction proceeds to the right at low temperatures and is reversed at a temperature approximating the boiling point of the solution. With hydrogen sulfide this reaction becomes

$$Na_2CO_3 + H_2S \rightleftharpoons NaHCO_3 + NaHS$$

which also goes to the left at the higher temperatures.

This process is usually carried out as a continuous process, absorbing the impurities from the gases in some type of tower or contact apparatus and releasing the absorbed gases in another part of the apparatus. With carbon dioxide it is necessary to heat the solution to a high temperature—that is, approximately 110–120° C.—in order to drive off the carbon dioxide and re-form the neutral carbonate. In the case of hydrogen sulfide the gas is absorbed in one part of the apparatus and blown with hot air in another part releasing the hydrogen sulfide and re-forming the neutral carbonate.

Alkaline bicarbonates, especially sodium bicarbonate,

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[1] Received March 14, 1931.

are not very soluble in water, consequently highly concentrated solutions cannot be used. A solution containing about 8 to 10 per cent of sodium carbonate or 15 to 20 per cent of potassium carbonate may be used for carbon dioxide removal, but for hydrogen sulfide removal, in order to prevent the excessive formation of thiosulfates, solutions stronger than 3 per cent are not economical. For this reason it is necessary to circulate a relatively large amount of solution in the system for the removal of a given amount of acidic gases. For the removal of carbon dioxide, the large amount of steam necessary to heat the solution for driving off this gas often renders this process entirely uneconomical.

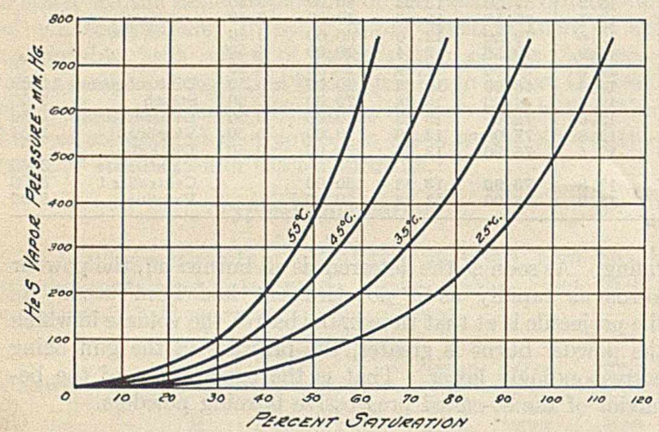

Figure 1—Equilibrium Pressure of Hydrogen Sulfide over 50 Per Cent Water Solution of Triethanolamine

Since 100 per cent saturation is arbitrarily assumed as the volume absorbed at about 30° C. with hydrogen sulfide vapor pressure of 760 mm., when the temperature is below 30° C. as above, the solution will be more than 100 per cent saturated.

Investigation of Organic Nitrogen Bases for Gas Purification

An experimental study of the problem of the economic removal of carbon dioxide from natural gas preparatory to its liquefaction for the separation of helium was started by the author several years ago and culminated in the discovery (*1*) of the use of a class of compounds that has proved to be highly efficient for the removal of both carbon dioxide and hydrogen sulfide from gases. This study covered practically the entire field of the organic nitrogen bases and disclosed the fact that certain amines and amino compounds have the property of absorbing carbon dioxide and hydrogen sulfide, forming pyrolytically unstable carbonates and hydrosulfides which, when heated to a temperature above 50° C., decompose and liberate the carbon dioxide and hydrogen sulfide and release the free base in its original form.

This reaction is quite different from that involved in the absorption of these gases by means of neutral alkaline carbonates, inasmuch as bicarbonates are formed only in small amounts and the free base is regenerated instead of simply the neutral carbonate.

The reaction involved in this process is thought to be as follows:

$$2RNH_2 + CO_2 + H_2O \rightleftharpoons (RNH_2)_2H_2CO_3$$

With hydrogen sulfide this reaction is thought to be

$$2RNH_2 + H_2S \rightleftharpoons (RNH_2)_2H_2S$$

Practically the whole field of organic nitrogen bases has been investigated with a view of obtaining data on the most satisfactory of the amines to be used for the separation of gases. To be suitable for this purpose a compound should have the following characteristics: (1) high specific absorption capacity for the acidic gases; (2) high boiling point, and consequently low vapor pressure to prevent loss of absorbent by vaporization; and (3) a high degree of stability of the molecule in order to prevent decomposition of the base and loss of absorbent through this means.

Some of the compounds tested were the ethanolamines, propylamines, and hydrazines, nicotine, aniline, and quinolin, and a great number of other amines and amino alcohols, both chain and cyclic, including primary, secondary, and tertiary amines, as well as monoamines, diamines, triamines, etc.; and certain heterocyclic nitrogen bases. It was found, however, that the lower members of the alkylamines are too volatile to be as economical as some of the others, while certain amines, such as aniline and other benzene derivatives, are not sufficiently basic to form carbonates, and some of the carbonates of other nitrogen bases, notably guanidine and piperidine, are not decomposed upon boiling the solution and consequently are not so adaptable to this process as some others. The following compounds were found to have the characteristics necessary to make them useful in this process: benzylamine, diaminopropanol, diethanolamine, diethylaminoethanol, dihydroxypropylamine, hydrazine hydrate, piperidylethanol, phenylhydrazine, triethanolamine, tetrahydro-*o*-toluidine, cyclohexylamine.

The ethanolamines (diethanolamine and triethanolamine) were found to be the most satisfactory compounds for immediate use; the first consideration being that they have a high specific absorption capacity, and the second that they are commercially available at a reasonable price and possess all the other properties necessary for this purpose.

Absorption Characteristics of Ethanolamines

The ethanolamines were discovered by Wurtz (*3*) in Germany and investigated by Knorr (*2*). These compounds have been available, however, only in very recent years. When this material became commercially available, larger quantities were obtained by the author in order to make a more thorough investigation of their properties and absorption characteristics.

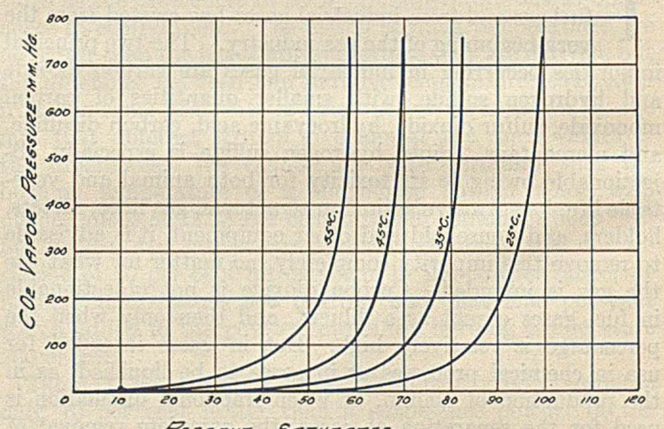

Figure 2—Equilibrium Pressure of Carbon Dioxide over 50 Per Cent Water Solution of Triethanolamine

Commercial triethanolamine and diethanolamine are viscous, hygroscopic liquids with a slightly ammoniacal odor. The formula for triethanolamine is $N(CH_2CH_2OH)_3$; for diethanolamine, $HN(CH_2CH_2OH)_2$. The physical properties are listed below.

	TRIETHANOLAMINE	DIETHANOLAMINE
Molecular weight	149.15	105.1
Specific gravity, at 20°/15° C.	1.12	1.101
Boiling point, ° C.	277 at 150 mm.	271 at 760 mm.
Vapor pressure at 20° C., mm. Hg	<0.0001	0.0002
Solubility in water	Completely	Completely
Weight per gallon	9.35	9.2
Alkalinity, 1 cc. = cc. normal acid	7.53	10.44

Since the ethanolamines are relatively weak bases, as compared with inorganic alkalies, when they react with carbon dioxide and hydrogen sulfide the compounds formed have a definite dissociation pressure which varies with every concentration of the absorbed gases and with the temperature. This relationship is shown graphically in Figures 1 to 4. These charts show the relationship between the amount of carbon dioxide and hydrogen sulfide absorbed in a 50 per cent solution of the bases and the partial pressure of the absorbed gases over such solutions at different temperatures. One hundred per cent saturation as shown on these charts is arbitrarily taken as the amount of gases absorbed when the hydrogen sulfide or carbon dioxide partial pressure is 760 mm. and the temperature 30° C. One hundred per cent saturation for triethanolamine corresponds to 50 volumes of carbon dioxide or hydrogen sulfide per volume of 50 per cent solution, while 100 per cent saturation for diethanolamine corresponds to 70 volumes of carbon dioxide or 100 volumes of hydrogen sulfide per volume of 50 per cent solution.

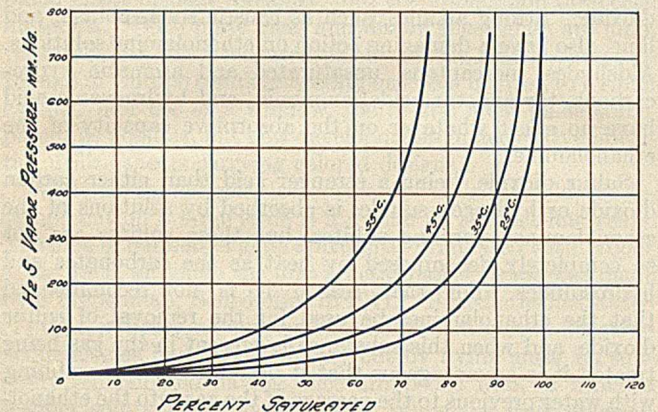

Figure 3—Equilibrium Pressure of Hydrogen Sulfide over 50 Per Cent Water Solution of Diethanolamine

In practical operation for the absorption of carbon dioxide and hydrogen sulfide, a 50 per cent water solution of these ethanolamines has been found to be satisfactory. Since these ethanolamines are mono-acid bases, theoretically 1 mol of the amine should absorb 0.5 mol of either carbon dioxide or hydrogen sulfide. This theoretical absorption, however, will be realized only when the partial pressure of the carbon dioxide or hydrogen sulfide is equal to 1 atmosphere and the temperature of the solution is 30° C. Where the partial pressure of the impurity is lower than 1 atmosphere, the amount of gas absorbed will be correspondingly less than theoretical, as shown in the charts.

When absorbing carbon dioxide and hydrogen sulfide from gaseous mixtures, the volumes absorbed per volume of circulated solution can be calculated from these charts. For example, suppose it is desired to remove the carbon dioxide from 1000 cubic feet of gas per minute when the amount of carbon dioxide equals 20 per cent of the total gas, and the gas is treated for this absorption at atmospheric pressure and 35° C. Calculations based on Figure 2 show that if a gas carrying 20 per cent carbon dioxide (152 mm. partial pressure) at 35° C. is in complete equilibrium with a 50 per cent solution of triethanolamine, the solution will be 74 per cent saturated or will hold in combination 37 volumes of carbon dioxide for each volume of solution circulated. It would therefore be necessary theoretically to circulate for this amount of gas about 41 gallons of solution per minute. Calculation will show that if sodium carbonate were used for the same purpose it would require the circulation of 125 gallons per minute. Consequently much larger equipment and higher operating costs would result.

Type of Equipment

The type of equipment developed for carrying out the process of gas separation by the use of ethanolamines is shown schematically in Figure 5. In the installations that have been made, the absorber consists of a standard bubble-type absorber tower, containing from 12 to 24 bubble trays fitted with a number of bubble caps. The gas enters the base, passes up under the caps, and the solution is pumped into the top, flows down over the trays, and absorbs the impurities as it proceeds on its way down the tower. With this arrangement countercurrent scrubbing is accomplished and the liquid leaves the absorber at the base, where it is in contact with the gas carrying the greatest amount of impurity.

The installation shown in Figure 5 has been based on conditions where the gas is treated at pressures above atmospheric. In such gas the pressure in the tower is sufficient to force the liquid through the outlet of the tower, through the heat interchangers and piping, to the top of the reactivator tower. For this reason, a standard type of liquid-level controller is shown.

In order to conserve as much heat as possible, heat exchangers are provided for heating the outgoing solution from the absorber with the hot reactivated solution which is being returned to the absorber. After the solution is heated in the heat exchangers, it is passed to the middle of the reactivator, which is similar in construction to the absorber, being fitted with bubble trays. As it passes down the reactivator tower, the solution increases in temperature and is scrubbed by the steam generated in the base of the reactivator tower and, since countercurrent conditions obtain, by the time it reaches the bottom is completely stripped of the absorbed carbon dioxide or hydrogen sulfide. The heating and boiling of the solution at the bottom of the reactivator is accomplished by means of low-pressure steam contained in the pipes as shown. The impurities, saturated with water vapor at the temperature of the feed plate of the reactivator, pass up the column and into the reflux condenser at the top, in which the water vapor is condensed and passed back to the top plate of the reactivator. This refluxed water covers the upper three or four plates of the reactivator tower and scrubs out any entrained absorbent that might otherwise be carried away by the escaping impurities. After reactivation the solution is pumped through the heat exchangers and cooler and then completes its circuit at the top of the absorber tower.

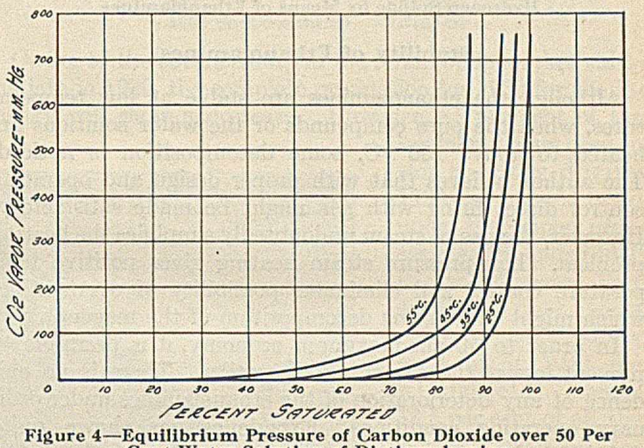

Figure 4—Equilibrium Pressure of Carbon Dioxide over 50 Per Cent Water Solution of Diethanolamine

This arrangement gives us a continuous process for the removal of carbon dioxide or hydrogen sulfide. Owing to the high specific-absorption capacity of the ethanolamines for these impurities, the size of the equipment is smaller than would be necessary if other known reagents were used. The carbon dioxide and hydrogen sulfide are removed completely and much less steam is required for reactivation than if sodium carbonate were used. This results in much greater economy in separation of carbon dioxide and hydrogen sulfide than has previously been possible.

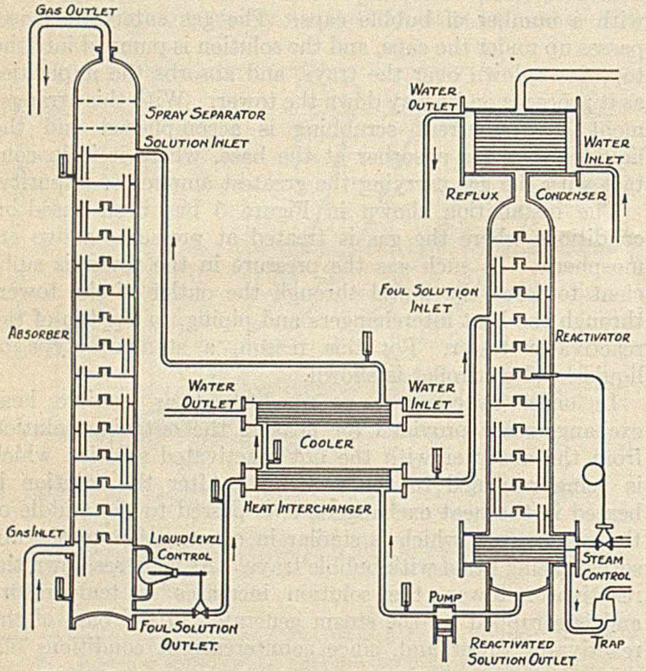

Figure 5—Apparatus for Absorption of Carbon Dioxide and Hydrogen Sulfide by Means of Ethanolamines

Stability of Ethanolamines

Although the ethanolamines are stable at low temperatures, when the pure compounds or the water solutions are heated to above 150° C. some decomposition is noticed. The author believes that with proper design and operating control direct firing with gas might be made satisfactory. However, the use of steam undoubtedly simplifies the heating problem. Low-pressure steam heating gives positive temperature control and eliminates possibility of overheating, which might cause some decomposition of the reagent.

In order to obtain maximum economy, it is desirable to prevent loss of the reagent in operation. There is no evidence of any deterioration of the ethanolamines under ordinary operating conditions. Experience has shown quite definitely that, if suitable precautions are taken to guard against leakage, the loss from pumps, fittings, etc., will be negligible. Ethanolamine is a very penetrating substance and will pass through pinholes and other places in the equipment that would not disclose any leakage when used with other liquids. With proper engineering practice this source of waste may be reduced to a minimum and the loss of the reagent kept so low that its replacement becomes a very small item of expense in the operation of a plant.

Strong mineral and organic acids must be completely eliminated from the gases to be treated, since such acids produce stable salts of ethanolamine and thus destroy its activity for the absorption of hydrogen sulfide and carbon dioxide. Strong alkalies, such as caustic soda, potash, and lime, also have a damaging action on ethanolamine solutions. Aldehydes, mercaptans, unsaturated and aromatic hydrocarbons, tar and tar acids, ammonia, and hydrocyanic acid have no effect whatever on the absorptive capacity of the ethanolamines.

Sulfur dioxide, being a stronger acid than either carbon dioxide or hydrogen sulfide, is absorbed by solutions of the ethanolamines, forming sulfites, but these sulfites are not so completely decomposed by heat as the carbonates and hydrosulfides. For that reason it is not recommended that the ethanolamines be used for the removal of sulfur dioxide, and when this substance is present in the gas being treated it is advantageous that it be removed by scrubbing with water previous to the passage of the gas into the ethanolamine solution. Whereas the strong alkalies when in contact with hydrogen sulfide and oxygen rapidly form thiosulfates in solution, the ethanolamines are not sufficiently basic to permit the rapid formation of thiosulfate under the same conditions. Some thiosulfate is formed under this condition, but the reaction is so slow that the solution is not harmed.

Applications

The application of this process is particularly indicated in the removal of carbon dioxide from natural gas, from hydrogen for use in ammonia synthesis and the hydrogenation industries, in the separation of hydrogen sulfide from natural gas, refinery gases, coke-oven gas, and manufactured gas. The greatest economy is obtained where the gas occurs at pressures higher than atmospheric, inasmuch as such high pressures tend to increase the partial pressure of the impurities, giving much better equilibrium conditions in the absorber, and a low rate of circulation of solution is required to remove the impurities.

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New Motion-Picture Films Depict Story of Steel

"The Story of Steel," from the mining of iron ore to the manufacture of finished steel products, is depicted interestingly in a series of educational motion pictures just released for free circulation by the United States Bureau of Mines. These motion pictures, which constitute a notable addition to the bureau's extensive collection of films that visualize the workings of American mineral industries, have resulted from extensive revision of a picture prepared several years ago. They have been produced by the bureau in coöperation with an industrial concern, and are available on both 35- and 16-mm. width of stock upon application to the Pittsburgh Experiment Station, U. S. Bureau of Mines, Pittsburgh, Pa.

Film 143, 2 reels, "Mining and Metallurgy," shows the geographical and geological location of the iron ore deposits; transportation of ore from mine to blast furnace by boat and railway; reduction of the ore in the blast furnace to pig iron or molten iron for further processing; and pouring of ingots, weighing 2 to 4 tons.

Film 144, 1 reel, "Rails, Rods, and Plates," shows the method of making these and other hot-rolled products from the ingots.

Film 145, 1 reel, is titled "Wire Products." First the rods are rolled to a smaller diameter and then, after exposure to acid and other baths, are cold-drawn through tapering holes of successively smaller diameters until ready for making into wire products.

Film 146, 1 reel, "The Manufacture of Pipe," includes heating and rolling 2- to 4-ton ingots; cutting into lengths; and rolling to a suitable length, thickness, and width for the desired pipe. The edges are beveled and the skelp is rolled to a circular cross section.

Film 147, 1 reel, "Sheets and Tin Plates," shows primarily the process of rolling a suitable-sized bar flat, doubling it, reheating and rerolling and redoubling until the pack is 8 sheets thick. After this pack is rolled down to the proper thickness, it is trimmed, and the sheets are tinned or galvanized.

Manufacture and Characteristics of Laminated Glass[1]

Willard L. Morgan

Triplex Safety Glass Company of North America, Clifton, N. J.

Laminated glass is a sandwich consisting of a layer of plastic between two sheets of glass to which the sheet of plastic has been caused to adhere by the combined effect of heat, pressure, and the application of special materials. Both plate glass and drawn sheet glass are used. Nitrocellulose has been used chiefly as the plastic sheet, although in Europe cellulose acetate has been utilized to a small extent. For use as a window, the plastic must be as transparent as possible, but new developments in decorative novelties utilize sheets carrying colored designs.

While laminated glass is a quarter of a century old, its development on a large scale is a matter of the last few years. The idea of laminated glass apparently originated with Woods (*4*) in 1906, although the first practical safety glass was made by a Frenchman, Benedictus, in 1911. Benedictus has stated (*1*) that, in brooding over an automobile accident in which an acquaintance had been seriously cut by flying glass, he suddenly remembered having once dropped a flask in which a lacquer solution had evaporated. While the flask cracked, all the glass particles remained fastened to the dry lacquer film. In safety glass we depend upon security from the dangers of flying glass splinters by reason of the fact that, while the glass will crack, all pieces will remain adherent to the plastic, which also operates to absorb the breaking force.

After developing several methods for producing laminated glass (*2*), Benedictus found that he secured best practical operation where a film of gelatin was used on the interior glass surfaces to secure adhesion of the celluloid. The gelatin, however, was not used as an ordinary wet glue, but in a form dry to sight and touch which became adhesive due to thermoplastic flow under heat and pressure (*3*).

The major portion of all laminated glass has been made by this process, although other methods are in use. In France it was made by the Société du Verre Triplex on a small scale previous to the World War, but it was not until the war that any considerable market was found for it. During this period it was used for such things as airplane and automobile windshields, bullet-proof glass for tanks, glass for submarines, battleship-bridge windows, and eye blanks for gas masks and aviators' goggles. In 1912 a British group took over the manufacturing and sales rights for Great Britain and its colonies from the French concern and the Triplex Safety Glass Company, Ltd., was organized. Successful production was established in 1914. After the war the market in the automotive industry offered the most promise of development. Adoption of safety glass by the British motoring public was rapid. Amory L. Haskell was very much impressed with the life-protective value which laminated glass offered to the motorist, and as a result of his determination to bring this safeguard to the American people the Triplex Safety Glass Company of North America was incorporated under license from the British concern, who in 1923 had secured the world rights from the French Triplex concern. At the present time the plant at Clifton, N. J., is the largest of its kind in the world. Previous to the last three years England had been the major producer of laminated glass, but the United States is now leading by a considerable margin. At present there are at least eleven concerns in this country interested in the production of safety glass.

The Triplex Safety Glass Company Factory at Clifton, N. J.

It has been variously estimated that from 33 to 65 per cent of all injuries received in automobile accidents are caused by flying glass. Consequently, while the idea that there was a non-shatterable glass required considerable sales education at first, the rapid adoption of this glass by the automotive companies has caused a rapid growth in the industry as indicated by the figures from the production of Triplex glass alone.

Production of Triplex Glass in United States

Year	Square feet
1926	1,153
1927	50,000
1928	2,000,000
1929	6,642,000
1930 (first 6 months)	3,215,000

Owing to the severe slump in the automobile market starting late in 1929, the complete production for 1930 for the industry will show a decrease. However, 85 per cent of the laminated glass used in this country during 1930 was manufactured under the Triplex process. At the end of 1930 it was estimated that 4,900,000 cars were equipped with safety glass in at least the windshield. This is 18.5 per cent of all the car registrations for 1930. This has grown from a usage in approximately 80 cars in 1926.

The automobile industry, in spite of its present importance, is not the only outlet for laminated glass. The present article, in addition to discussing the production of this glass, will summarize the development work leading into new fields of utilization. The production methods outlined below refer to standard-quality laminated glass such as that used in windshields, windows, and deflectors of the ordinary automobile.

Triplex Manufacturing Operations

Glass sheets are cut to size by means of metal templates. Each piece of glass is wiped on one side by hand with a clean-

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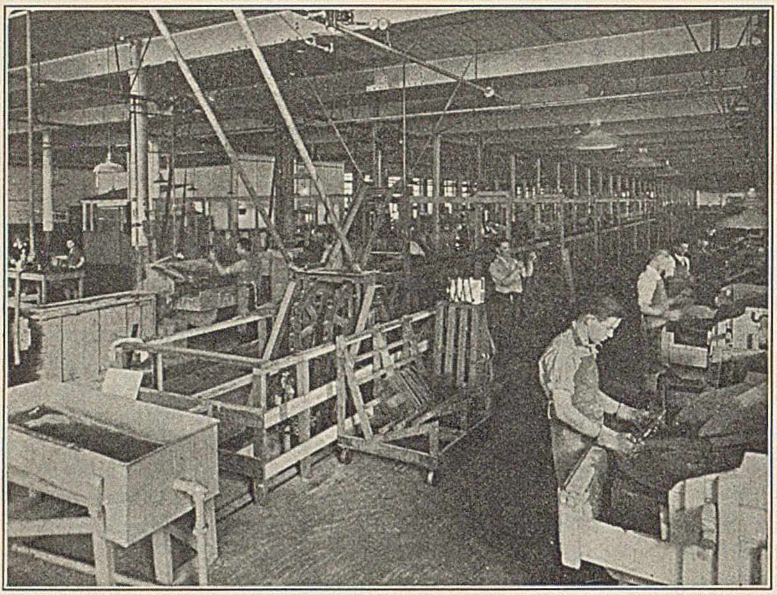
[1] Received March 30, 1931.



Finishing Edges of Deflectors

ing solution and is placed on a conveyor, which carries it through a washing machine with a series of revolving brushes, and thence into a drier. Emerging from the drier, the glass sheets are sprayed with a dilute solution of gelatin by means of an automatic device which moves a spray nozzle back and forth at right angles to the direction of motion of the conveyor. A very uniform coating of a special gelatin approximately 0.00001 inch thick is given the glass by this treatment. The gelatin dries substantially on contact with the warm glass as it passes along the conveyor.

The celluloid sheets, cut to size and previously carefully examined on dark and light backgrounds for dirt and surface imperfections, are placed on the glass and carried through other automatic spraying apparatus, where the celluloid is sprayed first on one side and then on the other with a mixture of plasticizers and high-boiling solvents to soften the surface slightly. The other glass is then laid on top and operators examine the loose sandwich of two glass sheets with the sheet of celluloid for any possible dirt inclusions, which are removed before clips are applied at the edge.

The problem of eliminating small dirt specks and of maintaining the slight haze of the plastic at a minimum calls for constant vigilance and extraordinary cleanliness and precaution in manufacture of both the laminated glass and the celluloid plastic. For this reason the glass conveyors are covered from the washing operation to the assembly operation. All spray operations are in closed chambers.

Salvaging Rejected Windshields by Cutting Deflectors from Satisfactory Areas

From the point at which the washed glass sheets emerge from the drier to the point at which the assembled sandwiches pass to the pressing operation, the processing and workers are contained in a long room constantly supplied with fresh air which has been filtered and washed. This room is vacuum-cleaned twice daily. Such precautions are necessary to reduce the contamination from dust particles.

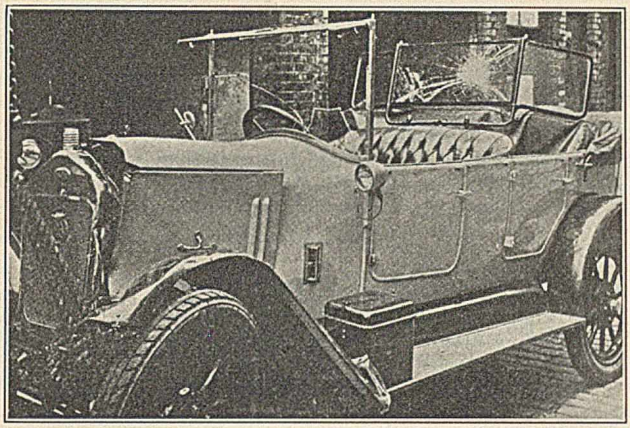
The conveyors carrying the assembled sandwiches travel between two lines of hydraulic presses. Girls lay up two sandwiches in each press between sheets of heavy paper and press these, first with a relatively low pressure followed by high pressure, the presses being operated from two separate pressure lines. Both surfaces of each press are steam-heated, the temperature being controlled by means of a Tagliabue controller on the steam line. Single-platen presses have largely been supplanted by those with double platens. Any irregularity in the platens is a source of trouble, since it places a strain on the glass. Some presses, however, are built with one surface very slightly convex, so that pressure is applied first along the center of the glass in order to squeeze any bubbles to the sides as the pressure is increased.

The pressing of laminated glass, depending upon the thickness of glass and the plastic used, is generally carried out at from 200° to 260° F. for from 6 to 20 minutes, with final pressures ranging from 150 to 350 pounds per square inch. Under these conditions there is a thermoplastic flow of the celluloid sheet. The surfaces are bonded to the glass, this action being aided by the use of the gelatin coating on the latter and the softening of the celluloid surfaces by means of the solvents sprayed on before assembling where such sprays are used.

The pressed sandwiches are transferred back to the conveyor line, which carries them to the sealing and finishing operations. Each sandwich has the celluloid removed approximately $^1/_8$ inch in from the edge so as to form a slot, which is then filled with a waterproofing pitch to seal the edge against atmospheric moisture. With some glass a special transparent waterproof coating is applied directly to the edge. Straight edges are then ground on a Weber automatic machine, and curves and corners are finished by hand grinding. Minor scratches in the glass surfaces are polished out, the finished pieces are inspected, and then they are wrapped and sealed for shipment.

Salvage Operations

Since the layer of celluloid in laminated glass prevents the use of rejects and scrap as cullet, salvage operations are mainly confined to the recovery of satisfactory areas of large rejected pieces, such as windshields, by cutting into smaller pieces, such as deflectors. Both glass sheets of a rejected piece are first cut to the dimensions of the new pieces made and the plastic is then cut by the insertion of a razor blade in the crack in the glass. Methods are also in use for reclaiming the raw



Ordinary Glass *vs.* Laminated

The girl in the front seat almost severed her jugular vein. The passenger riding in the rear seat was uninjured because the Triplex tonneau shield merely cracked.

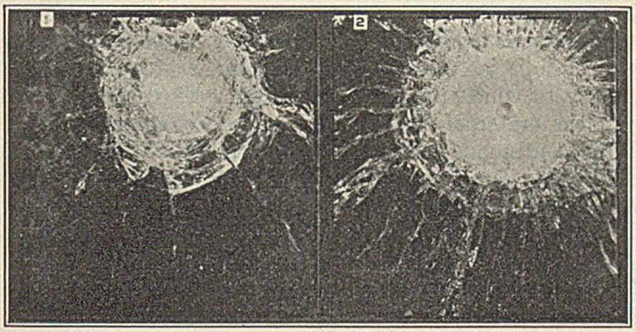
glass sheets depending upon the destruction of the plastic layer.

Major Problems in Production of Laminated Glass

There are a number of general problems which require continuous attention if satisfactory laminated glass is to be produced. The most important of these are the elimination of dirt inclusions; the securing of good, permanent adhesion; the selection of a plastic; and the control of the laminating process so that the safety glass will not develop color, brittleness, or bubbles and be as free of haze as possible. As celluloid is quite hygroscopic, it is also essential that the glass edges be protected from the separating action of rain and humid conditions by a waterproof seal which must be equally efficient in cold and warm weather.

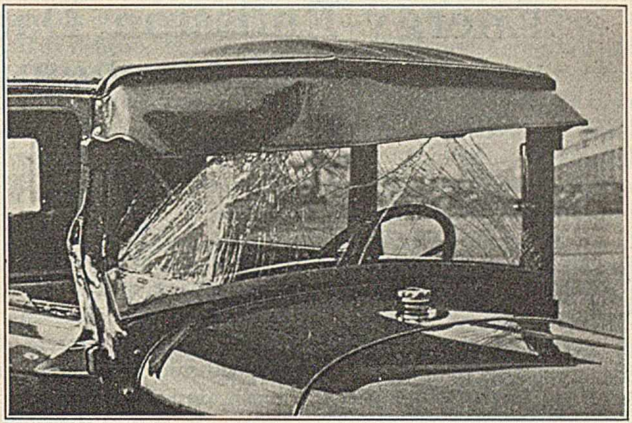
The constant battle against dirt has already been mentioned. The other problems involve more directly the efforts of the research and control laboratory.

The problem of satisfactory adhesion has been fairly well settled in different ways by several processes for glass made with celluloid. Instead of coating the glass sheet with gelatin, some processes spray a thin layer of pyroxylin solution on the glass, or use casein or albumin as an adhesive. The patent literature is full of references to the use of other special substances for this purpose. Likewise, a number of methods have been cited for the treatment of the celluloid sheet with softeners before assembly. Alcohol has been used for this purpose, while acetone, amyl acetate, castor oil, and many other substances and mixtures have been specified. Improved adhesion has also been attempted by artificial roughening of the inner surfaces of the glass by grinding, sand-blasting, or chemical treatment.



Bullet-Proof Glass, Showing Results of a Single Shot at Close Range

The plastic used in laminated glass has always been a problem. While great improvement has been made in the properties of celluloid sheets for this purpose, no two batches are precisely alike and the material must be checked constantly to insure satisfactory service from the finished product. The chief disadvantage of pyroxylin is its tendency toward discoloration under service conditions. However, the properties of the improved celluloid now used in laminated glass are such that no discoloration is noticeable after a year of ordinary service, but after two years there may be a very slight, though not objectionable color. A temperature of 120° F. is the approximate service limit for laminated glass containing celluloid. On the other hand, cellulose acetate, while resistant to temperatures up to the atmospheric boiling point of water, has the disadvantage of a tendency toward brittleness, more haze, and considerably higher cost. As yet none of the synthetic resins have appeared in commercial laminated glass use, probably because of their tendency to become brittle and lose their adhesion on exposure to ultra-violet radiation.



Close-Up of the Windshield of Laminated Glass

Further Developments

The manufacture of laminated glass is showing markedly the current trend toward mechanization. While the above description may indicate fairly simple manufacture, high rejections for many months of 60 per cent and over have attended any new independent enterprise in the field. Each handling of a piece of glass by a worker introduces a certain amount of dirt, breakage, cracks, chips, and particularly scratches. The spraying of glass automatically leads to more uniform adhesion, fewer bubble rejects, and, because of the better uniformity, less breakage in pressing. Consequently, each hand operation that can be replaced by machine results in higher yield and cleaner and better product. In the Triplex plant today less than one-half the workers handle three times the production of two years ago. As a consequence rejection is now kept at a very small minimum. Further mechanization, such as handling of celluloid sheets and assembly, can be expected.

The use of cellulose acetate as the plastic in laminated glass will probably develop, particularly for such industrial uses as require greater resistance to heat than celluloid affords. The cellulose acetate industry is still in an early stage, and material with improved properties at reduced cost may be available within a few years. It does not appear that cellulose acetate will displace celluloid for ordinary laminating purposes, such as automobile glass, until the acetate is improved by more satisfactory plasticizers.

In addition to its use in private automobiles, taxicabs, and busses, laminated glass is now finding an expanding market in railway service, where it is used for the windows in locomotive cabs, in club and parlor cars, and in street-railway cars. It is also being employed industrially for machine guards and windows on special test equipment. The uses developed during the war in the naval and air services also continue, and considerable multiple-layer laminated glass 1 to $1^1/_4$ inches in thickness is used as bullet-proof glass.

All of these applications are based on the safety feature of laminated glass. A new field is now being developed, however, in which this feature is secondary and the emphasis is upon the artistic effects which may be obtained by using color and design in the sheet of plastic. Table tops, tray bottoms, mirrors, wall paneling, soda fountains, display signs and novelties, art placques and silhouettes designed in mirror, and many other products of extremely attractive appearance have already been placed on the market. Celluloid can now be printed satisfactorily in four colors, with future prospects of additional variety if desired, so that marbles and grained and inlaid woods can be secured which rival the natural materials. The opportunities for new and striking artistic effects through the medium of laminated glass are numerous and future development of the industry may be quite as much along this line as along the established one of insuring safety.

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Energy-Emission Data of Light Sources for Photochemical Reactions[1]

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Data are presented giving the amount and spectral distribution of the radiant energy from a number of typical carbon arcs, most of which are in common use at the present time. This information is essential for the selection of the most suitable light source for a reaction involving the use of ultra-violet or visual light. It also illustrates the wide variety of types of spectral-energy distribution that can be obtained from different types of carbon arcs.

LIGHT sources, in the ordinary meaning of the term, are now being used for many purposes other than the production of visual light. Physicians and clinical workers make use of them for various therapeutic purposes, laymen for health maintenance, while technical workers use light sources for a wide variety of photochemical and analytical reactions influenced by radiation in various parts of the spectrum.

In order to determine the effectiveness of a given source of radiation for a specified purpose, it is not sufficient to measure its intensity simply in the broad bands of the spectrum designated as ultra-violet, visual, or infra-red, since many of the effects of radiation are produced by relatively narrow portions of these bands. As an example, the activation of ergosterol to form vitamin D is brought about only by ultra-violet of shorter wave length than about 3100 Å. Since this in many sources constitutes only a small fraction of the total ultra-violet and may be practically absent in some sources which contain appreciable amounts of ultra-violet of longer wave length, a determination of ultra-violet intensity tells nothing of the value of a light source for this purpose.

The evaluation of a source of ultra-violet or visual light for any of its various purposes may be obtained from measurements of the intensity and distribution of energy throughout the spectrum. When the response curve of a reaction under consideration is known, the effectiveness of a given source can be determined directly from its spectral-energy distribution curve by determining the intensity in that range of the spectrum to which the material responds. When the response curve is not known, information regarding it can be obtained by comparing the effectiveness of two different sources whose spectral-energy distribution curves are known.

Light Sources

The sources commonly used for the production of visual light, as well as ultra-violet and infra-red, fall into two classes. The first is represented by incandescent solids, which show an essentially continuous spectrum of which the commonest illustration is the ordinary tungsten-filament lamp. The second is the discontinuous or line spectrum caused by the thermal or electrical excitation of gas molecules, commonly produced by an arc or other electrical discharge.

Both types of radiation are found in the carbon arc. The crater or electrode tip is heated to incandescence and shows the typical continuous spectrum of an incandescent solid, while the arc stream, between the two electrodes, gives off the characteristic line or band spectrum of the molecules and atoms present in the arc. The relative amounts of the two types of radiation can be varied at will in accordance with the purpose to which the arc is to be put; thus, the radiation from the crater of the plain or projector carbon is almost all the continuous spectrum of the incandescent solid, while from a true flame arc it is practically all of the second type. In this case the incandescent solid electrodes produce only a very small fraction of the total ultra-violet and visual light, most of which comes from the arc stream between the two electrodes. The difference between the two types of arc is clearly shown in Figure 1, *A* and *B*.

An arc between two pieces of pure carbon will show, in addition to the radiation from the electrodes themselves, certain lines and bands, chiefly in the violet and near ultra-violet, characteristic of the carbon arc in air. This distribution of energy can be modified by incorporating other materials in the carbon which are vaporized by the arc and add their characteristic spectrum to that of the carbon itself. Such materials may be distributed throughout the electrode, but are more commonly concentrated in the center or core. The flame carbon arc thus offers a very versatile source of radiation, for by changing the nature of the material in its

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core the distribution of energy can be changed within wide limits at will.

Until recent years arcs have been used principally for the production of visual light, and therefore most of the compounds utilized as flame materials have been those which would add most to the visual light emitted by the arc. More recently the demand for various types of ultra-violet radiation has led to the development of arcs which meet the different special demands in this field.

Experimental Procedure

The energy-distribution curves reported herein were obtained by the use of two monochromators, or spectroradiometers, together with a separate thermopile calibrated in terms of absolute energy units and screens of known spectral transmission. The first monochromator, of which the optical parts are of crystalline quartz, is calibrated to measure radiation over the range 2300 to 7000 Å. which includes most of the ultra-violet and visual light. Its operation has been previously described (*3*, *8*). The second is an infra-red spectroradiometer made by the Gaertner Scientific Corporation of the type of the Wadsworth constant-deviation spectroscope. This was used for the range 6000 to 18,000 Å. The operation of this instrument is essentially the same as that of the spectroradiometer for the ultra-violet and visual with an additional correction for the variation in the reflecting power of the gold mirrors throughout the region measured.

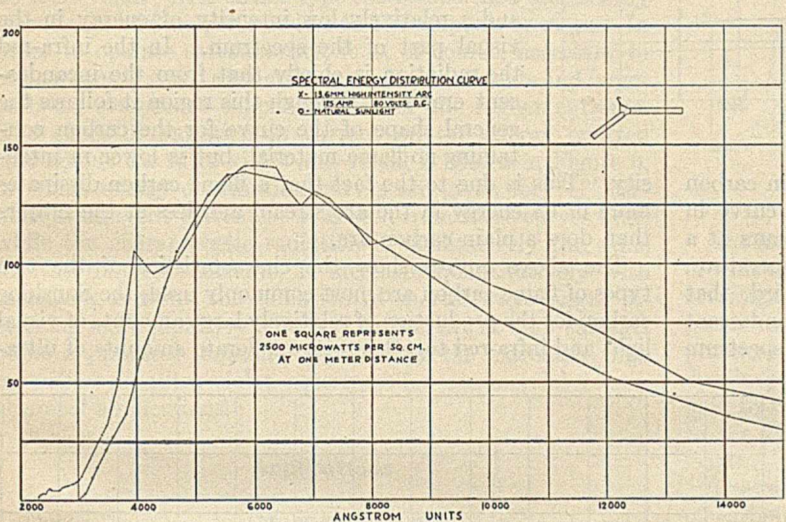
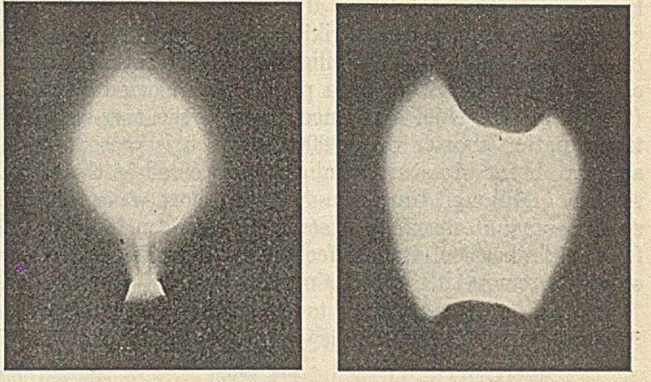


Figure 2

Both these instruments give relative energy-distribution curves only. By means of a procedure that has been described elsewhere (*8*) they are converted into curves expressed in absolute energy units. Briefly, this consists in isolating by means of suitable screens the amount of energy in wave bands corresponding to those covered by the spectroradiometer for any given light source, measuring this in absolute units by means of a galvanometer and thermopile, and correlating the corresponding areas under the energy-distribution curves to correspond to the absolute energy values so obtained. By this means curves are obtained in which unit areas represent unit amounts of energy, so that the intensity between any two wave-length limits may be determined simply by measuring the corresponding area under the curve. The two sets of curves obtained overlap in the region 6000–7000 Å., in which region quite satisfactory agreement is shown by the two methods of measurement.



A—D. c. projector carbon arc *B*—Sunshine flame arc

Figure 1

It is believed that the range of wave lengths chosen covers the entire region of interest to either biological or technical workers. The short-wave-length limit of 2300 Å. in the ultra-violet is fairly close to the limit of transmission of air, which, except in very thin layers, may be taken as approximately 2000 Å. Furthermore, commercially available sources of ultra-violet do not emit appreciable amounts of energy of shorter wave length than 2300 Å. On the long-wave-length side infra-red radiation of longer wave length than 14,000 Å. is completely absorbed by even a relatively thin layer of water. Its spectral distribution is of relatively little importance for most purposes, although its total amount may be significant as indicating the amount of heat given off by the light source.

Discussion of Results

Figure 2 shows the energy-distribution curve for a typical high-intensity carbon arc such as is used in searchlights and in motion-picture projection and photography. On this is superposed the energy-distribution curve for normal sunlight (*8*). The radiation from the arc as measured is the radiation from the positive crater only, as in most applications of this

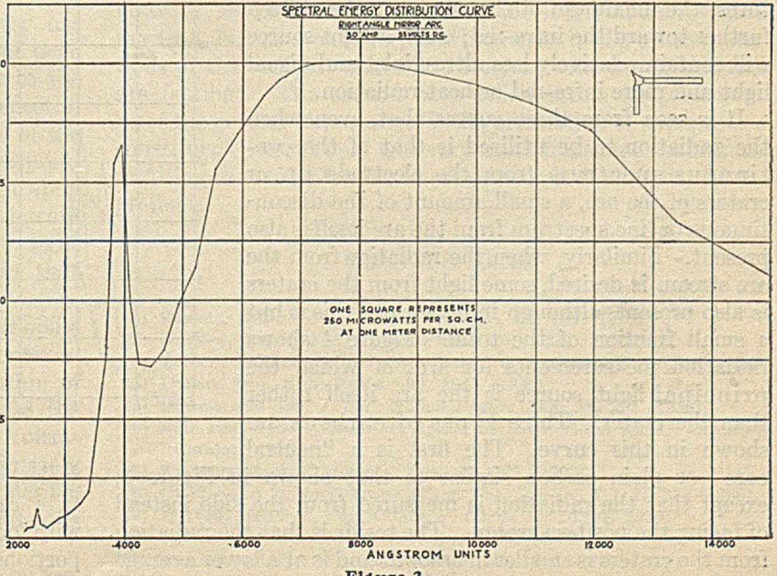


Figure 3

type of light source this is all that can be utilized. The curve shows the rather striking agreement between this light source and natural sunlight through the entire range of the spectrum, as has been previously reported by others (*1*, *2*, *5*). The chief difference between the two sources is the radiation shorter than 2900 Å. which is present in the arc but absent in natural sunlight as received at the earth's surface. Although this ultra-violet of short wave length is small in amount, its effects in some cases are considerable, and for the duplication of the effects of sunlight it may be necessary to remove it by means of a suitable filter.

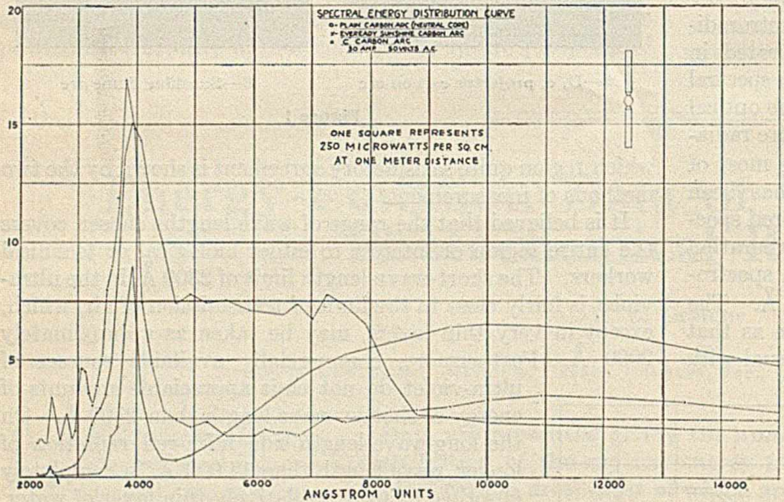


Figure 4

The energy distribution from the crater of a plain carbon arc is shown in Figure 3. This differs from the curve in Figure 2: first, in that the maximum intensity occurs at a longer wave length, corresponding to a lower temperature; second, that the total intensity is lower; and third, that superimposed upon the radiation from the incandescent solid there appears a larger amount of the line or band spectrum due to the arc itself. This is especially noticeable in the ultra-violet at about 2500 Å. and again near 3900 Å., which is near the commonly accepted lower limit of the visual portion of the spectrum. Energy-distribution curves for other incandescent solids such as the tungsten-filament incandescent lamp will follow the same general shape as this, except that, since they operate at lower temperatures, the maximum of the curve will be shifted further toward the infra-red; such a light source will contain relatively less ultra-violet and visual light and more infra-red or heat radiation.

It is seen from these curves that, even when the radiation to be utilized is that of the continuous spectrum from the electrode tip or craters of the arc, a small amount of the discontinuous or line spectrum from the arc itself is also present. Similarly, when the radiation from the arc stream is desired, some light from the craters is also present, although in most cases this is but a small fraction of the total. Figure 4 shows radiation measurements for arcs of which the principal light source is the arc itself rather than the crater. Three types of carbons are shown in this curve. The first is a "neutral core" or plain carbon similar to that shown in Figure 3, except that the radiation is measured from the side instead of facing the positive crater. The result is that the radiation from the craters is smaller in amount and is at a lower average temperature, so that the maximum of the curve is further toward the infra-red. Also, the amount of the characteristic radiation of the arc stream is increased. This is the radiation characteristic of the plain carbon arc, to which no flame material has been added.

"Sunshine" carbons, which contain cerium salts in the core, give an entirely different energy-distribution curve. The same bands are present as before, but in addition the presence of this flame material causes an emission of energy in the ultra-violet, increasing gradually in intensity from about 2900 to 4000 Å., which approximates the increase in intensity of natural sunlight itself throughout this region. There is also a high and fairly uniform intensity throughout the visual part of the spectrum, extending to about 8000 Å. in the infra-red. Most of the energy through this region is caused by spectrum-emission lines so closely packed together as to approximate the effects of a continuous spectrum. Beyond about 8000 Å. the intensity falls off rapidly, until at longer wave lengths practically the only radiation given off is that from the incandescent electrodes. In the same figure is shown the energy distribution of "C" carbons, which contain a mixture of metals, including iron, in the core. Radiation from this carbon is characterized by a series of groups of very intense lines throughout the ultra-violet, and a relatively low intensity of energy in the visual part of the spectrum. In the infra-red the radiation is chiefly that from the incandescent craters. Through this region it follows the general shape of the curve for the carbon containing no flame material, but is lower in intensity. This is due to the fact that a flame carbon dissipates more of its energy in the arc stream and less at the craters than does a plain carbon arc.

The above curves show the characteristics of the two types of flame carbon arc most commonly used, the Sunshine carbon for the production of relatively large amounts of visual light and infra-red together with moderate amounts of ultra-violet, corresponding to that found in sunlight itself, and the "C" carbon for producing high intensities of ultra-violet with only moderate intensities in the visual and infra-red portions of the spectrum.

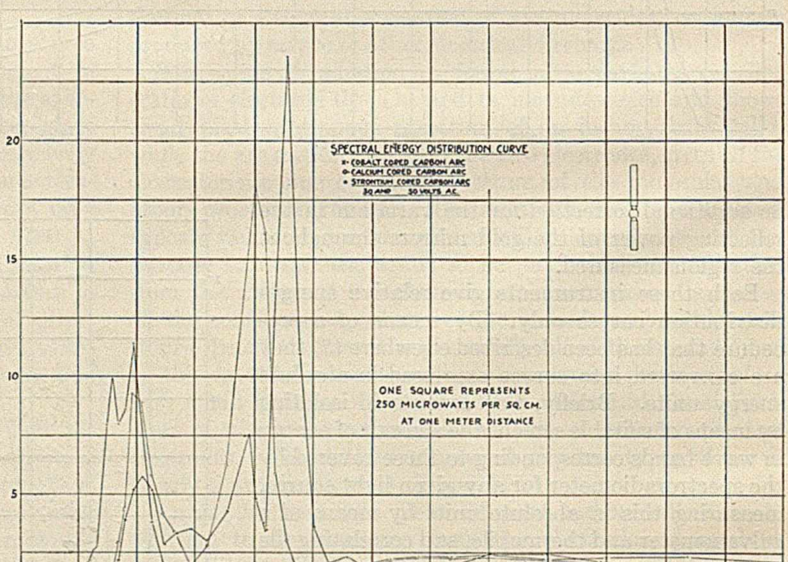


Figure 5

Figure 5 shows some of the possible effects that can be obtained by using other materials in the arc. For producing other, and sometimes unusual, distributions of energy in the ultra-violet, various metals are especially suitable. The carbon shown in the curve containing cobalt as the principal flame material is an illustration of this, giving a very high intensity of radiation near 2400 Å., also a peak near 3600 Å. with a low intensity of energy in the infra-red and visual regions of the spectrum.

Calcium compounds have been used in the carbon arc for many years. The energy-distribution curve of an arc containing this material is shown also in Figure 5. It contains relatively little energy in the ultra-violet, fairly strong emission in the violet, and another maximum extending from the green to the orange. This consists principally of two bands, one in the green and one in the orange, which give the light from these carbons a yellowish color.

Another instance of usual energy distribution is shown with carbons containing strontium compounds in the core, shown in the same figure. These are characterized principally by a very strong band centered around 6500 Å. in the red with a few lines and bands throughout the rest of the visual spectrum, having relatively little energy in the ultra-violet.

Except in the case of the high-intensity arc, which is normally operated at much higher currents, the energy-distribution curves all represent arcs operated at 30 amperes and 50 to 55 volts. Arcs of this type can be operated successfully at currents of 8 amperes or less to 100 amperes or more. In order to operate satisfactorily, it is, of course, necessary to use carbons of small diameter for the lower currents and larger carbons, sometimes copper-coated, for the higher currents. The effect of variation in current on the energy emitted throughout the ultra-violet and visual is shown in Figure 6, in which energy-distribution curves are given for "C" carbons at different currents. It is seen from these curves that, while the characteristic radiation is qualitatively the same for the different currents, it increases quantitatively with increasing current, the radiation of shorter wave length increasing more rapidly. The "C" carbon arc at high currents offers a practical method for obtaining the extremely high intensities of ultra-violet necessary for commercial photochemical applications.

Applications

The application of photochemistry to industrial chemical reactions has been summarized by Ellis (*6*), and more recently by Dorcas (*4*) and by Frankenburger (*7*).

It has been claimed that industrial photochemistry has not made the progress which a few years ago it had been expected to make. This is undoubtedly due in part to the fact that insufficient attention has been paid to the spectral composition of the radiation used and to the response of the reaction in question to different wave lengths. Future progress in this field should depend to a considerable extent upon determination of the most favorable part of the spectrum for carrying out the reaction, and selection of the light source which will give the maximum of intensity in that region.

Furthermore, portions of the spectrum other than the one desired may actually be harmful to the reaction in question. This has been investigated in the case of the activation of ergosterol to form vitamin D (*9* to *12*). In this case the desired reaction proceeds most satisfactorily with ultra-violet between the wave-length limits of approximately 2700 and 3100 Å. Longer wave lengths are not effective, while radiation of shorter wave length than about 2700 Å. is actually harmful, causing undesirable side reactions.

Another instance is the duplication in accelerated weathering tests of the weathering produced by sunlight. This is a very complex phenomenon, produced in most cases by the entire ultra-violet spectrum from the lower limit of the sun's spectrum at about 2900 Å. up to the beginning of the visual spectrum at 4000 Å. and, possibly, by the violet and blue of visual light. In cases in which light is an important factor in accelerated weathering tests, it is desirable to duplicate as closely as possible the effects of sunlight. To do this, the light should not contain radiation of shorter wave length than found in the sun, as this radiation is known to produce entirely different results; and all the wave lengths present in sunlight which contribute to the production of the observed effect should be present in the artificial light source.

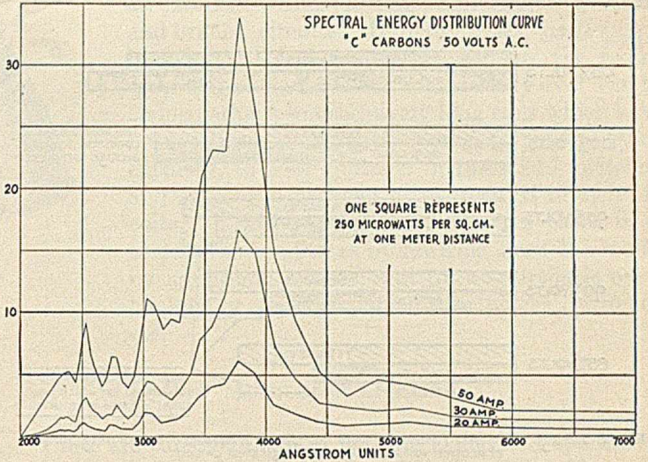


Figure 6

The fact that ultra-violet in many cases causes fluorescence, of which both the intensity and color depend on the material investigated, has been used as a basis for a great many proposals for its use in analytical determinations. The limited practical success that has been achieved in this field may be due in part to the fact that insufficient attention has been paid to the spectral composition of the light source used and to the variation in the response of the material with wave length.

The most familiar photochemical reaction is the synthesis of carbohydrates by living plants, in which case light furnishes all the energy for the reaction. A much more promising field for the commercial application of photochemistry, however, seems to be its use, not as the source of energy for a reaction, but as a catalyst, in which case it fills all the functions of the ordinary material catalysts with which chemists are familiar. The second use, which seems at present to be of the greater importance, is the production of changes in a constituent present only as a very small fraction of a mixture, resulting in a considerable improvement in the quality of the product.

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Good Lighting—An Executive Problem[1]

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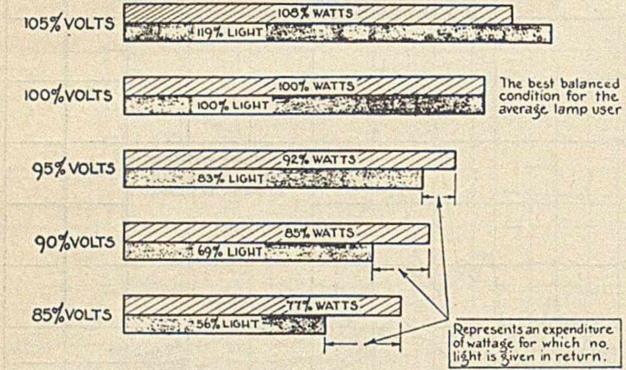
THOSE who are responsible for factory operation and efficiency no longer lift a quizzical eyebrow when illumination is mentioned as a necessary factor for successful plant operation. Thousands of executives have come to appreciate its relationship to efficiency, reduced shrinkage, decreased cost of production, and many other features, not so easily evaluated, but nevertheless having a definite bearing on successful operation.



For the average lamp user, the most light per dollar is obtained by burning lamps at proper voltage on a well regulated circuit.

Figure 1—Relation between Power Consumption and Light Obtained for Operation at Various Percentages of Rated Voltage

Advantages

Decreased cost of production, reduced spoilage, fewer accidents, and a higher morale among the workers are a few of the things which good lighting claims it can bring to the factory. These claims are supported by actual plant data.

Some time ago the White Sewing Machine Company combined their metal- and wood-working plants, which formerly occupied 1,075,000 square feet of floor area. When combined, the two plants occupied 800,000 square feet, of which the sewing-machine division occupied 200,000. This resulted in a combined space shrinkage of 25.6 per cent, but because of the installation of an up-to-date lighting system they were able to utilize every square inch of floor area, and therefore their output, instead of being diminished, was increased.

Tests made at the Timken Roller Bearing plant clearly point out that light is a very active agent in decreasing the cost of production:

Foot-Candles	% Increased Production per Employee	Cost of Light in % of Payroll
Old System:		
5	...	0.3
New System:		
6	4.0	0.8
13	8.0	1.6
20	12.5	2.4

A 12.5 per cent increase in production is shown, equal in dollars and cents to more than five times the cost of the better lighting, and a resultant decrease in cost.

The president of the Detroit Piston Ring Company, who frankly admitted his doubt that it was possible to reflect the effect of lighting on production, was convinced by a test which showed the better lighting had brought an increase of 25 per cent in his plant. These results are striking, but not unusual; such production increases and cost decreases are within the reach of factories everywhere.

"Accident Facts," published by the National Safety Council in 1929, estimates that during 1928 there were 24,000 fatalities arising out of, or in, the course of gainful employment; further, it estimates that during that same period the lost time from non-fatal accidents reached the staggering figure of 3,125,000—about one accident for every four persons engaged in industry, or one for every fourteen persons gainfully employed. R. E. Simpson, of the Travelers Insurance Company, states that there is warrant for assuming that defective vision and deficient or unsatisfactory lighting installations were contributing factors in 18 per cent of these accidents.

That these conditions could exist year after year is all the more reprehensible, because the remedy is so easily applied and has many beneficial results in addition to the safety involved. Accidents caused by carelessness, inattention, or ignorance can be eliminated only by a long-continued painstaking educational campaign, often involving a change in long-established habits. On the other hand, elimination of accidents due to inadequate or improper lighting is simply a matter of purchasing the proper equipment, installing and operating it under competent direction. In fact, it seems logical to include adequate illumination in the list of safeguards, for lamps and reflectors act as a guard; the resultant illumination points out the hazards and aids in avoiding them just as effectively as a railing points out the danger of and provides protection against the hazard of a revolving flywheel.

Figure 2—Comparison of Old Drop Lighting Installation with New Overhead System

The left half of the room is lighted with the old drop lights, which have been replaced in the right half by new overhead lights. Well-distributed glareless lighting has supplanted glare and gloom.

The lighting of a factory is no longer a responsibility in the janitor class of duties. The factory manager who thoroughly

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[1] Received March 26, 1931.

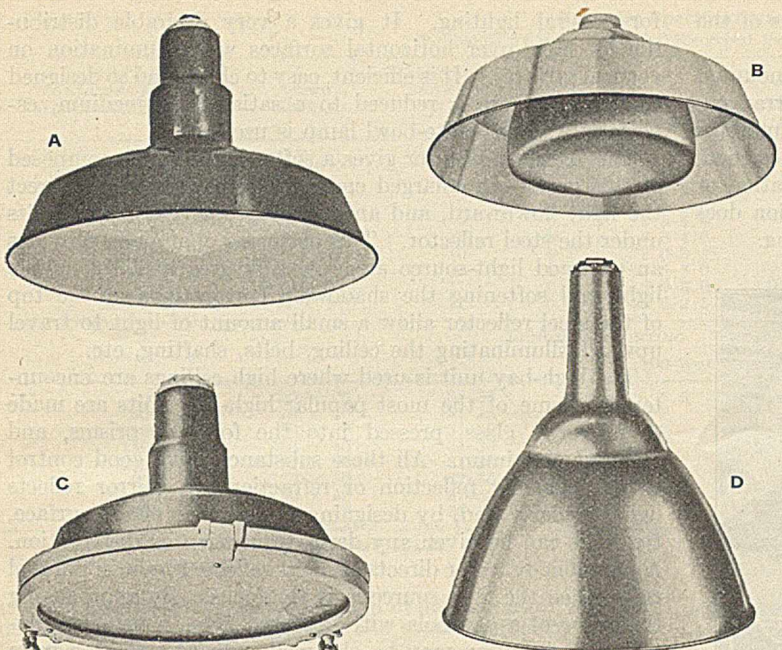

Figure 3—Standard Types of Reflecting Equipment

A—R. L. M. standard dome with high-wattage bowl frosted lamp
B—Glassteel diffuser for producing soft glareless light
C—Dust-tight unit to eliminate explosion hazards
D—High-bay unit for use where high mountings are necessary

familiarizes himself with the workings of each department and studies the problems pertaining to each should also be familiar with what good lighting is, as contrasted with bad lighting; what good lighting will do; and what are the lighting requirements of his particular plant. Then he will be able to specify proper lighting and supervise its maintenance so that every benefit which ordinarily would be derived is received.

Let us, therefore, consider a few of the reasons for the need of better lighting in the factory and some of the fundamentals which make good lighting as important as other accepted factors in economical plant operations.

The fact that the average plant is not in operation at night may lead the executive to believe that his present system is acceptable. Careful investigations will show, however, that, even in modern plants where provision has been made for plenty of daylight, there are places where daylight is not sufficient to insure good vision. Furthermore, during the winter, which is frequently a busy season, there are early morning and late afternoon hours and many cloudy days when artificial light is needed to supplement daylight. In old buildings, where little provision has been made for daylight, the need is even more apparent.

Daylight decreases rapidly as the distance from the windows is increased. This has led to the common practice of locating machines along the windows. Areas in the center of the room then become used only for storage or other inactive purposes, chiefly because of the lack of sufficient light. Where rentals are high, these storage areas contribute to high production costs. A well-designed lighting system will supply uniform illumination throughout the room, thereby increasing the value of the space farther from the windows and permitting the arrangement of machines according to continuity of process.

Voltage a Real Factor in Illumination Design

Wiring is the "pulse of good lighting." The value of voltage that will be actually available at the socket is too uncertain and plays too important a part in the performance of an incandescent lamp to leave it out of consideration in making a lighting layout.

One per cent in voltage changes the light output about 3.4 per cent. A difference of 5 volts will result in a difference of about 17 per cent in light output, and this lost light is of a much better color quality than that remaining, which becomes more and more yellow as the voltage is reduced and the filament temperature drops. Figure 1 indicates the relation between power consumption and amount of light obtained.

Ordinarily the voltage should be maintained several volts above the nominal circuit value at the service switch, to allow for the drop in interior wiring, which should be expected to run not less than 2 or 3 volts when the average lighting load is on. Such low values can only be obtained with an excellent wiring job with ample copper in feeders and branch circuits. In many cases, particularly in industrial and commercial service, the wiring drop will be found to run considerably over 3 volts, owing perhaps to excessively long runs which have been selected only with regard to safe carrying capacity, to poor contacts in fuses and switches, and to poorly designed or overloaded branch circuits. The best procedure in such cases is to correct the conditions by rewiring branch circuits, by additional feeders, and by a systematic overhauling or replacement of fuse blocks, switches, etc.

Methods of Lighting

There are three methods of lighting which find application in the industries. The first is so-called "local" lighting, with drop cords or small lights on individual machines. A lighting system which consists entirely of such local units is to be shunned, however. True, such a system usually means a high intensity of light immediately on the work, but there is too great a contrast every time the worker looks up from his operation and, as the eye has to adapt itself to the lower level of general illumination prevailing throughout the entire interior, it is safe to assume that many working minutes are lost. This method has been largely superseded by general overhead lighting, because it relieves brightness contrasts, brightens up the interior, makes supervision easier, and promotes a more sanitary condition. A direct comparison of

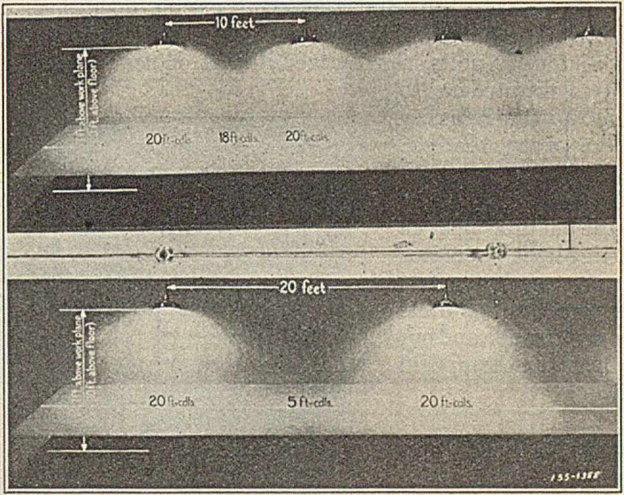

Figure 4—Pictorial Representation of the Conditions Obtained with Proper and Improper Spacing

drop lighting with overhead lighting in two sections of the same shop is illustrated in Figure 2.

General or overhead lighting units consist of lights mounted overhead and, in so far as possible, symmetrically arranged, usually according to bays, to produce approximately uniform illumination throughout a given area. If properly designed, such lighting makes possible good vision in any location or position and, where overhanging machine construction does not prevent, is the ideal method for industrial lighting.

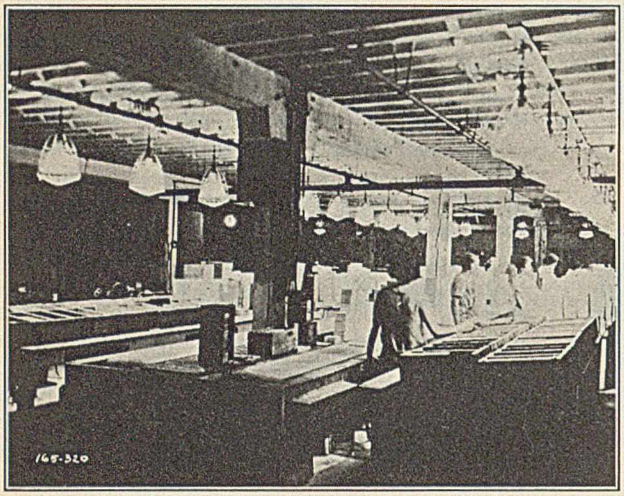

Figure 5—High-Intensity Lighting System in Shading Room of Tile Plant

Five-hundred-watt daylight lamps in prismatic reflecting units spaced 4 feet apart give uniform illumination of 150 foot-candles.

In certain industrial operations, particularly where fine work is being done, it is necessary that a high intensity of light be available. To give to these operations the intensity that is needed a new type of lighting, called "lighting plus," is coming into prominence. This means that, in addition to the general overhead system, producing some 15 or 20 foot-candles, there is superimposed upon specific operations an additional 100 or 125 foot-candles. This is done by means of high-intensity units, usually mounted at or near the ceiling and so directed as to build up the intensity where most needed. This system has practically all the advantages of the old drop light in getting light where it is most needed, and furthermore the units are out of reach and not so likely to be tampered with.

Reflecting Equipment

The essential requirements of reflecting equipment are permanence, durability, efficiency, and ease of maintenance. Figure 3 shows four important standard types of equipment.

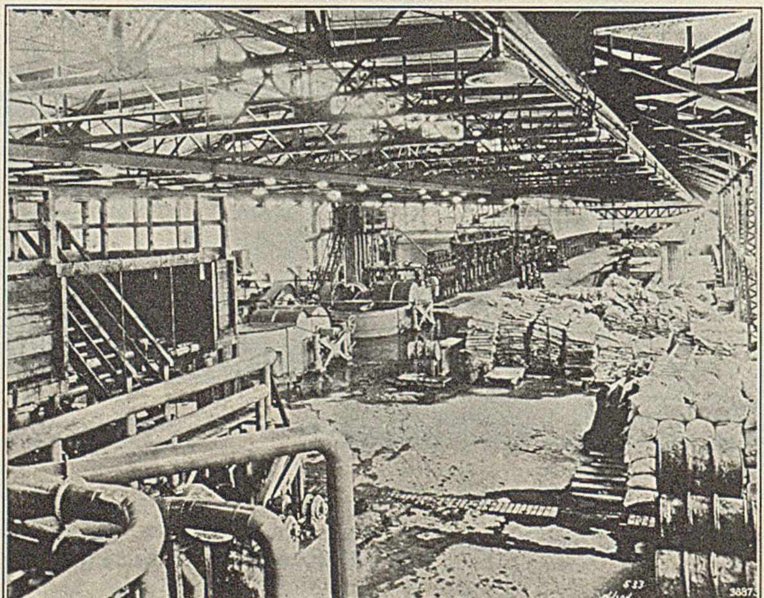

Figure 6—Modern Lighting Installation in a Large Paper Mill

Two different types of equipment are used in this room. R. L. M. dome reflectors equipped with 500-watt lamps furnish illumination for most of the space, while the paper machine is lighted by 500-watt lamps in Glassteel diffusers.

The R. L. M. standard dome reflector is the most widely used type for general lighting. It gives a very desirable distribution of light over horizontal surfaces with illumination on vertical surfaces. It is efficient, easy to clean, and so designed that direct glare is reduced to a satisfactory medium, especially when a white-bowl lamp is used.

The Glassteel diffuser gives a softer light. It is composed of two parts—an enlarged enameled steel reflector to direct the light downward, and an enclosing opal globe which fits under the steel reflector. This enclosing opal globe provides an enlarged light-source area, thereby greatly diffusing the light and softening the shadows. Perforations in the top of the steel reflector allow a small amount of light to travel upward, illuminating the ceiling, belts, shafting, etc.

The high-bay unit is used where high ceilings are encountered. Some of the most popular high-bay units are made of mirrored glass, pressed into the form of prisms, and oxidized aluminum. All these substances give good control of the light by reflection or refraction. A mirror reflects light regularly and, by designing the contour of the surface, the light can be given any desired direction or distribution. A parabolic reflector directs all light reflected by it in parallel rays, when the light source is at the focus. By approaching the curve of a parabola with mirrored glass, a very concentrated distribution may be obtained. Slight variation from this curve will spread the beam somewhat to give the typical high-bay unit distribution. Glass prisms can also be made to refract light to desired directions, and by scientifically designing a unit made up of glass prisms, concentrated distribution may be obtained. Oxidized aluminum reflects most of the light along the same direction as a mirror, except that it is slightly diffused. Again, by using an approximate parabolic curve, a concentrated distribution can be obtained.

Intensities

The more experienced the illuminating engineer, the less he feels inclined to give general figures as to how much light any factory operation requires. He has no hesitancy, however, in stating that more light than is generally used today may be used economically and profitably. In recent years a large number of factory managers, after making a careful scrutiny of the facts regarding lighting, have put in several times the amount they originally had.

There are four levels of illumination, as follows:

5–10 foot-candles. Satisfactory for work of a coarse nature such as rough assembling, rough packing, and the like, where the eyes are not called upon to see small details quickly and accurately. This value would also represent an abundance of light for warehouse, stockrooms, aisles, and passageways—enough light to dispel any sense of gloom.

10–15 foot-candles. Considered good light for most kinds of work on light-colored surfaces and for fairly close work on dark-colored surfaces. Not enough light, however, for examining fine details on dark, light-absorbing surfaces.

50–100 foot-candles. Necessary only in ex-

Franklin Specifications
(Published by the Society for Electrical Development, Inc.)

Area per Outlet Adequately Lighted	Approx. Spacing	Minimum Distance from Underside of Reflector to Floor[a]		Lamp Rating				
				100-Watt	150-Watt	200-Watt	300-Watt	500-Watt
Sq. ft.	*Feet*	*Feet*	*Inches*	*Approx. foot-candles*[b]				
75–85	9 × 9	8	6	5–6	8–11	12–15	20–23	40–44
85–95	$9^1/_2 \times 9^1/_2$	9	0	4–5	8–10	11–14	18–20	35–40
95–110	10 × 10	9	6	3.5–4.0	6–8	10–12	16–21	30–35
110–125	11 × 11	10	0	3.5–4.0	6–7	8–10	14–18	25–30
125–145	$11^1/_2 \times 11^1/_2$	10	6	3.0–3.5	5–6	7–9	12–15	21–25
145–170	13 × 13	11	6	2.5–3.0	4–5	6–7	10–13	19–23
170–200	$13^1/_2 \times 13^1/_2$	11	6	2.0–3.0	3.5–4.0	5–6	8–11	16–20
200–230	$14^3/_4 \times 14^3/_4$	11	6	2.0–2.5	3.0–3.5	4.5–5.5	7–10	13–17
HIGH-BAY MOUNTING								
				300-Watt	500-Watt	750-Watt	1000-Watt	1500-Watt
400	20 × 20	31–36		4.5	8.5	13	18	29
600	20 × 30	31–36		3	5.5	8.5	12	19
900	30 × 30	31–36		2	3.5	6	8	13
1200	30 × 40	31–36			3	4.5	6	10
1600	40 × 40	31–36			3	3	4.5	7
900	30 × 30	37–50			3.5	5	7.5	11.5
1200	30 × 40	37–50			2.5	4	5.5	8.5
1600	40 × 40	37–50				3	4	6.5

[a] Mount units 12 feet high wherever possible.
[b] Average conditions.

tremely fine, accurate operations and in inspections of very fine details; usually employed locally and supplemented by general lighting of lower value.

Spacing, Mounting Height, and Lamp Size

The design of a general lighting system is based largely on the desirability of uniform illumination throughout the entire area. To produce these results, it is necessary that lighting units be mounted fairly high. Too great spacing between units will give an uneven illumination, as indicated in Figure 4. This can be remedied either by raising the units where the ceiling height permits or by installing additional ones. It is apparent that, to get uniform illumination, it is necessary to maintain a certain ratio between spacing and mounting height. With the modern types of lighting units, the spacing should not materially exceed the distance between the floor and the bottom of the unit.

Special-Purpose Lighting

In flour mills, grain elevators, starch mills, cocoa mills, coal-grinding rooms, and similar places, there is one vital problem which is seldom present in the other industries—the prevention of explosions and fires due to explosive dust accumulations. Although the incandescent lamp is the safest of all illuminants, it should always be remembered that it is possible to start a fire with any incandescent lamp, gas-filled or vacuum, if it is operated in such a manner as to permit the excessive accumulation of heat. When such is the case, the temperature of the surrounding material rises until it reaches the point where the heat is dissipated just as rapidly as it is produced by the lamp. If this final temperature is high enough and if combustible materials are present, a fire will be started.

There are two general types of protection units for such service—the vapor-proof and the dust-tight. Vapor-proof units are designed for protection from explosive vapors, as well as dust, and accordingly they are suited for use in extra hazardous locations. In dusty atmospheres the dust-tight unit is entirely satisfactory. It is well to make sure that the lamp used is of the proper size; otherwise, it is obvious that the unit will be hotter than intended.

Some of the hesitancy about using dust-tight and vapor-proof units has been due to an impression that these units would cause serious temperature rise unless they were ventilated, and ventilation would, of course, destroy the safety value. It has been found, however, that fixtures and globes without ventilation, but with sufficient radiating surface, actually run cooler than many of those that are ventilated. Extensive tests showed that as a rule the wire and socket parts of a properly designed, non-ventilated unit were definitely cooler than when the fixture was ventilated. In most cases ventilation was found to lower the temperature of the glass bulb slightly, but this effect was negligible compared with the undesirability of a higher temperature at the lamp base and socket where heat is much more likely to cause premature failure of the lamps. As a result of this later knowledge on the subject, the regulations no longer require that properly designed fixtures or closing glass globes be ventilated.

Color Matching or Identification

Equipment employing accurate correcting filters, by means of which it is possible to duplicate daylight, are necessary where precision in color identification, grading, or other color inspection is required. Color factories, paint and dye mixing, chemical analyses, and textile and cigar sorting and grading are examples of industries where color correcting equipment is desirable.

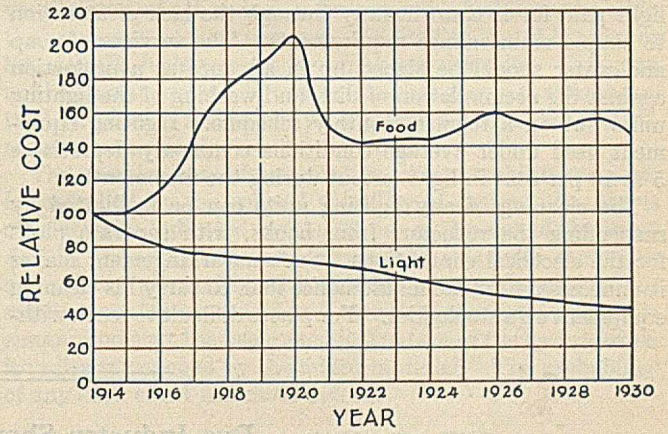

Figure 7—Relative Trends of Food Costs and Cost of Lighting since 1914

For color identification and discrimination, the ideal illuminant is one which does not favor any colors. White light is therefore the only kind that can qualify as a standard. Noon sunlight on clear days does not vary appreciably in quality, but cannot be depended upon throughout the year. In the northern hemisphere north skylight is less variable in quality and intensity than light from any other portion of the sky. As a result, color work gravitated to north windows.

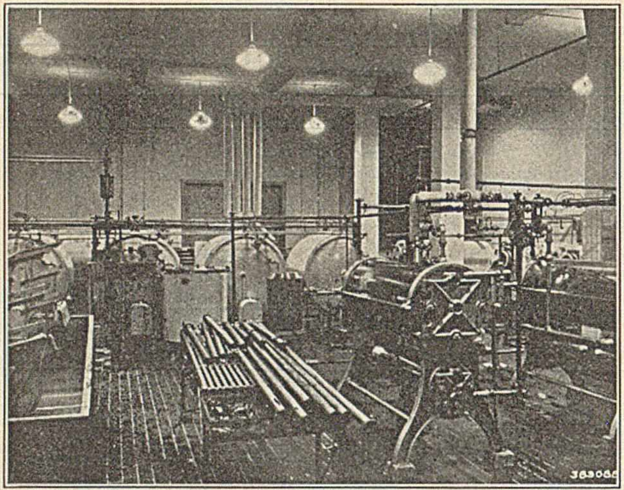

Figure 8—Pasteurizing Room Lighted with Eleven 200-Watt Lamps in Glassteel Diffusers

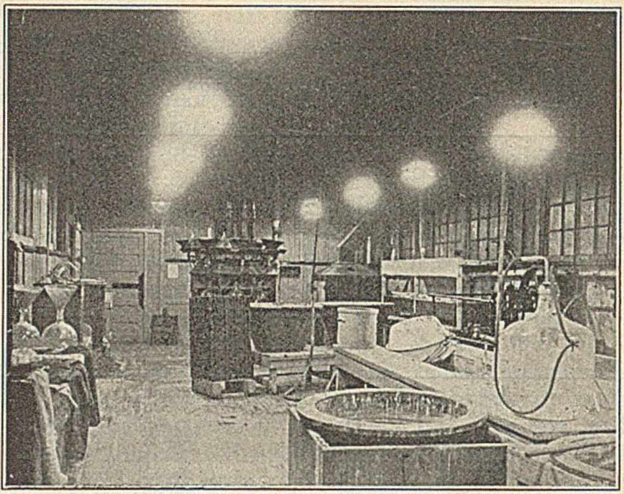

Figure 9—Uniform Lighting in Plant Laboratory

Where color-discrimination equipment is used, intensity is sacrificed because of the large amount of light which such units absorb.

An installation in which a very high intensity of light (150 foot-candles) has been directed onto the operation is shown in Figure 5. Those responsible for the installation advance the theory that under such a high intensity of light it is easier to distinguish between the different grades and colors of tile, than if a low-intensity, color-correcting unit were used; and, furthermore, because of this high intensity one is better able to tell the color appearance when they are utilized out of doors.

On the other hand, a tobacco plant has recently installed a color-correction system, believing that it is easier in this way to differentiate between the grades and shades of the tobacco leaf.

Maintenance

Experience has shown that in many cases one-half of the light paid for is thrown away through the lack of attention to simple maintenance requirements. The services of soap and water should be signed up in advance as a protection against the accumulation of dirt, and washing of the lighting units put on a regular monthly schedule. Lighting equipment used under average conditions commonly depreciates 5 to 10 per cent in light output during the first month.

The cleaning of any lighting units can be facilitated by suspending the reflectors from hooks, with separate plugs for the electrical connections. Such an arrangement makes it unnecessary for the maintenance man to carry his cleaning equipment up a stepladder. For places difficult to reach without accident risk, some form of disconnecting hanger is recommended.

A considerable portion of the light from a fixture strikes the walls of the room, the surface reflecting back a part of the light striking it and absorbing the rest. White walls reflect approximately 80 per cent of the incident light striking them; dark brown walls, on the other hand, reflect only 15 per cent of the light reaching them. Thus, when dark walls and ceiling are refinished in light color, the illumination in a room may be increased 50 to 100 per cent.

Cost of Artificial Light

Artificial light has steadily decreased in cost, until today its cost is now only approximately 2 per cent of a century ago. M. Luckiesh, nationally known illuminating engineer, in his book, "Light and Work," says:

> The great economic value of scientific developments is scarcely realized by the public. It is difficult to illustrate this value in dollars. This is equally true of lighting because there is so much value in increased safety, production, and happiness that can scarcely be appraised in money. However, the relative decrease in cost of electric light, compared with the relative increase in the cost of food, as shown in the chart, is extremely interesting because the cost of food is at least a rough gauge of all wages and the cost of necessities for all of us who work.

Adequate and proper artificial light can now be obtained at a cost equivalent to 1 per cent (seldom over 2 per cent) of the production expenses. The chart mentioned in this quotation showed the relative cost of food and light over a period of years. This chart has been continued from 1914 to 1930 in Figure 7. In spite of the generally increased level of costs, as reflected in the cost of food, the relative cost of lighting has decreased quite steadily over this period.

Dye Industry Shows Decrease in 1930

Outstanding features of the preliminary report of the Census of Dyes and Other Synthetic Organic Chemicals, 1930, by the United States Tariff Commission are:

A production of 86,585,000 pounds of dyes in 1930, representing a 22 per cent decrease from the peak output in 1929.

Sales of 89,867,000 pounds of dyes valued at $38,670,000, representing a decrease of 15 per cent by quantity and 16 per cent by value from sales in 1929.

Increase of 23 per cent in sales of unclassified and special dyes.

Decrease of 15 per cent in sales of domestic dyes of all classes, but decreases of only 2 per cent for vat dyes, other than indigo, 5 per cent for lake and spirit-soluble, 6 per cent for direct, and 10 per cent for basic dyes. Heavy decreases occurred in the mordant and chrome class (30 per cent) and sulfur dyes (24 per cent).

Sales exceeded production by 3.8 per cent in 1930, while in 1929 production exceeded sales by 5 per cent.

Decrease of 18 per cent in exports from 1929.

Decrease of 36 per cent in imports from 1929.

The decrease in production and sales in 1930, as compared with 1929, was less, however, than the decrease in either of the depression years 1921 or 1924. A 55 per cent decrease in production and 59 per cent decrease in value occurred in the depression year of 1921 over 1920. A new production record was reached in 1923 followed by a 27 per cent decrease in production and a 26 per cent decrease in sales value in 1924.

Gasoline Dopes[1]

H. C. Dickinson

Heat and Power Division, Bureau of Standards, Washington, D. C.

GASOLINE, whether sold as such or under any of the numerous trade names, is essentially a mixture of hydrocarbons, derived principally from petroleum, which possesses a range of volatility enabling its use as a fuel in motor-vehicle engines.

The commercial product has passed through a wide range of variations from the time when 74° gasoline was a troublesome by-product of kerosene refining in 1900, to about 1920 to 1923, when gasoline was practically anything which would burn in a motor-vehicle engine. Since that time, as a result of extended research fostered by the two industries most concerned, the product is being more and more definitely manufactured to meet the present known requirements of motor vehicles. Changes in sources of crude oil, in methods of refining, and in design of vehicles, as well as in latitude and the seasons, jointly affect the nature of the products marketed. Better coördination is now maintained between the petroleum and the automotive industries, while the public is reasonably well protected by competition.

In view of this apparently very satisfactory condition, one may ask—why gasoline dopes? In the first place, no natural product is perfect, and gasoline, notwithstanding the care in its manufacture, is as yet essentially a natural product in that all its constituents are derived from natural or synthetic crudes over which the producer has very limited control as to composition.

As a result of the normal failure to reach perfection, the motor vehicle offers a new field for the former dopesters of human ills. In fact, the psychological factors which have played such a large part in the distribution of drugs and medicines are equally potent in their effect on the marketing of fuel dopes.[2] Fortunately, however, it is possible in dealing with the motor vehicle to do away with the purely subjective reactions which make it so difficult to measure the effects of drugs. Yet even with the purely mechanical problems of the motor vehicle, considerable skill and ingenuity may be required to avoid prejudice, particularly when results must depend upon the performance of a vehicle concerning which accurate physical measurements are difficult. One of the most common claims made by vendors of fuel dopes is that results can be had only on the road, and not when the engine is mounted on a proper test bench with accurate measuring and recording instruments.

In order to analyze the possibilities of improvement in motor gasolines by the addition of dopes, by which term we refer to those substances which are to be added in small amounts such as an ounce or so to the gallon, it will be well to state the requirements of a motor fuel for satisfactory use, and to consider what are the chances of improving its character by means of dopes as above defined. These requirements are somewhat as follows:

Starting Properties

The engine must start. To be sure, the oil and the battery and the starting motor have much to do with this, but we are discussing fuel and must assume that these other elements are in order. To start an engine enough of the fuel must be vaporized at the existing temperature to form an explosive mixture. Since only the lighter fractions of the gasoline will vaporize at starting temperature, and since the lower the temperature the less will vaporize, excess fuel must be added to supply enough of the lighter portions to produce an explosion. It has been found that a well-designed choke mechanism will enable the carburetor to supply for starting a mixture of about 1 pound of fuel per pound of air—i. e., from twelve to fifteen times the normal amount of fuel. Many careful tests have shown how to determine with some accuracy the temperature at which any given fuel will start with this mixture ratio.

It is further shown that to secure an initial explosion requires a partial pressure of hydrocarbon vapor in the engine cylinder of the order of 10 mm. of mercury. Such a concentration of fuel vapor in the charge can result only from the evaporation of a substantial proportion of the fuel supplied. For instance, if it is possible for the carburetor to supply an amount of fuel equal in weight to the amount of air—i. e., twelve to fifteen times the normal charge—it will be necessary to evaporate 4 or 5 per cent of the fuel.

Obviously, the starting characteristics of a fuel cannot be revolutionized by the addition of any foreign material in amounts much less than 1 per cent. Claims that any dope promotes easy starting are therefore open to very serious question and should not be accepted without adequate proof.

Sufficient Vaporization

A good gasoline must vaporize in the manifold sufficiently to avoid too much crankcase dilution and to give good distribution of the fuel to the different cylinders. Before crankcase ventilators and other devices for removing fuel from the oil in the crankcase became common, the limit in use of heavier or less volatile fuels was set by crankcase dilution. This may not be true at present, but experience has shown that for practical purposes a fuel is not satisfactory if too much of it remains unvaporized.

The completeness of evaporation, like the ability to start, is controlled by the general volatility of the gasoline and is satisfactorily indicated by the 90 per cent point of the usual A. S. T. M. distillation test. Obviously, this point cannot be appreciably affected by the addition of any material in the small amounts here considered, except on the very improbable assumption that the basic chemical nature of the hydrocarbon is radically changed by the added material. The probability of any such effect is remote indeed.

Vapor Pressure Not Too High

A gasoline must not have too high initial vapor pressure, due to an excess of very volatile constituents or to fixed gases in solution. Otherwise it may form vapor in the supply lines and carburetor, resulting in "vapor lock," or stoppage of the engine due to interference with the normal fuel feed.

Formerly this trouble was infrequent, since there was a dearth of volatile fractions in most gasolines. Of late, cracking processes and increased recovery of natural-gas gasolines have made vapor lock more common. So far as the writer is informed, no dope has ever been proposed to remedy this fault.

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[1] Received March 2, 1931. Publication approved by the Director of the Bureau of Standards of the U. S. Department of Commerce.

[2] The author here uses the popular term "gasoline dopes" in its commonly accepted sense. Any substance which is used or proposed for mixture in amounts less than, say, 1 per cent with gasoline for the purpose of improving its properties would fall under this definition.

Knocking Characteristics

The tendency of gasolines to knock or detonate has been under much discussion in relation to the action of fuel improvers. Unlike the other properties of fuels mentioned above, this characteristic is dependent on the chemical rather than the physical properties of the hydrocarbons present, and is in some cases greatly modified by the presence of small amounts of inhibitors.

The subjects of detonation and anti-detonants have been given much careful study, a review of which would be entirely out of place in this discussion. A brief summary of present information, however, is necessary to a clear understanding of the present situation regarding fuel dopes.

For convenience, we shall adopt the recently recommended octane-number method of designating the knock character of fuels. The reference standards for this purpose are mixtures of pure normal heptane and pure isoöctane (2,2,4-trimethylpentane), the octane number of any mixture being numerically equal to the percentage of isoöctane by volume that it contains. The octane number of a fuel is the same as that of the standard which it matches when tested by an approved method.

There are in general two methods of improving the knock rating of an ordinary gasoline: (*a*) to blend it with other fuels such as benzene, special cracked gasoline, alcohol, or better grades of gasoline which have high octane numbers; in which case the rating of the blend will be intermediate between that of the constituents with some approach to proportionality; and (*b*) to add one of several special anti-detonants which will produce a similar result. The first alternative is not of interest in a discussion of fuel dopes as here defined, since the quantities used in blending are entirely outside the range being considered and the results are roughly proportional to the amounts used. Some of the anti-detonants, however, are essentially fuel improvers. Among these the best known are iron carbonyl, nickel carbonyl, and organic compounds of lead, selenium, and tellurium.

The intensive research which has been devoted to the subject of anti-detonants leaves slight ground for expectation that any of the other readily available chemical compounds will serve this purpose. Tetraethyl lead, the only one of those mentioned which has found general application in this country, is not marketed separately, but only when combined in finished fuels, on account of the danger of handling the concentrated volatile lead compound.

In view of these facts, claims which are made as to the knock-suppressing power of fuel dopes should be accepted only after adequate tests. Routine tests have been run on about one hundred fifty of such dopes by the Bureau of Standards at the request of various submitters, and without exception the reports have shown no definitely measurable effect on detonation. These tests, of course, did not include tetraethyl lead or other of the recognized knock suppressors since, as noted above, these are not available for distribution as dopes.

Power Development

The maximum power of a motor-vehicle engine is determined mainly by the size and design, including the speed at which the engine develops its maximum power. Once the engine-vehicle combination is designed, the user is more concerned with the maximum torque which the engine will deliver at various speeds than with the horsepower at the optimum speed. The ability of an engine in this respect is usually expressed as brake mean effective pressure (BMEP), which is a generalized figure comparable for engines of all sizes. It is defined as the mean pressure in the cylinders, during the working stroke, which would be required to develop the measured brake horsepower at a given speed. It varies with speed and with engine design, but for most automobile engines within the normal range of speeds it lies between 80 and 120 pounds per square inch.

Claims made for different fuels and fuel dopes on the basis of increased car ability necessarily imply an increase in BMEP.

It has been shown, both on theoretical grounds and from direct measurements, that for a given engine and for fuels which do not knock, the BMEP, within the rather wide range of proper explosive mixtures, depends very accurately on the amount of oxygen taken into the cylinder and burned to carbon dioxide and water. It follows, therefore, as has been shown experimentally, that the BMEP is affected only to a very minor extent by the character of the fuel, except in so far as the volume of oxygen taken into the cylinder is affected thereby. Since the vapor volume of the usual liquid fuels in an explosive mixture seldom varies more than 1 per cent, it is obvious that neither fuel dopes nor different fuels which do not affect detonation can greatly affect the BMEP and therefore the ability of a car.

It may be of interest to note that ethyl alcohol, having a higher heat of evaporation than gasoline, may give a per cent or so greater BMEP because of the greater cooling and contraction of the air in passing through the carburetor.

Carbon Deposits

The collection of so-called carbon in engine cylinders is a nuisance and expense, as it may be necessary to remove it to avoid excessive detonation and other troubles. Claims for the removal or prevention of carbon deposits commonly have been made for fuel dopes. Since the collection of carbon under normal operating conditions involves a rather long time and is greatly affected by engine and operating conditions, conclusive evidence as to the carbon-removing properties of dopes dissolved in the fuel is very difficult to obtain.

It has been shown that, under some conditions at least, the formation of carbon deposits reaches an equilibrium dependent on the operating factors mentioned above, and that, given a badly carbonized engine, the deposit may be greatly reduced by a few hours' running at high load under favorable conditions. Obviously, reduction in carbon deposit following the use of dopes is not necessarily the result of their use. Apparent removal of carbon as manifested by reduced knock follows the use of knock suppressors, but as noted above, none of them appear to be available in the form of dopes.

Although there are various recognized solvents which will dissolve the binder in the normal carbon deposit, and permit the carbon to be blown out of the exhaust, it does not appear that the mixing of these in relatively small quantities with the fuel should be an effective method for their use. There is no valid evidence of the effectiveness of any fuel dopes as herein defined in the removal or prevention of carbon deposits, and conclusive proof would be difficult if not impossible to obtain.

Satisfactory Mileage

Another requirement of a motor fuel is that it shall give a satisfactory number of ton-miles of transportation per gallon used. Increased economy is very often claimed for gasoline dopes.

The combining proportions of air and gasoline are rather closely 15 to 1 by weight. On the other hand, the maximum horsepower of an engine is usually developed at about twelve pounds of air per pound of fuel and, under some conditions, particularly in the warming-up period, an even richer mixture is required to give satisfactory acceleration and general performance. These figures are, moreover, much affected by the uniformity of distribution to the different cylinders, and by the type and adjustment of the auxiliary accelerating devices employed on most carburetors. Therefore, almost without exception carburetors are set for a mixture ratio that is much too rich for maximum fuel economy. In fact, in many cases the settings are so rich as materially to reduce the maximum power of the engine when warmed up to normal operating conditions. These over-rich settings also promote excessive carbon formation and result in much less satisfactory general performance.

Obviously, here is a fruitful field for improvement. Any device that will induce or compel the user to run on a leaner mixture often will have the obvious advantages of reducing the fuel consumption, reducing the carbon deposit and thus the tendency to knock, and improving the general performance of the vehicle at the expense perhaps of some little delay in warming up the engine in cold weather.

Fuel dopes are frequently accompanied by instructions to use a leaner mixture. When such instructions have been followed, they have sometimes seemed to accomplish favorable results. There is also some evidence that certain dopes may affect the rate of fuel feed through carburetor passages. It is safe to say, however, that an adjustment of the carburetor would have accomplished the same or better results.

Conclusions

Gasoline dopes which are sold for addition in small quantities to gasoline can be accepted as of value only on conclusive evidence that they are effective. They cannot be expected to improve starting, decrease crankcase dilution, or prevent vapor lock. So far as information is at hand, no materials which in small quantities reduce knock are sold separately for mixture with gasoline. Maximum power cannot be affected by small additions of any known substances, except as they affect fuel knock. Carbon formation and fuel economy are so dependent on adjustments and operating conditions that proof of the value of dopes is more difficult. In the testing of some one hundred fifty such dopes at the Bureau of Standards, exclusive of the well-known knock suppressors, not a single instance of any important improvement has been observed in any feature of engine performance.

Economics of Recovering By-Product Carbon Dioxide[1]

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The recent development of solid carbon dioxide refrigeration has directed special attention to the quantities of gaseous carbon dioxide generated as a by-product of many industrial operations. Some of these have value as sources, but this value is controlled by many factors. In this article the major economic considerations which affect the value of such by-product sources as raw material for the solid carbon dioxide industry have been discussed.

THE recovery and purification of carbon dioxide from lime kilns and from the calcination of magnesite is not a novel thought. As a matter of fact, operations manufacturing liquefied carbon dioxide from both these sources were in more or less successful use in Europe a quarter-century ago. The early files of the German *Zeitschrift für die gesamte Kohlensäureindustrie*, as well as the American *Carbonic Acid*,[2] are replete with references to the technology of carbon dioxide manufacture from lime kilns. A complete historical description of some workable processes will be found in "The Carbonic Acid Industry," by J. C. Goosman.[3] The manufacture of carbon dioxide from lime-kiln gases has nevertheless been a dead issue in the United States for more than two decades, because economic justification for such operation has been lacking. Even recent proposals for producing pure carbon dioxide direct from kilns by steaming and regenerative heating have their counterparts in the art of two decades ago.

Recently several lime operators and others attempting to exploit limestone deposits have had their interest quickened by the growth of the infant industry of solid carbon dioxide under the trade-mark "Dry-Ice." It has seemed to them that the recovery of by-product carbon dioxide from their operations, actual or contemplated, for the manufacture of solid carbon dioxide might show an attractive profit, or at least help to bear some of the overhead burdens of the lime business.

Now, it is not to be denied that carbon dioxide can be recovered at some cost from lime-kiln stack gases, nor is there any insurmountable technological difficulty in liquefying the carbon dioxide so purified and converting it to solid form, if patent, sales, and distribution difficulties are ignored. Furthermore, in most parts of the United States the manufacture of pure carbon dioxide gas could be accomplished on a large scale from lime- or magnesite-kiln gases for a small fraction of current retail solid carbon dioxide selling prices, provided steady operation on a large scale, small radius of shipment, and economical selling and distribution are assumed. Careful analysis of more than a score of lime-kiln proposals within the past two years, however, has failed to disclose a single case which has established any sound present justification for the manufacture of solid carbon dioxide under such conditions from such a source. It is the purpose of this paper to discuss some of the factors that have been taken into consideration in the evaluation of the gases considered.

Size of Industry

The solid carbon dioxide industry today is by no manner of means a tonnage industry, since the approximate total sales of all plants in the United States in 1930—some 30,000 tons—is less than the carbon dioxide produced from one modern blast furnace in a single month, and represents an annual consumption of only about one-half pound per capita. The statement is frequently made loosely that solid carbon dioxide is a "coming thing," "has a great future," "will grow fast,"

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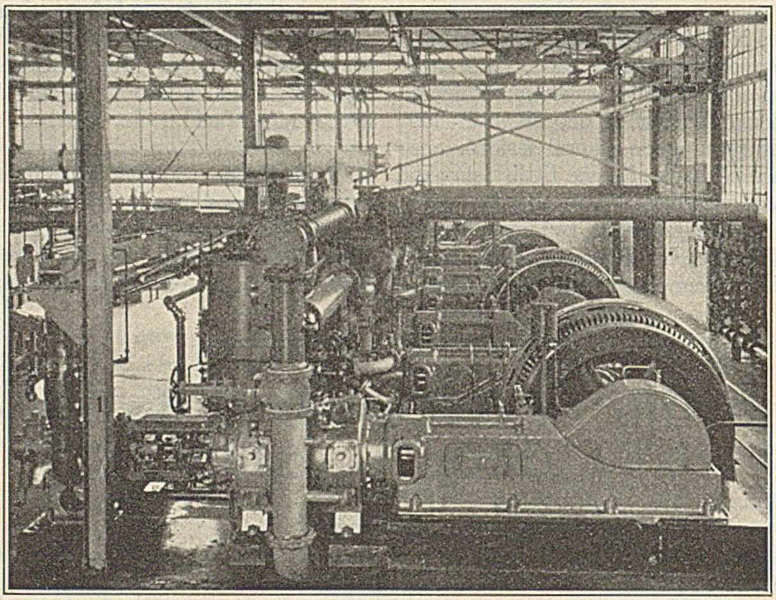
[1] Received March 18, 1931.

[2] No longer published; formerly issued, commencing January, 1905, by the Carbonic Acid Publishing Co., 5504 Fifteenth Ave., Brooklyn, N. Y.

[3] Published in 1905 by Nickerson, Collins & Co., Chicago, Ill.; now out of print.

and with all of these viewpoints the writer is in the heartiest accord. It does, indeed, seem a logical refrigerant for many purposes, and will unquestionably eventually find largely increased use at decreased selling prices.

It is always possible to justify almost any kind of industrial operation by assuming a stable price favorable to the operation and neglecting to consider competitive sources of supply. Sound operators will, of course, avoid such assumptions. It is necessary that we keep constantly in mind the current proportions of the industry in relation to the supply of raw material. Complete figures on the sale of solid carbon dioxide have not been published, but Figure 1 shows the growth and seasonal fluctuation of the Dry-Ice Corporation sales from 1926 through 1930. This represents a large majority of the total volume sold.



Battery of Three-Stage Compressors in the Niagara Falls Plant of the DryIce Corporation of America

These compressors have a capacity of 120 tons per day of carbon dioxide working between a nominal pressure and more than 1000 pounds per square inch.

In presenting this curve attention is directed to two things—(1) the consistency with which the seasonal variation of demand is repeated with its unfavorable sharpness of summer peak, and (2) the orderly manner and definite proportion in which the volume of demand increases from year to year. The contention has been advanced by many that this orderly progression in volume of business has been attained in a market stabilized at an admittedly arbitrary introductory price. They maintain that at some lower price level, the selection of which has usually been based upon an idle hypothesis of a hoped-for volume of sales or on a scale of manufacture unattainable under present conditions, new markets will rapidly open up for fabulous quantities of the material. Inasmuch as this type of reasoning is common, and by no means peculiar to solid carbon dioxide, the point can be passed with little comment. It must be noted, however, that solid carbon dioxide has properties widely different from water ice. When new users desire to adopt it as a refrigerant, they must purchase new equipment for use with it and frequently they must change their methods. This sometimes involves changes by the producer, not only in technological methods, but in selling methods and in the type of market approached when methods of distribution are altered. This is indeed a happy circumstance for a responsible supplier, since the changes described require considerable time for their accomplishment, regardless of price, process, or any other consideration. The time lag thus introduced in the development of new business is ample for the construction of production facilities to meet the demand, and the informed manufacturer, quite aside from the current situation in respect to patent control and sales competition, can afford to view with complacence the expansion activities of those less endowed with experience in the industry or information as to its rate of sound development.

Notwithstanding this, the properties of solid carbon dioxide combined with the appeal of the catchy and novel trademark, "Dry-Ice," and the fanciful contradiction which it suggests to the public mind, give to Dry-Ice *news value*. The natural and inevitable consequence of this news value has been a certain amount of editorial comment portraying solid carbon dioxide in general and Dry-Ice in particular as a romance of modern business, which perhaps it is. The natural consequence of the editorial comment has been the development of much activity that is more romantic than businesslike. However, it is obvious that the rate of increase in the total volume of solid carbon dioxide marketed bears some reasonable relation to the actual willingness of users to purchase it at a price, and to the rate at which they can possibly adapt equipment and methods for its use. Let us, then, consider a few points in connection with the evaluation of low-pressure pure carbon dioxide gas.

Evaluation of Supply of Carbon Dioxide Gas

The chief premise in such a discussion is that carbon dioxide gas per se is absolutely valueless. Like air and water, the amount of the supply in some form in every civilized community is far in excess of any conceivable demand. To dwell on this point would be only a waste of time, inasmuch as we must start with all the carbonaceous fuel consumed and add to it all the carbonates calcined, the carbohydrates fermented, and sundry other sources.

It will probably be accepted without further support, then, that carbon dioxide can acquire value only by having something peculiar about it to distinguish it from other less desirable carbon dioxide in the same vicinity or at least available to supply the same market.

The selection and valuation of by-product carbon dioxide sources is thus always a competitive question, in that no source anywhere now known to us possesses a sufficiently outstanding advantage against all other possible sources for supply of the same market to have any possible chance of dominating such a market by reason of the nature of the source alone. Several choices are open to any one willing to risk paying anything at all for them. Thus one can find advocates for at least a half-dozen widely varying types of supply for the New York market, and it is perfectly safe to say that there are at least three times as many other sources and processes not now advocated, or at least not receiving publicity, which under some imaginary set of conditions could be used to meet the demands of the market. Certainly a corner on the supply of carbon dioxide is a practical impossibility and deserves to rank with perpetual motion as axiomatically untrue. Raw carbon dioxide, in short, bears much the same relation to the solid carbon dioxide business that a supply of air bears to the oxygen business.

Nevertheless, by-product carbon dioxide under some conditions and in some places does have value which it may acquire by reason of six factors: (1) purity, (2) pressure,

(3) location, (4) seasonal value, (5) safety factor, and (6) time value.

The net valuation of any source must be based on all six of these factors and sometimes others peculiar to the individual situation. In any event, these six factors are additive, and a particularly unfavorable situation in regard to any one of them will often render a given source unattractive, even though the other five are favorable. Conversely, a particularly favorable situation in regard to one factor sometimes will offset unfavorable situations in regard to others.

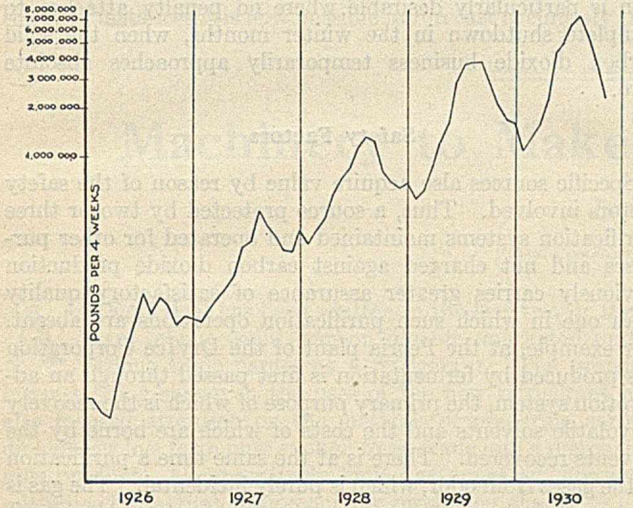


Figure 1—Dry-Ice Sales by 4-Week Periods

Purity

Let us first consider, then, purity value. The ideal in this respect is obviously 100 per cent carbon dioxide—i. e., complete freedom from odor, moisture, oil, solids, and gaseous impurities. The criterion of lesser purities is, of course, the cost of correcting them to the ideal condition or to a sufficiently close commercial approach to it. The value involved, however, is a relative one, and no absolute value is implied or possible for gas of a definite purity. This is because the present or future market is so limited in relation to enormous available supplies that only the purest gas available for supplying a given market has any purity value whatever. All other sources for supplying the same market have a negative purity value equivalent to their extra purification costs at the existing volume of production and annual load factor. It should be noted that low costs for purification based on fanciful assumption of non-existent annual load factor and volume of demand are not in question, and any process, regardless of its nature, which requires considerable investment must be scrutinized very closely, particularly if there is any question about the volume of sales that can be realized.

Figure 2 shows in convenient form the arithmetical relation between capital charges, taken conservatively at 15 per cent for depreciation, interest, and taxes, to the annual tons marketed per ton of installed capacity. It is obvious that, except at a very low investment per ton of capacity, capital charges per ton produced mount very sharply at low load factors, and must be still further increased to allow for evaporation losses between point of production and consumer. This curve refers only to purity values. Investment shown is hence only investment in process equipment for delivering pure carbon dioxide to compressor suction and is entirely aside from investment in refrigerating machinery and solid-forming equipment. The latter, of course, involve additional investment charges which could also be presented in a similar way but the refrigerating and press investment charges are relatively constant for equal capacity, while investment in purification equipment is almost nil in favorable by-product locations but becomes quite large if expensive absorption systems are employed.

Just what constitutes a reasonable expectance of sales from a given plant capacity is, of course, not germane to this paper, nor is the bearing of patent control and effective sales promotion method of interest in a purely economic discussion of this kind. However, it will be apparent from a casual inspection of the annual demand curves presented in Figure 1 that the indicated figure of 125 tons per ton of installed capacity as a reasonable expectance for actual production in a wholly non-competitive field is a fair maximum. Some recently installed plants have produced as low as 30 to 50 annual tons per ton of installed capacity in strictly non-competitive markets. As a matter of fact, 125 tons per ton of capacity in economically sized plants are now attainable in only a few large cities.

Summing up this point, the purity value depends upon purity relative to the most attractive source for supplying the same market, corrected for differences in purification cost on the basis of actual volumes produced.

Pressure

A few sources of carbon dioxide acquire a definite value by reason of their pressure, but here again value can be based only on some conception of relative desirability. Gas wells yielding carbon dioxide under substantial pressure are generally in such remote locations that their operation could probably be made to pay only on a basis of a volume production large enough to support efficient manufacture with low overhead charges and transportation in large enough quantities to bring the transportation cost within reason. These conditions do not now exist, but for the above reason a positive value of pressure per se in its influence on by-product value can exist only in relation to a plant in which the volume produced is far beyond present proportions.

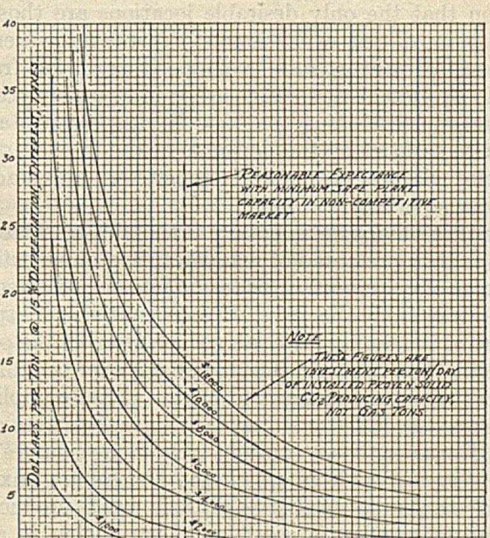


Figure 2—Per Ton Capital Costs of Process Equipment for Delivering Pure CO_2 to Compressor Suction

Viewing pressure value from another angle, at the Niagara Falls plant of the DryIce Corporation of America the maximum production of Dry-Ice per kilowatt-hour has been 13 pounds, with fluctuating operation the year round it has averaged 8.7 pounds; the average cost of power has been approximately $1.00 per ton. Depreciation, fixed charges, and maintenance on compression equipment amounted to $1.40 per ton.

From this we might conclude that the value of pressure in any case is not large in relation to the selling prices now existing, but such a conclusion would not begin to express the facts. In every geographical district where carbon dioxide issues from the ground under pressure there are several wells producing the gas under diverse ownership. This means that, even if a positive pressure value could be assigned to a given source of gas, it would be negatived by the willingness of another well owner or driller to consider something less as sufficient to cover this value. From this point of view any credit for pressure value must be dropped out of consideration in a competitive cost analysis. The common occurrence of carbon dioxide gas wells in certain petroleum-producing regions leads to the thought that future drilling for oil and gas over a period of years is quite likely to confirm the view that control of known well-gas supplies is unimportant.

Location

Location is perhaps the most important consideration generating value for by-product carbon dioxide. By the same token it is perhaps the most difficult to appraise correctly. Here again we are faced with constantly changing premises, and the locations which appear to have the greatest value for, say, the next five years are by no means necessarily those that might have the greatest ultimate value.

If we set up the idle hypothesis that the market for vast quantities of solid carbon dioxide is a likelihood of the near future and that this market will be distributed approximately in proportion to population, we must immediately come to the conclusion that the only desirable locations are those at or near the point of use, which is to say in the larger centers of population. However, such a supposition is far from the facts, and at present no market exists in any single center of population, not excluding the New York metropolitan area, sufficient to support by the demands of the local trade alone a producing plant of economical proportions, manufacturing, say, 100 tons per day.

It is rather obvious elementary economics to state that a dilemma is then presented of manufacturing on a costly scale at the point of consumption, or manufacturing on an economical scale away from the point of consumption and spending all or part of the saving for the transportation of the product. No final and clear choice in this dilemma is ever possible, since both types of operation seem to have a definite application, and each may seem better suited to definite situations existing locally. However, if we consider only those sources of by-product carbon dioxide in which the owners are anxious to dispose of substantial tonnages of their waste product, only the second alternative is possible. Distribution to a fairly wide area is necessary and apparently will be necessary for some time to come. This injects into our conception of location value that of center of gravity of surrounding markets, which will perhaps be sufficient explanation of the fact that the largest producing unit is now located at Niagara Falls. In addition to power, water cost, and other favorable factors, the ability to ship with a reasonable haul to more of the northeastern part of the United States than is possible from seaboard points was an important consideration. The location of the largest producing unit in the midwest at Peoria, in so far as transportation is concerned, was dictated by similar considerations.

To state the point briefly, a central location a reasonably short distance from a number of markets quite obviously has greater location value than either a more remote point or a point located in one market but not easily accessible to surrounding markets, particularly when the market at a single center of population is not large enough to support an economically sized plant.

Seasonal Value

By-product sources may also acquire value by reason of their seasonal nature. Thus, a source which produces heavily during the summer months and little or not at all in the fall and winter has an obvious advantage in supplying a seasonal industry with corresponding peaks. Such seasonal operation is particularly desirable where no penalty attaches to complete shutdown in the winter months, when the solid carbon dioxide business temporarily approaches absolute zero.

Safety Factors

Specific sources also acquire value by reason of the safety factors involved. Thus, a source protected by two or three purification systems maintained and operated for other purposes and not charged against carbon dioxide production obviously carries greater assurance of satisfactory quality than one in which such purification operations are absent. For example, at the Peoria plant of the DryIce Corporation gas produced by fermentation is first passed through an adsorption system, the primary purpose of which is the recovery of volatile solvents and the costs of which are borne by the solvents recovered. There is at the same time a purification of the gases from odor, which is purely incidental. The gas is next passed through a water-absorption system whose primary purpose is to obtain other products and which has been operated for several years without regard to the recovery or sale of carbon dioxide. A third purification system is employed to clean up any remaining traces of odor, while a fourth system is employed for the removal of permanent gases. It should be obvious that this gas has an appreciable value, some desirability over a source similar in every other respect but not so well protected from the hazard, ever present with any system, of occasional small quantities of material of unsatisfactory quality.

Further comprehended in the term "safety factor value" is the implication of assured continuity of supply. Thus a plant having by-product carbon dioxide whose output of primary product is sold entirely through very conservative channels, and whose operation has been at a constant rate over a period of years, is obviously more desirable than the source of which these things cannot truthfully be said. Further assurance of continuity of supply is obtained when the proportion of solid-producing capacity to total carbon dioxide available is quite small, since it will then require a substantially complete shutdown of the parent plant to influence materially the operation of the solid carbon dioxide plant.

Time Value

In the expression "time value" is comprehended a concept of the valuation based on all the other factors of any kind being timely in relation to the actual state of development of the market for the product. Thus, no positive value whatever can be assigned to by-product carbon dioxide under any circumstances unless there is considered to be a profit obtainable from its recovery. Such a profit presumes that operations are undertaken when the increased amounts of solid carbon dioxide produced are made available to the market at approximately the same time and in approximately the amounts that can be absorbed, or perhaps a little faster to allow for unforeseen conditions. Much progress has been made in this direction in the past few years by the reduction of the time necessary to provide additional producing capacity, but there is still a naive tendency on the part of seasoned engineers, studying by-product carbon dioxide in general and Dry-Ice in particular, to base conclusions on the unwarranted assumption that the product manufactured can be sold without difficulty at some price necessary to yield a profit in their own mind's eye, and that the market is in no danger of over-supply and its usual train of economic consequence.

To cite an example of rapid construction, the ground was broken for the Peoria plant on April 10, 1930, and, on July 17, a unit of 50 tons capacity was placed in operation, producing at once steady and dependable quantities of salable product. In many instances it is now possible to forecast accurately the rate of market development at least four months in advance by following closely the progress of the principal users and prospective users in modifying their equipment and methods. For example, a change in refrigerated truck transportation of any large hauler of meat or frozen products requires several months for its accomplishment. Improved speed of plant construction, better intelligence as to the rate of introduction of new equipment and methods, and the construction of large seasonal storages, now aggregating 7000 tons of solid carbon dioxide capacity, have eliminated all hazard of any shortage of supply of the product and made it possible to undertake further developments along sound conservative lines.

Machinery to Make Solid Carbon Dioxide[1]

Terry Mitchell

Frick Company, Inc., Waynesboro, Pa.

A GREAT deal has been written in the last two or three years about solid carbon dioxide, marketed under various trade names as a refrigerant. The growing interest being shown in the uses of the new refrigerant has also focused attention on the methods of preparing carbon dioxide gas in a form pure enough to be made into a merchantable product. Comparatively little has appeared, however, outlining the actual equipment for producing the ice.

The plant making solid carbon dioxide comprises, briefly, a three-stage compression system, carbon dioxide condensers, three-stage liquid coolers, snow chambers, and auxiliaries such as mixers, intercoolers, filters, etc. The several stages of liquid cooling are synchronized with the corresponding stages of compression to give better efficiency, reduce the size of the machinery, and save horsepower.

The physical basis of the manufacture of solid carbon dioxide is the reduction in pressure and cooling of the carbon dioxide below its triple point, which is at −70° F. In practice the liquid carbon dioxide may be allowed to expand to a pressure between 5 and 15 pounds gage, corresponding to a temperature of about −100° F. Under these conditions part of the liquid carbon dioxide turns into ice and the remainder into gas, the latter representing the amount required to cool the liquid to the ice temperature and to take out the heat of fusion. It is evident that the yield of ice, per pound of carbon dioxide handled, will be much greater if the liquid is precooled to a low degree. In this system the liquid is chilled to as low a temperature as possible, corresponding to the lowest suction pressure in the three-stage compression plant, before it enters the ice-making cylinders.

Removal of Impurities

The principal present-day sources of carbon dioxide gas are coke fires, fermentation vats, lime kilns, and "oil" wells. Gas from any ordinary source known at present is too impure for direct conversion into the solid for refrigeration purposes, but must be purified to an extraordinarily high degree by processes more or less elaborate, depending on the nature and amount of impurities present. The removal of inert gas, moisture, and substances causing odors, is particularly important. The gas obtained from alcohol plants and from natural wells in Mexico and some other places is sufficiently pure to require only simple treatment. The purified gas is fed into the system under a few pounds pressure by a rotary blower.

Removal of moisture is necessary to prevent freezing and clogging with water ice in the low-temperature parts of the cycle. In commercial plants, water is removed from the gas before it enters the system by freezing, sulfuric acid driers, or in some cases by absorbers using activated charcoal. The apparatus in the gas circuit between the stages of compression is provided with valves from which any water, precipitated by the higher pressure existing between these stages, may be drained. Whatever water vapor is condensed with the liquid tends to accumulate and freeze in the liquid carbon dioxide coolers. In cases where the gas is not dried thoroughly, continuous operation may be insured by installing these coolers in multiple, with by-pass piping arranged so that one cooler can be thawed out while the other is in service.

Even a small amount of machine oil in the gas causes a yellow discoloration in the blocks of ice, and they cannot then be sold. Other impurities, depending upon the source from which the gas is taken, must be guarded against by special means.

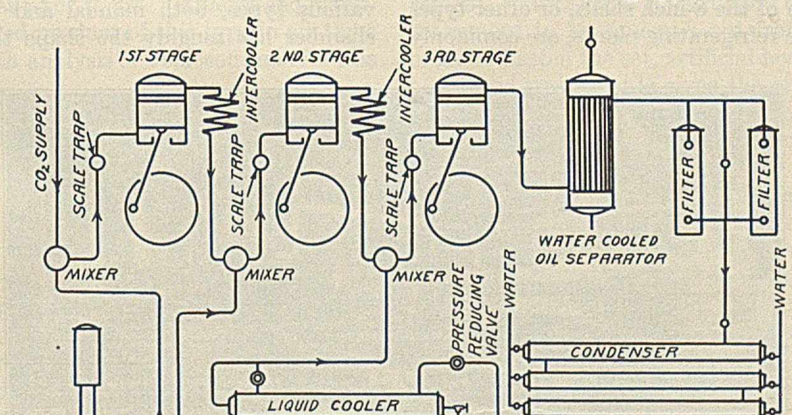


Diagram of Machinery for the Manufacture of Solid Carbon Dioxide

Compressors

The compressors are of either the vertical single-acting enclosed type,

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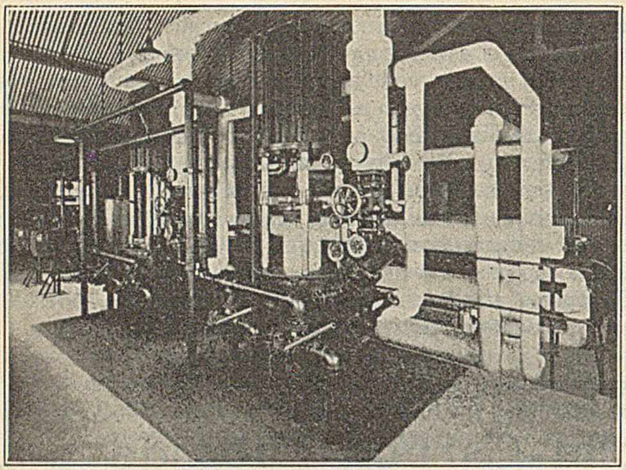
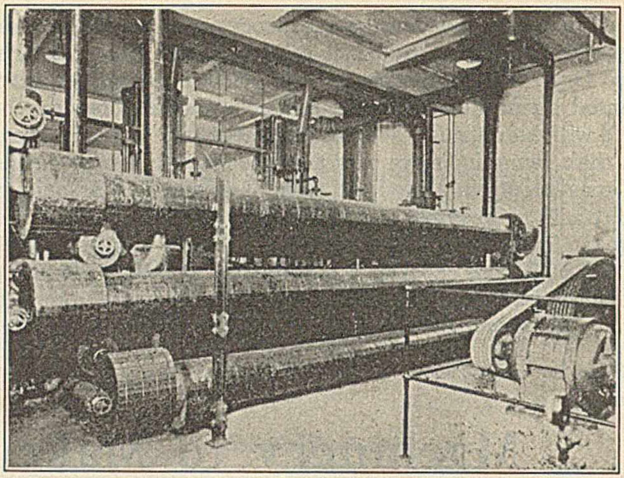
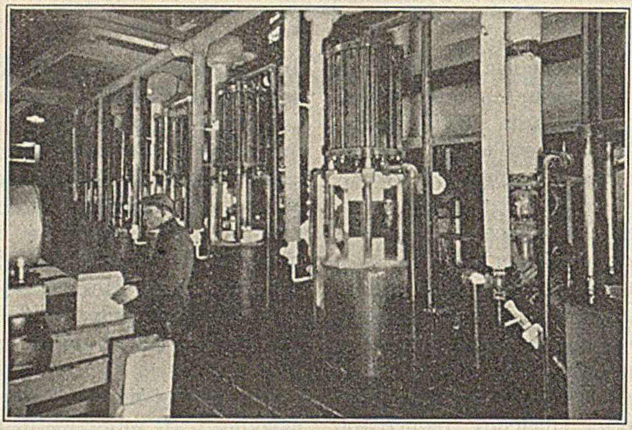
[1] Received February 12, 1931.



Machines for Making Carbonic Ice or Solid Carbon Dioxide. Liquid Coolers and Compressors in Rear



Typical Installation of Liquid Coolers



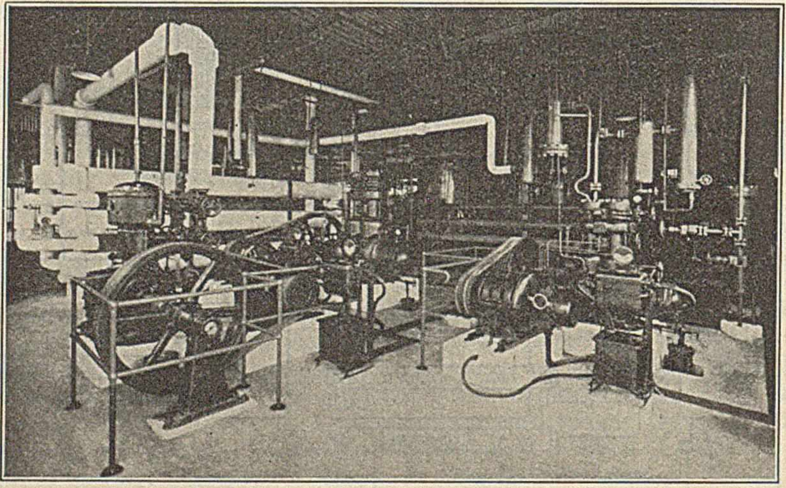
Six Hydraulic Machines Producing Nearly 50 Tons of Solid Carbon Dioxide per Day

each with two cylinders, or the horizontal double-acting design. Where the plant capacity is large enough, duplex-coupled enclosed machines, driven by a single motor placed between them, are used for the first stage, in which the pressures are such that ordinary ammonia compressors are applicable. Larger plants have two machines for the second stage as well. Another way is to use multistage machines with booster compressors to handle the large volume of low-pressure gas. Intercoolers, through which cold water is circulated, are employed between the various stages. Before entering the filters and condensers, the gas passes through a tubular oil separator of the water-cooled type.

Condensers and Liquid Coolers

Condensers of the standard shell-and-tube design with seven water tubes in each of the 8-inch shells, or other types as built for carbon dioxide refrigerating plants, are commonly used. Similar 8-inch shells with the multipass tubes are employed as liquid coolers. Pressure-reducing valves are fitted in the line between the receiver and the first-stage cooler and also between the first- and second-stage coolers.

An expansion line is branched off after the liquid passes through the reducing valve, and this admits carbon dioxide to the tubes of the cooler; the main body of the liquid fills the space around the tubes, inside the shell.



Three-Stage Compression System and Liquid Carbon Dioxide Coolers—Solid Carbon Dioxide Plant

The gas evaporated in the first-stage cooler is conducted to a mixer, where it joins with the suction gas entering the third-stage compressor.

In a similar way the partly cooled liquid is carried to a lower temperature in the second-stage cooler, the gas evolved in each case being handled at the highest pressure possible, for the sake of economy.

The third cooling stage is really a heat exchanger, and is labeled as such on the diagram. In this shell the low-temperature blowback gas from the ice-making chamber is passed around the tubes, the liquid being inside them. The gas recovered from the ice chamber is finally taken back to the first-stage mixer and reënters the system.

Snow Chambers

The snow machines illustrated are of vertical design, hydraulically operated, and were developed from tests with various types, both manual and power-driven. The snow chamber has roughly the shape that would be required to accommodate a square post; the sides of the square opening measure 10 inches. By varying the length of the chamber of the machine it can be arranged to produce blocks of ice up to 20 inches long. Although the 10-inch cubes, weighing from 40 to 50 pounds, have been accepted as standard in the trade, it is likely that larger blocks will be preferred in the future, these blocks to be sawed into smaller pieces after the ice has been delivered to the user. These larger blocks will be 10 inches square in cross section, and will therefore fit into the storage and shipping boxes now in use, but the length of the blocks may be increased to 20 inches to save time in handling and to aid in preventing evaporation.

The cast-iron snow chamber is heavily insulated, as can be seen in the photographs. Inside the chamber is fitted a square piston or ram, worked by a hydraulic cylinder below the floor level; a similar hydraulic cylinder controls the head or cover of the chamber. The operating levers and water valves are clearly shown in the foreground of one of the views. The hydraulic cylinders being of ample size, a simple centrifugal pump provides the necessary water pressure. An open surge tank is part of the water system.

A blowback valve and suction pipe are installed above the expansion connection, due precautions being taken to keep the flakes of snow from entering the blowback line and eventually clogging the heat exchanger. The vertical design of the machine keeps the pressure of the ram from setting up uneven strains on the frame or foundation of the unit. The tendency of the moving parts to freeze fast, and the inclination of the top of each block of ice to be soft and porous, with broken corners, have also been overcome.

The loose snow formed in the chamber can be given either one or two compressions, by manipulation of the controls, and by admitting an extra amount of liquid before opening the blowback valve a heavy, more solid block of ice can be formed if desired.

The machines are usually operated on a continuous schedule, 24 hours a day. The pressures and temperatures throughout the system will be different under various conditions but average pressures of 100, 350, and 900 pounds gage, respectively, for the three stages, are typical.

Plants of the type described are in operation in this country and abroad. The largest installation, having a capacity of about 50 tons of solid carbon dioxide per day, is in Philadelphia.

Quick-Setting Silicate of Soda Cements for Acid-Proof Tank and Tower Construction[1]

Foster Dee Snell and Howard Farkas

130 Clinton St., Brooklyn, N. Y.

Silicate of soda cements for acid tank and tower construction may be considered as of three types. The first is a mixture of inert material with sodium silicate, and hardens by slow drying. The second is a mixture of inert and acid material with sodium silicate and hardens both by drying and by reaction to liberate silicic acid. The third is a mixture of inert and alkaline or neutral material with sodium silicate, which by reaction will produce an insoluble silicate to give a set preliminary to drying. The neutral or alkaline self-hardening cements do not set so hard initially and are therefore better able to take up the strains incidental to further building operations.

Details of representative types of acid-proof lining construction are given.

IN THE construction of solid masonry, acid tanks, towers, and chimneys, or for lining metallic casings, a cement that will not deteriorate rapidly is essential. The cements most widely used for this purpose are prepared by mixing suitably blended inert materials, such as siliceous aggregate, with specified amounts of high-silica sodium silicate. The majority of such cements are sold as a carefully graded dry mixture, and the silicate solution of a specified grade is added just prior to use. At least one manufacturer offers a ready-mixed product of this type in air-tight containers. A typical mesh analysis of a siliceous mix for this purpose is as follows:

	Mesh	%
Retained on	20	0.02
	40	0.41
	60	2.69
	80	2.37
	100	6.63
	200	17.38
Through	200	70.50

The silicate solution almost always used is that having a ratio of 1:3.86, sold in the trade as water glass. This contains 6.4 per cent Na_2O and 24.7 per cent silicon dioxide, and has a reading of approximately 34° Bé.

When applied as the acid-proof mortar between chemical bricks, such a cement dries out to form a strong bond, which, after treatment with acid, becomes highly resistant to further attack by acids. The chief objection to the product is that the silicate requires a considerable length of time to dry out. About a week must be allowed for the cement to harden, during which time no stress can be placed on the masonry because of the softness of the mortar. The contraction in drying is often serious. Control of this factor by grading of the aggregate is limited by the viscosity of the sodium silicate solutions used and the resulting thickness of the film about the particles of cement. Only 4 to 12 courses of brick, according to size, can be laid per day with this type of cement. More rapid construction causes some of the partly set cement to be squeezed out from the lower courses. In order to hasten the set, artificial heat is often used.

An acid treatment is given the cement joints after hardening has taken place to render them fully acid-tight. The bonding strength of the wet mortar is dependent on the adhesiveness of the colloidal silicate solution. During drying it becomes less readily soluble in water, and when fully dried it has a considerable water resistance. As soon as the mortar joints are painted or sprayed with sulfuric acid, the sodium silicate with which it comes into contact is decomposed to give silicic acid and sodium sulfate, along with the unaffected filler. During use acid gradually penetrates the joint or lining, so that the bond is more or less completely transformed from that of dried silicate of soda to that of silicic acid. Even though silicic acid is insoluble in water and of itself has no adhesive or bonding strength, the cement so transformed in place has a very definite and satisfactory bonding strength. The final result is therefore a cement lining or joint which is both acid- and water-proof. Such a cement carefully handled and properly air-dried gives a tensile strength up to 1700 pounds.

When food products with delicate flavors are to be handled,

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[1] Received February 20, 1931. Presented before the Division of Industrial and Engineering Chemistry at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931.

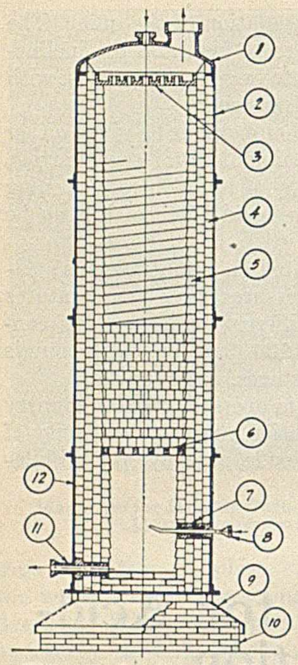


Figure 1—Denitrating Tower with Triple Lining, Set Inside of a Metallic Casing

(1) Chemical-ware cover
(2) Metallic casing
(3) Chemical-ware distributor
(4) Radial brick lining
(5) Chemical radial brick, spirally set, minimizing the capillary flow
(6) Chemical-ware grill
(7) Special block
(8) Steam jet
(9) Drip pan
(10) Chemical-brick base
(11) Outlet connection
(12) Backing of acid-proof cement

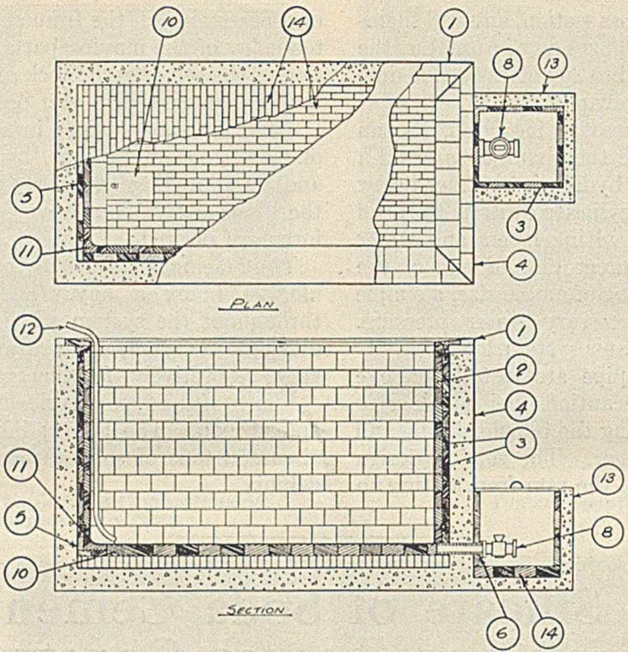


Figure 2—Rectangular Brick-Lined Pickling, Galvanizing, or Storage Tank, with Outer Valve Control and Sump Drain

(1) Chemical-brick coping
(2) Chemical-brick facing
(3) Chemical-brick lining set on edge
(4) Outer retaining wall or metallic casing
(5) Backfill of acid-proof cement
(6) Outlet connection
(8) Outlet valve
(10) Special block to keep steam from cement joints
(11) Special corner-shaped brick
(12) Steam pipe
(13) Outside valve control chamber
(14) Chemical brick set on edge

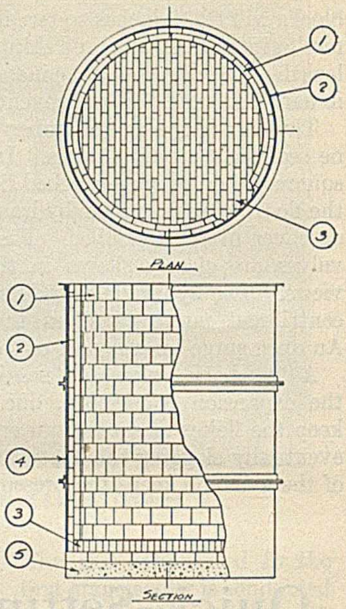


Figure 3—Cylindrical Brick-Lined Tank with Double Radial Brick Lining for Side Walls

(1) Chemical radial brick lining
(2) Backfill of acid-proof cement
(3) Straight chemical-brick set on edge
(4) Outer retaining wall or metallic casing
(5) Brick or cement base

painting the joints with sulfuric acid is often objectionable. In such cases very good results are secured by treating the joints, after thorough air-drying, with a 10 per cent solution of calcium nitrate, calcium chloride, or calcium acetate. A dilute lime-ammonia solution may also be used. The product of the reaction, when treated with the lime compounds, is insoluble in water and therefore does not affect the flavor of the contents of the tank.

Methods of Hastening Rate of Set

The addition of a minor percentage of material to the ingredients of a cement of this type for the purpose of increasing the rate of set by chemical reaction with the silicate is a decided improvement provided other defects are not introduced. A bond of uniform hardness throughout is formed in a shorter period of time.

Any material added to the cement which will react with the silicate to neutralize the alkali present and precipitate silicic acid causes the cement to harden more quickly than drying out of the silicate solution. Such an addition agent either is an acid itself or gives an acid reaction in solution.

A number of patents have been issued and pending patents are claimed on cements to which an acid material has been added. Various products of this kind are on the market. In one product (*7*) organic acids, such as oxalic, stearic, or oleic acid, are added to the cement. These react on addition of the aqueous silicate solution to cause precipitation of colloidal silica. Another patent (*5*) claims the use of any salt which will liberate acid in solution, thereby causing precipitation of silicic acid by reaction with the alkali of the sodium silicate.

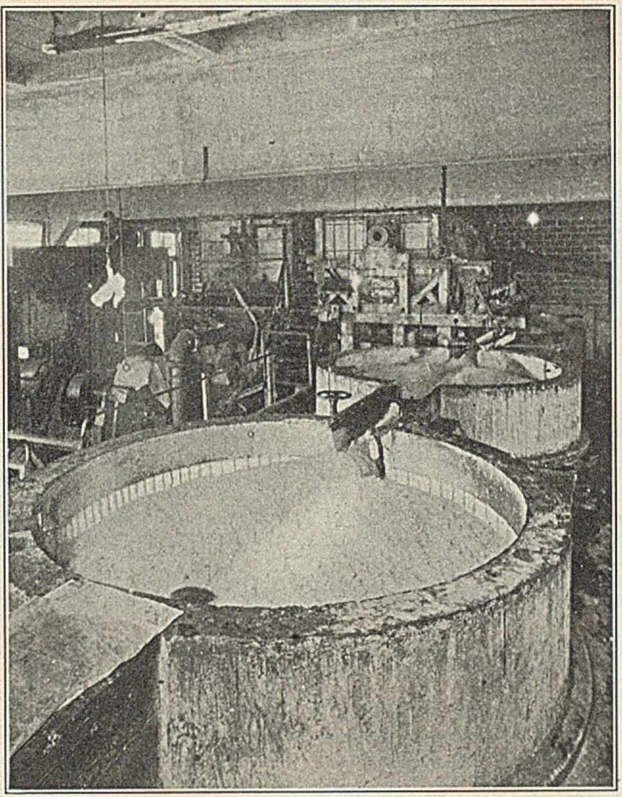
Some German products recently introduced into this country are described in a series of British patents (*3*). One type of product consists of a form of hydrated silica, such as opal, chalcedony, siliceous sinter, certain flints, etc. The essential feature of this type of aggregate is its reactivity with sodium hydroxide, to the extent that it will combine with the alkali of the silicate solution. Another type contains a small percentage of powdered silicon or an alloy of silicon with a metal such as iron. On reaction with the silicate solution, this type liberates hydrogen, which gives a porous cement and presents an element of danger in its use. A third type contains a small percentage of any of a series of acid salts such as fluosilicates or salts of fluoric, fluorotantalic, or fluorostannic acid.

It is possible to obtain similar results by the addition of a neutral or alkaline agent instead of an acid material. The reaction involved is that of sodium silicate or silicic acid in the silicate solution with the neutral or alkaline material to form an insoluble silicate and water or a neutral salt. Hardening by chemical reaction thus takes place in the same way as when precipitation of silicic acid occurs. The addition of a small percentage of calcium sulfate (*1*) or of lead carbonate (*2*) is claimed to increase the rate of set. Calcium phosphate (*4*) has also been used.

Laboratory Tests of Cements

In order to obtain a general comparison of the different kinds of products consisting primarily of siliceous aggregate, typical samples of the various grades were prepared in the laboratory for tests, without regard to patent coverage. The alkaline type contained 0.5 per cent of commercial light aluminum hydroxide. The acid type contained 1 per cent of commercial sodium fluosilicate. The neutral type contained 1 per cent of a mixture of 5 parts of light aluminum hydroxide with 4 parts of sodium fluosilicate. This mixture is neither acid to methyl orange nor alkaline to phenolphthalein. The aggregate used was the same in every case and had approximately the mesh analysis given earlier in this paper. The 34° Bé. sodium silicate with a ratio of 1:3.86 was used in every case. Although a more alkaline silicate has been recommended for this purpose with an imported acid type of cement, the acid ingredient of that compared was adjusted for the more siliceous silicate. This leaves only one variable, the setting agent. In every case 100 grams of dry cement were well mixed by hand with 60 to 70 grams of sodium silicate just before use. The data obtained are summarized in Table I.

Since the value of the added material resides in its ability to make the cement harden without drying out, test pats of cement containing the materials being compared were placed in a humidity cabinet at saturated humidity. The hardness of the pats was then compared by physical examination at 24-hour intervals. At 48 hours they show a regular gradation from lack of set in the product without addition agent to a hard, brittle set in the case of the acid setting agent.



Brick-Lined Tanks in Continuous Bleaching System at Plant of Oregon Pulp & Paper Company, Salem, Ore.

As another method of comparison pairs of bricks were cemented together with mortar joints about $^1/_8$ inch (3 mm.) thick and left in the laboratory for 48 hours. They were then compared qualitatively. The strength of bond is in agreement with the rate of set in saturated humidity. Failures of quick-setting cements may result from using the cement after solidification has proceeded to such a point that it does not bond properly with the brick.

The time of workability of the mix, prepared according to directions, at a room temperature of 22–24° C., was observed and recorded. The mix was considered workable as long as it could be applied to a brick and adhere. The variation in the workability is also in line with the setting in saturated humidity.

Direct comparison of the degree of contraction of the cements as a property of the type of setting agent may be unfair. That property depends to a considerable extent on the grading of the aggregate used and the commercial gradings in different commercial cements are not the same. In general, the contraction of a cement is least in the quickest setting cements and greatest in the slow-drying type tested.

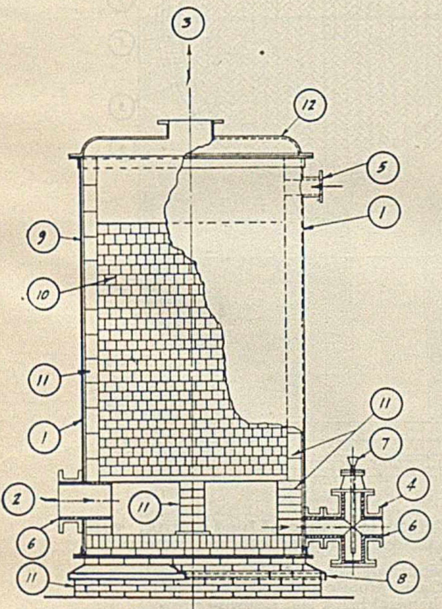


Figure 4—Acid-Spray Tower with Metallic Inlet and Outlet Connections Lined with Chemical Ware

(1) Metallic casing
(2) Gas connection
(3) Gas connection
(4) Acid outlet connection
(5) Acid connection
(6) Chemical-ware pipe lining
(7) Diluting tube
(8) Drip pan
(9) Backing of acid-proof cement
(10) Packing rings
(11) Chemical brick lining
(12) Metallic cover

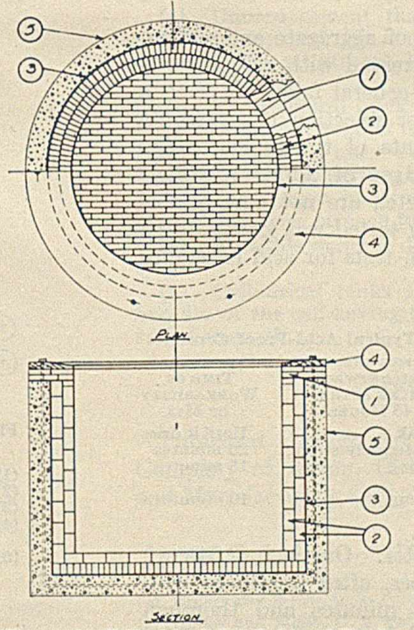


Figure 5—Cylindrical Brick-Lined Tank, Using Straight and Arched Brick Shapes

(1) Chemical-brick facing (straight and wedge shapes)
(2) Chemical-brick lining set on end (straight and arch shapes)
(3) Backing of acid-proof cement
(4) Wooden coping
(5) Concrete or metallic outer shell

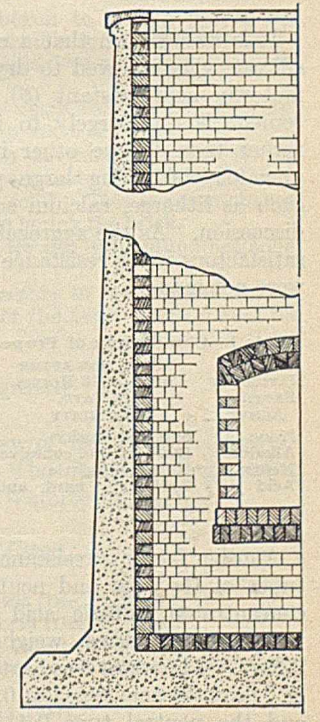


Figure 6—Stack with Bonded Chemical-Ware Lining for Low-Temperature Corrosive Gases

In these the grading of the aggregate and the quantity and kind of sodium silicate were constant.

Cements with the alkaline setting agents set to a rubbery consistency in 48 hours. With acid setting agents the set is more complete, to a hard and brittle mass. Precipitation of silicates in the cement, therefore, gives a moderately self-hardening product, whereas precipitation of silicic acid gives a quick-setting product.

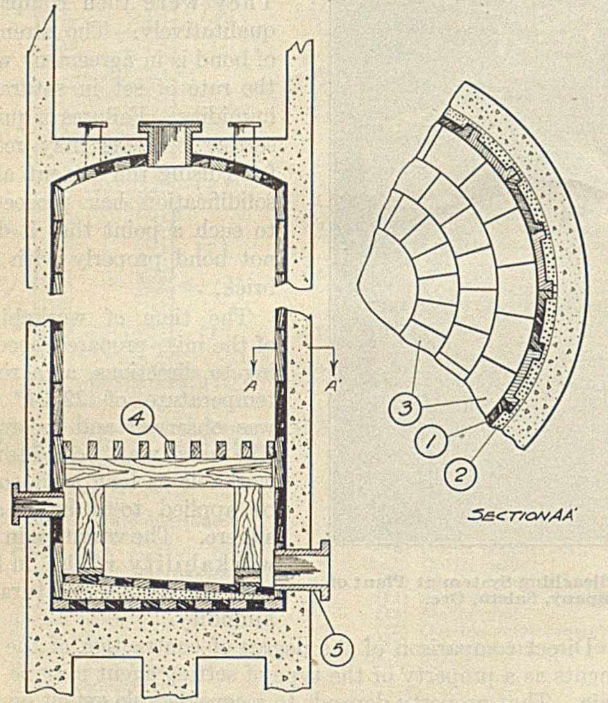


Figure 7—Acid Absorption or Scrubbing Tower

(1) Chemical-ware radial-shaped tile
(2) Acid-proof cement grout
(3) Chemical-ware radial brick floor and dome
(4) Racks (design optional)
(5) Clean-out
Section AA'—Lining section detail showing plan of radial brick on floor and dome

It is well known that a mixture of aggregate and sodium silicate when allowed to dry and treated with acid is satisfactorily acid-resistant (*6*). Any general failure of such a cement is due largely to improper selection of aggregate rather than to the other ingredients of the cement. Aggregates containing large percentages of added materials such as litharge, calcium sulfate, etc., are not part of this discussion. As the aggregate being tested was known to be satisfactory in its resistance to acid, tests for acid resistance were not made.

Table I—Comparison of Properties of Typical Acid-Proof Cements

Nature of Setting Agent	Condition after Setting 48 Hours in Satd. Humidity	Adhesiveness of Bond between Bricks after 48 Hours	Time of Workability of Mix
None	Soft and mushy	Weak	Until it dries
Alkaline	Rubbery and cohesive	Moderately strong	20 minutes
Neutral	Hard and brittle	Strong	15 minutes
Acid	Extremely hard and brittle	Strong	10 minutes

Another factor is resistance to water. One-inch (2.54-cm.) cubes of the acid and neutral types, after treatment with concentrated sulfuric acid for 10 minutes and thorough washing, were dried, weighed, and immersed in water for 7 days. The water was heated to boiling for 1 hour each day. In 7 days the acid type lost 0.15 per cent of the original weight and the neutral type 9.4 per cent. This would indicate more satisfactory resistance of the acid type to water, a condition relatively unimportant. If used in a leaching cycle, while the cement may require resistance to water at times, the cycle is usually such that at other times an acid solution is present. If the solutions should penetrate the cement to increasing depths as the tank is used, that cement would also receive acid treatment from the solution.

Grades of Cement

Apparently there may be three grades of cement, differentiated according to the time of set. An ordinary cement composed of a mixture of graded aggregate and silicate will answer the requirements of the plant superintendent who is able to allow ample time for setting of the mortar. In saturated humidity it will never set and under normal conditions it requires from 7 to 10 days for satisfactory set. The rapid hardening which occurs with the cement containing an added acid ingredient will appeal to those who must put the construction to use as soon as possible after erection. This cement sets in 24 hours. Cement containing neutral or alkaline material occupies a position between these two and has some characteristics of each. It will harden in a comparatively short time, but will remain soft and workable long enough to permit ample time for handling. In the self-hardened condition it is flexible enough to allow for the strains incidental to building without fracturing but sets sufficiently to carry the load of the additional courses being laid. It adheres well to chemical brick, metals, wood, glass, etc. In general it seems to have the widest applicability of the types studied.

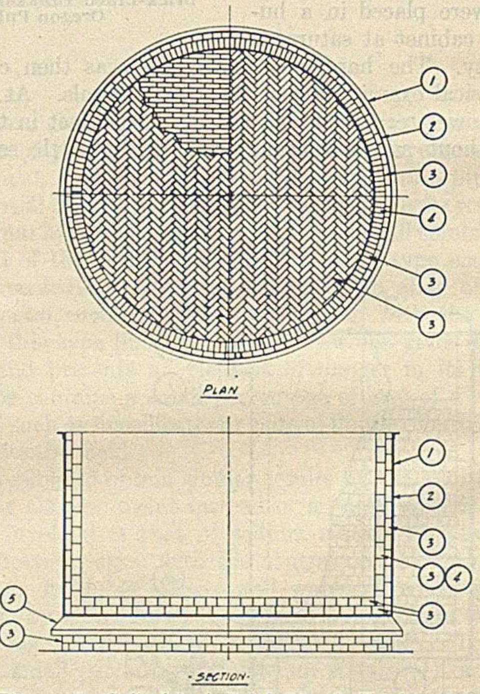
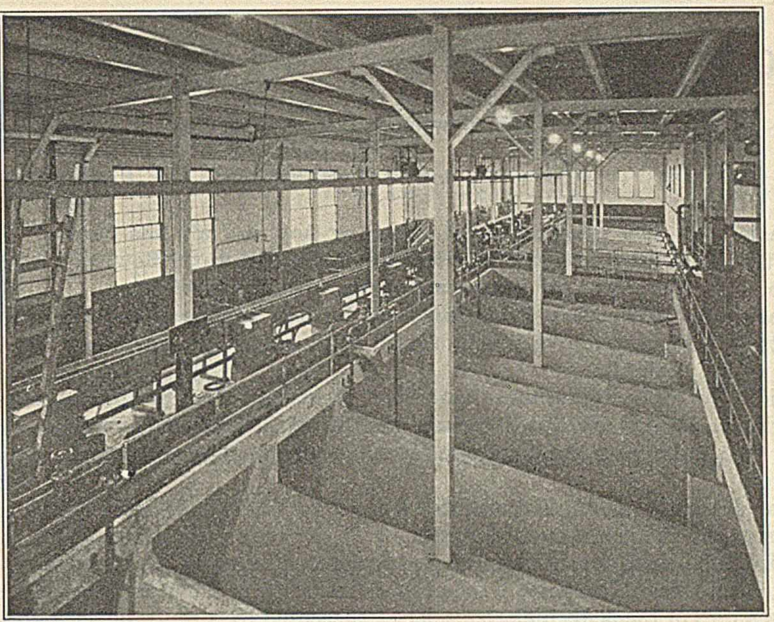


Figure 8—Cylindrical Brick-Lined Tank, with Botton Laid Up in Herringbone Pattern

(1) Outer retaining wall or metallic casing
(2) Backfill of acid-proof cement
(3) Straight chemical brick laid sidewise
(4) Chemical arch brick set up with No. 3 straight brick
(5) Drip pan

Acid-Proof Construction

Acid-proof masonry for chemical-plant construction is very widely employed in Germany, and its use in this country and in Canada is gaining in popularity for such work as Gay-Lussac and Glover towers, pickling tanks, chemical storage tanks, chimneys, gutters, acid floors, etc. The



Brick-Lined Bellmer Bleachers in the Plant of Restigouche Company, Ltd., Athol, New Brunswick

first installations of brick- and cement-lined towers and tanks in the United States were made more than twenty years ago and many such jobs are still in use today. Some of the advantages of this construction are:

(1) If properly installed, acid-proof masonry work has a long life. There is very little depreciation.

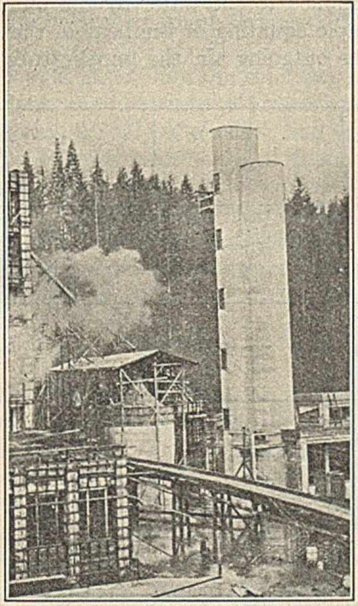
(2) It has great resistance to high heat and quick thermal changes. Acid-proof masonry is capable of handling hot acid gases up to about 1500° F. For high-temperature work a specially compounded chemical brick should be specified.

(3) It is very resistant to abrasion. Frequently it has been found desirable to line an acid-resisting metallic casing with masonry work, not only to minimize corrosion, but also to protect the casing from abrasion and mechanical wear.

(4) The cost of installation is relatively low.

The accompanying drawings offer practical suggestions based on the best lining practice.

Acid-proof masonry work is resistant to all acids except hydrofluoric. Installations in use handle sulfuric, nitric, acetic, citric, tartaric, phosphoric, butyric, formic, and many others, as well as solutions of aluminum sulfate, chlorine, ferric chloride, dyestuffs, bromine, aluminum chloride, etc.



Jenssen Acid Towers with Acid Storage and Recovery Tanks under Construction at Rainier Pulp and Paper Co., Shelton, Wash.

Wherever possible, acid-proof masonry should be erected by specially trained mechanics. The average brick mason is not adaptable for this work because it is hard to make him realize the importance of watching all details. Extreme care is always necessary. Some of the larger chemical manufacturing companies have developed a trained personnel and a very high rate of efficiency has resulted. Practically all failures have been traced to the presence of faulty joints due to careless workmanship or improper manipulation of materials. The following precautions should be taken:

(1) Half of a standard-shaped barrel or a low tub should be used to prepare the mix. The paddles should be of hard wood, about 1$^1/_2$ × 3 to 2 × 5 inches and about 2 to 4 feet long, depending upon whether a quick- or slow-setting cement is being mixed. Galvanized-iron pails of about 8- or 10-quart size will be found convenient containers for serving the brick masons. They should be thoroughly cleaned and dried before using.

(2) In the case of a slow-setting cement, only a quantity that can be used within an hour or two should be mixed at a time. Similarly, only about a 15-minute supply should be mixed at one time in the case of the neutral or alkaline cement, and about a 10-minute supply when using the acid type.

(3) From 60 to 70 pounds of 34° Bé. silicate of soda are used with every 100 pounds of the dry cement. The mixing must be thorough and complete. All lumps must be broken up until there are no traces of dry cement or excess silicate. The silicate should be poured into the mixing tub first, and then the powdered cement added. The cement should also be agitated thoroughly while using. No water must be allowed to come into contact with the dry cement.

(4) Unused cement that has begun to take a partial set should not be used. It is not permissible to add new silicate to such partially set cement, because this does not renew the plasticity of the mix.

(5) The chemical brick must be clean and dry before using. In extremely cold weather it is well to warm the brick.

(6) The joints must be as thin as the uniformity of the chemical brick will permit, by no means more than $^1/_8$ inch.

(7) The cement joints must be solid. This is accomplished by pressing down on each joint when laying the brick.

(8) A double lining is desirable for use in handling hot solutions.

(9) Cylindrical tanks are preferable to rectangular vessels because of the self-keying feature of the brick which makes for added strength.

Acknowledgment

Published through the courtesy of the U. S. Stoneware Company of Akron, Ohio, and The Stebbins Engineering and Manufacturing Company, of Watertown, N. Y.

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Evaporation of Water by Hot, Dry Air[1]

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The evaporation of water by hot, dry air has been studied and the relative importance of water flow, air flow, and air temperature has been determined.

Water flow, including both form of spray and rate of circulation, has been found to be the most important variable.

The fact that a high level of efficiency is obtainable under widely differing conditions should encourage the more frequent use of such a scheme of evaporation.

THE application of hot-air evaporation to the concentration of solutions on an industrial scale differs materially from the analogous applications of humidification and dehumidification as commonly carried out. Previous studies of evaporation such as is here contemplated have been made chiefly to obtain data for the designing of Glover, Gilchrist, and Gaillard towers for concentration of sulfuric acid. In these cases the temperatures at which evaporation is effected are higher than those of the present study and the vapor pressures of the acids differ considerably from that of water at the same temperature.

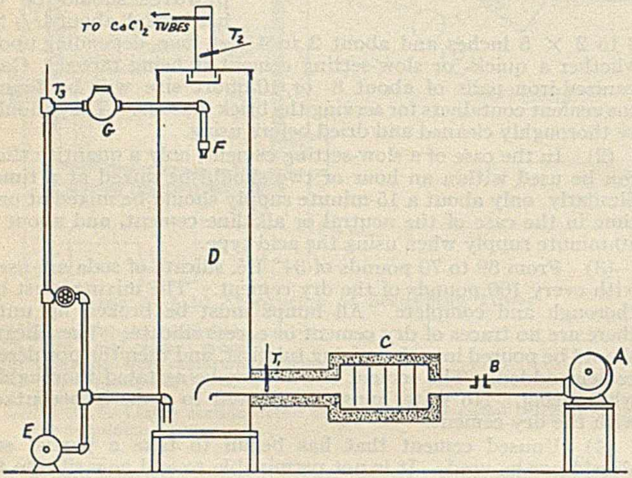

Figure 1—Apparatus for Study of Evaporation by Hot Air

In this paper a study is made of the evaporation of water by hot, dry air, to determine by small-scale operation how nearly equilibrium is attained in such systems. The term "equilibrium" is used to denote that the air leaving the tower is at the temperature of the water being circulated and is saturated. As has been stated in a well-known text (*1*), "In view of the simplicity of the apparatus and the ease of operation, it is surprising that towers of this sort, fired directly with flue gases from a furnace, are not more widely used."

Apparatus

The apparatus is shown in Figure 1. An air stream, controlled by a throttling device on the fan inlet, was blown by a fan, *A*, measured by a calibrated pitot tube, *B*, and heated by passing over a number of electrical resistances, *C*, controlled by a rheostat.

The air could thus be easily controlled from a zero to the maximum flow, and its temperature controlled more accurately than would be possible on a small scale with a fuel-fired furnace.

The hot air, the temperature of which was measured by a thermometer, T_1, placed in a well of thin-walled copper tubing far enough from the heater so that it was not affected by radiation from the heating wire, passed up an unpacked galvanized-sheet-iron tower, *D*, countercurrent to a spray of water which was continuously circulated by a pump, *E*. The tower was 30.5 cm. (12 inches) in diameter and 122 cm. (4 feet) high. The lower end of the spray nozzle was 28 cm. (11 inches) below the top of the tower.

The water was drawn off at the bottom of the tower and sprayed in at the top through *F*. The rate of flow was controlled by a valve in a by-pass around the pump and was measured by a water meter, *G*. The temperature of the outgoing air was indicated by a thermometer, T_2, and that of the circulating water by a thermometer, T_3, both of which were placed in wells of thin-walled copper tubing.

The humidity of the outgoing air was determined by drawing off a measured volume of air which was dried by passing through calcium chloride tubes, the tubes being weighed before and after the experiment. In no case did the second tube show any gain in weight, so in the latter experiments the second tube was not weighed. The humidity of the ingoing air was measured by a sling psychrometer.

Determination of Heat Content of Dry Air

In such a system, thermally insulated from its surroundings, if the heat supplied to the water by the pump is negligible, then by a simple equating of the heat in the entering air to the heat in the outgoing air, the temperature of the exit air may be determined for any inlet-air temperature as shown in Figure 2. In this figure air temperature is taken as abscissa, and heat content above 0° C. as calories per gram of dry air is taken as ordinate. Since no heat is lost within the system, the heat content of the inlet and exit air will be the same. The heat content of dry air at the inlet temperature may be found on the curve labeled "dry air;" then, reading across

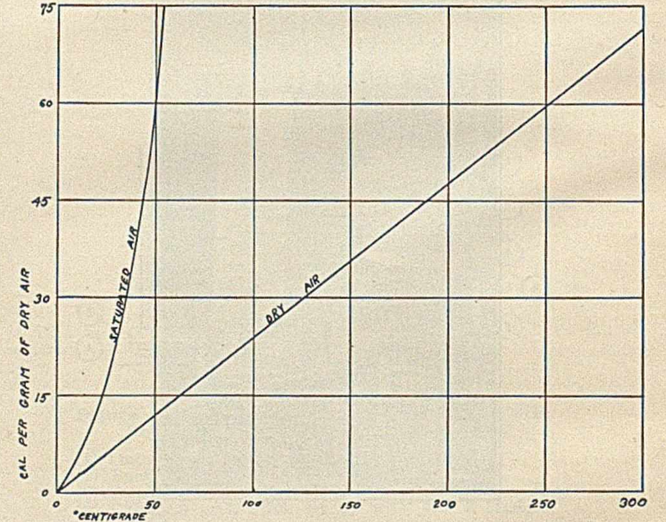

Figure 2—Heat Content of Dry and Saturated Air

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[1] Received March 5, 1931. This paper is based on an undergraduate thesis presented by the junior author, R. H. Newton.

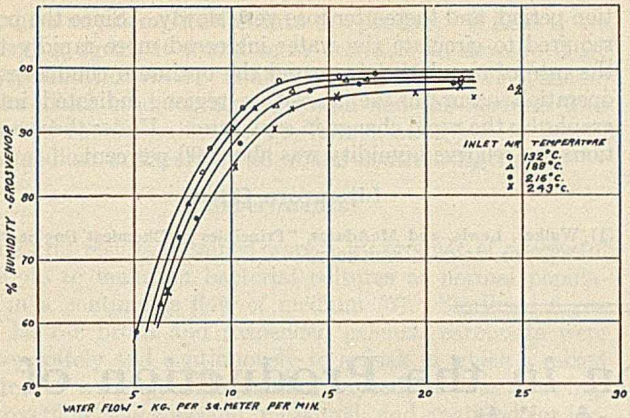

Figure 3—Nozzle 1: Air Flow Constant at 5.60 cm. per Second in Tower

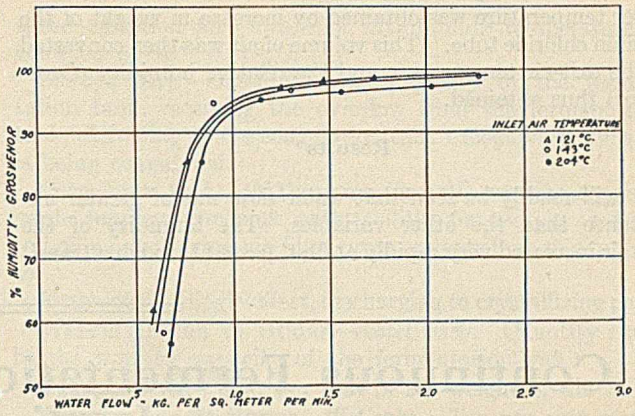

Figure 4—Nozzle 2: Air Flow Constant at 6.02 cm. per Second in Tower

Grosvenor Humidity *vs.* Water Flow: Hot-Air Temperature as Parameter

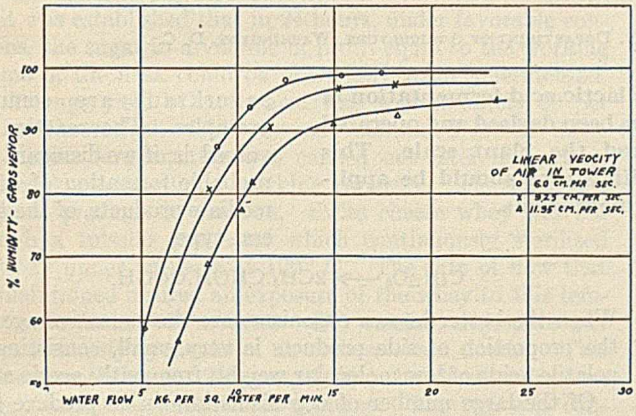

Figure 5—Nozzle 1: Hot-Air Temperature Constant at 132.2° C.

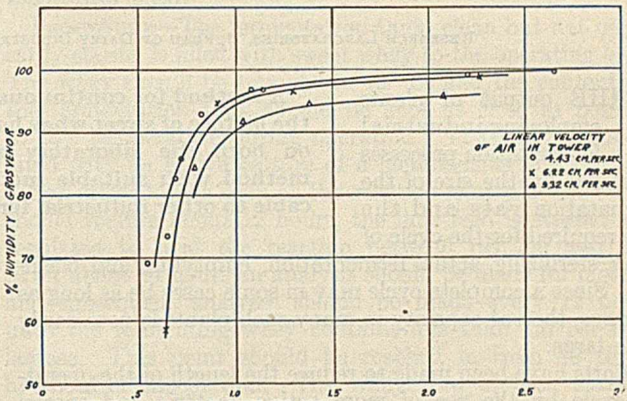

Figure 6—Nozzle 2: Hot-Air Temperature Constant at 143.3° C.

Grosvenor Humidity *vs.* Water Flow: Air Flow as Parameter

horizontally—i. e., at constant heat content—to the saturated line gives the temperature at which this air will leave if saturated.

Deviations from these equilibrium conditions must in practice be dependent on: (*a*) rate of water circulation, (*b*) form of water spray, (*c*) rate of air flow, and (*d*) temperature of hot air. The relative importance of these variables was studied experimentally. (*a*) and (*b*) obviously depend on the more fundamental variables—time and area of contact—but these quantities can neither be measured nor calculated, so that the directly measured values are of greater importance in the design of such towers.

Operation

The apparatus was run with hot-air temperature, hot-air flow, and water flow adjusted to the desired figure until a steady state was reached, as was indicated by unchanging temperature of the outgoing air. This required about 45 minutes. The humidity of the entering and outgoing air was then determined by the methods indicated. The conditions were then altered and other determinations made after a steady state had again been reached under the new conditions. Two types of spray nozzles were used as follows:

Nozzle 1. Schutte Koerting, 4.5-mm. orifice, 1.25-cm. ($^3/_8$-inch standard) pipe connection, 45-degree spray. Capacity, 600 to 1100 liters per hour (160 to 280 gallons per hour).

Nozzle 2. Schutte Koerting, 2.5-mm. orifice, 0.9-cm. ($^1/_4$-inch standard) pipe connection, 90 degree spray. Capacity, 60 to 230 liters per hour (15 to 60 gallons per hour).

A series of runs was made to determine the effect of each variable.

The air flow was maintained constant at 229 liters (8.1 cubic feet) per minute and the Grosvenor humidity of the exit air determined as a function of water flow at a series of temperatures. These results are shown graphically in Figure 3 for nozzle 1 and in Figure 4 for nozzle 2.

The hot-air temperature was then maintained constant and the Grosvenor humidity of the exit air determined as a function of water flow at a series of different rates of air flow. The results are plotted in Figure 5 for nozzle 1 and in Figure 6 for nozzle 2.

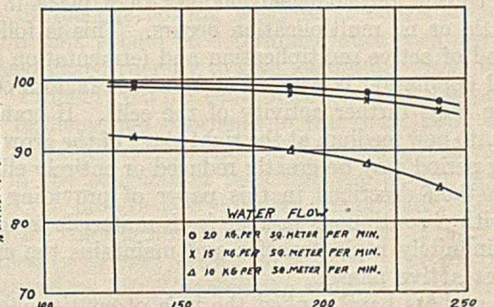

Figure 7—Grosvenor Humidity *vs.* Hot-Air Temperature: Water Flow as Parameter

Nozzle 1: Air Flow Constant at 5.60 cm. per Second in Tower

The effect of hot-air temperature on the Grosvenor humidity of the exit air at a number of different rates of water flow, air flow being constant, is shown in Figure 7 for nozzle 1.

The Grosvenor humidity of the plots refers in all cases to the humidity at the exit-air temperature. The weight of water absorbed from a certain volume of air measured at the meter temperature was obtained by increase in weight of the calcium chloride tube. This volume of air was then converted to the exit-air temperature and the relative humidity (Grosvenor) thus obtained.

Results

It will readily be seen that water flow was of greater importance than the other variables. The humidity of the exit air increased very rapidly at first, passed through a transition period, and thereafter rose very slowly. Since the power required to circulate the water increased more rapidly than the rate of circulation increased the optimum conditions for operation occur in the transition region, indicated in the graphs by the rapid change in curvature. Under these conditions the relative humidity was about 90 per cent.

Literature Cited

(1) Walker, Lewis, and McAdams, "Principles of Chemical Engineering," p. 391, McGraw-Hill, 1927.

Continuous Fermentation in the Production of Lactic Acid[1]

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A method for continuous lactic acid fermentation of the lactose of sweet whey has been devised and operated on both the laboratory and the plant scale. This method with suitable modifications should be applicable to other industrial fermentations.

THE output of plants employing industrial fermentation processes is limited by the size of the fermentation vats and the time required for the cycle of filling, sterilizing, actual fermentation, emptying, and cleaning. Since a complete cycle may in some cases be as long as ten days, the vat capacity in many such plants is necessarily made large.

Efforts have been made to reduce the length of the operating cycle by the use of more active bacteria and special treatments to accelerate the chemical action of the bacteria. These means have been found to be valuable, but to a limited degree.

During the time required for cleaning, sterilizing, and emptying the equipment and for the growth of the inoculating organism to its maximum effective numbers, very little actual fermentation takes place. If these time-consuming factors could be eliminated and the actual fermentation process carried on continuously, the ratio of equipment cost to production could be considerably reduced.

When a suitable medium is inoculated with a culture of the lactic type, growth and fermentation pass through a definite series of phases. There is first the lag period, in which certain physiological changes take place in the cell but little or no multiplication occurs. This is followed by a period of active multiplication and fermentation until the normal population is reached and various factors come into play to limit further activity of the cells. If transfers are made into new medium at the right stage of the growth curve, the lag period may be greatly reduced or entirely eliminated. The method described in this paper of providing the culture with a continuous flow of fresh materials is equivalent to an infinitely rapid transfer and maintains the culture at its most active phase.

The authors have applied the idea of continuous fermentation to the production of lactic acid from the lactose of whey, with the hope that their results may be applied, not only in lactic acid production, but also, with suitable modifications, to other commercial fermentations.

Theoretical

The fermentation of sugars to lactic acid is frequently encountered. The souring of milk and the production of sauerkraut are common examples. The reaction involved is, if we disregard the probable formation of intermediate products, of the general type,

$$C_6H_{12}O_6 \longrightarrow 2CH_3.CHOH.COOH$$

When the better known organisms are the causative agents, the proportion of side products is very small, consisting of volatile acids of low molecular weight, frequently acetic acid.

Of the large number of organisms known to produce lactic acid to some extent, the best known are the common *Streptococcus lactis* of souring milk and several of the lactobacilli such as *L. bulgaricus* and *L. casei*. The lactobacilli have the advantage of being able to continue the fermentation until a pH value is reached approximately one unit lower than is possible when *S. lactis* is used. This advantage becomes of greater importance when the acid is partly neutralized from time to time, as is done in the commercial fermentation. With the accumulation of lactates in the solution, a limiting concentration of undissociated lactic acid becomes more definitely the factor inhibiting the fermentation and thus the actual limiting pH value gradually increases (*1*, *2*). The higher the pH value in the fermenting solution, the greater the likelihood that contaminating organisms will succeed in utilizing part of the sugar and in converting it to undesired products, such as butyric acid. Hence the advantage of using an organism able to withstand high acidity and high concentration of undissociated lactic acid, when practically complete utilization of sugar is desired. A mycoderm in a culture of a lactobacillus has the associative effect of accelerating the action of the lactobacillus and is frequently used for this purpose.

The abandonment of preliminary sterilization of equipment and media in industrial sugar fermentations is possible only when other means can be used successfully to prevent loss of sugar and formation of undesired products. If the fermentation can be carried out within pH and temperature ranges unfavorable to foreign fermentations, it is a very desirable situation. This is the case in the lactic fermentation. At 44° C. and between pH 5.0 and pH 5.8 the lactic fermentation may be kept clean of active contamination.

Preservation of unsterilized sugar media may be accomplished by use of low temperatures, high acidity, or high alkalinity. Obviously, the means used to bring the preserved media to the proper condition for fermentation should not

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[1] Received January 2, 1931.

introduce any complication into the process. If acid is the preserving agent, it would seem desirable to develop it by the fermentation itself. If alkali is the preservative, it should be the alkali used for neutralization and the medium thus preserved should be fed to the fermentation vat in lieu of both medium and part or all of the neutralizing agent.

Experimental

The first results obtained were a by-product of successful attempts to maintain bacterial cultures at normal population in a continuous flow of medium (*3*). Sterilized 6 per cent lactose broth and suspended calcium carbonate were fed separately and continuously to a flask in which a mixed culture of a lactobacillus and a mycoderm was growing. The overflow was collected, measured, and analyzed for lactic acid and unfermented sugar. Rate of feed and other conditions were varied, both intentionally and accidentally, so that continuously uniform results were not obtained; but it was established that in 24 hours, under favorable conditions, the sugar in a volume of broth equal to the working volume of the flask could be practically entirely fermented. The average yield of lactic acid was approximately 80 per cent of theoretical. This run was continued for 20 days.

A similar fermentation was carried out later in a glass-lined tank of 30 gallons' working capacity. The tank was sterilized previous to the run. Swiss cheese whey was fed through a tubular preheater which continuously sterilized the whey under pressure at 120° C. The rate of flow that was maintained insured an exposure of the whey to this temperature for at least 30 minutes. Dry calcium carbonate was fed continuously by means of an endless-chain device. This run went smoothly for 2 days and then the sterilizer became clogged with coagulated milk proteins. The run was continued successfully for another 24 hours with raw whey. It was demonstrated that there is no inherent difficulty in carrying out sterilization continuously. The trouble was due to the heat-coagulability of certain components of the raw material.

Another run was made in the same equipment over a period of 14 days. Raw whey pretreated with hydrated lime as a temporary preservative was fed to the fermentation tank. Dry hydrated lime was fed at such a rate as would maintain the reaction in a range favorable to lactic fermentation but unfavorable to butyric acid production. It was again demonstrated that a volume of whey equal to the working volume of the fermentation vat could be practically entirely fermented in 24 hours under conditions of continuous flow. Crude calcium lactate was recovered from a 6-liter sample of the overflow and analyzed for its percentage of lactic acid. Calculations showed that the yield was 90 per cent of theoretical based on the lactose originally present.

Two runs each lasting a week were carried out in larger equipment at the Grove City Creamery, Grove City, Pa. A fermentation vat of 4500 pounds capacity was used and the product of the fermentation was isolated as crude calcium lactate. The earlier figures as to rate of fermentation and yield were substantiated.

Recommendations regarding equipment and procedure are outlined in the following paragraphs.

Recommended Equipment and Procedure

EQUIPMENT—*Whey storage.* Feeding constantly to the fermentation tank at a rate such that the contents of the fermentation tank will be displaced every 24 hours.

Lime reservoir and feeding device. Feeding hydrated lime at such a rate as to maintain a reaction between pH 5.0 and 5.8 in the fermentation tank.

Fermentation tank. Insulated, covered, equipped for slow-speed agitation and means of maintaining temperature of contents at 43° ± 1° C.

Storage tank. One-fourth the capacity of the fermentation tank, receiving the overflow from the fermentation tank, delivering to the coagulation tank except when a charge is being coagulated.

Coagulation tank. Of the same (or half) working capacity as the fermentation tank, with facilities for heating contents to boiling, delivering via filter press or centrifuge to evaporator.

Evaporator. Single-effect, discharging to crystallizing pans.

MATERIALS PER 24 HOURS—*Sweet whey.* Quantity equal to the working capacity of the fermentation vat.

Hydrated lime. Four per cent of the weight of the whey.

PRODUCT PER 24 HOURS—*Wet cake.* Ten per cent of the weight of the whey, containing 50 per cent calcium lactate, equivalent to 40 per cent lactic acid or 80 per cent of the theoretical yield.

PROCEDURE—The fermentation tank, clean but not necessarily sterile, is filled with sweet whey to the operating level. The whey should be brought to 43° C. and the contents of the fermentation tank should be kept as close as possible to this temperature during operation. The whey is inoculated with an active culture of a lactobacillus and the agitation started. As soon as the reaction is at pH 5.0, which should require about 12 hours, the lime feed is started and regulated to hold the reaction between pH 5.0 and 5.8. After about 24 hours an analysis should be made for lactose, and subsequent analyses should be made every 12 hours until the fermenting whey contains less than 1.0 per cent lactose. This point should be reached in from 48 to 72 hours after inoculation. The whey feed is then started. A volume of whey equal to the volume of the fermentation tank should be fed each 24 hours at first and until a more efficient rate can be determined. The whey in storage should be pretreated with hydrated lime to prevent undesired fermentations.

The necessary controls are the following: The whey in storage should be tested with phenolphthalein paper after each addition of a new supply. If the test paper does not show pink, hydrated lime should be added until it will. The reaction of the contents of the fermentation tank should be tested frequently to insure that the pH value is kept between 5.0 and 5.8. Bromocresol green paper may be used (*4*). It gives a green color in this range. Potentiometric measurements may be desirable at first. The lactose percentage of the overflowing whey as it comes from the fermentation tank should be determined once each day and the whey feed gaged thereby to give maximum fermentation efficiency. Probably 0.5 per cent lactose is about the proper goal, since fermentation continues in the coagulation tank.

As often as sufficient fermented whey collects, it is heated to boiling in the coagulation tank and the boiling is continued until the protein is completely coagulated. Lime is then added till the solution turns litmus paper blue to convert the excess lactic acid to calcium lactate. The coagulum is then removed by filtration and the solution is evaporated to a density of about 25° Bé. (10 to 1). The hot liquid is run into crystallizing pans. When it is cold, the cake of calcium lactate is broken up and dried.

If it is desired to purify the calcium lactate somewhat, the condensing ratio may be made 5 to 1. Cooling will then give a semi-fluid crystal mass, which may be filtered in a centrifuge and lightly washed. The filtrate and washings may be returned to the evaporator or, if the lactose content is appreciable, fed to the fermentation vat.

In case it is desired to make lactic acid directly, sulfuric acid may be added to the hot coagulated whey to convert the calcium lactate to the free acid and then the coagulum and calcium sulfate filtered off together. The filtered lactic acid solution may then be evaporated to the desired concentration.

Application to Other Fermentations

The method of using alkali as a preservative for medium in storage is obviously particularly applicable to fermentations producing acid. The procedure of inoculating the medium in storage with the culture used in the fermentation, whereby the acidity of the partially fermented medium acts as its own preservative, is another possible means of accomplishing the same purpose. For many fermentations, however, it would be necessary to sterilize raw medium either continuously or intermittently. The prevention of contamination of the fermenting medium with organisms producing undesirable substances may frequently be prevented by proper control of H-ion concentration. It must be remembered in this connection that the growth of acid-producing organisms is usually inhibited by the undissociated form of the acid produced, the concentration of which is a function of both the H-ion concentration and the total concentration of the acid (*1*).

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(1) Kolthoff, *Tijdschr. vergelijk. Geneeskunde*, **11**, 268 (1925).

(2) Rogers and Whittier, *J. Bact.*, **16**, 211 (1928), and unpublished work.

(3) Rogers and Whittier, *Ibid.*, **20**, 127 (1930).

(4) Whittier, *J. Dairy Sci.*, **14**, 26 (1931).

The Rate of Calcination of Limestone[1,2]

C. C. Furnas

North Central Experiment Station, U. S. Bureau of Mines, Minneapolis, Minn.

Calcination of limestone takes place in a very narrow zone which is the phase boundary between calcium carbonate and calcium oxide. This zone advances from the outside to the inside of the piece at a constant rate for each temperature, independently of particle size or degree of calcination. Curves and data are given for rates of calcination and temperature histories of particles. Most of the resistance to heat transfer into the piece appears to be in the narrow zone of calcination, and not in the body of the calcined material. The calcination data may be used to determine the surface area of the particles.

IN THE United States alone approximately 5 million tons of limestone per year are burned for use as lime; 20 million tons are calcined in metallurgical furnaces to be used as flux, and several times this much, of the order of 75 to 100 million tons, are calcined in the manufacture of cement. Yet there is but little information available on the rate at which calcination takes place. As far as the author knows, there are only three published investigations on the matter. In the first (*2*), the data were very meager and indefinite. The size of material used was not specified, and other attending conditions of the system were not mentioned.

In the second (*3*) it was apparently assumed that heat transfer and calcination were synonymous or, more correctly, that they occurred together, which is not necessarily true. A particle of limestone may acquire a calcining temperature and remain that way for a long time before calcination actually takes place. This second paper, then, is a clever correlation of the data of temperature acquisition in limestone, but its applicability to lime burning is doubtful.

In the third piece of work (*7*) nine different limestones were calcined at various temperatures for varying lengths of time. The data show the relative ease with which different limestones may calcine, but the actual rates reported are hardly applicable to burning limestone in practice, for the material used was mostly of small size (−4 mesh) and the calcining was done in porcelain crucibles heated from the outside. The results obtained are really those for a confined bed of fine material and do not give much information as to the specific rate of calcination within the limestone itself. It may be said, however, that none of the data reported in Linzell's paper are qualitatively different from those of this present paper.

Because of its importance in the heat-transfer phenomena of the blast furnace, the Bureau of Mines has undertaken a short study of the rate of calcination of limestone, and the data are reported in this paper.

Summary of Results

The data obtained may be summarized in such a simple manner that it seems best to present a statement of the results first and then to offer the experimental proof just as in geometry a theorem is first stated and then proved.

Calcination proceeds only from the outside of the piece inwards over a very narrow zone, practically a line. The data reported in this paper are given as rates of advance of this line of calcination from the outside to the inside of the piece. As a first approximation, this line of calcination advances at a constant linear rate (measured in centimeters per hour), dependent only on the temperature of the surroundings and independent of size or shape of particle, degree of calcination, or amount of previous heating.

The summarized data are given in Figure 1. The equation of the plotted curve is very simple, being

$$\log_{10} R = 0.003145t - 3.3085 \qquad (1)$$

where R = rate of advance of the line of calcination in centimeters per hour
t = temperature, ° C.

This equation is purely empirical and no theoretical importance should be attached to it.

Obviously, since the rate of penetration of the line of calcination is constant throughout the entire period, the length of time required to calcine is directly proportional to the size of the piece. In Figure 2 are given computed curves for the time required for complete calcination of pieces of different sizes at different temperatures. The size is defined as the greatest thickness of the piece, where thickness is defined as the smallest of the three dimensions as contrasted with breadth and length.

This makes the problem of time of calcination a very simple one. Undoubtedly, particle size and degree of calcination do have an effect on the rate, but under the conditions of size and temperature studies these effects, if they were there, were

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[1] Received March 13, 1931. Presented before the Division of Industrial and Engineering Chemistry at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931.

[2] Published by permission of the Director, U. S. Bureau of Mines.

not of sufficient magnitude to appear above the normal variation of the data. The particles varied from an equivalent spherical diameter of 2.5 to 8.5 cm.; the degree of calcination, from 39 to 100 per cent. Without further experimental work, confidence should not be placed in these data for particles less than 1 cm. or greater than 15 or 20 cm. in diameter.

Details of Experiment

The study was divided into two parts: (1) calcination when hot gases flow through a bed of particles, and (2) calcination of single pieces in a graphite-walled induction furnace. The latter experiments were conducted at a higher temperature than could be obtained with the gas-flow apparatus.

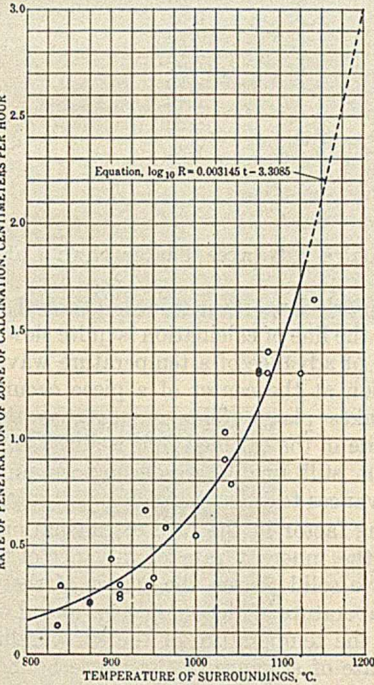

Figure 1—Rate of Penetration of Line of Calcination, Related to Temperature

The gas-flow apparatus was the same that had been used previously for heat-transfer determinations (*1*), and is shown in Figure 3. Briefly, hot gases from the pot furnace, *F*, are pulled through the column of broken solids, *C*, and the temperature histories of the gas stream at the top and the bottom of the column are recorded by thermocouples T_2 and T_1. It was found that the experiments could be conducted equally well by using a shielded gas burner in place of the pot furnace.

In addition to the thermocouples indicated in Figure 3, the beads of two additional thermocouples were placed in the center of pieces of limestone on top of the column. A hole would be drilled through the stone, one of the wires pushed through, butt-welded to the other wire, and the junction would be pulled back to the center of the piece. These thermocouples gave the temperatures of the center of the piece.

For the experiments above 1000° C., a 35-kilovolt-ampere Ajax-Northrup induction furnace was used. The heating element was a hollow graphite cylinder, 8 cm. inside diameter. In making a run, the furnace would be heated to somewhat above the desired temperature and then a single piece of limestone would be suspended in the center of the furnace, one thermocouple imbedded in the center of the piece and another placed on the surface. Every effort was made to keep the surface temperature constant. During experiments the carbon dioxide evolved from the limestone would be partially converted to carbon monoxide by the graphite walls and would burn at the top of the furnace.

All temperature records were kept on a Leeds and Northrup multiple-point recorder.

The temperature history of the gas stream at the top of the column in the gas-flow experiments affords a means of determining the heat-transfer coefficients from the gas stream to the column of material (*1*).

The amount of calcination after a run was determined by loss of weight. The distance which the line of calcination had penetrated was determined by averaging a great many measurements of the width of the calcined band.

The limestone used had the following analysis:

	%		%
CaO	54.33	Al_2O_3	0.30
Fe	0.36	CO_2	43.10
SiO_2	0.50	Loss	43.10
MgO	1.14		

The complete operating and computed data are given in Table I. These data show wide variations of particle size and degree of calcination. In one of the runs the limestone was preheated before putting it into the furnace. A careful study of the complete set of data shows that none of these variables has a consistent, significant effect. It is very probable that continued, careful experimentation would give results which were reproducible enough to show small variations with the other variables, particularly if a greater size range were studied.

Mechanism of Reaction

Limestone decomposes according to the reaction

$$CaCO_3 = CaO + CO_2 \qquad (2)$$

The reaction is endothermic, absorbing about 43,000 calories per formula weight. It can be shown by theoretical considerations that such a reaction cannot take place, except at the boundary between these two phases (*6*). Since the two solid phases are fixed in position, it might be expected that the line of calcination would start at the outside of the piece and advance inward. If there were chance calcium oxide molecules on the interior of the piece and the necessary heat were available at that point, then centers of calcination might start at various places on the interior of the piece. However, several hundred pieces were examined during the course of these experiments and in every one calcination had proceeded by the advance of a definite line or phase boundary from the outside toward the center.

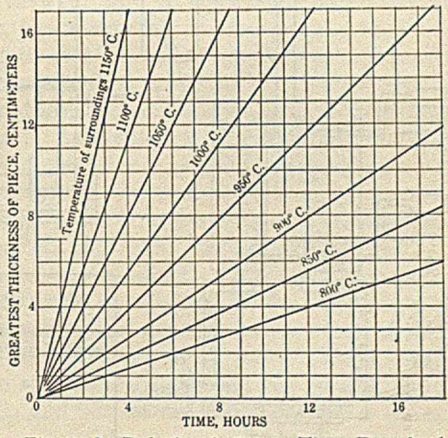

Figure 2—Relation between Time Required for Complete Calcination, Temperature, and Thickness of Particle

Table I—Data on Heat Transfer and Calcination of Limestones

Max. Temp.	Run	Av. Equiv. Spherical Diameter of Particle	Time	Wt. Loss during Run	Calcination Completed	Av. Measured Depth of Penetration of Calcination	Computed Rate of Penetration		Rate of Gas Flow	Coef. Heat Transfer Gas to Solid[a]
° C.		Cm.	Sec.	%	%	Cm.	Cm./sec. × 10⁴	Cm./hr.	Std. l./sec./cm.²	
A—GAS FLOWING THROUGH COLUMNS OF MATERIAL										
835	163C	4.1	8100	30.7	72.2	0.29	0.36	0.13	0.08	0.0016
840	162	2.5	5400	25.0	58.0	0.45	0.84	0.30	0.13	0.0047
875	166C	7.3	10190	30.5	70.8	0.64	0.62	0.22	0.08	0.00065
875	166D	7.3	10190	30.5	70.8	0.66	0.65	0.23	0.08	0.00065
900	163B	4.1	8400	30.7	71.3	0.82	0.98	0.35	0.08	0.0016
910	165C	6.3	7500	32.6	75.6	0.52	0.69	0.25	0.08	0.00078
910	166B	7.3	11100	30.5	70.9	0.84	0.76	0.27	0.08	0.00065
910	165E	8.0	7500	18.6	43.2	0.80	1.07	0.38	0.08	0.00078
940	164A	3.0	3900	26.2	60.8	0.71	1.83	0.66	0.13	0.0032
945	166A	7.3	12000	30.5	70.9	1.05	0.88	0.32	0.08	0.00065
950	165B	6.3	8100	32.6	75.6	0.79	0.98	0.35	0.08	0.00078
965	163A	4.1	9590	30.7	71.2	1.55	1.62	0.58	0.08	0.0016
1000	165A	6.3	8700	32.6	75.6	1.32	1.52	0.55	0.08	0.00078
B—SINGLE PIECES IN INDUCTION FURNACE										
1035	170	7.3	5940	37.2	86.3	1.48	2.50	0.90		
1035	176	4.0	3480	43.1	100.0	1.0	2.87	1.03		
1040[b]	169	4.0	5940	37.1	86.0	1.3	2.19	0.79		
1075	171	6.6	3300	35.2	81.5	1.2	3.63	1.31		
1075	172	5.7	1800	25.8	59.8	0.65	3.61	1.30		
1085	173	4.6	1800	36.9	85.5	0.65	3.61	1.30		
1085	174A	3.6	900	31.2	72.3	0.35	3.89	1.40		
1085	174B	3.7	900	31.7	73.5	0.35	3.89	1.40		
1125	175	5.6	3600	37.8	87.6	1.30	3.61	1.30		
1140	168	6.0	3300	39.8	92.2	1.50	4.55	1.64		

[a] Measured in calories per second per degree difference per cubic centimeter of bed.

[b] Limestone was preheated to 500° C. before putting it into the furnace.

Distinction between Calcined and Uncalcined Material

The calcined portion is always soft and pure white. The uncalcined portion remains hard and is gray, probably owing to the presence of traces of unoxidized carbon from organic matter. Figures 4, 5, and 6 show cross sections of typical pieces of partially calcined stone. The division line between the two phases is very sharp. Figure 6 is the photograph of a piece which was ground into the shape of a sphere. The dark, uncalcined portion has retained its spherical shape, showing that the phase boundary advances uniformly in all directions.

The dark appearance of the central portion is not sufficient proof that there areas are uncalcined. However, several samples were taken at various positions in the dark regions and calcined in platinum crucibles. All samples showed full loss of weight, indicating that no calcination had taken place inside of the white band.

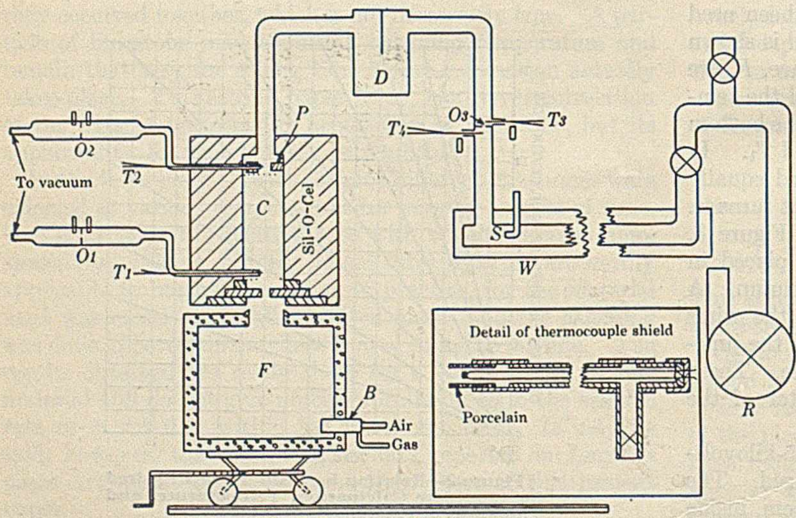

Figure 3—Heat Transfer Equipment

One investigator (4) has reported that there is a zone of partially calcined calcium carbonate inside of the completely calcined portion. If this is true, the zone is very narrow, for none of the samples of this investigation showed any such partial calcination close to the phase boundary.

Temperature Advances Faster than Calcination

It is particularly important to note (Table I) that the rate of advance of the line of calcination is quite slow, much slower than the rate of advance of a temperature wave. Temperature acquisition at the center of a piece occurs long before calcination takes place. This means that the portion of the piece inside of the calcined zone is always in a metastable condition, but still unable to decompose until the phase boundary advances to it.

The limiting factor in the rate of calcination at low temperatures is the inherent rate of advance of this boundary line of the two solid phases, the center of the piece coming up to the temperature of the outside far ahead of calcination. However, as the temperature of the surroundings is raised, the specific rate of advance of the phase boundary is so increased that resistance to heat transfer begins to have an effect and the center temperature, although it is sufficiently high for calcination, lags behind the outside temperature until calcination is completed. This means that, after the temperature reaches a certain point, the 43,000 calories per formula weight being absorbed at the phase boundary are being demanded so rapidly that no additional heat gets past the boundary to go into the center of the piece.

Temperature of Interior of Pieces

These two effects are shown in Figure 7. At the lower temperature (curve *B*), the temperature of the center rose to that of the outside in the usual manner for the heating of a solid body. However, calcination lagged far behind this temperature, for it was only 72 per cent complete after 160 minutes of heating.

At the more elevated temperature the center came up to a definite temperature and stayed there while calcination proceeded. At various places in the literature it will be found that "calcination temperatures" are reported as being from 900° to 950° C. In the run under consideration the temperature in the center remained constant at about 940° C. It is evident, then, that this so-called "calcination temperature," which apparently is meaningless because calcination theoreti-

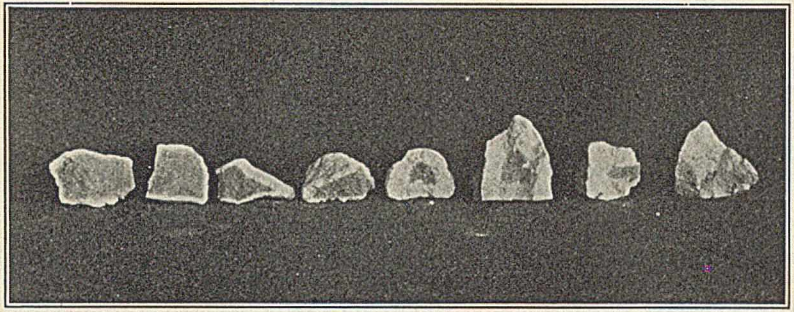

Figure 4

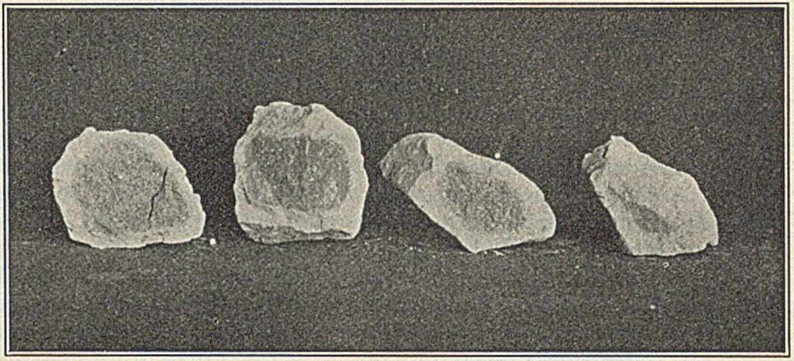

Figure 5

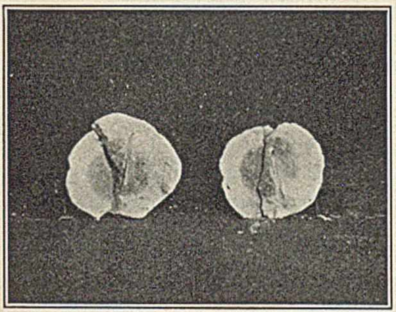

Figure 6

Cross Sections of Typical Pieces of Partially Calcined Limestone

cally should proceed at any temperature if the carbon dioxide pressure is low enough, is actually a measure of the temperature which the center of a piece maintains while calcination is proceeding at more elevated temperatures.

The difference in the temperature histories of the surface of the pieces in runs *A* and *B* is due to the fact that run *A* was a single piece in an induction furnace, the surface temperature coming up almost at once. Run *B* was that of a piece at the top of a bed of material and the whole bed had to be heated before the top piece acquired temperature.

From a consideration of Figure 7 it would seem that, if the outside of a piece is heated to some temperature greater than 1000° C., then the center should maintain a constant temperature between 900° and 950° C. until calcination of the piece is complete and then it should rise to the temperature of the outside. This is exactly what happens, as is shown in Figure 8. This curve is for the temperature history of a piece which was completely calcined before being taken from the furnace.

Calcination Not Analogous to Heat Transfer

From the preceding discussion it can be seen that it is erroneous to consider that heat flow and calcination are analogous (*3*). If the external temperature is below 950° C., then the center acquires temperature much ahead of calcination. If the external temperature is greater than 950° C., then the arrival of the center temperature to that of the outside is evidence that calcination is complete to the center, but the temperature history has not been in any way similar to the simple heating of a body.

Carbon Dioxide Pressure

The runs that were made at low temperatures were for the system where gas flowed through a column of broken limestone. The total pressure was approximately atmospheric and the carbon dioxide was 5 to 10 per cent. No significant variations could be found with variations of the carbon dioxide percentage.

In the high-temperature runs the pieces were placed in a graphite-lined induction furnace. The total gas pressure was 1 atmosphere. The gas evolved in the furnace then was 100 per cent carbon dioxide, but it was in contact with hot graphite and was partially converted to carbon monoxide. The percentage of carbon dioxide in the gas ranged from 30 to 50 per cent. No significant variations which could be attributed to difference in gas compositions could be found between the high- and low-temperature runs.

Probable Driving Force of Reaction

It seems reasonable to suppose that the major driving force of the calcination is the equilibrium carbon dioxide pressure of the calcium carbonate. If this is true, the rate of calcination might be expected to be approximately proportional to the equilibrium carbon dioxide pressure.

Measured equilibrium carbon dioxide pressures for calcium carbonate are shown in Figure 9 (*5*). It will be observed that the shape of the curve, when related to temperature, is the same as that for rate of calcination as shown in Figure 1. However, the sharp rise in the equilibrium carbon dioxide curve begins at a lower temperature than the corresponding rise in the rate curve. This would indicate that another factor besides the carbon dioxide pressure tends to limit the speed of reaction. As pointed out before, this limiting factor at elevated temperatures is probably the resistance to heat transfer. So there are two tendencies in calcination, specific rate of advance of phase boundary and rate of heat transfer, which are alternately controlling factors in the rate.

Fortunately for simplicity of the problem, as a first approximation, the rate of advance of the calcination zone for all temperatures is constant and independent of the size of the piece. This independence of particle size indicates that the resistance to heat transfer is for the most part at the line of calcination and not throughout the body of the calcined material.

Rate of Carbon Dioxide Evolution

In some instances it is important to consider the rate of evolution of carbon dioxide during the course of the calcination. Obviously, if the line of calcination advances at a constant rate, this rate of gas evolution is proportional to the area of the calcining surface, which decreases as the reaction proceeds toward the center. If the particles are considered

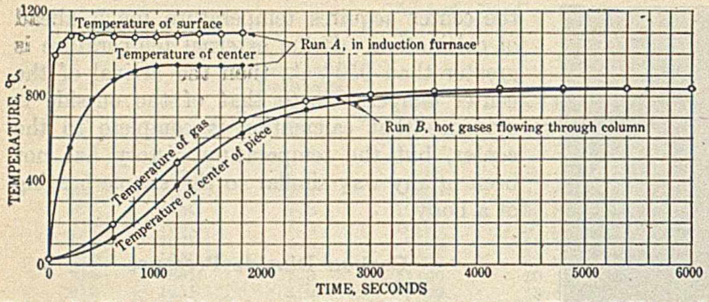

Figure 7—History of Surface and Center Temperatures of Typical Pieces of Limestone during the Calcining Period at Different Temperatures

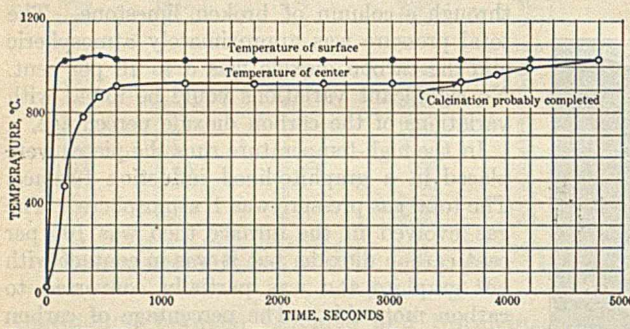

Figure 8—Temperature History for Complete Calcination at Elevated Temperatures

spheres, then the rate of gas evolution for pure calcium carbonate will be given by the equation

$$\frac{dG}{d\theta} = \frac{4\pi Rd\ 22.4}{100}(r - R\theta)^2 \qquad (3)$$

$\frac{dG}{d\theta}$ = rate of gas evolution from one piece in liters per hour
θ = time in hours since beginning of calcination
R = rate of calcination as determined by Equation 1
r = outside diameter of particle
d = specific gravity of limestone

This equation may be written

$$\frac{dG}{d\theta} = 2.82Rd(r - R\theta)^2 \qquad (4)$$

Surface Area

This study furnishes a means of making an approximate determination of the surface area of irregular pieces of limestone. If a piece of limestone is calcined for a short distance inward, the volume of calcined material is approximately the surface area times the thickness of the calcined layer. The amount of calcination—that is, the volume calcined—is determined by loss of weight. The boundary of the calcined zone is very sharp and uniform around the piece. After breaking the piece, the thickness of this zone may be determined by the average of several measurements. Dividing this average thickness into the volume calcined gives the surface area. A number of such determinations were made. It was found that for irregular pieces of limestone the surface area was 20 to 50 per cent greater than for a sphere of the same volume.

Rates of Calcination of Different Limestones

In order to determine the effect of composition of limestone upon the rate of calcination, two samples of two other limestones used in commercial blast-furnace work were calcined. The samples were ground into the form of spheres, 5 cm. in diameter, and the rate of calcination was determined in the induction furnace. The data on the two samples are given in Table II.

Table II—Data on Calcination of Limestones

	Sample A	Sample B
	%	%
Analysis:		
CaO	49.60	43.40
MgO	4.38	9.25
SiO_2	0.52	0.26
Al_2O_3	0.05	0.11
Ignition loss	44.60	45.00
Diameter of sphere, cm.	5.2	5.1
Specific gravity	2.66	2.55
Temperature of calcination, ° C.	1075	1050
Rate of calcination, cm. per hour	1.55	1.77

By referring to Figure 1 it can be seen that these rates are distinctly greater than that of the average curve given there. In all probability this increased rate is due to the presence of the greater percentage of magnesia (4.38 and 9.25 per cent, as compared with 1.14 per cent in the first limestone). The dissociation pressure of magnesium carbonate is many times that of calcium carbonate at the temperatures considered, and hence might be expected to increase the rate of reaction quite appreciably.

It is evident that, for limestones which are quite different from the one studied, tests should be conducted to determine their specific decomposition rates. This could easily be done by placing one or more spheres of limestone in a muffle furnace, at 1000° C., and the rate of calcination determined by loss of weight after a certain time (about 1 hour). It would be necessary to keep the temperature of the furnace controlled quite accurately, as the temperature has the major effect upon rates of calcination.

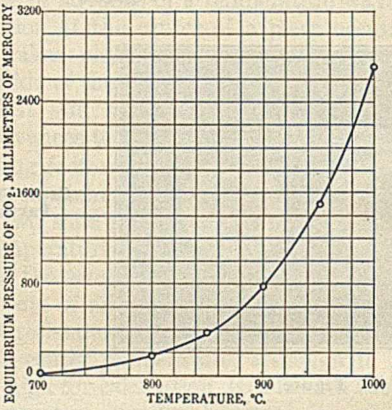

Figure 9—Johnson's Data of Equilibrium Carbon Dioxide Pressures in the Decomposition of Calcium Carbonate

After the rate was determined for one temperature, the rates for other temperatures can be estimated from Figure 1, as the other curves should run approximately parallel to this curve.

The determination of the rate of calcination is quite simple and can easily be done in almost any laboratory.

Acknowledgment

The author wishes to acknowledge the aid and suggestions of T. L. Joseph, H. F. Holbrook, and E. P. Barrett, of the U. S. Bureau of Mines, during the course of this work.

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Photographic Flame Studies in the Gasoline Engine

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An apparatus is described with which by photographic means simultaneous flame and pressure studies have been made of individual explosions in the gasoline engine. These records clearly show the relation between the rates of flame travel and the resulting rates of pressure rise in knocking and in non-knocking explosions. They indicate that the phenomenon of knock in the gasoline engine, which heretofore has been recognized by its characteristic sound and by the shape of its pressure record, is due to a many-fold increase in the rate of inflammation within the latter portion of the charge.

The records indicate that during the combustion process in the engine there is a relatively narrow combustion zone which moves progressively through the charge, and that, after the burning of the fuel in the combustion zone is over, the products of combustion continue to emit light for some time. The intensity of this afterglow increases as the pressure in the combustion chamber begins to rise rapidly, and during the period of maximum pressure it is most intense in those portions of the products of combustion which were formed in the early part of the explosion before the pressure had risen above the compression pressure. In some respects these flame records taken from the gasoline engine are similar to those obtained by investigators who have studied combustion in bombs.

By MEANS of an apparatus developed especially for the purpose, photographs have been taken of combustion in the gasoline engine as it appeared through a narrow quartz window that extended over the entire length of the combustion chamber. A simultaneous record of the changes in pressure in the engine cylinder was also obtained by photographic means. The flame records, which were taken on moving films, consist essentially of photographic plots of time after ignition against distance from the spark plug to the combustion zone; while the pressure records consist of plots of time after ignition against pressure in the engine cylinder. The data were obtained while the engine was running under its own power and pulling a full load.

These records clearly show the relation between the rates of flame travel and the resulting rates of pressure rise in knocking and in non-knocking explosions. This information supplements the data secured with the auxiliary sampling valve (*10*), which proved to be inadequate for differentiating between the rates of flame propagation in knocking explosions and those in non-knocking explosions during the combustion of the last portions of the charges.

In surveying the literature, no description has been found of similar experiments made with the gasoline engine, but several investigators have described the results of such studies made in bombs (*1*, *2*, *4*, *5*, *8*, *9*, *11*). In 1928 Maxwell and Wheeler (*8*, *9*) called attention to the need of flame studies of this type in a gasoline engine, but apparently the difficulties involved have not heretofore been overcome. Some of the records of combustion in the gasoline engine obtained with this new apparatus are shown herein, and they are compared with those of other investigators who in a similar way have studied combustion in bombs.

Apparatus

Engine—The engine and auxiliary apparatus required to insure proper control of the conditions of engine operation did not differ appreciably from that described in a previous publication from this laboratory (*10*). The following improvements were made, however: First, in order to keep the inlet and outlet jacket water at a constant temperature of 100° C., the old evaporative cooling system was replaced with another which was equipped with a circulating pump; second, to make it possible to change quickly from one fuel to another, the conventional carburetor was replaced with a Venturi tube and a jet that was fed from either of two float bowls; third, in order to synchronize the flame and pressure records, a special form of ignition system was used.

In the ignition system the timing of the spark was controlled by connecting a rotating contactor in series with the primary. The rotating contactor consisted essentially of a brush insulated from the engine which rode upon a Bakelite disk that was mounted upon the crankshaft. This disk, which was 6 inches (15.2 cm.) in diameter and 0.75 inch (1.9 cm.) wide, carried two narrow brass plates buried in its surface and connected electrically to the crankshaft. Since these plates were spaced 20 degrees of revolution apart, two surges of current passed through the primary of the ignition system during each revolution of the crankshaft. With this ignition system, then, two ignition sparks passed through the spark plug near the end of the compression stroke, the first of which ignited the charge. As is shown below, the second spark was for the purpose of accurately timing the record of events, and since it had no appreciable effect upon the operation of the engine, the ignition system was quite satisfactory for these experiments.

Cylinder Head—A special cylinder head fitted with a quartz window that extended all the way across the ceiling of the combustion chamber was built for this research. It was provided with a means of mounting a combustion camera above the window. A general view of the cylinder head and combustion camera fastened in place upon the engine is shown in Figure 1.

In order to incorporate certain features essential in this work, it was necessary to make the shape of the combustion chamber differ considerably from the conventional shapes now in commercial use. In designing the combustion chamber the following factors were given primary consideration: First, in order that the spark might serve as a means of synchronizing the flame records with the respective pressure records, it was desirable to locate the spark plug in a position where its terminals would be visible through the quartz window. Second, in order to study the motion of the burning zone through that part of the charge which burned last, it was necessary to locate the spark plug at one end of the combustion chamber. To avoid the disturbing effects of hot spots, such as the exhaust valve, upon the flame travel, the spark plug was located over the intake valve, and the last part of the charge to burn was then at the opposite end of the combustion chamber over the piston. Third, it was desirable to

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have a compression ratio of 5.0 to 1 so that the engine would knock when operated with straight gasoline as the fuel. Cross sections of the combustion chamber are shown in Figures 2 and 3, and the ceiling of the combustion chamber is shown in Figure 4.

As is shown in Figure 2, a slot for the quartz window was cut through the central portion of the cylinder head to permit light to pass from the combustion chamber to the lens of the combustion camera. With this arrangement it was necessary to give considerable attention to the apportionment of the water spaces. In this engine water was circulated from the cylinder block into water spaces *A* and *B* of Figure 2 through four 0.5-inch (1.27-cm.) holes not shown in the sketch. The outlet from the engine (also not shown) was located in water space *A*, and water spaces *A* and *B* (Figure 2) were connected by means of water spaces *A* and *B* of Figure 3. The success of this arrangement of the cooling spaces may be judged by the fact that the engine showed no tendency to preignite, even when knocking quite violently.

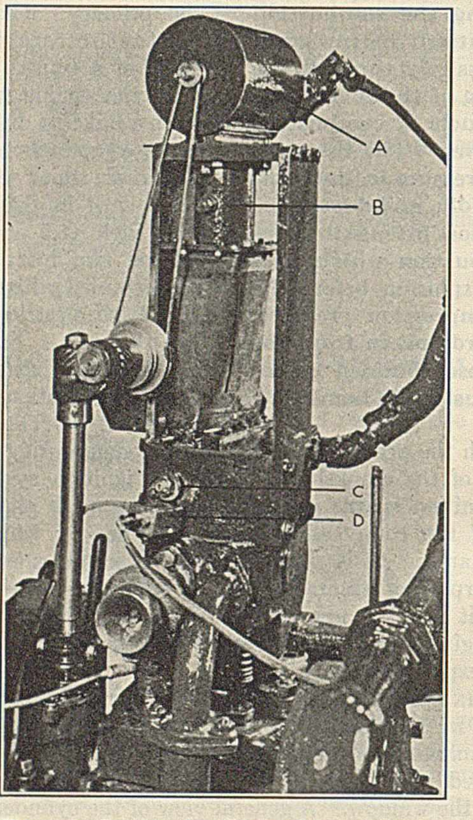

Figure 1—Combustion Camera Mounted upon Engine

A—Film drum
B—Cylindrical tube which supported lens carrier
C—Nut and washer on end of window retainer
D—Spark plug indicator

METHOD OF MOUNTING QUARTZ WINDOW—The quartz window, which was 5 inches (12.7 cm.) long and 0.375 inch (0.952 cm.) wide, was cemented into a window retainer which was held in place with a nut and washer (Figure 1). A general view of the window retainer is shown in Figure 5, and a cross section of the quartz window itself is outlined in position in Figures 2 and 3. To minimize the difference between the coefficient of expansion of the quartz window and that of the window retainer itself, this part of the apparatus was made of Invar. The general shape of the window retainer was that of a tapered plug with a diameter of 0.81 inch (2.1 cm.) at the small end and 1.1 inches (2.8 cm.) at the large end. This was ground to fit a tapered hole in the cylinder head (*D* in Figure 3).

The most successful of the several methods used for cementing the quartz window into the window retainer is as follows: In order to keep any extraneous grit or cement off the window, the polished sides were first covered with strips of paper which were held in place with Carter's liquid paste. A piece of string asbestos which had previously been dipped in a paste of litharge and glycerol was next carefully laid along the shoulders of the window retainer at the bottom of the groove *G* (Figure 5) and the excess of the litharge and glycerol on the side walls of groove *G* cleared off. The window was then pressed into position and spaced equidistant from the side walls of groove *G* by placing copper strips along either side.

After the litharge and glycerol paste had set, the space between the side walls of the groove *G* and the window was filled with a mixture of feather asbestos and porcelain cement. This mixture was firmly pressed into place with a piece of spring steel about 0.005 inch (0.0127 cm.) thick. After baking the window in the window retainer overnight in an oven at 80° C., the paper was removed from the polished sides of the window. This part of the apparatus was then placed in the engine and tested for leaks. If any developed, they were plugged with more asbestos and porcelain cement.

COMBUSTION CAMERA—The camera consisted of a film drum suitably mounted on top of the engine and a Meyer Plasmat (F 1.5) lens enclosed in a light-tight compartment and adjusted to focus an image of the quartz window upon the surface of the film drum. The lens was mounted inside the cylindrical tube, shown in Figure 1, upon a lens carrier. The lens carrier was clamped in position on the inside of the cylindrical tube by means of a nut threaded to fit a stud that projected from the lens carrier through an oblong hole in the cylindrical tube. This arrangement made possible the adjustment of the height of the lens and thereby provided a means of focusing the image of the quartz window upon the film drum.

The film drum and the mechanism for operating the shutter are shown in Figure 6. The film drum itself was taken from a General Electric oscillograph and adapted to this apparatus. It was driven indirectly from the camshaft of the engine by a system of pulleys as shown in Figure 1. The film drum was equipped with a shutter which consisted of a brass cylinder about 0.75 inch (1.9 cm.) in diameter and with a slot 4 inches (10.2 cm.) long and 0.06 inch (0.16 cm.) wide cut through its center. Thus, by moving the shutter arm, which was attached to one end of this cylinder as is shown in Figure 6, the film-drum shutter was rotated about in its housing, thereby cutting off the passage of light from the lens to the film drum, unless the slot through the brass cylinder was in a vertical position.

In this research it was desirable to permit light from only one explosion to fall upon the film drum. This was accomplished by opening and closing the film-drum shutter at the right time by means of the auxiliary apparatus shown attached to the film drum in Figure 6. By connecting the electromagnet in series with an electrical contactor driven from the crankshaft of the engine and with a source of direct current, a surge of electricity was passed through this magnet during the time interval that it was desired to have the shutter open. The operation of the film-drum shutter then was as follows: The shutter arm was pulled around into the cocked position in the dark room and left in this position until the picture was snapped. At this time a surge of current passed through the magnet causing the ratchet lever to rotate in a clockwise direction, thereby releasing the shutter arm which was quickly turned about by the shutter-arm spring to a vertical position shown as position 2 in Figure 6. When the circuit through the electromagnet was broken, the ratchet-lever spring pulled the ratchet lever back into its original position, permitting the shutter arm to rotate around into position 3, as shown in Figure 6.

Pressure Recorder—The pressures in the combustion chamber were measured with an electrical pressure indicator of the spark-plug type which was connected electrically to a single-element oscillograph. Both of these instruments and their uses have been described in previous publications from this laboratory (*6*, *7*).

Means of Synchronizing Flame and Pressure Records—Since the shutter on the oscillograph was opened by a surge of direct current through a small electromagnet, simultaneous records of the same explosion were obtained on the film drum and in the oscillograph by connecting the electromagnet in the oscillograph and that on the film drum in series with the electrical contactor and the source of direct current.

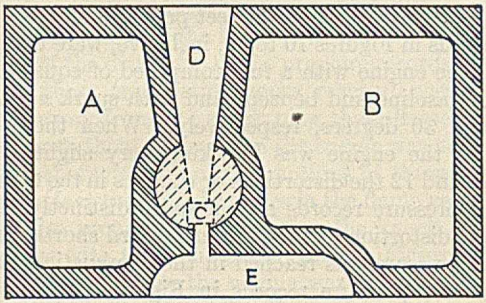

Figure 2—Transverse Section of Cylinder Head

A, *B*—Water space
C—Cross section of quartz window
D—Cross section of light-tight compartment leading to lens
E—Cross section of combustion chamber

As mentioned above, two ignition sparks were photographed upon each flame record. Both of these instants in the combustion period were also marked simultaneously upon the pressure records in the following way: The secondary (two turns) of a tiny transformer was permanently connected in series with the oscillograph element, and the instants that the ignition sparks were induced in the ignition system were marked upon the pressure records as kinks in the pressure line by connecting the primary (also two turns) of this tiny transformer in series with the condenser and the rotating contactor of the ignition system.

Materials

Eastman Portrait Panchromatic cut film was used both in the combustion camera and in the oscillograph.

The gasoline used was a regular commercial grade and the benzene was a c. p. grade.

The lead tetraethyl used was supplied in the form of Ethyl fluid by the Ethyl Gasoline Corporation.

Procedure

After the window had been fastened in place, the engine was allowed to run, avoiding rich mixtures as much as possible, for at least one-half hour to permit it to come to equilibrium. During this time the optical system of the oscillograph was cleaned and adjusted to produce as bright a line as possible upon the screen. The film drum was also loaded and cocked.

As soon as the jacket temperature reached 100° C., the engine was stopped until the window and window retainer had been removed and cleaned. While the jacket temperature was being raised to 100° C. again, the lens was placed on the lens carrier and the film drum mounted upon the drum platform as shown on Figure 1. Then, after the conditions of engine operation (speed, spark advance, mixture ratio, and fuel) were rechecked, the picture was snapped. Since the film-drum shutter mechanism was connected electrically with that on the oscillograph, the mechanical part of this operation consisted simply of making an exposure with the oscillograph.

The films carrying the latent images of the flame and pressure records were developed in total darkness following the procedure recommended by the Eastman Kodak Company.

Data

A number of typical flame and pressure records obtained with the apparatus described above are shown in Figures 7 to 17, inclusive. On all these records time is read from left to right. On the flame records at the top, for example, the white spots designated as *A* are actual photographs of the ignition sparks which started the combustion in the respective explosions. The white spots marked *B* are also photographs of ignition sparks, but these sparks jumped across the spark-plug terminals 20 degrees of revolution after the combustion started and have no apparent effect upon the combustion process. They were placed on these records solely as reference points. On the pressure records the breaks in the pressure lines marked *A* were induced in the oscillograph circuit at the respective times of ignition of the charges. The breaks in the pressure lines designated as *B* were induced in the oscillograph circuit at the instants that the ignition sparks marked *B* jumped across the spark-plug terminals. The units along the ordinates of the flame records at the top of the figures represent distances from the spark plug in inches and the units along the ordinates of the pressure records at the bottom of the figures represent pressures in pounds per square inch.

The pressure records, then, are simply graphs on which the pressures in the combustion chamber are plotted against time expressed in degrees of revolution of the crankshaft of the engine. The flame records, on the other hand, are graphs which show the progress of the flame front through the central portion of the combustion chamber plotted against time in degrees of revolution. If part of the freshly burned gases did not continue to glow for some time after the combustion zone passed by, the flame records would appear as bands which correspond to projections of the combustion zones in the engine. The slopes of these bands would be determined by the film and flame speeds, while the distances across them measured parallel to the time axis would depend (provided the width of the quartz window was neglected) upon the actual duration of the combustion process along a vertical line at the corresponding point in the combustion chamber. The distances across these bands measured along the ordinates would depend upon the actual widths of these projected combustion zones. The bands corresponding to projections of these combustion zones or flame fronts upon the film drum appear along the upper left-hand edges of these flame records. In Figures 7, 8, and 9 the combustion zones are shown between the two small arrows marked *C*. These combustion zones are quite prominent upon these records before the

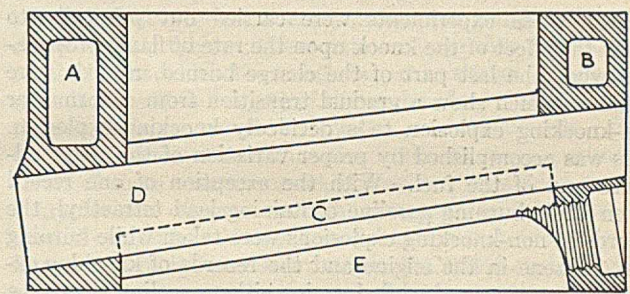

Figure 3—Longitudinal Section of Cylinder Head

A, *B*—Water space
C—Cross section of quartz window
D—Cross section of tapered hole in cylinder head
E—Cross section of combustion chamber
F—Location of spark-plug indicator

pressure in the combustion chamber begins to rise rapidly. During the time of maximum pressure in the engine the freshly burned gases emit so much light that it is difficult to distinguish between the combustion zones and the afterglow on some of the prints. On the negatives, however, the combustion zones are fairly distinct all the way across the combustion chamber. The actual duration of the combustion process as measured on these records varies between 3 and 10 degrees of revolution, while the actual widths of the projections of these combustion zones vary between 0.375 and 1.5 inches.

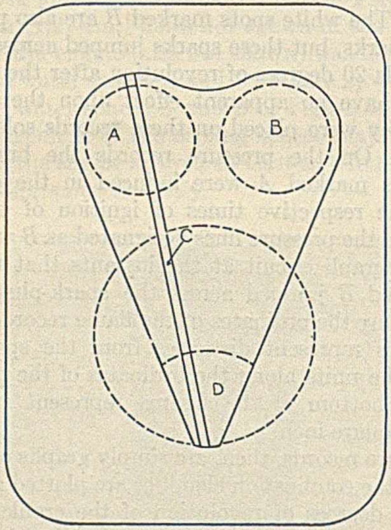

Figure 4—Ceiling of Combustion Chamber

A—Intake valve
B—Exhaust valve
C—Location of quartz window
D—Location of detonating zone

Since these experiments were carried out primarily to study the effect of the knock upon the rate of flame propagation when the last part of the charge burned, records were obtained which show a gradual transition from a normal or non-knocking explosion to a decidedly knocking explosion. This was accomplished by proper variation of the spark advance and of the fuel. With the exception of one record taken while burning gasoline containing lead tetraethyl, the records of non-knocking explosions were taken while burning C. P. benzene in the engine and the records of knocking explosions were secured while burning either gasoline alone or a mixture of gasoline and benzene. In all the runs the engine speed was kept at 800 r. p. m., the jacket temperature at 100° C., and the throttle wide open. The fuel level was kept at such a height that the analysis of the exhaust gases showed the presence of less than one per cent of either carbon monoxide or oxygen. This analysis checks quite closely with that obtained when the engine is operated with the theoretical amount of air in the fuel-air mixture.

The records in Figures 7 to 9, inclusive, were taken while operating the engine with benzene as the fuel and with spark advances of 20, 25, and 30 degrees, respectively. Since the compression ratio used in this work was 5.0 to 1, and since the fuel was benzene, these are records of non-knocking explosions. These flame records indicate that combustion zones passed through every portion of the charge and that the burned gases behind the flame front continued to glow for some time afterwards. If the directional velocities of the gases in the combustion chamber are neglected, the combustion zones on the upper left-hand edges of these flame records indicate that the duration of the combustion process was equivalent to about 4 degrees of revolution. These data indicate that the flames started out very slowly from the spark plug and barely moved for a time interval equivalent to about 5 degrees of revolution of the crankshaft. After the flames or combustion zones in Figures 7 and 9 started, they traveled the entire length of the combustion chamber at fairly constant rates of speed (74 and 60 feet per second, respectively). The projections of the combustion zones appear to have become somewhat wider as they approached the end of the combustion chamber. The speed of the combustion zone in the flame in Figure 8 gradually increased until it approached a point approximately 0.5 inch from the spark plug. From this position it traveled at a rate of 110 feet per second until a point about 3.25 inches from the spark plug was reached. At this time the flame slowed down and traveled the remaining distance to the end of the combustion chamber at a speed of about 33 feet per second.

The records in Figures 10 to 12, inclusive, were taken while operating the engine with a fuel composed of equal parts by volume of gasoline and benzene and with spark advances of 20, 25, and 30 degrees, respectively. When these records were taken the engine was knocking very slightly, but in Figures 11 and 12 the distortions or changes in the types of the flame and pressure records appear quite distinctly. Except for a slight distortion of the pressure record shortly after the maximum pressure was reached in the combustion chamber, the flame and pressure records in Figure 10 do not differ appreciably from those of normal, non-knocking explosions. The flame records in Figures 11 and 12 are similar to those in Figures 7 to 9, inclusive, in that the flames do not appear to have moved away from the spark plug until an interval of time equivalent to about 5 degrees of revolution of the crankshaft had elapsed. At the end of this interval, however, the flames in Figures 11 and 12 traveled away from the spark plug at the rate of approximately 80 feet per second and continued at this rate until they arrived at a point about 4 inches away from the spark plug. Through the next 0.5 inch of distance traveled the apparent rates of flame travel in these two explosions decreased quite rapidly. Then the remaining distances to the end of the combustion chamber were negotiated at "detonating" velocities. This exceedingly rapid rate of combustion of the last parts of the charge to burn in each of these explosions produced the small kinks on the pressure cards at the time of maximum pressure. In the case of the flame record in Figure 11, auto-ignition apparently took place near the end wall of the combustion chamber just as the knock began. During the period of the knock the flame then spread down toward the spark plug from the point of auto-ignition to meet the oncoming combustion zone, as may be seen from the backward slope of the nearly vertical portion of the flame record at the top.

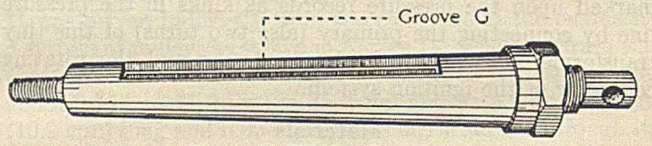

Figure 5—Window Retainer

The records in Figures 13 to 15, inclusive, were obtained while operating the engine with a fuel composed of 25 per cent benzene and 75 per cent gasoline (by volume) and with spark advances 20, 25, and 30 degrees, respectively. When the records on Figure 13 were taken, the engine was knocking incipiently, the degree of knock being of about the same intensity as when the records of Figures 11 and 12 were taken. The flat top on the pressure record in Figure 13 indicates that there was a rather mild knock in this explosion. This type of pressure record is probably due to the very light character of this knock and to the fact that the volume of the combustion chamber, because of the motion of the piston, was increasing quite rapidly at the time of the knock. The flame record in Figure 13 appears to be of the same general type as those described above until the combustion zone approached a point about 4 inches away from the spark plug. At this time auto-ignition took place in the unburned portion of the charge at a point about midway between the oncoming combustion zone and the end of the combustion chamber. From the point of auto-ignition, combustion in the unburned portion of the charge spread out toward the end of the combustion chamber and back to meet the normal combustion zone. In this explosion again the knock began just as auto-ignition occurred in the last part of the charge to burn.

When the records in Figures 14 and 15 were taken the engine was knocking quite severely. This fact is shown on these flame and pressure records by the many-fold increase in the rate of inflammation of the last portions of the charge and by the degree of the distortion of the pressure records. Until the time that these combustion zones reached positions about 3.5 inches away from the spark plug these flame records are very similar to those taken when the engine was not knocking. A striking characteristic of the motions of these combustion zones is the fact that the decreases in the flame velocities were not nearly so pronounced just before the knock occurred, as was the case with the combustion zones in Figures 11 and 12, which were taken while the engine was knocking incipiently. There is little evidence on the films carrying these flame records to indicate that spontaneous ignition took place in the unburned portion of the charge just as the knock began. However, the records do show the presence of a faint luminosity in the unburned portion of the charge which was visible for a time interval equivalent to about 2 degrees of revolution before the knock began. At present it is not certain whether this faint luminosity in these flame records is due to reflection of light from the inside of the window retainer or to some form of slow oxidation in the unburned portion of the charge just before the knock occurred; but the records do show that, at the time the knock began, the entire volume of the charge left to burn burst into a highly luminous flame.

The flame and pressure records in Figures 16 and 17 show the effect of lead tetraethyl on the knock. The records in Figure 16 were taken when the engine was being operated with straight gasoline as the fuel and was knocking quite violently, while the records in Figure 17 were taken when the engine was not knocking and was being operated with gasoline containing 0.15 per cent by volume of lead tetraethyl. The remaining conditions of engine operation in these two runs were kept as nearly identical as possible. The flame and pressure records on Figure 16 are similar to those in Figures 14 and 15, which were taken while the engine was knocking quite severely, and the flame and pressure records on Figure 17 are similar to those on Figure 8, which were taken while the engine was running normally and was not knocking. In Figure 16 there is some indication of auto-ignition at a point about two-thirds of the distance from the oncoming combustion zone to the end of the combustion chamber at the time the knock began.

An examination of the pressure records of knocking explosions indicates that the rise in pressure at the time of the knock requires a measurable period of time, sometimes as much as 5 degrees of revolution. Since it has been shown (*7*, *8*) that the pressure indicator and the oscillograph reproduce faithfully the form of the phenomenon studied at this frequency with a lag of 0.6 degree of revolution at 800 r. p. m., it is believed that the phenomenon of knock does actually require a short interval of time for its occurrence. The flame records substantiate this conclusion, as the duration of the combustion process appears to vary from 2 to 5 degrees as the flames pass through the detonating zone. This apparent duration seems to decrease as the intensity of the knock increases.

In Table I are tabulated the determinations of the angles of revolution at which the knock occurred in the knocking explosions described above. Measurements were made on both the flame and the pressure records. In columns 2 and 3 of Table I are measurements taken from the pressure records of the angles of revolution at which the knock began and ended, respectively, and in column 4 are measurements taken from the flame records of the angles of revolution at which the knock began. Since at the time of maximum pressure it was very difficult to determine exactly the point on the flame records where the combustion zone ended and the afterglow began, no determinations from these records of the angles at which the combustion was completed are included in this table. These data indicate that the angles of revolution at which the knock began as shown by the flame records are within 1 degree of the angles of revolution at which the knock began as shown by the pressure records. Since these differences are within the limits of the experimental errors of these measurements, it has been concluded that the characteristic distortion of the pressure records from the normal or non-knocking shape is due to a many-fold increase in the rate of inflammation within the latter portion of the charge.

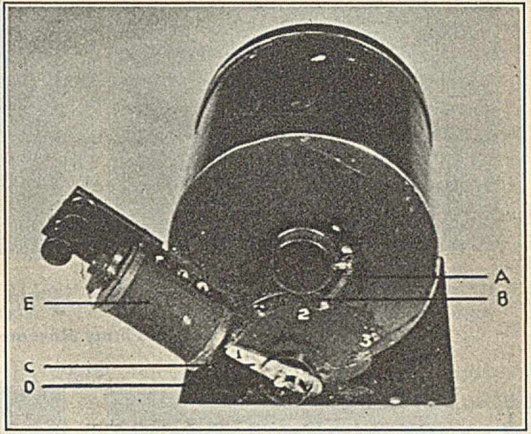

Figure 6—Film Drum, Showing Auxiliary Apparatus Which Operated Shutter

A—Ratchet-lever spring
B—Ratchet lever
C—Shutter arm
D—Shutter-arm spring
E—Electromagnet

Table I—Measurements of Time of Occurrence of Knock

(Degrees of revolution after top dead center)

Figure	From Pressure Records		From Flame Records
	Time knock began	Time knock ended	Time knock began
10	..	24.0	..
11	11.0	14.0	11.5
12	5.5	9.0	5.0
13	..	22.0	17 to 21.5
14	10.0	12.5	10.0
15	3.5	6.5	3.5
16	14.0	17.0	14.5

An attempt was made to compare the time at which combustion was completed in the combustion chamber with the time at which maximum pressure was realized. In case of the flame records it was not possible to determine accurately the angle at which the combustion was completed, because of the difficulty involved in distinguishing between the combustion zone and the afterglow at the time of maximum pressure, but it was possible to determine quite accurately the time at which the flame front contacted the end of the combustion chamber. The results of measurements taken from the pressure records of the angles of revolution at which

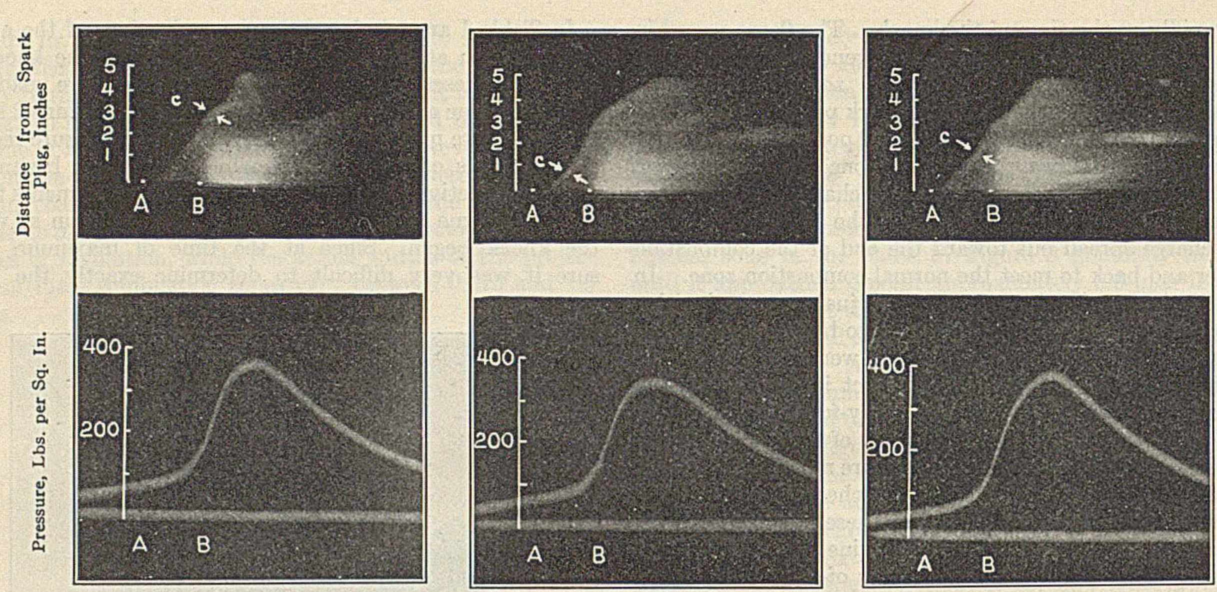

Figure 7—Charge Ignited 20 Degrees of Revolution before Top Dead Center

Figure 8—Charge Ignited 25 Degrees of Revolution before Top Dead Center

Figure 9—Charge Ignited 30 Degrees of Revolution before Top Dead Center

Flame Movement in a Mixture of Benzene and Air

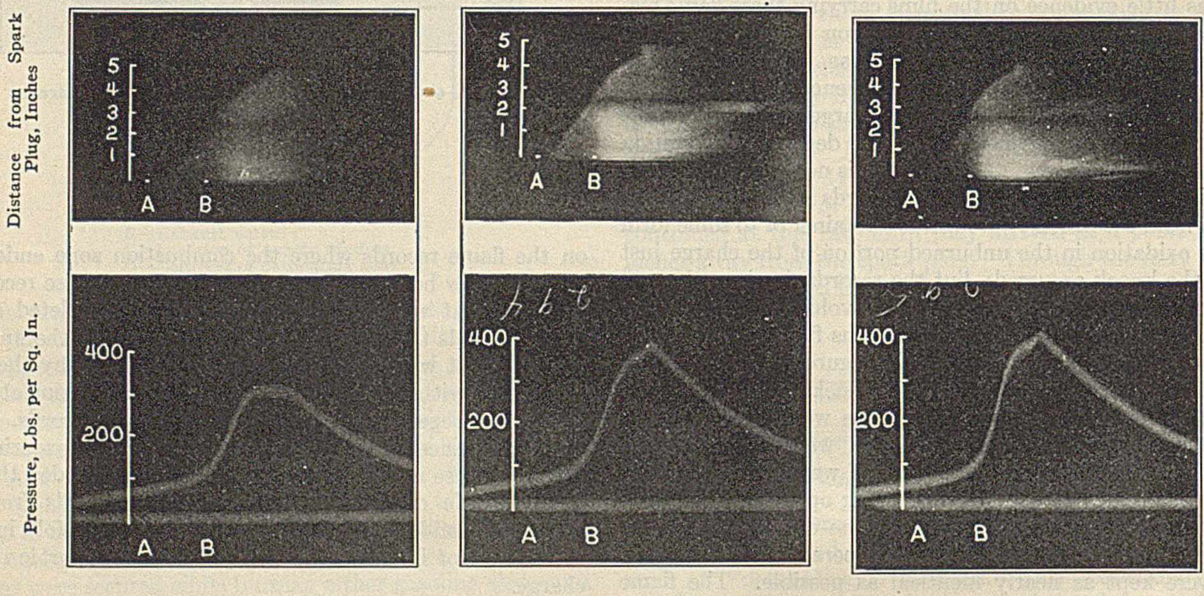

Figure 10—Spark Advance of 20 Degrees

Figure 11—Spark Advance of 25 Degrees

Figure 12—Spark Advance of 30 Degrees

Flame Movement in Engine When Operated with a Fuel Composed of 50 Per Cent Gasoline and 50 Per Cent Benzene

maximum pressure was attained in the combustion chamber and of measurements taken from the flame records of the angles of revolution at which the flame contacted the end of the combustion chamber are tabulated in columns 2 and 4 of Table II.

Table II—Comparison of Time of Maximum Pressure in Combustion Chamber with Time of End of Flame Propagation

(Degrees of revolution after top dead center)

Figure	Time of Max. Pressure	Time of Max. Pressure, Cor. to Constant Volume	Time of End of Flame Propagation	Approx. Duration of Projected Combustion Zones (Col. 3 − Col. 4)
7	16.0	20.5	13.0	7.5
8	13.0	23.0	17.0	6.0
9	8.0	10.0	7.0	3.0
10	18.0	24.0	23.0	1.0
11	14.0	14.0	11.5	2.5
12	9.0	9.0	5.0	4.0
13	24.0	26.0	21.0	5.0
14	12.5	12.5	10.0	2.5
15	6.5	6.5	3.5	3.0
16	17.0	17.0	14.5	2.5
17	18.0	24.0	20.0	4.0

The angles of revolution listed in column 3 of this table are the angles at which maximum pressure would have been realized if the piston had not moved from the top-dead-center position. These values were arrived at by measuring the pressures on the pressure records at 2-degree intervals and correcting these measurements for the volume changes due to the motion of the piston. The data tabulated in column 5 are the differences between the data in columns 3 and 4, respectively. These values are approximately equal to the observed durations of the combustion processes as determined by measuring the distances across the projections of the combustion zones on the flame records at the end of the flame propagation.

Discussion of Results

One of the most significant facts that is brought out by these flame and pressure records is that the phenomenon of knock which heretofore has been recognized in the gasoline engine by its sound and by the characteristic shapes of the

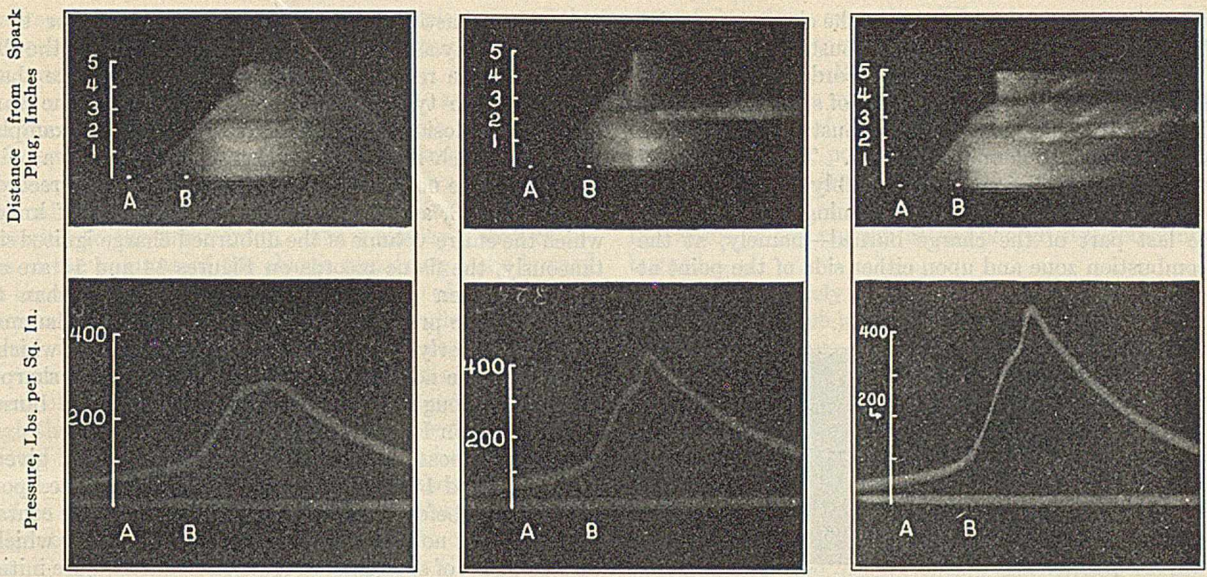

Figure 13—Spark Advance of 20 Degrees Figure 14—Spark Advance of 25 Degrees Figure 15—Spark Advance of 30 Degrees

Flame Movement in Engine When Operated with a Fuel Composed of 25 Per Cent Benzene and 75 Per Cent Gasoline

pressure records is due to a many-fold increase in the rate of inflammation within the latter portion of the charge. In other words, just at the time that the knock begins there is a many-fold increase in the amount of charge beginning to burn, with the emission of light, per unit time. During the course of the present work this characteristic of the knock has been observed in hundreds of knocking explosions in the engine both photographically and visually. The visual observations were made by replacing the film drum with a rotating mirror. Further, the absence of this characteristic increase in the rate of inflammation has been observed in hundreds of non-knocking explosions in the engine.

The flame records, in general, substantiate the results of experiments made with the auxiliary sampling valve (*10*), which indicated that a narrow combustion zone within which the combustion reaction completed itself moved across the combustion chamber. For the sake of clarity it might be well to state at this point that we mean by the combustion zone that region in which oxidation of the hydrocarbons in the fuel takes place, and we do not include the reactions of the products of combustion which are brought about by changes of temperature and pressure. As was mentioned above, the combustion zones are quite distinct upon the negatives of the flame records. They were still more pronounced when the flames were observed in the engine by visual means because the combustion zone was greenish blue and the afterglow was a bluish white or a reddish yellow depending upon the mixture ratio. These records, then, indicate that a combustion zone passes through every portion of the charge and that the products of combustion continue to glow for some time afterwards.

It is believed that the shape of the flame front is convex to the direction of the flame travel as it moves away from the spark plug and passes through the charge. Some evidence for the validity of this belief has been pointed out in the study of the motions of the combustion zone with the sampling valve (*10*). With this instrument it was found that the combustion zone moved more rapidly through the middle portions of the combustion chamber than along the side walls. This peculiarity of the flame travel is probably due to the cooling effect of the walls of the combustion chamber. Consequently, it would be expected that the portion of the charge midway between the ceiling and the floor of the combustion chamber would burn a little more quickly than those portions nearer the walls. Thus, when photographic records of the flames are taken in the manner described above, projections of the convex flame fronts appear upon the records. Therefore, it does not seem to be possible to determine the actual thickness of the flame front at any point in the charge from these records.

The records of the motions of the combustion zones in Figures 10, 11, and 12 just before and during the time of the knock are characteristic of those taken while the engine was knocking incipiently. One of the significant peculiarities of some of these records is the arrest in the flame movement just before the knock occurred. In case of the flame record in Figure 11, for example, it does not seem possible that this decrease in flame velocity is due to a change in volume of the combustion chamber caused by the receding motion of the piston, because the knock occurred at 10 degrees of revolution after top dead center. At this angle of revolution the volume of the combustion chamber had increased only about 5 per cent. In case of the flame record on Figure 12 this arrest in flame movement also appears, and in this explosion the knock occurred at 5 degrees after top dead center. This means that this peculiar decrease in flame velocity occurred in this explosion when the volume of the combustion chamber was practically constant. Consequently it is believed that this phenomenon is similar to the check in the flame progress which was observed in a bomb by Maxwell and Wheeler (*8*, *9*). Kirkby and Wheeler (*5*) find that in bombs this arrest in the flame movement comes at the moment that the "skirt" of the flame contacts the walls of the combustion chamber and that it is accompanied by an arrest in the rate of pressure development. Since the arrests in the rates of flame propagation on Figures 11 and 12 are accompanied by decreases in the rates of pressure rise, it is believed that this may be the correct explanation of this phenomenon in the engine.

During the time of the knock the motions of the combustion zones in Figures 11, 12, and 13 are very interesting. Each of these three different types of knock is frequently recorded when the engine is knocking incipiently. The flame and pressure records in Figures 11 and 13 show that spontaneous ignition occurred in the unburned portions of the charges ahead of the respective flame fronts just at the time the knock began, as indicated by the corresponding pressure records. In other words, at the beginning of the knock in these two explosions the flame records indicate that spontaneous ignition occurred in the unburned portion of the charge at a point distinctly in advance of the normal combustion zone. During the time of the knock the flame recorded in Figure 11 traveled at high velocities from the point of spontaneous ignition both toward the end walls of the combustion chamber and back toward the normal combustion zone. The distortion of the pressure record in Figure 13 is probably due to the fact that the charge in this explosion was burning at three places when the last part of the charge burned—namely, at the normal combustion zone and upon either side of the point at which spontaneous ignition occurred.

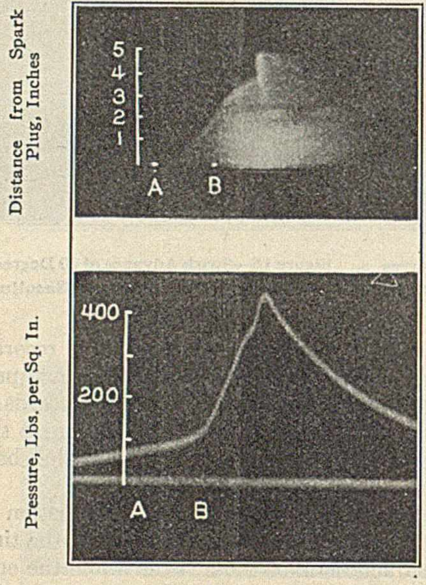

Figure 16—Flame Movement in a Theoretical Mixture of Gasoline and Air in Engine When Charge Was Ignited 20 Degrees before Top Dead Center

The flame records in Figures 14 and 15 show the presence of a faint luminosity in the unburned portion of the charge which was visible for a short interval of time before the knock occurred. As was pointed out above, the presence of this luminosity in the unburned charge at this time may be due either to reflection inside the window retainer or to slow oxidation of the fuel throughout this portion of the combustible mixture. If it is due to slow oxidation, this process apparently had continued until a critical point was reached. At this time the records indicate that the entire volume of the charge in the detonating zone burst into flame simultaneously and that the sharp increase in pressure shown at the time of the knock by the pressure records resulted therefrom. On the flame record shown on Figure 16 there is evidence that spontaneous ignition occurred at a point about 0.5 inch from the end wall of the combustion chamber. From the point of spontaneous ignition the flame spread with great rapidity both toward the end of the combustion chamber and back toward the normal combustion zone. This exceedingly rapid rate of flame spread might be expected if the unburned portions of the charge were near a critical stage.

In regard to the way in which inflammation takes place at the time of knock there seem to be three possibilities. First, at the beginning of the knock spontaneous ignition may occur at a point or at a number of points in advance of the normal combustion zone. This flame then spreads rapidly through the remaining unburned portions of the charge. Second, all of the unburned charge visible through the window may burst into flame simultaneously at the beginning of the knock, instead of at one or several points in advance of the normal combustion zone. Third, the velocity of propagation of the normal combustion zone may increase sharply or to substantial infinity as it passes through the last part of the charge to burn. The records in this paper offer evidence that all three of these types of inflammation occur in the various knocking explosions in the gasoline engine. As examples of knock in which spontaneous ignition occurred at a point in advance of the normal combustion zone, the flame records on Figures 11, 13, and 16 are cited. As examples of knock in which the entire volume of the unburned charge ignited simultaneously, the flame records on Figures 14 and 15 are cited. (Records taken under engine conditions other than those covered in the present paper show this type of inflammation still more clearly.) As an example of knock in which the velocity of the normal combustion zone increased sharply as it passed through the last part of the charge to burn the flame record on Figure 12 is cited.

With the possible exception of the indication given by Figures 14 and 15 of slow oxidation in the unburned portion of the charge before knock began, the flame records contained herein present no evidence as to the mechanism by which the various forms of spontaneous ignition mentioned are initiated. This discussion is therefore concerned simply with the evidence that spontaneous ignition does occur within the knocking portion of the charge, and not with the possible prior events that bring spontaneous ignition about.

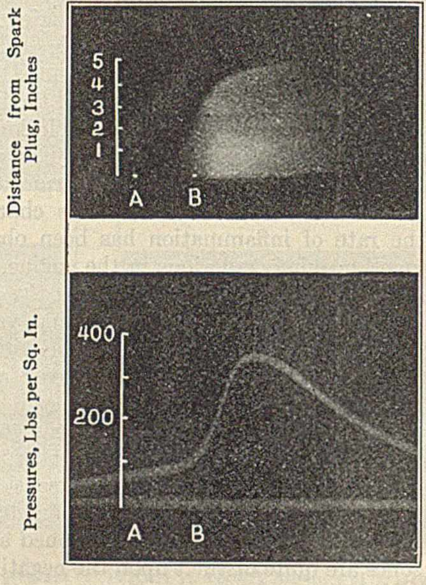

Figure 17—Flame Movement in Engine When Operated with a Spark Advance of 20 Degrees and with a Fuel Which Consists of Gasoline Containing 0.15 Per Cent of Lead Tetraethyl by Volume

It may perhaps be well also to point out the difference between the spontaneous ignition shown on these records and what is commonly called pre-ignition. Pre-ignition is ignition that comes before the time of the ignition spark. Pre-ignition may possibly be due to spontaneous ignition in some cases, but it may also be caused by some hot spot in the engine cylinder, such as an improperly cooled exhaust valve. No pre-ignition occurred during these tests, and every one of the spontaneous ignitions recorded came at least 30 degrees after the spark.

Theories about the detonation phenomenon which agree more or less closely with the facts as observed from these records at the time of the knock have been advanced previously by other investigators, who have for the most part based their opinions upon the results of experiments in bombs. However, experimental data which indicate that any of these speculations might be the correct explanation of the fuel knock in the gasoline engine have apparently never before been obtained.

No attempts have been made to relate the rate of pressure rise to the volume of gas burned per unit time. The reason for this is the lack of information about the transverse shape of the flame front in this combustion chamber and about the directional velocities of the gases in the combustion chamber with respect to the flame front. For a similar reason calculations of the volumes of the charge remaining to be burned at the time the knock begins and calculations of the increases in pressure caused by the knock are not included.

A very interesting phenomenon which is shown on these flame records is the afterglow, or the emission of light by the products of combustion after the combustion zone has passed through the charge. The reasons for believing that this light is emitted by the products of combustion are based upon the experiments with the sampling valve, upon the differences in the colors of the afterglow and of the combustion zone as directly observed, and upon the experiments of David and Davies (*3*). These workers found that, while Clerk "zigzag" indicator diagrams were being obtained, the products of combustion in a special gas engine emitted light for as many as four successive compressions. These results are explained as being due to the formation of carbon dioxide and water molecules which are in an abnormal state, and to the emission of light by these abnormal molecules when the pressures and the temperatures are increased. They believe that the average life of these abnormal molecules may be as long as several seconds. The results of the experiments with the sampling valve are subject to the criticism that it is not known how soon or at what stage the combustion reactions were stopped in the valve itself. But the appearance of the flame records and the conclusion of David and Davies that luminous emission during gaseous explosions does not result solely and directly from chemical combination agree with the conclusion reached from the sampling valve studies—namely, that the true combustion process in the engine occurs within a comparatively narrow zone which moves through every part of the charge.

Some interesting observations have been made of the afterglow on the flame records shown herein. On all the flame records the intensity of the light in the products of combustion increases sharply when the pressure begins to rise rapidly in the combustion chamber. At this time the burned gases between the spark plug and the combustion zone begin to emit light. A significant fact about the afterglow is that the intensity of the light is at a maximum in those portions of the products of combustion which were formed before the pressure began to rise rapidly in the combustion chamber. In case of the flame records of severe knock shown on Figures 14, 15, and 16, a sharp increase in the luminosity of the products of combustion is visible all the way back to the spark plug at the time of the knock. This is believed to be due to the effect of the sharp increase in the pressure upon the products of combustion at the time of the knock. This phenomenon is being investigated further in this laboratory, and it is hoped to discuss it more in detail in a later paper.

Conclusions

1—Starting at the spark plug a flame, or narrow combustion zone, moves progressively through the charge. Oxidation of the fuel is apparently complete within this narrow zone of combustion, but the products of combustion to the rear of the flame front continue to emit light for some time.

2—During normal or non-knocking combustion, the time required for the average flame to travel across the combustion space (under the conditions of these tests) was about 40 degrees of crankshaft revolution.

3—A knocking explosion differs from a non-knocking one only in the way the last portion of the charge burns. The difference is this: Whereas in a non-knocking explosion the flame continues to move at a comparatively constant velocity clear to the end of the combustion space, in a knocking explosion the latter portion of the charge inflames at a much higher rate than normal. This rate is often so high that at the instant of knock the flame appears simultaneously throughout the whole of the portion of the charge still remaining to be burned.

4—The extremely high rate of inflammation in that portion of the charge which burns at the instant of knock is apparently due to auto-ignition occurring within it. This may be caused by temperature induced within that part of the charge by adiabatic compression.

5—The violence of the knock is determined by how large a portion of the total charge is involved in the spontaneous inflammation, or the amount of it still remaining to be burned at the instant knock occurs.

6—The very rapid, and often substantially instantaneous, inflammation that occurs within the portion of the charge which burns at the instant of knock is accompanied simultaneously by a very rapid rise in cylinder pressure. The magnitude of this pressure rise increases along with the intensity of the knock.

7—The one effect upon combustion of the presence of lead tetraethyl in the gasoline is to prevent the extremely rapid inflammation of the latter portion of the charge, and the accompanying pressure rise, which is the knock. Lead tetraethyl has no effect upon the velocity or the character of the flame prior to the time at which knock would have occurred in its absence.

Acknowledgment

The authors take pleasure in acknowledging their indebtedness to E. J. Martin for many valuable suggestions freely given in connection with this work, to A. Straus for supervising the design of the apparatus, and to J. W. O'Donnell for assistance in the control and operation of the engine during the tests.

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Bread Containing Vitamin D to Be Marketed

An agreement has been reached whereby the General Baking Co. will pay a royalty on every loaf of bread it markets, in which the vitamin D element is incorporated. This royalty will go to the Wisconsin Alumni Research Foundation and the Pediatric Research Foundation of Toronto, through whose joint efforts the patents and processes have been worked out. Under the contract these institutions will devote their profits to child welfare and nutritional research. The laboratories of the Pediatric Research Foundation have assumed the responsibility of continuously analyzing the bread to insure and guarantee that it shall supply the vitamin D to the degree research has proved to be adequate and efficacious. It is understood that this introduction of irradiated ergosterol in white bread will involve no increase in price. The two beneficiaries of the agreement, Wisconsin and Toronto, are non-profit institutions.

Solubilities of Gases in Liquids at High Pressure[1]

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THE application of high pressures to industrial processes has led to engineering operations that frequently require a knowledge of solubilities of gases in liquids at pressures higher than those for which such data ordinarily are available. Examples of this type are the separation of gases by preferential solution in a suitable scrubber liquid and the condensation of vapors in the presence of non-condensable gases. Occasionally also the rate of a chemical reaction in the liquid phase is controlled by the solubility of a gaseous reactant.

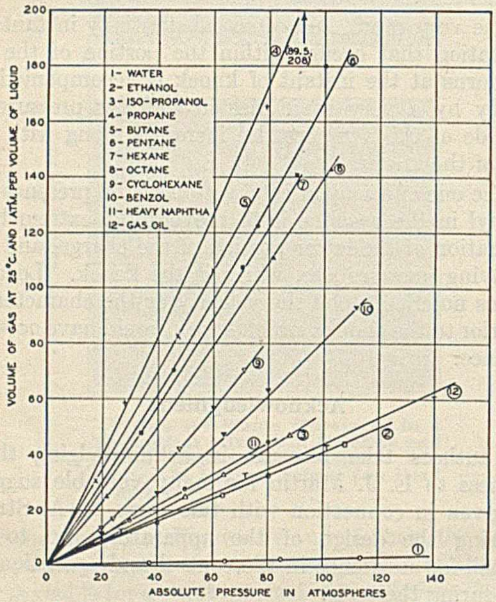

Figure 1—Solubility of Methane at 25° C.

Within experimental error the curve for isopropanol may also be considered as representing solubilities in methanol, normal propanol, isobutanol, and normal butanol.

The determinations of Larson and Black (*3*) on nitrogen and hydrogen in liquid ammonia, and those of Wroblewski (*9*), Sander (*4*), and Hachnel (*5*) on carbon dioxide in water and some organic solvents seem to be the only data on gas solubilities at real high pressures available in the literature. Finlayson (*2*), in attempting to develop a method of separating oxygen and nitrogen in air, studied the behavior of these gases toward various solvents at pressures not exceeding 160 pounds per square inch (10.9 atm.); and the solubilities of air and natural gas in kerosene, mineral seal oil, and various crudes have been determined by Dow and Calkin (*1*) at pressures up to 350 pounds per square inch (23.8 atm.). Larson and Black's data show that the amount of nitrogen and hydrogen dissolved in liquid ammonia is roughly proportional to the pressure up to 150 atmospheres. In the case of carbon dioxide, however, the linear relationship breaks down after the pressure has exceeded a few atmospheres, and thereafter the solubility is lower or higher than that calculated from the atmospheric data according to the solvent used (*4*).

Since these data did not permit of any generalization as to the behavior of other combinations of gases and liquids, a systematic study of the subject was undertaken. This work involved solubility determinations for a number of the common industrial gases in a variety of solvents, covering a wide range of pressure but limited to room temperature. Preliminary experiments by Simard and Sturznickle (*7*) on methane, nitrogen, and hydrogen in water and a series of alcohols gave results which showed in a qualitative way that the solubilities in such systems came close to being straight-line functions of pressure.

Experimental Procedure

Most of the solubilities were determined by saturating the liquid with gas at suitable intervals of pressure and measuring the ratio of solute to solvent in a sample drawn off for analysis. To this end a small amount of solvent was introduced into an evacuated steel cylinder of 2 liters capacity. The gas was then forced in at the highest pressure available and the cylinder agitated in a water bath maintained at 25° C. After the pressure had become constant, the cylinder was taken from the bath and inverted in a vertical position for withdrawal of a sample of the solution. The liquid and the gas separating from it on release of the pressure were collected over mercury in one of three burets, so designed that the volumes could be measured with the same degree of accuracy at any ratio of gas to liquid.

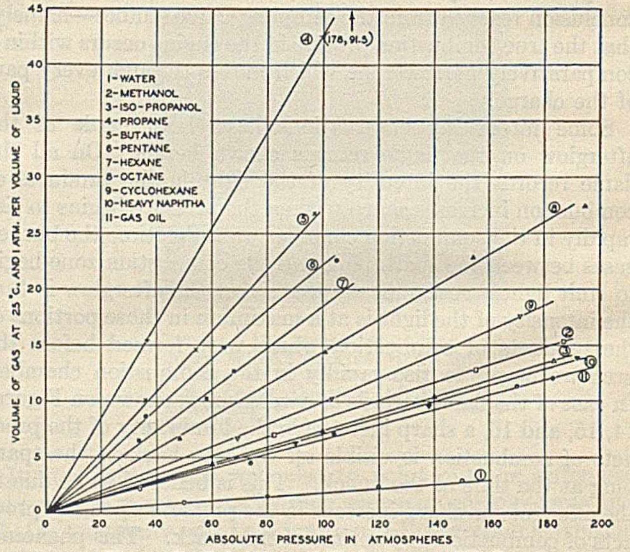

Figure 2—Solubility of Hydrogen at 25° C.

Within experimental error the curve for isopropanol may also be considered as representing the solubilities in ethanol, normal propanol, isobutanol, normal butanol, and benzene.

When the solvent was liquid at room temperature, as was usually the case, the two volumes were read directly and corrections made for the vapor pressure of the liquid and the atmospheric solubility of the gas. Since the liquid was atomized by the sudden release in pressure, complete separation of solute from solvent occurred without any sign of supersaturation, and it was only necessary to wait for drainage of the liquid before the volumes could be read. If the whole sample was in the gas phase, it was analyzed in an

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[2] Present address, Standard Development Co., Elizabeth, N. J.

Table I—Solubilities of Gases in Liquids at Various Pressures

LIQUID	PROPANE		PROPYLENE		HYDROGEN SULFIDE		ETHYLENE		OXYGEN	
	Pressure range	Equation	Pressure range	Equation	Pressure range	Equation	Pressure range	Equation	Pressure range	Equation
	Atm.		*Atm.*		*Atm.*		*Atm.*		*Atm.*	
Gas oil	0–7	$y = 19.1\,(x)$	0–5	$y = 12.1\,(x)$	0–15	$y = 4.17\,(x + 1.7)$	0–41 41–60	$y = 2.84\,(x)$ $y = 12.1\,(x - 30)$	0–70	$y = 0.154\,(x)$
Carbon tetrachloride							0–32 32–60	$y = 7.8\,(x)$ $y = 35.1\,(x - 24.5)$	0–70	$y = 0.31\,(x)$
Ethanol							0–33 33–60	$y = 2.8\,(x)$ $y = 5.5\,(x - 15.6)$		
Heavy naphtha			3–7	$y = 15.1\,(x + 0.7)$	0–9.0	$y = 5.5\,(x)$	0–6	$y = 5.0\,(x)$		
Water									0–70	$y = 0.028\,(x)$
Formic acid									0–70	$y = 0.047\,(x)$
Pentane									0–100	$y = 0.576\,(x)$

y = Volume of gas at 25° C. and 1 atmosphere per volume of liquid.
x = Absolute pressure in atmospheres.

ordinary gas-analysis apparatus, or the solvent was frozen out with carbon dioxide snow. In working with liquids of high vapor pressure, such as the lighter hydrocarbons, it was necessary also to determine the composition of the gas phase in the high-pressure cylinder. With less volatile solvents, however, the pressure of the vapor was usually an insignificant part of the total pressure in the cylinder.

The sample taken for analysis was so small that the pressure drop in the steel cylinder was negligible. After check runs had been made at one pressure, gas was bled from the steel cylinder and further determinations were made at successively lower points. To make sure that no error due to supersaturation in going from a higher to a lower pressure was introduced, the procedure was reversed in several experiments, but without any difference in the results.

Another method, involving measurement of the gas dissolved in a measured amount of liquid by the pressure drop in a previously calibrated reservoir, was used successfully in checking some high solubilities determined by the other procedure. A carefully calibrated Bourdon gage was used for measuring all pressures.

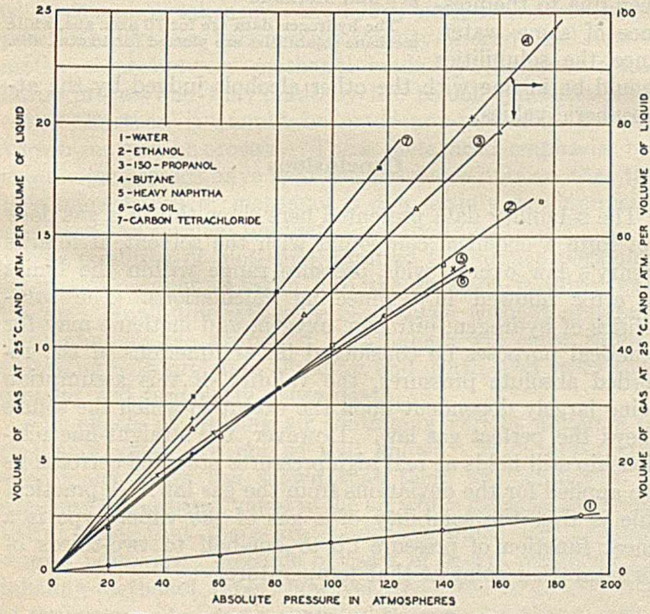

Figure 3—Solubility of Nitrogen at 25° C.

Within experimental error the curve for isopropanol may also be considered as representing the solubilities in methanol, normal propanol, isobutanol, normal butanol, and benzene.

Inasmuch as the work was undertaken to obtain data for engineering use, a somewhat low accuracy, compared with that of ordinary physical measurements, was tolerated in order to simplify the procedure. Although the individual determinations were as a rule checked within 2 per cent, it is believed that the total error of this method is such that the results should not be considered accurate to better than ±5 per cent.

The materials used for the solubility measurements were in general of the highest purity available. The heavy naphtha had a specific gravity of 0.8003 with a vapor pressure of 80 mm. at 25° C. For the gas oil the corresponding figures were 0.8319 and 2 mm. The other hydrocarbons were from 98 to 99 per cent pure.

Discussion of Results

The majority of solubilities determined were for hydrogen, nitrogen, and methane in various alcohols and hydrocarbons as well as water. Except for some of the alcohol curves, which fell so close together that it was impossible to include them all in the plots, Figures 1 to 3 give these results expressed as volumes of gas dissolved per volume of liquid as a function of absolute pressure. The gas volumes are measured at 25° C. and 1 atmosphere. Within the experimental error the curves for isopropanol may be considered representative of a group of alcohols, as indicated under the individual diagrams. The solubilities of hydrogen and nitrogen in benzene also coincide with the isopropanol curves.

The solubilities are not strictly linear functions of pressure, although the deviations from a straight line are hardly noticeable for hydrogen in any of the liquids studied or for nitrogen in the solvents other than heavy naphtha and gas oil. There is a general tendency, however, for the hydrogen and nitrogen solubilities to increase less rapidly with pressure than called for by a straight-line relationship. On methane pressure has the opposite effect, as shown by the curves in Figure 1. That this trend in curvature is due in part to deviations from the perfect gas law is brought out by Figure 4. Here the solubilities of the three gases in isopropanol are plotted against the pressure which the solute would have exerted had it obeyed the perfect gas law, and the resulting straight lines show that the solubilities in question follow Henry's law within the whole pressure range studied. This correction is not sufficient, however, to eliminate the more marked curvature in the case of some of the hydrocarbons.

Regardless of whether the failure to straighten some of the curves is due to factors other than experimental errors, it is apparent that all the data in Figures 1 to 3 might for practical purposes have been obtained from the corresponding atmospheric solubilities. This is illustrated by the following examples chosen at random:

Solubility of methane in methanol at 50 atm. abs. (49 atm. gage):

(1) Read from Figure 1 (curve 3) the value is 24.8
(2) Estimated from solubility at atmospheric pressure:
0.438 (*6*) × 50 = ... 22.0
(3) Estimated from atmospheric solubility with correction of pressure:
Corrected pressure = 54 atm. (*8*) 0.438 × 54 = ... 23.7

The corresponding values for hydrogen in benzene at 100 atm. abs. are:

(1) 7.3 (2) 7.6 (3) 7.6

For nitrogen in gas oil at 100 atm. abs. the following solubilities result:

(1) 9.7 (2) 11.3 (3) 11.1

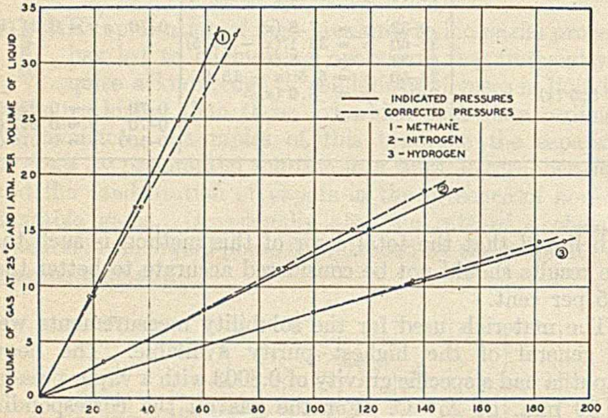

Figure 4—Effect of Pressure Correction on Solubility Curves for Isopropanol

Judging from these examples, high-pressure solubilities of the three permanent gases, hydrogen, nitrogen, and methane, in other liquids may be estimated with engineering accuracy from Henry's law. In other words, the solubilities of these gases in any solvent may be predicted over a wide range of pressure from one experimentally determined point. That a knowledge of the solubility at atmospheric pressure serves this purpose is borne out by the illustrations given above. This may be expressed by the relation $v = k\,p$, where v, the volume of gas dissolved, is measured at atmospheric temperature and pressure. If p is the pressure in atmospheres absolute, k becomes equal to the atmospheric solubility. To obtain better accuracy, p should be corrected for the deviation from the perfect gas law.

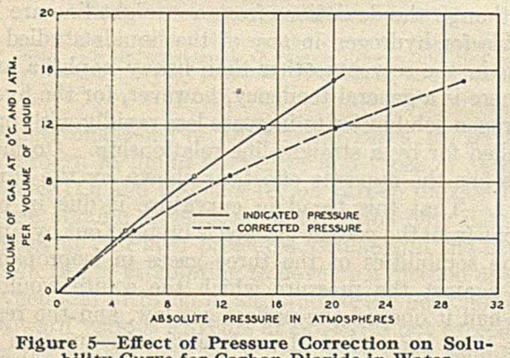

Figure 5—Effect of Pressure Correction on Solubility Curve for Carbon Dioxide in Water

The data for oxygen in five solvents, given in the last two columns of Table I, show that this gas belongs to the same class as hydrogen, nitrogen, and methane. However, in dealing with gases of the vapor type, the linear solubility relationship holds only over a limited pressure range. This is illustrated by the data in Table I for propane, propylene, hydrogen sulfide, and ethylene. The approximate vapor pressures of these materials at 25° C. are, respectively, 10, 11, 20, and 65 atmospheres, and it will be noted that their solubilities in various liquids obey Henry's law only up to about one-half to two-thirds of the saturation point. The behavior of ethane is similar to that of ethylene, as shown by qualitative experiments not recorded in the table.

As would be expected, Henry's law cannot be applied when there is a tendency for the solute to combine chemically with the solvent. An example is carbon dioxide dissolved in water. According to Hachnel's data (*5*), represented by the solid line in Figure 5, the linear function breaks down at about 5 atmospheres, and from then on the solubility increases less and less rapidly with rising pressure. Correcting the pressure of the carbon dioxide for its deviation from the perfect-gas law only increases the curvature, as shown by the dotted line. On the other hand, carbon dioxide behaves normally in many organic solvents. Thus, the data given by Sander (*4*) for carbon dioxide in ethanol, propanol, benzene, and some derivatives of benzene obey Henry's law, since the solubility curves become straight lines when the pressure correction is applied.

Figure 6 gives further aid to the estimation of solubilities in the hydrocarbons. Here the data for methane and hydrogen are plotted as functions of the hydrogen-carbon ratio of the solvent, and it will be noted that all the aliphatic hydrocarbons, as well as cyclohexane, fall on smooth curves. In the alcohols, however, neither the number nor the arrangement of the carbon atoms affects the solvent power to any appreciable extent. Hydrogen is somewhat more soluble in methanol than in the other alcohols, as would be expected from the known solubilities at atmospheric pressure. The lower curves for nitrogen and methane in ethanol may have been due to the presence of some water, since the solubilities should be in line with the other alcohols judged by the atmospheric values.

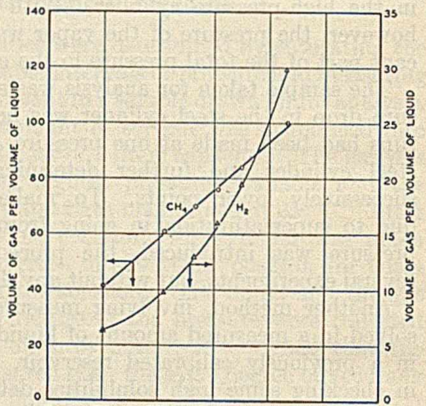

Figure 6—Effect of Hydrogen-Carbon Ratio of Solvent on Solubilities of Hydrogen and Methane

The hydrogen data are for 70 atm. abs. while methane solubilities are plotted for 48 atm. abs.

Conclusions

The solubility data presented here show that if a gas does not form a chemical compound with the solvent, it follows Henry's law over a wide pressure range within the limits of error allowed in engineering calculations. The solubilities of hydrogen, nitrogen, oxygen, and methane may for practical purposes be considered linear functions of the recorded absolute pressures, the validity of this assumption being largely dependent upon the extent to which the solute obeys the perfect gas law. However, the straight-line relationship still holds at real high pressures provided corrections are applied for the deviations from the gas law. A practical rule is that the solubility of a gas of the vapor type is a linear function of pressure up to one-half to two-thirds of its saturation point at that temperature.

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Methanol Antifreeze and Methanol Poisoning[1]

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Although both crude and refined methanol have been used for many years as a radiator antifreeze in communities where there are wood-distillation plants, it has not heretofore been distributed widely for that purpose, principally because its cost to the consumer has exceeded that of denatured ethyl alcohol. With the advent of synthetic processes for making methanol from stack gases, water gas, and coal gas, it is now available in large quantities. While it is difficult to ascertain the exact quantity consumed due to inability to obtain information as to the total methanol that dealers have on hand, it is estimated that 4,000,000 gallons have been used in automobile radiators during the past season.

Obviously, the physical and chemical properties of methanol are satisfactory for its use as an antifreeze. However, owing to the existence of much conflicting and confusing data regarding the poisonous effect of methanol, an investigation was desirable as to its toxicity, not only from its particular use as an antifreeze, but from a consideration of fundamental information which could be used in evaluating the dangers from manufacturing and handling this product. The United States Bureau of Mines was requested to make the investigation, and as this bureau is interested in both the manufacture and the health hazards of this new product of the mineral industry, it acceded to the request and entered into a formal agreement with the Carbide and Carbon Chemicals Corporation, the Du Pont Ammonia Company, and the Commercial Solvents Corporation, to carry out the investigation coöperatively. The investigation is in progress at the bureau's Pittsburgh Experiment Station under the direction of its chief surgeon, and with the advice and consultation of the U. S. Public Health Service and a group of toxicologists and public health officials.

This report has been prepared mainly to acquaint persons interested in this type of investigation with the plan, procedure, and the test equipment that is being used. As much of the work is still in progress it will not be possible to give much detailed information regarding the results obtained. However, summary statements regarding the health hazards from antifreeze methanol will be made where they are justified by the results obtained to date. When the investigation has been completed, a detailed report will be published.

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It has been stated in a previous publication (*1*) that the observations and discussions of the poisonous effect of methanol which have been recorded in the literature are conflicting and confusing. It has been shown beyond doubt that methanol is a poison and will produce serious poisoning when enough is taken into the body; also, that there is no practical difference between the toxicity of crude and refined methanol or between methanol made by the wood-distillation process and that made by the recent synthetic processes. Further, it cannot be made non-poisonous by any known method or process. These facts need emphasis, because some persons have held the erroneous opinion that the poisonous action of methanol is due mainly to impurities and that the purified product is relatively less toxic.

The quantity of methanol required to produce poisoning when the product is taken into the stomach is fairly well known. Small amounts have been taken without apparent harm, but on the average 1 to 2 ounces will cause serious poisoning with probable blindness and death, and twice that amount will frequently cause death.

The effects of inhaling air containing various amounts of methanol vapor are not so well known. Wide experience over many years has shown that there are conditions of exposure to methanol vapor in the air which cause no apparent harm; also, that there are conditions which will produce serious poisoning. Records of cases of severe poisoning by inhaling methanol vapor, however, show the large majority of serious cases to have occurred in the use of methanol, principally as a solvent for paints and varnishes, in relatively small confined and unventilated places. The use of shellac dissolved in methanol for coating the interior of beer vats has been an important source of trouble of this kind. The potential health hazards from air containing methanol vapor thus depend on the degree of exposure; accordingly, the safety of methanol for antifreeze purposes depends on whether or not the exposure involved in a particular usage will exceed the range of tolerable exposure.

Less is known of the dangers to health from absorption of methanol through the skin. In reviewing the literature, no conclusive information could be found that serious poisoning has been acquired in this manner. A few cases are described as possibly being due to skin absorption. In these the exposure was either so slight that it is rather difficult to believe that the trouble was due to absorption of methanol through the skin, or the situation was complicated by the possibility of high concentrations of vapor in the air breathed. When one considers the large amounts of methanol that have been used and the frequency with which it has undoubtedly come in contact with the skin, it is apparent that no appreciable hazard exists from this manner of exposure to methanol as an antifreeze. It is understood that death has been caused in animals by application of methanol to the skin; but from all the information that can be obtained, the quantities applied and the mode of application are not comparable with reasonable practice in the use of an antifreeze.

Scope of Bureau of Mines Investigation

In general, the investigation undertaken by the Bureau of Mines is an extended study of the toxicity of methanol when acquired by inhaling air containing its vapor and when acquired by absorption through the skin. The study will not include work on the toxicity of methanol when taken into the stomach, because the ingestion of enough methanol to cause poisoning is not an apparent hazard from its legitimate use as an antifreeze.

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[1] Received March 11, 1931. Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

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The phases of the investigation which have been in progress during the past year, and which are being continued, are: (1) a laboratory investigation of the toxicity and physiological action of methanol when acquired by inhalation and skin absorption; (2) a field investigation of the concentration of methanol to which persons are exposed in private garages, public garages, in the operation of automobiles, and in dispensing it for antifreeze purposes; (3) a study of the exposure and health experience of persons engaged in the manufacture of methanol; and (4) a study of the use of agents to guard the public against the use of methanol for beverage purposes.

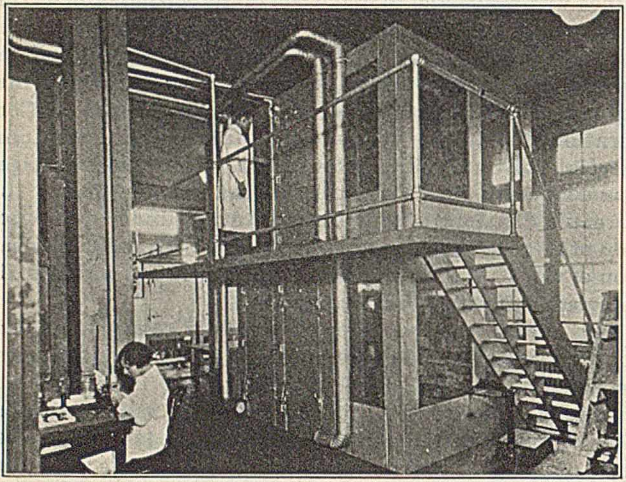

Figure 1—Battery of Four Chambers Used for Exposing Animals to Methanol Vapor

Laboratory Experiments with Animals

Kinds of Animals Used and Observations Made—Monkeys, dogs, and guinea pigs are being used in the laboratory study. The animals are observed for symptoms, special attention being paid to ophthalmoscopic examination of the eyes. The blood and urine are analyzed for methanol and formic acid. In addition, certain clinical determinations are made, such as pH, sugar, and albumin in the urine, and non-protein nitrogen and total and pre-formed creatinine in the blood. Blood examinations are made for hemoglobin, red blood cells, white blood cells, differential counts, and blood platelets.

At the end of the predetermined exposure periods or in case of death, the animals are autopsied and specimens of tissue taken for microscopic examination.

Range of Concentrations. Inhalation Experiments—It is aimed to cover concentrations and periods of exposure ranging from those which cause no effect to those which produce definite effects. The concentrations which are being studied at present are 1000, 4000, and 15,000 p. p. m. methanol vapor in air. The periods of exposure are 4, 8, and 24 hours daily or continuous exposure.

Test Procedure and Equipment for Inhalation Experiments—It has been the experience of the writers that more often than not, and particularly with long-term experiments which require repeated exposure to obtain threshold response, the experimental technic has a more deleterious effect than the gas or vapor in question. To minimize these influencing factors as much as possible, the Bureau of Mines uses equipment with which exposure can be made under well-ventilated, comfortable housing conditions to which the animal has become accustomed during a pre-test period.

The apparatus for exposing animals to methanol vapor–air mixtures is shown in Figures 1, 2, 3, and 4. Briefly, the apparatus consists of a battery of four gas-tight chambers of approximately 288 cubic feet capacity. They are constructed entirely of metal-covered framework and wire-embedded plate glass. The doors are of the refrigerator type and close against tubular rubber gaskets. Each chamber is fitted with all-metal cages for housing the animals. The vapor-air mixtures are made by continuous vaporization of a known quantity of methanol and dilution of these vapors by a known volume of air.

Referring to Figure 3, air is exhausted from chamber *a* at a constant rate of eight air changes an hour by means of exhaust fan *b*, controlled by the pressure at plate orifice *c*, indicated by manometer *d*. Fan *b* connects to each unit of the battery through take-offs from a header, *u*. All chambers are operated at the same rate of air change; individual variations in pressure on the orifices due to variation in pipe resistance to the header are balanced by means of slide gates in the ducts between each chamber and the header. The exhaust is delivered to a chimney through the roof at a point where it will not contaminate the intake to the chambers. Figure 4 shows the manifold system used for avoiding zone ventilation in collecting the air from within the chamber and delivering it to the exhaust duct.

The air removed from the chamber is supplied at slightly less than atmospheric pressure by an intake through an expansion box, *v* (Figure 3, also see Figure 4). The air which enters the expansion box is a mixture of two-thirds fresh air from the exterior of the room, *e*, and one-third fresh room air that has passed through the vaporizer, *f*, and which contains the desired quantity of methanol vapor. The methanol vapor is prepared by continuous, complete evaporation of a known and constant amount of liquid methanol. Evaporation is effected by dropping the methanol onto a gauze ribbon suspended in a glass jacket, *f* (also see Figure 2), through which air passes countercurrent to the flow of methanol down the ribbon. Evaporation is complete on the ribbon, thus assuring a vapor composition identical with the liquid composition. The liquid methanol is delivered to the wick by a chemical-proportioning pump, *g*, which can be readily adjusted to give a flow of a few drops a minute to a steady stream. The flow from the pump to the vaporizer is observed by means of a sight glass, *h*, whose drop size is calibrated and thereby affords a means of checking the rate. The quantity of methanol delivered to the vaporizer in unit time is measured by means of a graduated supply reservoir, *r*.

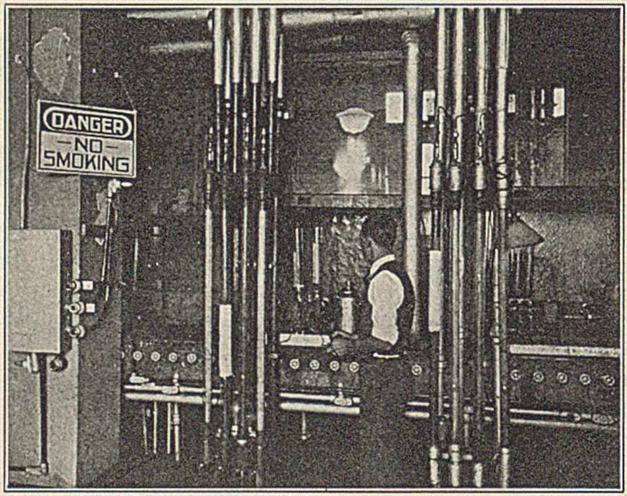

Figure 2—Proportioning Pumps and Vaporizers Used for Preparing Methanol Vapor–Air Mixtures

The air used for vaporizing the methanol is delivered to

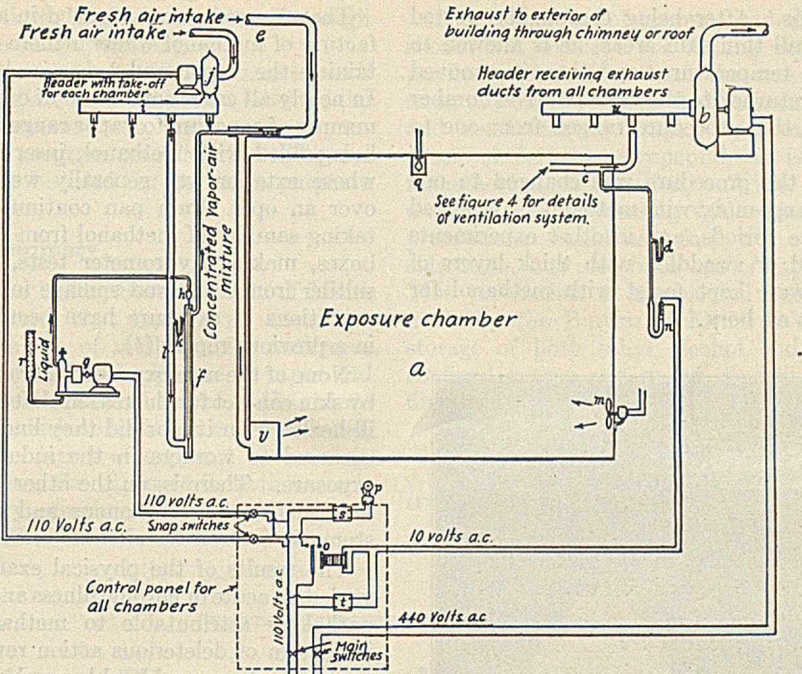

Figure 3—Diagrammatic Sketch of Apparatus for Preparing, Controlling, and Making Exposures to Vapor-Air Mixtures (Shown as a Single Unit of a Battery of Four Chambers)

the vaporizer from a header supplied by a motor-driven pressure blower, *j*. As previously stated, the quantity is one-third that admitted to the chamber, *a*, and is controlled by maintaining a constant pressure on a plate orifice, *l*, as indicated by manometer *k*. The concentrated vapor-air mixture (three times the desired concentration) is led through a duct to the main fresh-air intake, where it is diluted to the desired concentration. It escapes into the main fresh-air stream through a number of small holes which facilitate mixing. Further mixing takes place in the duct to the expansion box *v*, and in the expansion box.

A fan, *m*, with motor outside the chamber to exclude sources of ignition of a possible explosive atmosphere, continuously stirs the air in the chamber and, assisted by the exhaust system shown in Figure 4, prevents stratification and zone ventilation. The air from the fan is directed toward the door and the expansion box, and away from the animals so that they would not be subject to draughts.

The quantity of methanol delivered by the pump is observed hourly and the concentration of vapor is calculated from these observations, ventilation conditions being maintained constant. The calculated concentration is frequently checked by chemical analysis.

Safety Features of Exposure Equipment—The danger from explosions in working with such comparatively large volumes of a combustible vapor-air mixture is obvious. An explosion of the volume contained in one of the chambers described would wreck the laboratory and very possibly take the lives of attendants. While reliance is placed on attendants to operate the apparatus safely, the outcome of human fallibility or of unforeseen accident is too well known to trust the attendant alone. Therefore, in the design of the test equipment, several precautions have been taken to prevent the occurrence of a concentration of vapor high enough to fall within the explosive range, which for methanol is between 6.0 and 36.5 per cent by volume in air.

The major conditions which might result in the formation of an explosive mixture are: the interruption of ventilation by failure of the exhaust fan, *b*, with a continuation of the admission of methanol vapor, or an increase in the volume delivered by pump, *g*, to that which will create an explosive mixture under normal ventilation, or both. To overcome these a pressure-actuated electrical contact, *n*, is connected to the same line as the orifice-plate manometer, *d*, so that any drop in pressure on the orifice will break a circuit to a relay solenoid, *o*, which in turn will open the circuit to pump *g* and also to the vaporizer air-supply fan, *j*, thus stopping the admission of methanol vapor. At the same time the relay opens the circuit to *g* and *j*, it closes the circuit to a bell, *p*, the ringing of which attracts the attention of an attendant so that the animals will not suffer from lack of ventilation. To avoid too rapid pumping, the volume of the reservoir *r* is kept below the quantity required to produce an explosive vapor-air mixture in the chamber, even though the entire content is delivered practically instantaneously to the vaporizer. Further, the length of the ribbon, or rather the surface is kept below that which will allow vaporization of enough vapor to produce an explosive vapor-air mixture under normal air supply; and finally, the duct from the vaporizer is inserted in the fresh-air duct in a manner that will tend to discharge the vapors back through the fresh-air duct should the conditions favoring an intake of air by the chamber be interrupted.

It may be mentioned that where it is necessary to make toxicological investigations with vapor-air mixtures which fall near or within the explosive range, the experiments are conducted in a pressure-resisting chamber equipped with a parchment-covered relief door. A chamber of this kind has been described in a previous publication (*2*).

Apparatus for Skin-Absorption Experiments—Figure 5 shows the apparatus used for skin-absorption experiments with dogs. It consists of a stanchion or "pillar" arrangement that closes tightly around the neck for holding the dog and at the same time keeping his head in a small chamber supplied with fresh air to prevent the possibility of inhalation of methanol vapor. This fresh-air chamber is maintained at a positive air pressure of 0.5 cm., as indicated by a manometer at the top. The dog stands in a zinc-coated iron drain pan which catches the methanol drippings and from which they are conveyed through a drain line to a receptacle. Methanol is poured along the back of the dog until it runs down his

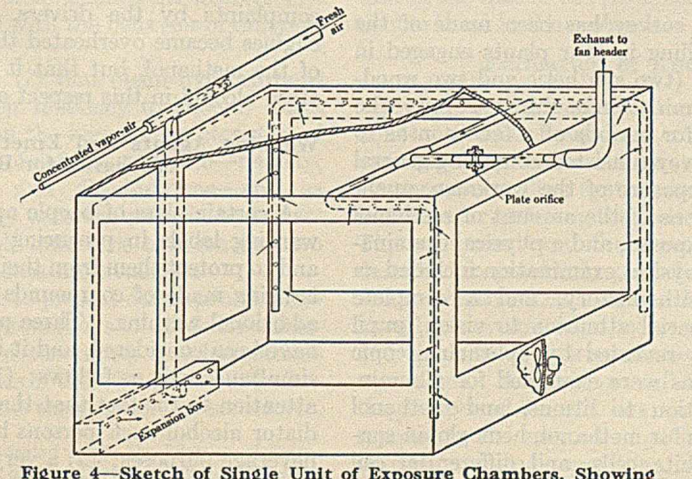

Figure 4—Sketch of Single Unit of Exposure Chambers, Showing Ventilation System

sides and legs in streams. After being thoroughly wetted including abdomen and all thin skin areas, he is allowed to dry completely at room temperatures and then is removed from the apparatus and returned to the kennel. The number of daily applications by this procedure ranged from one to three.

In some experiments the procedure was changed to one whereby the animal was kept moist with methanol by repeated application for 30-minute periods, and in other experiments the animal was wrapped or swaddled with thick layers of cotton bandage which were kept moist with methanol for periods of 30 minutes to an hour.

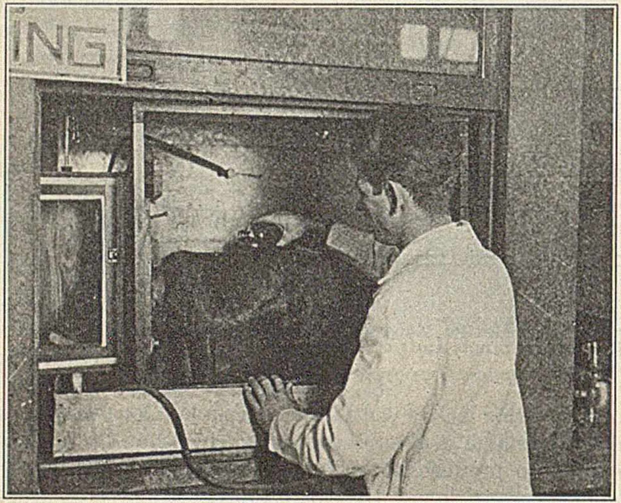

Figure 5—Apparatus for Subjecting Dogs to Skin Applications of Methanol

Summary of Results to Date from Laboratory Experiments with Animals—As laboratory work with animals is still in progress, it seems inadvisable to report detailed findings until all the work, particularly the long-term experiments included in the plan of the investigation, has been completed. It has been found that there is a range of concentrations of vapor in air and periods of exposure which cause no apparent harm, and that there are also conditions which cause methanol poisoning in monkeys, dogs, and guinea pigs. The conditions which cause harm to these animals, however, are of much greater severity than would accompany the use of methanol antifreeze.

Exposure and Health Experience of Men in the Methanol Industry and Men Using Methanol Antifreeze

Field Investigations—A survey has been made of the conditions of exposure prevailing in four plants engaged in the manufacture of methanol (two synthetic and two wood-distillation), and physical examination of thirty-six men who have worked in these plants for periods of a few months to ten to fifteen years. This survey consisted of making general observations of duties and exposure of the workmen, quantitative chemical determinations of the amount of methanol to which the workmen were exposed, and a physical examination of the workmen. The physical examination included an occupational history, a health history, and a complete physical examination with special attention to vision, pupil reflex, and eye pathology as revealed by ophthalmoscopic examination. Urine specimens were examined for albumin, sugar, specific gravity, reaction to litmus, and methanol content; and blood specimens for methanol, hemoglobin content, number of red and white cells, and differential cell counts.

These persons were engaged in all operations of the manufacture of methanol wherein there was exposure to air containing the vapor and exposure by contact with the skin. In nearly all cases both types of exposure were present. The manner of exposure to vapor ranged from working over drums being filled with methanol, inserting bungs in filled drums whose exterior was generally wet with drippings, working over an open drain pan continuously wet with methanol, taking samples of methanol from drums and stillhouse lookboxes, making hydrometer tests, and general exposure resulting from leaks and spillage in the working places. The conditions of exposure have been described in more detail in a previous report (*1*).

None of the men expressed fear of exposure to the vapors or by skin contact for the reason that they had never experienced ill health from it, nor did they know of serious effects having occurred to workers in the industry from this manner of exposure. There is, on the other hand, universal knowledge that methanol is poisonous and cannot be taken into the stomach.

The results of the physical examination of these men revealed no acute or chronic illness and no defective vision or eye pathology attributable to methanol. There was also no indication of deleterious action revealed by blood and urine analysis. In a considerable number of cases of comparatively severe exposure, methanol was found in both the blood and urine when the specimens were taken after several hours' work. This confirms actual exposure and the acquiring of methanol but, on the other hand, it substantiates experience that certain amounts of methanol can be acquired without apparent harm. Specimens taken the following morning from several of these persons showed methanol to be practically absent in most cases and markedly reduced in the others. In all cases the amounts in the blood and urine were far below those that have been found in the laboratory part of the study to be harmful to dogs.

In addition to this study of workmen at plants where methanol is produced, a study was made of twenty-four drivers of trucks in which methanol antifreeze was used exclusively for a period of approximately $2^1/_2$ months (November 15 to December 20, and January 3 to February 17). A mixture of approximately equal parts antifreeze methanol and water was maintained in the radiators at all times; this mixture provides freezing protection to approximately −25° F.

The drivers of these trucks were examined at the time of starting the period of use and then were reëxamined at the end of the period, with particular attention given to eye pathology. A comparison of the findings for these examinations revealed no evidence of harm. Also, there were no complaints by the drivers. They stated that when the engines became overheated they occasionally noted the odor of the methanol, but that it was very similar to denatured ethyl alcohol in this respect and caused no discomfort.

Warning Agents and Emetics to Discourage the Use of Methanol for Beverage Purposes

A certain class of people apparently overlook or disregard warning labels in procuring alcohol for beverage purposes, and to protect them from their own folly or ignorance a study is being made of compounds which might be added to give additional warning. Three possible types of warning agents have been considered, and it is probable that all may be used simultaneously, as follows: (1) a color of bright hue to draw attention to the fact that the substance differs from the radiator alcohol such persons have also previously misused for beverage purposes; (2) a very unpleasant taste to emphasize further the fact that the substance is not suitable for beverage purposes; and (3) an emetic to produce vomiting if enough of the methanol is taken to cause poisoning.

It is believed that ample precautions will have been taken if these four means of warning are used—a poison label on the container, a color, an unpleasant taste, and an emetic, together with an educational program teaching that methanol never has been and cannot be used for beverage purposes without serious consequences.

Summary

The information which the United States Bureau of Mines has obtained to date indicates that there is no hazard to health from the reasonable use of methanol for antifreeze purposes. Many of the conditions of exposure to vapor and by contact with the skin, which were observed in the manufacture of methanol and for which no health hazard was found, are very comparable to the degree of exposure observed in usage as an antifreeze. Also, the exposure in both cases is below that which laboratory experiments with animals have indicated to be harmful either from inhalation of vapor or absorption through the skin.

The users, manufacturers, and distributors of methanol should not construe the finding that there is no apparent public-health hazard from the reasonable use of methanol as an antifreeze to mean that methanol is safe for all purposes and conditions of usage. Rational precautions must be observed for this compound, as is necessary in the safe manufacture, distribution, and use of many chemical commodities. When dealing with volatile combustible liquids, precautions should be taken, not only from a health consideration, but also from one of explosion and fire hazards. This precaution is emphasized because the investigations made by the Bureau of Mines have revealed instances of storage of both ethyl alcohol and methanol antifreeze in confined spaces and under conditions which constituted a fire and explosion hazard.

Literature Cited

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Detonation Characteristics of Some Aliphatic Olefin Hydrocarbons[1]

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The relative tendencies to knock in an engine have been measured for twenty-five olefin hydrocarbons. These measurements were made, not on the hydrocarbon alone, but in admixture with gasoline, and the results have been expressed on a molecular basis using the antiknock effect of aniline as the standard of comparison.

Upon this basis there appear very great differences among the knocking properties of these compounds, and even among isomers, including those in which the structural difference lies only in the position of the double bond.

Definite relationships between molecular structure and tendency to knock have been found for these compounds. With the straight-chain olefins it was observed (1) that in a homologous series the tendency to knock increased with increasing length of the saturated carbon chain, (2) that in an isomeric series the tendency to knock decreased progressively with centralization of the double bond, and (3) that the tendency to knock is roughly determined by the length of the longest saturated carbon chain. Branched-chain olefins show a somewhat similar behavior; the tendency to knock decreases upon the introduction of a double bond, and the knocking tendency apparently is related, not only to the position of the double bond, but also to the branched structure o the molecule.

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It HAS previously been found that the paraffin hydrocarbons exhibit a wide variation in their tendency to knock in an engine, even among different isomers (*6*). This present paper is concerned with the behavior of different aliphatic olefin hydrocarbons.

It was pointed out long ago (*7*) that olefin hydrocarbons differ from the paraffins in their tendency to knock. Data have been published (*1*, *2*, *8*) on the knock characteristics of several isolated aliphatic olefins of definite structure—namely, 2-pentene, trimethylethylene, and diisobutylene—and as might be expected from analogy with the paraffin hydrocarbons, there appears considerable difference between the two isomeric pentenes upon which data are available.

It is the purpose of this paper to present data upon twenty-five unsaturated aliphatic hydrocarbons of definite structures and to point out some of the rather simple relations between the knock characteristics of these hydrocarbons when burned in a gasoline engine, and their molecular structures. The structure is to be considered not only as the arrangement of the carbon atoms, which have been found to be important in the case of the paraffins, but also as the position of the double bond in the molecule.

Evaluation of Knocking Properties

As in previous work (*6*), the tendencies of these hydrocarbons to knock have been compared in a single-cylinder, variable-compression engine which was equipped with an evaporative cooling system and fitted with a bouncing-pin indicator for matching the fuels in respect to antiknock quality. This equipment and the method of operating it have been described in previously published work (*4*).

The relative knocking tendencies under these conditions have been evaluated in terms of aniline, a knock suppressor, and the unit of this evaluation has been called the aniline equivalent. A positive aniline equivalent indicates that the compound knocks less than the reference gasoline and represents the amount of aniline, expressed as the number of centigram-mols per liter, which must be added to the reference fuel to produce a fuel that is equivalent in tendency

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to knock to a 1-molar solution of the compound in the reference gasoline—that is, to a solution containing 1 gram-mol of the compound made up to a volume of 1000 cc. with the reference gasoline. A negative aniline equivalent indicates that the compound knocks more than the reference gasoline, and represents the amount of aniline, expressed again as centigram-mols per liter, which must be added to the molar solution of the compound in the reference gasoline to make it equivalent in tendency to knock to the reference gasoline.

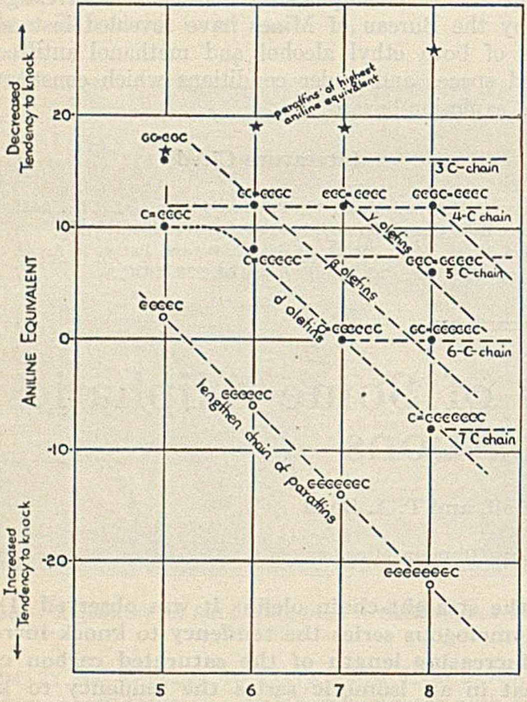


Figure 1—Detonation Characteristics of Straight-Chain Olefins

For example, the aniline equivalent of 3-heptene (mol. wt. 98) is 12. This means that 98 grams of the compound made up to a liter with gasoline (about a 14 per cent solution of the hydrocarbon by volume) is equivalent in knock to a liter solution of aniline (mol. wt. 93) in gasoline containing $^{12}/_{100} \times$ 93 grams of aniline (about 1.2 per cent solution by volume). Similarly, the aniline equivalent of −8 for 1-octene (mol. wt. 112) means that 112 grams of the octene and $^{8}/_{100} \times$ 93 grams of aniline made up to a liter with gasoline knocks the same as the reference gasoline. This makes the solution contain about 16 per cent octene and 0.9 per cent aniline by volume.

The precision of the measurement obtained in this way has been found to be usually within ±1 unit of aniline equivalent for compounds upon which two or more determinations have been made. Those compounds upon which check determinations have been made with samples from different sources are so indicated in the tables. Unfortunately some of these hydrocarbons have been available in limited quantities, so that only one determination of knocking tendency was possible and, although one determination represents the average of four or five separate bouncing-pin readings, the precision is possibly less in some cases than the figure given, due to unavoidable variations in engine conditions during the period while the measurements were being made.

In order to convey some conception of the magnitude of this scale of knock rating, it may be stated that, when tested alone or without admixture with gasoline, 1-octene, which has an aniline equivalent of −8, and 2, 4-dimethyl-2-pentene, which has an aniline equivalent of 18, begins to knock at compression ratios of 3.4:1 and 8.8:1, respectively, under certain specified conditions in the engine used in this work (*5*). These pure hydrocarbons are equivalent in knock to a mixture of 45 per cent 2, 2, 4-trimethylpentane in *n*-heptane and of 30 per cent benzene in the isoöctane, respectively. In other words, the respective octane numbers (*3*) are 45 and 130. The reference gasoline was equivalent to a mixture of 55 per cent of the isoöctane and 45 per cent *n*-heptane; its octane number was 55. These data are indicative only of the range covered by the aniline equivalent scale; they do not permit translation of this scale to another directly.

The aniline-equivalent method of expressing knock ratings provides a convenient and uniform basis for comparing compounds representing a wide range in tendency to knock. This basis furnishes a measure of the partial knock effect of each compound in gasoline at concentrations which are comparable with those in which such a compound might actually be present in commercial fuels. At concentrations below about 40 per cent by volume the computed aniline equivalent, either positive or negative, has been found to be substantially independent of concentration for a number of compounds investigated. This is, of course, due to the fact that there is direct proportion between amounts of aniline and amounts of compound which are equivalent in respect to knock; and the aniline equivalent might be defined as the amount of aniline, per unit amount of compound, added to a given quantity of gasoline. But the aniline equivalent as computed at concentrations below 40 per cent by volume has been found to be not necessarily an index to the behavior of the compound in greater concentrations with gasoline, or even in the pure state.

Although the numerical values of the aniline equivalents reported in this investigation depend somewhat upon experimental conditions and, of course, upon the reference fuel, there is no evidence at this time that the relative knocking tendency of one olefin hydrocarbon with respect to another when measured in this way is materially altered by reasonable changes in engine conditions.

The use of a molecular basis for evaluating the knocking properties of the compounds is especially convenient because of the consistent relationships between molecular structure and knock rating which then become apparent. It is the main purpose of this paper to present and to discuss some of these relationships.

Sources of Hydrocarbons

The twenty-five olefin hydrocarbons, data upon whose knocking behavior are presented here, have all been carefully synthesized by laboratory methods. Many of them have been prepared by P. L. Cramer, R. H. F. Manske, and F. K. Signaigo in the General Motors Research Laboratories. For a number of the olefins, and especially for the series of isomeric straight-chain octenes, the writers are indebted to Graham Edgar and the staff of the Ethyl Gasoline Corporation, and for the 2-hexene to G. M. Maverick and the Standard Oil Development Company. The sample of 2-methyl-2-butene was donated by Thomas Midgley, Jr., and the diisobutylenes, by F. C. Whitmore.

The preparation of the olefins in a state of absolute purity is not an easy matter. In almost every case there is the possibility of the presence of at least two isomers, the *cis* and *trans* modifications, and no attempt has been made to separate these isomers. In some cases, also, there is the possibility of isomerism in which the position of the double bond varies. For this reason only those olefins are included in which, judging from the method of preparation and the physical properties, the possibility of impurity from this source is reduced to a minimum. Perhaps the best indication of the purity of these compounds, and the structure as represented by the structural formulas given, is the consistency of the relations between their structure and their detonation characteristics, since a relation between these two sets of properties has previously been observed for the paraffin hydrocarbons.

To present a complete picture of the aliphatic olefin hydrocarbons of 5, 6, 7, and 8 carbon atoms, or those boiling within the present gasoline range is a matter of considerable difficulty. This arises from the enormous number of isomers which are possible of existence. Thus the number of paraffin isomers of 5, 6, 7, and 8 carbon atoms are (excluding geometric isomers) 3, 5, 9, and 18, respectively. The possible number of olefin hydrocarbons, however, is 5, 13, 27, and 68, respectively. Of the 68 possible octenes, only 8 have been previously reported in the literature as having been prepared in a state approaching purity.

For these reasons the twenty-five hydrocarbons upon which data are presented have been selected so as to comprise, not only those whose probable purity was high, but also those which would exhibit clearly the general relations between their chemical structure and their behavior when burned in a gasoline engine.

Data on Straight-Chain Olefins

The data on the straight-chain olefins are shown in Table I, which gives the structure of the compound, its aniline equivalent, and also the aniline equivalent of the corresponding paraffin. For convenience these data are shown graphically in Figure 1, where the aniline equivalent of each compound has been plotted against the number of carbon atoms in its molecule. The points representing the different compounds are designated by a conventional abbreviated structural formula of that hydrocarbon. In these designations, the hydrogen atoms are not represented; thus, the point CC═CCCC represents 2-hexene with 6 carbon atoms and an aniline equivalent of +12, and the point marked C═CCC-CCC represents 1-heptene with 7 carbon atoms and an aniline equivalent of 0. For comparison, the series of straight-chain paraffins is also represented in the figure.

Table I—Straight-Chain Olefins

HYDROCARBON	STRUCTURE	ANILINE EQUIVALENT	ANILINE EQUIVALENT OF CORRESPONDING PARAFFIN	INCREASE IN ANILINE EQUIVALENT DUE TO UNSATURATION
1-pentene	C═C—C—C—C	10	1	9
2-pentene	C—C═C—C—C	16[a]	1	15
1-hexene	C═C—C—C—C—C	8	−6	14
2-hexene	C—C═C—C—C—C	12	−6	18
1-heptene	C═C—C—C—C—C—C	0[a]	−14	14
3-heptene	C—C—C═C—C—C—C	12[a]	−14	26
1-octene	C═C—C—C—C—C—C—C	−8[a]	−21	13
2-octene	C—C═C—C—C—C—C—C	0	−21	21
3-octene	C—C—C═C—C—C—C—C	6	−21	27
4-octene	C—C—C—C═C—C—C—C	12[a]	−21	33

[a] Two or more complete determinations.

The data plotted show a number of interesting relationships between the structures of these olefins and their tendencies to knock.

(1) A first series of relationships is indicated by the dotted lines directed towards the lower right-hand corner of the chart. The line through the paraffins *n*-pentane, hexane, heptane, and octane shows a decrease in aniline equivalent with an increase in molecular weight. Similarly, the line drawn through 1-hexene, 1-heptene, and 1-octene, which is approximately parallel to the paraffin line, also shows the decrease in aniline equivalent accompanying the addition of CH_2 groups to an olefin. It is to be observed that 1-pentene does not lie on the straight line, and there are other indications that the lines for the *n*-paraffins and α-olefins would cross if they could be extrapolated to the gaseous hydrocarbons of low molecular weight. A general phenomenon similar to the regularity observed with the olefins is also marked by the line through 2-pentene, 2-hexene, and 2-octene, where again the lengthening of the saturated chain decreases the aniline equivalent or increases the knocking tendency. This relation also holds with the double bond in the 3 position, as in the case of the line drawn through 3-heptene and 3-octene. It is possibly significant that the lines as drawn are approximately parallel. It appears that the lengthening in this way of the longest saturated carbon chain of a straight-chain olefin produces a substantially constant change in the tendency of the olefin to knock. This relation is quite similar to the effect observed in paraffin hydrocarbons, and is substantially the same quantitatively.

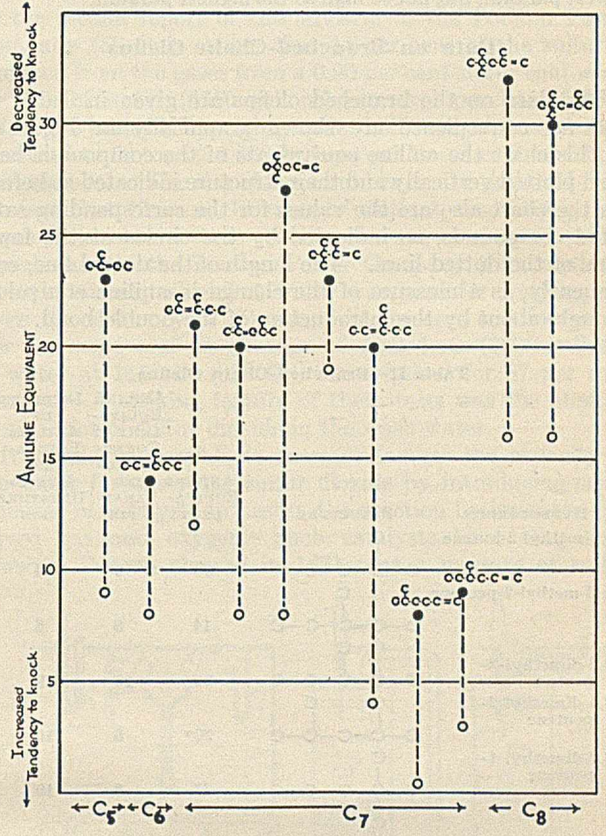


Figure 2—Detonation Characteristics of Branched-Chain Olefins

(2) Another relation between molecular structure and tendency to knock in an engine is illustrated by the vertical lines on the chart. The vertical line through the octenes passes successively through the isomeric 1-octene, 2-octene, 3-octene, and 4-octene. In this isomeric series the aniline equivalent increases, and the tendency to knock decreases, as the double bond is centralized or is located closer to the center of the molecule. There is a similar relation in the case of the heptenes, hexenes, and pentenes. It is also interesting to see that each time the double bond is moved towards the center of the molecule by a distance of one carbon atom, in these isomeric series, it accompanies a substantially constant increase in aniline equivalent.

(3) Let us also consider the relations as illustrated by the horizontal lines shown on the chart. The upper line passing approximately through 1-pentene, 2-hexene, 3-heptene, and 4-octene represents a substantially constant aniline equivalent and also passes through compounds whose longest saturated carbon chain is 4 carbon atoms long. A similar line through 1-hexene and 3-octene indicates the 5-carbon chain and the line through 1-heptene and 2-octene, a 6-carbon atom chain. Parallel lines may be drawn through 1-octene and 1-pentene, respectively. This series of horizontal lines has a substantially regular interval between them, indicating that, irrespective of molecular size, a decrease in the length of the longest saturated carbon chain produces an increase in the aniline equivalent.

(4) The area on the chart occupied by the straight-chain olefins is possibly of significance. The line through these olefins defines a line of maximum knock and it appears that the aniline equivalents of these worst olefins decrease with increase in molecular size. A line through 2-pentene, 3-heptene, and 4-octene

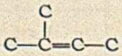
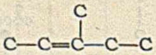
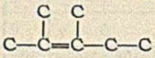
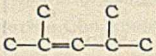
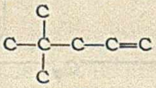
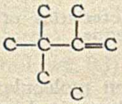
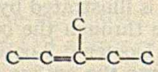
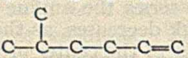
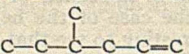
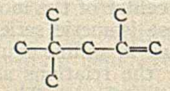
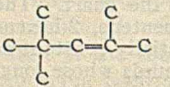
defines a line of minimum knock, since these represent the most centralized structures possible for straight-chain olefins of their molecular size; and it appears that, as the molecular weight increases, these best of the straight-chain olefins have substantially the same aniline equivalents.

The area occupied by the straight-chain olefins may also be compared with that occupied by the paraffin hydrocarbons. To define the latter area, stars have been placed on the chart to represent the branched paraffins of highest aniline equivalent; a line through these points and the line through the normal or straight-chain paraffins defines the area occupied by the paraffins. The straight-chain olefins lie within this space. For a given molecular size and within the range covered by these data, any straight-chain olefin has a higher aniline equivalent than the lowest paraffin, but not so high as the highest paraffin.

Data on Branched-Chain Olefins

The data on the branched olefins are given in Table II, and for convenience are shown graphically in Figure 2. In this chart the aniline equivalents of the compounds have been plotted vertically and their structure indicated as before. On the chart also are the values for the corresponding saturated compounds, as indicated by the circles at the lower ends of the dotted lines. The length of the dotted line, consequently, is a measure of the change in aniline equivalent brought about by the introduction of the double bond.

Table II—Branched-Chain Olefins

Hydrocarbon	Structure	Aniline Equivalent	Aniline Equivalent of Corresponding Paraffin	Increase in Aniline Equivalent Due to Unsaturation
C_5: 2-methyl-2-butene	 $C-\overset{\substack{C\\\vert}}{C}=C-C$	23	9	14
C_6: 3-methyl-2-pentene	 $C-C=\overset{\substack{C\\\vert}}{C}-C-C$	14	8	6
C_7: 2,3-dimethyl-2-pentene	 $C-\overset{\substack{C\\\vert}}{C}=\overset{\substack{C\\\vert}}{C}-C-C$	21	12	9
2,4-dimethyl-2-pentene	 $C-\overset{\substack{C\\\vert}}{C}=C-\overset{\substack{C\\\vert}}{C}-C$	20[a]	8	10
2,2-dimethyl-4-pentene	 $C-\overset{\substack{C\\\vert}}{\underset{\substack{\vert\\C}}{C}}-C-C=C$	27	8	19
2,2,3-trimethyl-3-butene	 $C-\overset{\substack{C\\\vert}}{\underset{\substack{\vert\\C}}{C}}-\overset{\substack{C\\\vert}}{C}=C$	23[a]	19	4
3-ethyl-2-pentene	 $C-C=\overset{\substack{C\\\vert\\C\\\vert}}{C}-C-C$	20	4	16
2-methyl-5-hexene	 $C-\overset{\substack{C\\\vert}}{C}-C-C-C=C$	8	0	8
3-methyl-5-hexene	 $C-C-\overset{\substack{C\\\vert}}{C}-C-C=C$	9	3	6
C_8: 2,2,4-trimethyl-4-pentene	 $C-\overset{\substack{C\\\vert}}{\underset{\substack{\vert\\C}}{C}}-C-\overset{\substack{C\\\vert}}{C}=C$	32	16	16
2,2,4-trimethyl-3-pentene	 $C-\overset{\substack{C\\\vert}}{\underset{\substack{\vert\\C}}{C}}-C=\overset{\substack{C\\\vert}}{C}-C$	30	16	14

[a] Two or more complete determinations on samples from separate sources.

These olefins with branched chains are of special interest as they represent the structural condition of a double bond combined with a varied branched structure. The position doubtless affects the detonation characteristics, as was found to be the case for the straight-chain olefins; and it has previously been found that the arrangement of a branched structure is of great influence on the aniline equivalent. It is to be expected that the knocking tendencies of these compounds will be related both to the position of the double bond and to the arrangement of the carbon atoms. On account of the enormous number of possible isomers of 5, 6, 7, and 8 carbon atoms, which comprise 113 compounds, a complete survey of these hydrocarbons is out of the question at present, and attention is confined to those upon which data are presented.

It is clear from the chart that these hydrocarbons exhibit a wide variety of tendencies to knock, and show a number of interesting regularities:

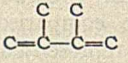
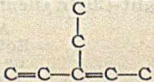
(1) All these hydrocarbons show greater aniline equivalents than the corresponding saturated paraffin compounds. The differences do not appear constant. By analogy with the straight-chain olefins, it might be expected that the greatest change would accompany the introduction of a double bond so as to break up a long chain of CH_2 groups, and there is some qualitative indication that this is so sometimes.

(2) It is to be expected that an olefin of the paraffin of highest aniline equivalent would be a compound also of a high value. In the case of the heptenes the most centralized structure is found in 2,2,3-trimethyl-3-butene, which has only one possible position for the double bond. This compound has an aniline equivalent greater than the corresponding paraffin, which is the highest heptane. An olefin of the highest octene, 2, 2, 3, 3-tetramethylbutane, of most branched structure, does not exist. Approximations to the best octene would probably include 2, 2, 4-trimethyl-3-pentene, which, however, is not so high as the tetramethylbutane. Absolute determination of whether the best aliphatic hydrocarbon of 8 carbon atoms is an olefin or paraffin would involve, of course, the preparation of an enormous number of hydrocarbons.

Data on Aliphatic Diolefins

Another variation in structure with the aliphatic olefins is the case of the introduction of two double bonds into the molecule, forming diolefins. Attention is confined to the four diolefins, data upon which are shown in Table III.

Table III—Diolefins

Hydrocarbon	Structure	Aniline Equivalent	Aniline Equivaof lent Corresponding Paraffin	Increase in Aniline Equivalent Due to Unsaturation
2,3-dimethyl-1,3-butadiene	 $C=\overset{\substack{C\\\vert}}{C}-\overset{\substack{C\\\vert}}{C}=C$	38	19	19
1,5-hexadiene	C=C—C—C—C=C	6	−6	12
2,4-hexadiene	C—C=C—C=C—C	29	−6	35
3-ethyl-1,3-pentadiene	 $C=C-\overset{\substack{C\\\vert\\C\\\vert}}{C}=C-C$	24	4	20

These compounds show a behavior, with respect to their tendency to knock in an engine, in good agreement with what might be expected from the known behavior of the olefins already considered. Thus, the two hexadienes have aniline equivalents greater than *n*-hexane, and the 2,4-hexadiene, with more centralized double bonds, has a much greater aniline equivalent than 1,5-hexadiene, whose double bonds are much less centralized and leave a greater length of unbroken and unbranched carbon chain. The 3-ethyl-2, 4-pentadiene, and the 2,3-dimethyl-1,3-butadiene in which there are present the conjugated double-bond systems as well as side chains, exhibit a somewhat similar behavior.

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Metallic Ions as Catalysts for the Removal of Sulfur Dioxide from Boiler Furnace Gases[1,2]

H. F. Johnstone[3]

UNIVERSITY OF ILLINOIS, URBANA, ILL.

THE recent development of the central power station resulting from the integration of facilities formerly located in numerous small plants has brought renewed interest in the problem of the removal of sulfur compounds from the furnace gases. Utilization of low-grade fuels, in the form of both coal and refinery wastes, has also aggravated the question. The extensive publicity given to the investigations on this subject by the London Power Company has been followed with interest in this country (*5*). This paper reports the preliminary results of an investigation in the Chemical Engineering Division of the University of Illinois Engineering Experiment Station on the general subject of stack gases. The research is a coöperative investigation conducted with the Utilities Research Commission, Inc., of Chicago. The data have been taken for the most part from a progress report to the experiment station and to the commission dated September 20, 1930.

The primary object of the work was to increase the solubility of sulfur dioxide in water, or aqueous solutions, to such an extent that the amount of water required for the removal of sulfur dioxide from gases containing very small concentrations of this constituent would be reduced to a point that would make the process economically and mechanically feasible. A specific example is its application to the scrubbing of gases from boiler furnaces. Another is its application to the removal of sulfur compounds from smelter fumes. A secondary object of the work was the production of sulfuric acid from the sulfur compounds in the gases being scrubbed. The higher the concentration of the acid produced the easier would be its disposal either as a trade waste or as a useful by-product.

In another paper the author has shown that between 70 and 90 per cent of the sulfur in coal appears in the flue gases after combustion according to the method of firing used (*1*). Of this portion approximately 97 per cent exists as sulfur dioxide and 3 per cent as sulfur trioxide or sulfuric acid vapor. These values correspond to an average concentration of about 0.325 per cent of the dioxide and 0.008 per cent of the trioxide in the gases from a high-sulfur coal. Because of these very small concentrations, the amount of water required for removal of the sulfur dioxide is enormous. Thus, it may be shown that, assuming no oxidation of the dissolved gas, for the removal of 75 per cent of the sulfur dioxide in the gases from 1 ton of coal containing 4 per cent sulfur, 21,000 gallons of water would be required at 25° C. If the temperature of the water were 50° C., 57,300 gallons would be required. When it is considered that many modern power plants burn as many as 4000 tons of coal a day, the stupendous volume of water required for washing the gases and the enormous size of the mechanical equipment for pumping and scrubbing become apparent.

Although in actual practice some oxidation of the dissolved sulfur dioxide by the oxygen from the flue gases takes place, the amount of water required approximates these figures. In the second report of the advisers to the London Power Company (*5*), it is shown that 44 per cent of the sulfur is removed from the gases from a 0.90 per cent sulfur coal when 27 tons of water (6750 gallons) are used per ton of coal. When the boiler is operating under half load, this amount is increased to 50 tons (12,500 gallons) per ton of coal for 67 per cent removal. The size of the scrubber can be gathered from the fact that 10.5 and 13 seconds' contact, respectively, are required to obtain these results. It was also noted in the experiments of the London Power Company that, contrary to expectations, when hot water was used for washing the gases the efficiency of the scrubbing process was increased. For the same coal an average of 15.2 tons (3800 gallons) of water at 145° F. (63° C.) was required for 87 per cent removal. A striking feature of these tests was the absence of any odor of sulfur dioxide in the wash water.

It should be possible to increase further the capacity of the water for absorbing sulfur dioxide by introducing small amounts of catalysts to hasten the reaction between the dissolved gas and oxygen. Such catalysts have long been known. Deacon showed in 1871 that a mixture of sulfur dioxide and air in the presence of copper sulfate is converted to sulfuric acid. Later the same invention was made by Roessler and was specially applied to the absorption of acid smoke. Wyld states that the process is hardly applicable to the manufacture of sulfuric acid, but possibly to that of copper sulfate from waste sulfur dioxide. The same process, extended to include salts of manganese, iron, and tin, was patented by Clark in 1888 (*7*). Titoff (*6*) investigated various catalysts for the oxidation of sodium sulfite solutions and

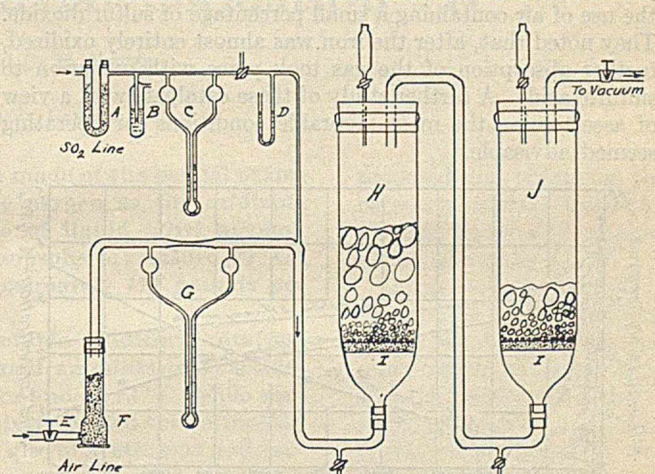

Figure 1—Apparatus for Determining the Catalytic Effect of Metallic Ions on the Removal of Sulfur Dioxide from Gases by Water

A—Drying tube containing anhydrone
B—Pressure regulator containing sulfuric acid
C—Flowmeter for sulfur dioxide; 25 to 100 cc. per min.
D—Manometer
E—Needle valve on compressed-air line
F—Drying tube containing calcium chloride
G—Flowmeter for air; 5 to 25 liters per minute
H—Scrubbing tower containing washing solution
I—Coarse porous plate
J—Scrubbing tower containing standard sodium hydroxide solution, hydrogen peroxide, and indicator

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[2] Published by permission of the Director of the University of Illinois Engineering Experiment Station.

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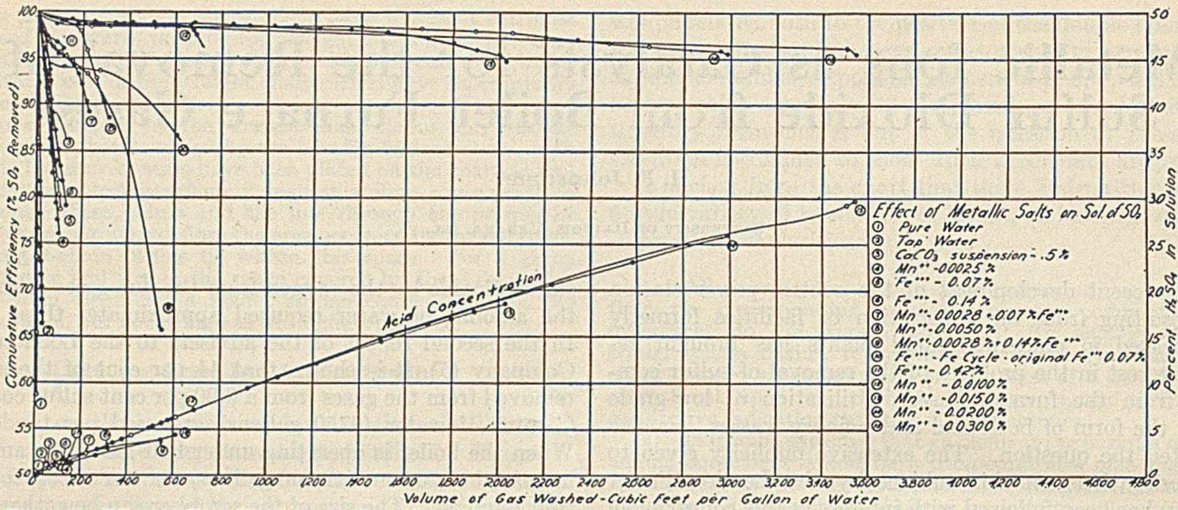

Figure 2—Effect of Metallic Ions on Capacity of Water for Absorbing Sulfur Dioxide from Air Mixtures Containing 0.325 Per Cent Sulfur Dioxide

concluded that the reaction is monomolecular with regard to the sulfite concentration and that, within certain limits, the concentration of oxygen has no influence on the velocity of oxidation. These results were later confirmed by Reinders and Vles (*4*), who found, on further investigation of the catalysis by salts of copper, iron, nickel, and cobalt, that each catalyst has its activity over a characteristic pH range. Thus, copper and iron salts are active from a pH of 4 to 12 and show an optimum at pH 8 to 10, while nickel and cobalt are active only in alkaline solutions. Recently Ralston (*3*), Leaver (*2*), and others, developed a method for oxidizing the ferrous sulfate in spent leaching solutions to ferric sulfate by the use of air containing a small percentage of sulfur dioxide. They noted that, after the iron was almost entirely oxidized, further absorption of the gas took place with oxidation to sulfuric acid. A further study of these catalysts with a view of ascertaining the most favorable conditions for operating seemed advisable.

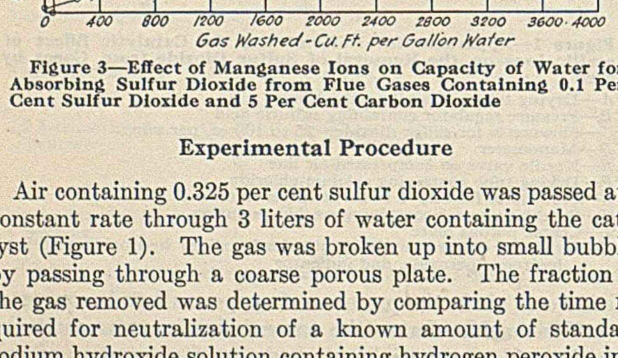

Figure 3—Effect of Manganese Ions on Capacity of Water for Absorbing Sulfur Dioxide from Flue Gases Containing 0.1 Per Cent Sulfur Dioxide and 5 Per Cent Carbon Dioxide

Experimental Procedure

Air containing 0.325 per cent sulfur dioxide was passed at a constant rate through 3 liters of water containing the catalyst (Figure 1). The gas was broken up into small bubbles by passing through a coarse porous plate. The fraction of the gas removed was determined by comparing the time required for neutralization of a known amount of standard sodium hydroxide solution containing hydrogen peroxide in a second tower with that required when no sulfur dioxide was removed. The efficiency of the scrubber was thus determined at short intervals and both the differential and cumulative efficiencies could be calculated. The sulfates of iron, manganese, and nickel and various combinations of these and with copper, zinc, and chromium were used for catalysts. The concentrations varied from 0.028 to 4.2 grams per liter of the metallic ion.

Results

The results for iron and manganese ions are shown in Figure 2. Nickel ions showed no catalytic effect in concentrations up to 1.5 grams per liter. The curves show that, in concentrations as low as 0.0028 per cent, manganese ions exert a strong catalytic action, increasing the capacity of the water for absorbing sulfur dioxide by approximately 600 per cent at this concentration. As the concentration of manganese ions is increased the effect of the increasing acidity of the solution on the catalysis is overcome. For a concentration of 0.03 per cent manganese an acid concentration of 29.6 per cent sulfuric acid may be attained before the differential efficiency falls to 30 per cent. During this time 3540 cubic feet of gas per gallon were scrubbed with an average efficiency of 95.5 per cent.

The catalytic effect of ferric ions is somewhat less than that of manganese. Definite promoter action is shown when a very small concentration of manganese is added to dilute ferric solutions. In the case of iron salts as catalyst the capacity of the solution for dissolving sulfur dioxide is greatly increased by circulating the solution over scrap iron whereby the concentration of the catalyst is increased and that of the acid decreased.

Copper Ions as an Inhibitor

An interesting case of negative catalysis, or inhibitor action, was discovered when an attempt was made to repeat the experiments with manganese ions in a scrubber constructed of brass. It was found that the presence of a trace of copper ions was sufficient completely to inhibit the action of manganese in any concentration. Removal of the copper by precipitation as copper sulfide was not sufficient to prevent the inhibition. Copper ions, however, have no effect on the catalysis by ferric ions. The presence of the ions of zinc, nickel, chromium, and the alkali metals neither inhibits nor promotes the catalysis by manganese ions.

When lime is added to the scrubbing water in the absence of any catalyst, there is no oxidation of sulfur dioxide and, while the efficiency is high at first, as soon as an amount of the gas necessary to form calcium sulfite and to saturate the water is absorbed the efficiency drops to zero. This indicates that the partial pressure of sulfur dioxide over solutions of calcium bisulfite is greater than that in the gases and therefore this salt will not be formed when flue gases are washed with water containing lime. On this basis the amount of calcium oxide required per ton of coal containing 4 per cent sulfur is 140 pounds.

Experiments Using Flue Gases

Application of the laboratory results was made with a small single-effect rotary scrubber having a capacity of about 100 cubic feet per minute. On account of the small capacity the water used for washing was recirculated from a reservoir. The pump, valves, and connecting piping were constructed of lead and the washer was lead-lined to prevent the attack of the acid. The flow of water was maintained constant at 8 gallons per minute. Gases were drawn from the breeching of the university power plant after the air preheater. Since they were somewhat diluted by leaks in the blower, they entered the washer at about 250° F. and having a composition of 5 per cent carbon dioxide, 15 per cent oxygen, 0.1 per cent sulfur dioxide.

The effect of the presence of manganese ions on the capacity of the washing water for absorbing sulfur dioxide is shown in Figure 3. The initial concentration of manganese was 0.025 per cent, although it was increased somewhat by evaporation. The efficiency of the washer was determined by finding the sulfur dioxide–carbon dioxide ratio before and after the washer. This expediency was necessary in order to eliminate the effect of air leaks between the points of sampling and also the effect of fluctuations in the sulfur dioxide content of the gases. Although the efficiency of the washer operating on flue gases was a great deal lower than that of the laboratory scrubber, it compared favorably with that obtained by other large-scale methods. Furthermore, since the time of contact between the gas and liquid in this washer was of the order of only $^1/_{20}$ second, the great increase in efficiency per unit time is apparent. The results further show that with the catalyst the volume of water required is approximately 270 gallons ($1^1/_4$ tons) per ton of coal.

Further work on the application of these catalysts to the removal of sulfur dioxide from flue gases is in progress.

Acknowledgments

The author wishes to express his appreciation to D. B. Keyes, in charge of research in chemical engineering at the University of Illinois, for his kind suggestions concerning the work. Thanks are also due George A. Lorenz for a part of the laboratory measurements.

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Studies in Liquid Partial Oxidation—II[1,2]

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A catalytic study has been made of the partial oxidation of ethyl alcohol, using oxygen as the oxidizing agent, and in the presence of liquid ethyl alcohol. The work was first done at atmospheric pressure (72° C.) and then repeated at approximately 170 pounds per square inch (100° C.).

Certain soluble and insoluble oxidizing catalysts caused the formation of small amounts of acetaldehyde at atmospheric pressure and at 72° C. while certain insoluble oxidizing catalysts caused the formation not only of acetaldehyde but also of acetic acid and carbon dioxide at the higher pressure and temperature.

THE partial oxidation of organic liquids using air as the oxidizing agent in the presence of a catalyst is a subject that has received very little attention in spite of its importance. It is important because the liquid phase, with its high specific heat, permits a better control of temperature. Temperature control is an essential factor in partial oxidation. On the other hand, the use of the liquid instead of the vapor phase presents at least two new difficulties. One is the question of contact between gas, liquid, and catalyst; and the other, the development of a catalyst which will operate at relatively low temperatures. Most of these organic liquids are volatile and partial oxidations operated under pressure in order to keep the organic compound in a liquid condition are dangerous.

The question of contact has already been investigated at the University of Illinois, and various methods have been proposed for obtaining the necessary contact between the gas, liquid, and catalyst in the laboratory (*1*, *2*).

It was thought advisable to attempt the liquid-phase partial oxidation of ethyl alcohol, using oxygen as the oxidizing agent and testing the action of all the common types of catalysts. Approximately one hundred fifty catalysts were tried in this investigation.

Apparatus and Procedure

The apparatus used for these semi-quantitative tests was a Schott filter funnel, which consists of an ordinary glass tube funnel with a sintered glass disk. The alcohol, together with the dissolved or suspended catalyst, was placed above the porous plate and oxygen was forced in at the bottom through the plate and up through the liquid. The bubbles of oxygen formed on the surface of the porous plate were, of course, extremely small. The top of the funnel was closed with a tinfoil-coated rubber stopper, through which was passed a Hopkins condenser to return as much alcohol as possible from the exit gases. Eight funnels were used at the same time. Each funnel was surrounded by a steam-heated water bath which maintained the temperature of the alcohol between 70° and 75° C.

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[1] Received March 6, 1931. Presented before the Division of Industrial and Engineering Chemistry at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931. Published by permission of M. S. Ketchum, Director of the Engineering Experiment Station, University of Illinois.

[2] The details of this work together with other experimental results will be published later in the form of a bulletin of the Engineering Experiment Station.

Both 95 per cent and anhydrous alcohol were used. At the end of the run the sample was tested for aldehyde by the Schiff's reagent and titrated for acetic acid.

Oxidation at Atmospheric Pressure

It was found that at atmospheric pressure, under which these first catalytic studies were made, no acetic acid was formed. Except in one instance, the oxidation went only as far as aldehyde. Cerium oxide in the presence of alkali produced acetic acid, formic acid, aldehyde resin, and carbonic acid. The reaction was carried out in either the acid or neutral condition in most of the other cases, however.

Group I. Metals in Group I of the periodic system, such as copper and copper-zinc couple, gave strong tests for aldehyde. Copper salts, such as copper acetate and copper chloride, also indicated the formation of aldehyde. Potassium, sodium, lithium, and gold salts did not show any catalytic activity.

Group II. Soluble mercury salts, such as the acetate, showed catalytic activity, but the insoluble salts, such as mercuric iodide, did not. Soluble salts of zinc and cadmium also showed activity—for example, the acetates—but not insoluble cadmium salts. Calcium and barium salts showed no activity.

Group III. In this group the same relation between solubility and activity appeared. The soluble aluminum salts, such as the acetates, showed activity, while the insoluble chloride did not. Perborate, boric acid, and thallium salts showed no activity. However, boron as a metal in the amorphous state, aluminum, lanthanum, and indium all showed some activity.

Group IV. Lead and tin salts, especially the soluble ones, were particularly active, also the lead and tin metals. Titanium salts and titanium metal acted the same way. On the other hand, thorium, zirconium, cerium, and germanium salts all showed negative results.

Group V. Vanadium pentoxide and vanadium acetate proved effective. Phosphotungstic acid and phosphomolybdic acid, as well as phosphorus pentoxide, were active. Potassium arsenate, bismuth acetate, vanadium trichloride, potassium pyroantimonate, antimony pentoxide, columbium chloride were all inactive, as was antimony metal and phosphorus and antimony pentoxide.

Group VI. Chromous acetate, potassium dichromate, chrom alum, and selenious acid were all effective, as could be predicted, probably acting more as oxidizing agents than as oxidizing catalysts. Uranium acetate, molybdic acid, tungstic acid, sodium tungstate, chromium acetate, and selenium and tellurium powder were all inactive.

Group VII. Manganese acetate, sulfate, oxide, and metallic manganese were all quite active.

Group VIII. The soluble iron, cobalt, and nickel salts, such as the acetates, were quite active. The insoluble salts, such as the citrate, tannate, etc., were inactive. Palladium, iron, cobalt, and nickel as metals were all quite active. Cobalt acetate and nickel acetate in the presence of sulfuric acid seemed to be inactive, also insoluble oxides such as iron oxides.

The few rare earths tried were inactive.

Hopcalite, consisting of a combination of oxides of manganese, copper, silver, and cobalt, was quite active.

At atmospheric pressure the well-known oxidizing catalysts in the form of soluble salts were active catalysts in this liquid-phase partial oxidation reaction. The insoluble oxidizing catalysts, such as hopcalite and others, would operate as catalysts within the liquid phase. It is quite apparent that the mechanism of oxidation in the two cases must be different.

Oxidation under Pressure

In order to obtain the advantage of increased thermal activation at higher temperatures and still retain the temperature-regulating benefit of the liquid phase, it is necessary to use higher pressures. In the case of such mixtures of oxygen and an inflammable compound, however, the danger of serious explosions increases rapidly as the pressure is increased. The following experiments were made to study the oxidation of alcohol under a moderately increased pressure and temperature (100° C.).

The catalyst to be tested was dissolved or suspended in the alcohol. A 10-cc. sample of the mixture was titrated with 0.1 *N* sodium hydroxide using phenolphthalein as indicator. Another 10-cc. portion of the mixture was placed in a beaker within a modified Parr bomb. The bomb was then closed tightly, a lead gasket being used in place of the ordinary rubber ring. The theoretical amount of oxygen gas required to oxidize the alcohol present to acetic acid was then forced into the bomb from a similar bomb previously filled to twice the desired pressure. The resulting pressure in the oxidation bomb was 170 pounds per square inch (11.3 atmospheres) at room temperature. The bomb was then heated for 24 hours in a boiling-water bath. The bomb was kept within a heavy steel shield during the filling and heating. After cooling to room temperature, the pressure was slowly released by passing the gases through wash bottles containing water, barium hydroxide, and neutral sodium sulfite, respectively. The bomb was opened and the liquid residue, which usually amounted to 8 cc., was rinsed into a flask and titrated with 0.1 *N* sodium hydroxide. Wherever possible, aldehyde was determined in the liquid residue and in the gases by the neutral sulfite titration method of Seyewitz and Bardin (*3*). When the quantity of aldehyde was too small for that determination, a qualitative test was made on the neutralized liquid residue with Schiff's reagent.

The results obtained with about forty of the substances previously tested as catalysts were closely parallel to those obtained with the same substances at atmospheric pressure and 70–75° C. In most cases there was no formation of carbon dioxide or acetic acid. The extent of the oxidation was the formation of very small concentrations of acetaldehyde, paraldehyde, and acetal.

With hopcalite catalysts and with cerous hydroxide suspended in sodium carbonate solution, however, there was considerable oxidation of the alcohol to acetaldehyde, acetic acid, and carbon dioxide. The following data are representative of the results obtained with these catalysts:

CATALYST	ALDEHYDE	ACETIC ACID	CARBON DIOXIDE
	Gram	*Gram*	*Gram*
4-Component hopcalite	Not detd.	0.0684	0.086
2-Component hopcalite	0.016	0.0070	Not detd.
Cerous hydroxide in sodium carbonate solution	Trace	0.0276	Not detd.

A further study of the mechanism of this oxidation is being made.

Acknowledgments

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The authors wish to express their appreciation of the financial assistance by the Chemical Foundation, of which Francis P. Garvan is president and W. W. Buffum, general manager.

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Special Control Apparatus in the U. S. Naval Sulfuric Acid Plant[1]

H. Marvin Coster

Naval Powder Factory, Indian Head, Md.

THIS sulfuric acid plant was built in 1918 by the du Pont Company as a part of the U. S. Naval Powder Factory at Indian Head, Md. It has been in constant operation ever since, except for about eleven months in the fiscal year 1924–25 and one week in 1929. It is of the Schröder-Grillo contact type, with the usual platinum on magnesium sulfate contact mass, burns sulfur as the raw material, and delivers sulfuric acid as oleum of a strength which may be expressed as 50 per cent free (dissolved) SO_3, 90.82 per cent total SO_3, or 111.25 per cent (100 per cent H_2SO_4).

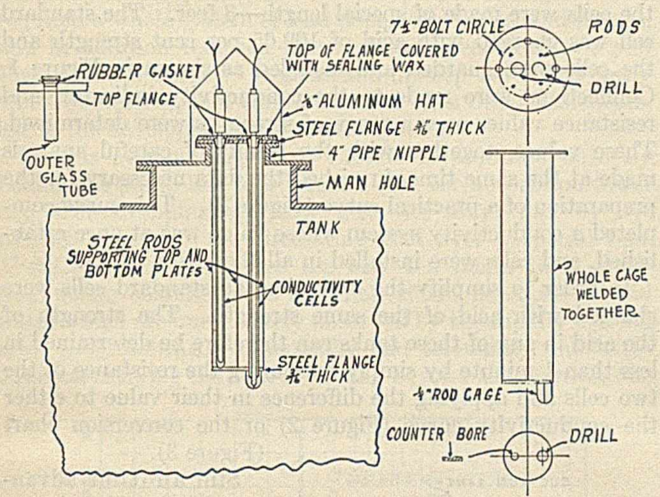

Figure 1—Conductivity Cell Guard and Sketch of Installation

The plant operates on the same basic principle common to all contact plants of this type, but in the development and application of special control apparatus it appears to be unique. It is therefore the purpose of this article to discuss only these developments.

Sulfur Dioxide Recorder

In 1922, with the coöperation of the Bureau of Standards, what is believed to be the first sulfur dioxide recorder in this country was developed and installed here. This recorder operates on the thermal conductivity principle for gas analysis (*5*), which is so well understood generally that it will not be discussed. Today several companies are making and selling excellent recorders. The apparatus in use at this plant consists of a Leeds & Northrup four-point resistance recorder, a Bureau of Standards thermal-conductivity cell, an Edison battery, and a purifying unit developed here. It keeps before the plant a continuous record of the percentage of sulfur dioxide in the entrance gas so that the operator is able to feed to the converter a gas of uniform sulfur dioxide content, which keeps an even load on the converter and insures a maximum conversion of sulfur dioxide to trioxide at all times. During the four years that it has been in constant operation no repairs have been necessary and no care has been required other than the usual weekly oiling, greasing, and battery-charging. Today it is operating perfectly, practically replacing the well-known Reich starch-iodine test for sulfur dioxide.

Conductivity-Measuring Unit

In 1928 a method was developed and apparatus installed for determining oleum strengths in the absorption system by conductivity measurements. Some conductivity measurements had been made on oleum from this plant by the Leeds & Northrup Company in 1920, but because of a minimum in the curve, work was discontinued and analysis by this method given up as impractical.

In the proper application of the plant's processes, definite information is demanded on the temperature and strengths of acid in the absorption system. Because of the high strength and the high freezing point (109.3 per cent H_2SO_4 freezes at 95° F. or 35° C.) of this acid, there is always more or less difficulty and danger in the sampling. The results obtained by analysis are not always accurate, as it is very difficult to prevent a loss of sulfur trioxide in both sampling and melting the sample. Obviously, there had long been a great need for more definite analysis at more frequent intervals and with less difficulty.

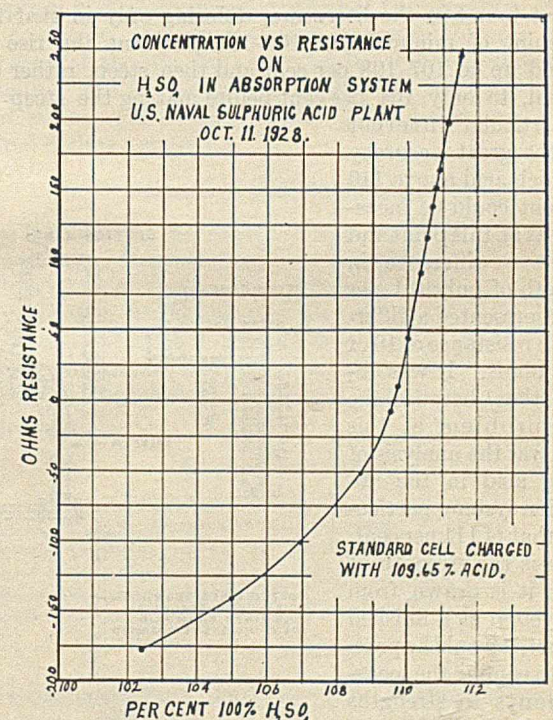

Figure 2

The conductivity of an electrolyte is determined by measuring the resistance of the solution between two electrodes immersed in it. The reciprocal of the measured resistance is the conductance of the solution. The resistance of the solution is commonly measured by the alternating-current Wheatstone bridge method employed by Kohlrausch. There are Landolt-Börnstein tables for conductance *vs.* concentration of pure sulfuric acid in distilled water.

Leeds & Northrup found that the relation between conduc-

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[1] Received February 4, 1931. Authority to publish granted by Bureau of Ordnance, U. S. Navy Department.

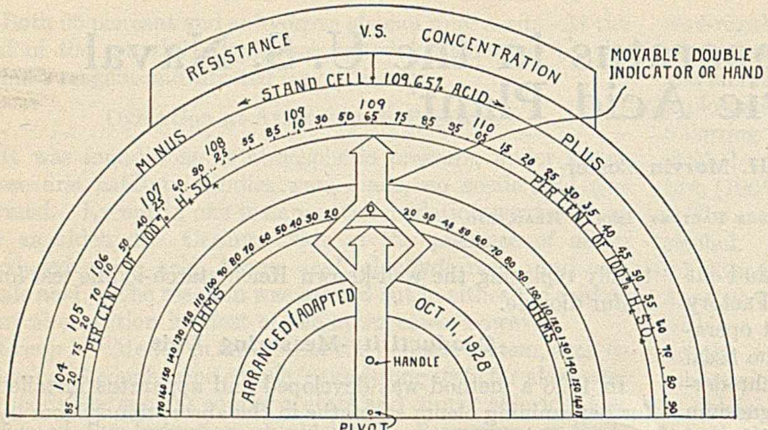

Figure 3—Conversion Gage, Ohms Resistance to Acid Strength

tivity and sulfuric acid concentration over a range of 96 to 99 per cent was quite variable, and so developed cells and a recorder for this determination. But with oleum—acid above 100 per cent H_2SO_4—because of a minimum in the curve, practical information was not available (*1*, *3*, *6*).

With a conductivity-measuring unit consisting of a cell made by fitting to a Dewar jar, a hard-rubber cover through which passed a thermometer and two glass tubes into which the platinum electrodes were fastened, and with the usual apparatus and a telephone, resistance values at a standard temperature were determined on samples selected from the plant to cover a wide range of strengths. These values, when plotted using ohms resistance as ordinates and acid strengths as abscissas gave a curve (Figure 6) which in general conformed to that found in the literature, differing only in that from the point of minimum at 102–103 per cent the rise was gradual up to 107–108 per cent and then steep, rather than gradual, to only 104 per cent before making the steep rise. Of particular interest was the great accuracy at which acid above 110 per cent could be measured, as at this point and above a difference in strength of only 0.1 per cent represented a difference in resistance of 10 or more ohms. It was obvious that, because the chief problem at this plant was the analysis of strong acid in the absorption system, particularly that of 111 per cent, which is the strength at which it is drawn from the system as a finished product, it would be practical to confine the measurements to strengths always known to be considerably higher than those falling near the minimum in the curve.

A Leeds & Northrup conductivity indicator designed to operate on alternating current simplified the conductivity measurements and permitted the preparation of a very accurate curve for acid as manufactured here.

To be of maximum value in the plant the cells had to be of a type which could be permanently mounted in the acid inside the tanks. Following the Leeds & Northrup Company's suggestion, conductivity cells of the Bishop type (*2*), so satisfactorily used on acid strengths below 100 per cent, were secured. These cells operate in pairs. One, known as the standard cell, is filled with acid of a strength somewhere near that of the acid to be measured. This cell, together with the second cell, called the measuring cell, is immersed in the tank of acid. Obviously, when the acid is of the same strength as that of the standard cell, the ratio of the resistance will be one to one. By employment of the standard cell temperature compensation is entirely automatic. The difference in the readings of the two cells fixes the point on the conductivity curve.

To reach to an adequate depth in tanks 6 feet in diameter, the cells were made of special length—3 feet. The standard cell was charged with acid of 109.65 per cent strength and the cells were guarded and installed as shown in Figure 1. Connections were made to the conductivity indicator, and resistance values over a range of strengths were determined. These values, together with the results of careful analysis made at the same time, furnished the data necessary for the preparation of a practical curve (Figure 2). This curve completed a conductivity system whose value was at once established, and cells were installed in all the oleum tanks.

In order to simplify the operation, all standard cells were charged with acid of the same strength. The strength of the acid in any of these tanks can therefore be determined in less than 1 minute by simply measuring the resistance of the two cells and applying the difference in their value to either the conductivity curve (Figure 2) or the conversion chart (Figure 3).

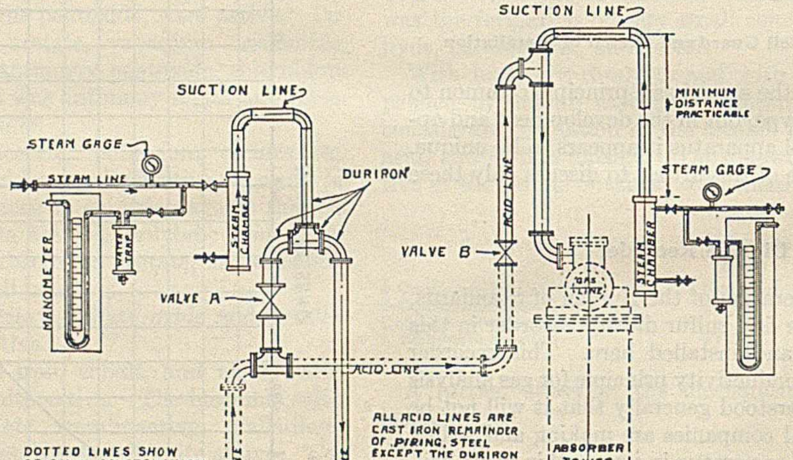

Figure 4—Automatic Acid Diluter

Still another advantage is its application to the determination of the temperature of the acid in the absorption system. Previously, approximate temperatures were determined by mounting long-stemmed thermometers at convenient places in the pump lines. Because the value of the acid in the standard cell changes with the temperature, these values were determined over a wide range of temperatures and a curve was plotted from these results. By the new method the acid temperature and the strength are read in one operation. In addition, should a continuous record of the changes in acid strengths ever possess any practical value, a recorder can be easily adapted to this system.

The increased safety to the men in handling so dangerous a product as oleum, as well as the saving in the cost of analysis, is important; but these advantages are slight as compared with the value to the absorption system for, with the conductivity cells mounted in the fuming, whirling oil of vitriol, it is only necessary to press a button and read with ease and accuracy the changes which so vitally influence the absorption of sulfur trioxide.

Automatic Acid Diluter

In 1930 a system new in design and principle for adding the necessary water to the absorption system was installed. By the absorption of sulfur trioxide all the units except the last are allowed to increase in acid strength. This strength is held as near to 98.3 per cent as is practical, as this acid has a minimum vapor tension of both sulfur trioxide and water and so is able to extract the sulfur dioxide completely from the gas and cause no formation of mist.

In the method employed heretofore, strong acid was diluted by mixing with water and this mixture added as necessary to keep the unit to the proper strength. This required a whole system of lead pots, coils, boxes, and pumps, and in addition required much of the operator's time and that of a lead burner. Repairs and upkeep were both costly and troublesome, and these, together with other difficulties, led to the development of the new system.

In this system (Figure 4) suction is produced both by raising the pump line to a height above the absorption tower and then dropping suddenly into the tower and by bypassing a part of the circulating acid over a special line. These suction lines, which are also the pump lines, draw from steam chambers, fed by small steam lines, steam and water which are immediately absorbed by the rapidly moving acid, thus diluting automatically and constantly and without even carrying the heat of mixing beyond the Duriron tee.

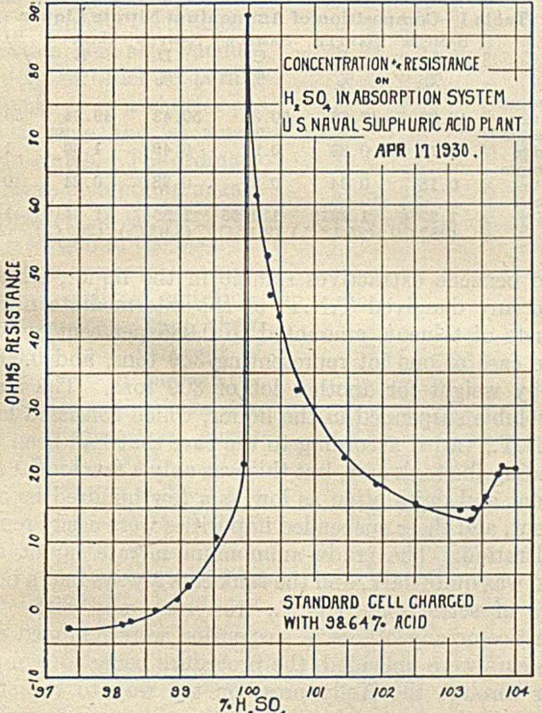

Figure 5

Whenever the quantity of water being drawn in by the pump line is insufficient to hold acid to the required strength, the auxiliary unit is put into operation by opening valve *A*. This unit has about twice the capacity of the regular unit, and with the two operating together more than enough water can be introduced to hold acid to any strength. At the present rate of production only about 100 pounds of water per hour are required, which amount in a steam cost to less than thirty dollars a month. To determine variations in strength, conductivity measurements are applied to curve (Figure 5) provided it is previously known whether the acid is weaker or stronger than 100 per cent. In case of doubt, however, it is but necessary to draw a small sample and note the presence or absence of sulfur trioxide fumes.

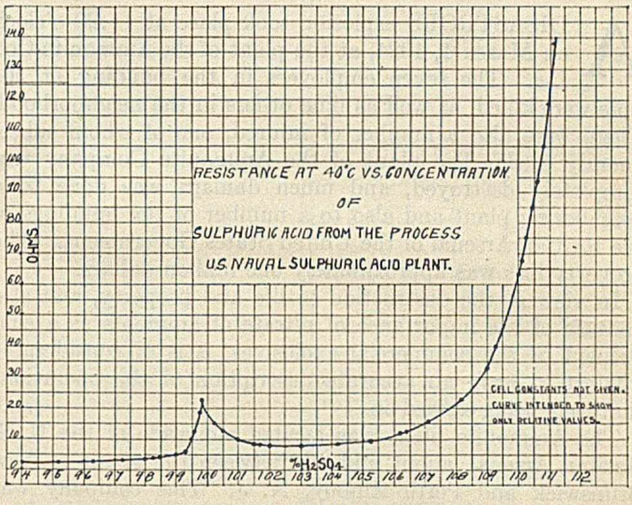

Figure 6

The new system has now operated for a year with practically no expense and with both a maximum sulfur trioxide absorption and a maximum reduction in formation of sulfuric acid mist. Its original cost amounted to only about 1 per cent of the old and, even under the present reduced production and including the added cost incurred by the use of steam, will effect a saving (*4*) of more than fifteen hundred dollars annually.

Summary and Conclusion

The installations described herein have each had a part in the twelve-year run just completed in which there was not an acid loss of more than a few hundred pounds, not a serious injury to a man, and an average conversion and yield of more than 95 and 94 per cent, respectively, was maintained. Today they are making adjustment simple, control easy, operation definite, and giving a conversion and yield never before equaled here.

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(2) Bishop, U. S. Patent 933,015 (Aug. 31, 1909).
(3) DeBlois, *Chemistry Industry*, **46**, 257 (1927).
(4) Naval Powder Factory, Report, 1929–30.
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Oil Consumption and Supply Survey Planned

A voluntary Committee on Petroleum Economics has been appointed by the Secretary of the Interior to make a survey of the supply and demand in the petroleum industry over a period of six months beginning April 1, 1931. This committee is appointed at the request of the American Petroleum Institute and consists of E. B. Swanson, Bureau of Mines, chairman; John W. Frey, Bureau of Foreign and Domestic Commerce; Martin Van Couvering, petroleum engineer; Alfred G. White, National Industrial Conference Board; and Howard Bennette, Western Petroleum Refiners Association. Two similar reports were made in 1930 as the result of a request of the American Petroleum Institute, and the data thus compiled served as a guide in securing more orderly production and diminution of wasteful and extravagant methods.

Recovery of Ammonium Nitrate from Amatol[1]

Explosion at Ammonium Nitrate Plant of Ammonite Company

R. Norris Shreve

Purdue University, Lafayette, Ind.

A DISASTROUS explosion took place at 11:20 o'clock on March 1, 1924, at the plant of the Ammonite Co., Inc. The seven employees in the building at the time were killed, as well as nine others in the neighborhood. There were also a number of injured, one of whom subsequently died. The plant of the Ammonite Company was completely destroyed, and much damage was done to a neighboring plant and also to a number of the buildings of the Raritan Arsenal of the United States Government. The property loss was approximately one million dollars.

In view of the destruction to life and property, and also because of the importance of nitrate of ammonia as a constituent of the commercial explosives, it is of considerable interest to have an accurate description of the operations that were being carried on.

The Ammonite plant was located alongside of the U. S. Raritan Arsenal, about midway between the towns of New Brunswick and Perth Amboy, N. J. This company was engaged in the manufacture of ammonium nitrate from a solution obtained from the breaking down of shells containing amatol, this latter operation, however, being carried out at the various governmental arsenals. The solution of ammonium nitrate was shipped in tank cars to the plant of the Ammonite Company. This ammonium nitrate liquor was purified, evaporated, grained, and prepared for use in the commercial explosives.

History of Site

The Ammonite Company occupied a one-story building, together with neighboring land and tanks. Many years ago an adjacent site had been used for a powder mill and a few of the old foundations remained in the vicinity. A number of years before, and during the war, a neighboring plant had been engaged in the manufacture of gun cotton. When leased by the Ammonite Company, the building had in it bales of cotton linters, camphor, and miscellaneous pieces of old equipment. These materials were gradually removed and were all out at the time of the explosion. When the occupancy started, the building had a sand floor that was quite dusty as trucks were accustomed to drive into this building for unloading or loading. However, except for sandy dust, the building appeared clean. There was no evidence that gun cotton had ever been handled in the building, or that the old powder mill in the vicinity had any relation to the explosion.

Before installing equipment, the Ammonite Company leveled off the sand and laid a thin concrete floor over the southern half of the building where the equipment was installed and the manufacturing operations were carried on.

Raw Materials

Amatol, as a rule, consists of a mixture of 20 parts of T.N.T. and 80 parts of ammonium nitrate, though certain shells contained 50 parts of T.N.T. and 50 parts of ammonium nitrate. At the end of the war there were in storage large quantities of these shells for which there was no use, and at a number of government arsenals these shells were broken down to recover the various materials composing them. This work was largely done by a salvaging company (Columbia Salvage Corporation) under the supervision of government officials.

The amatol was separated into its constituents while in the steel shell, by being subjected to a jet of steam which condensed sufficiently to dissolve the ammonium nitrate and also retained enough heat to liquefy the T.N.T., there flowing from the shell a hot solution of ammonium nitrate mixed with melted T.N.T. This was conducted to a suitable separating device which drew off most of the T.N.T. in the form of a liquid (temperature 95° C.), which was allowed to flow into containers and there to solidify. The hot ammonium nitrate liquor was run through a series of cooling and settling tanks for the removal of practically all the remaining T.N.T. This was done not at the Ammonite plant, but at the various arsenals (*6*). This cooled ammonium nitrate liquor carried in solution and also in suspension a small quantity of T.N.T. and other toluene-nitration products. Table I gives the percentage composition by weight of composite samples of about 2000 tons of this liquor. The reaction of the liquor was almost invariably slightly alkaline, owing to the addition of a small amount of ammonia before shipment in order to prevent nitric acid attack upon the steel of the tank cars.

Table I—Composition of Ammonium Nitrate Liquor

	Sample A %	Sample B %	Sample C %	Sample D %	Sample E %	Sample 68 %
Ammonium nitrate	48.30	47.68	50.32	50.43	49.54	53.05
Ammonium chloride	0.75	0.83	0.92	0.49	1.36	1.40
Ammonium sulfate	0.18	0.24	0.29	0.28	0.24	0.14
Specific gravity	1.2286 (28° C.)	1.2310 (25.7° C.)	1.2555 (9.1° C.)	1.2547 (8.6° C.)	1.2410 (26° C.)	1.2554 (28° C.)

The benzene extractives soluble in the liquor, which included any dissolved T.N.T. or the intermediate nitration products of toluene, amounted to 0.085 per cent by weight in the case of one lot representing 300 tons, and 0.098 per cent by weight for another lot of 300 tons. The amount of insoluble suspended in the liquor, which consisted largely of T.N.T., varied according to the care that had been taken in loading the tank cars, but this was only a few tenths of one per cent and quite often as low as a few hundredths of one per cent, and these suspended impurities were easily removed by filtration. The crude ammonium nitrate liquor as received was quite dark, and the tank cars always had a bottom sludge of settled-out T.N.T., iron rust, and dirt. These impurities or any others in suspension were removed as the tanks cars were unloaded, the procedure being to pump this liquor through the Kelly press on the way to the storage tanks or to the plant. In the winter some ammonium nitrate crystals separated, and before pumping out the tank cars it was necessary to warm the contents with steam for somewhat more than one hour.

Development of Process

When the proper procedure for handling this ammonium nitrate liquor was under consideration, it was known that

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[1] Received January 23, 1931. This article was delayed in publication until certain legal affairs were adjusted.

another plant had been operating successfully and safely by a simple atmospheric evaporation of screened ammonium nitrate liquor from the hot aqueous extraction of amatol, followed by atmospheric graining. Open enamel-lined steel pans provided with aluminum steam pipes were employed for the evaporation, and a material was obtained from which practically all the water had been removed. This material was run into ordinary open grainers similar to those shown in Figure 3 except that there was no top. The open or atmospheric evaporating pans and grainers were operated without any attempt to remove the very small amount of T.N.T. dissolved by the ammonium nitrate liquor.

In designing the Ammonite plant, consultation was had with a number of chemical engineers and special precautions were taken to obtain greater safety of operation and better products, and also to cut down decomposition. In the first place, it was decided to employ vacuum concentration, and also vacuum graining, in order to permit operation over a shorter period of time and at lower temperatures. The ordinary procedure in handling nitrate of ammonia is to carry the concentration in the open atmospheric evaporating pan, provided with air agitation, to such a stage that there is only 1 to 3 per cent of moisture left in the molten material, in which case the fudging temperature varies from 150° to 138° C. This hot liquid mass is then run into steam jacketed open grainers, where under agitation the material is grained and the rest of the water driven off. Here the granulated ammonium nitrate is also cooled by use of water in jacket. However, by the use of the vacuum apparatus lower temperatures would be employed.

Furthermore, in order to remove any dissolved T.N.T. or other nitrogenous impurities, as well as the color, it was

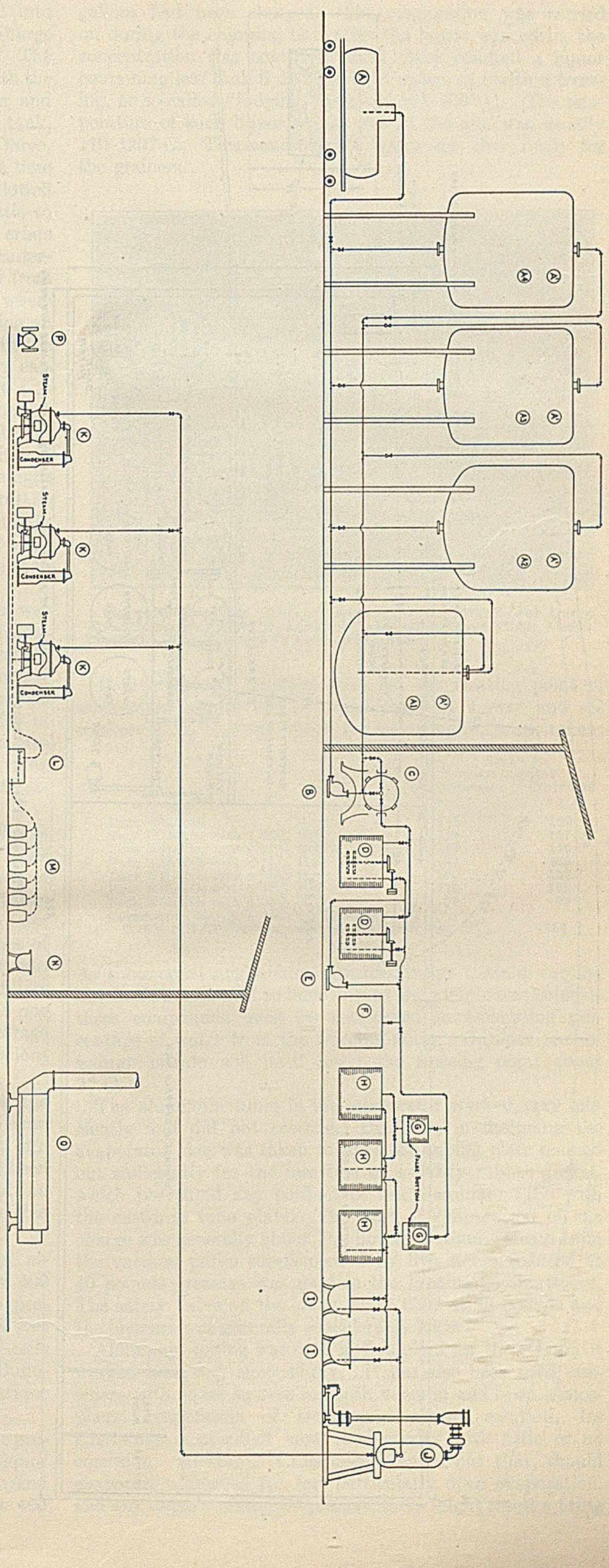

Figure 1—Flow Diagram Operation of Ammonite Plant

A—Standard 8000-gallon railroad tank car containing ammonium nitrate liquor

B and *E*—Pumps: motor-driven, Gould $1^1/_2$-inch centrifugal

A'—Temporary steel storage tanks: *A*1 and *A*2, 22 feet 6 inches dia. × 25 feet deep; *A*3 and *A*4, 24 feet dia. × 25 deep

C—Filter press, Kelley No. 150

D—Purification tanks: cypress, brick-lined, 10 feet dia. × 8 feet deep, agitated

F—Spent Darco tank: cypress 10 feet dia. × 8 deep

G—Sand filters: cypress, 5 feet 8 inches dia. × 3 feet 6 inches deep above sand; cloth filter above sand

H—Storage tanks: cypress, brick-lined, 10 feet dia. × 8 feet deep

I—Preheating kettles: cast iron 6 feet dia. × 4 feet deep, heated by steam in tubes

J—Evaporator: Buffalo Foundry and Machine Co. No. 10 horizontal tube, cast-iron, single effect, heated by steam in tubes

K—Grainers: Buffalo Foundry and Machine Co., 6 feet dia. cast-iron crystallizers

L—Sieve: wooden frame, 3 × 3 × 6 feet upper section consisting of movable screen

M—Barrels: lined with paraffined Arkell safety liners; average contents 325 to 350 lbs.

N—Kettle: cast-iron Dopp for melting wax and rosin for waterproofing ammonium nitrate grains

O—Boiler: 100-h.p. economic type Casey-Hedges Scotch marine boiler, internally fired, 72 inches dia. × 17 feet 3 inches; tubes 3 inches dia. × 14 feet long; boiler covered with 2-inch lagging; stack 32 inches dia. × 60 feet high

P—Vacuum pump 12 × 12 inches dry type; belt driven

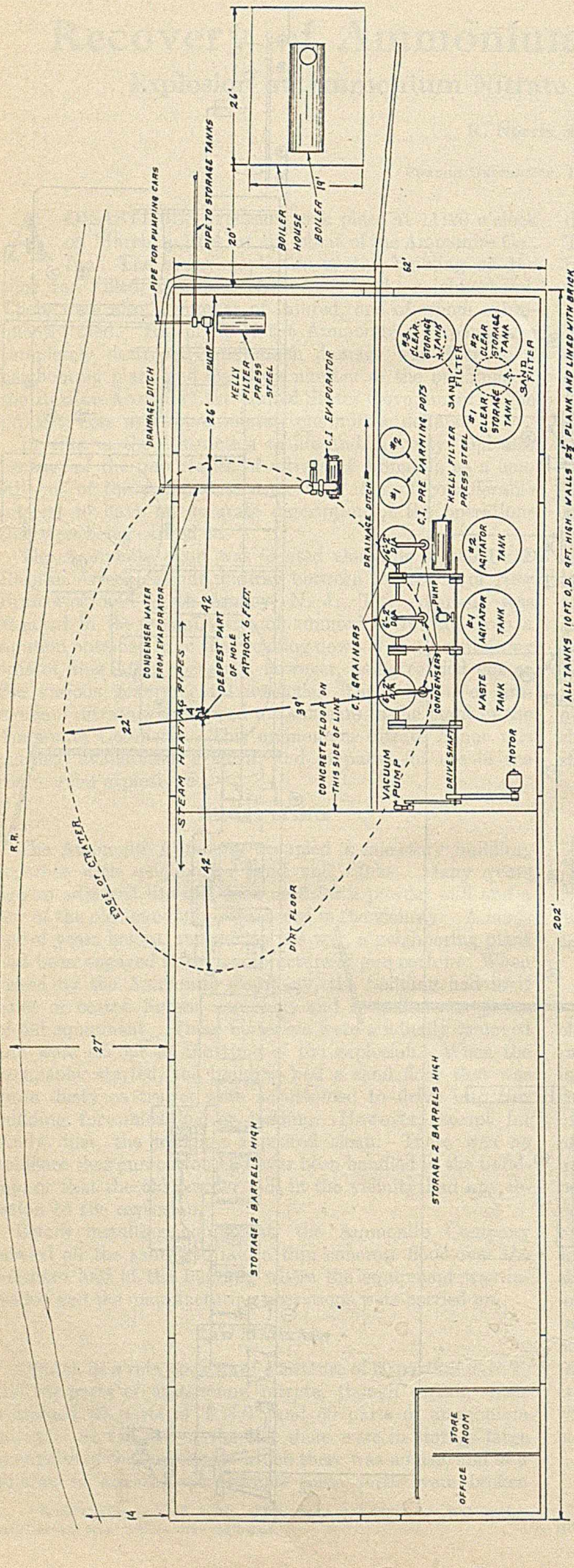

Figure 2—Plan of Ammonite Plant

considered wise to give the crude liquor, after filtration, a treatment with an activated carbon. Several different grades were tested, and grade known as Darco, which experimentation had shown considerably reduced the soluble benzene extractives as well as the coloring material, was finally adopted. As a matter of fact, most of the material experimented on contained 0.167 per cent by weight of benzene extractives, which was much higher than that present in the liquor subsequently received at the plant. In this case there was no trouble in reducing the benzene extractives by means of a 2-hour cold treatment with 0.38 per cent of Darco to considerably under 0.02 per cent. The resulting liquor was a very light lemon color, and gave a product upon evaporation and graining which was almost white, even when operating in iron vessels.

Factory Procedure

Upon the basis of extensive laboratory tests, and upon the known procedures as carried out in nitrate of ammonia plants, as well as the writer's experience in the large-scale production of ammonium nitrate, the Ammonite Company plant was designed, and operations started in the fall of 1923. The main steps in the operation involved crude filtration, purification, sand filtration, evaporation, and graining and coating.

A diagrammatical representation of the equipment and the flow of material is given in Figure 1. Figure 2 shows the relative positions of the different pieces of apparatus in the building. The vacuum grainers are shown in Figure 3, which also depicts, in the background, the brick-lined treating tanks. Figure 4 shows the vacuum evaporator.

Crude Filtration—One charge of 3000 gallons of crude ammonium nitrate liquor was filtered each day. The equipment consisted of 2-inch Goulds centrifugal pump connected to a motor and a No. 150 Kelly filter.

Procedure. The crude liquor was pumped through the Kelly filter, either directly from the tank cars or, more often, from one of the four 60,000-gallon storage tanks on the property into one of the two agitating tanks. The slime gathered upon the cloths of the Kelly press, and was cleaned out about once a week. Usually this amounted to only about 100 pounds and it was washed away with a very large quantity of water. This slime was never stored in the building, but was always immediately removed therefrom through a door by the Kelly press, and washed away in the ditch, also by this same door. This ditch also carried the large amount of water from the vacuum condensers. This slime contained some T.N.T., but it also had in it the other impurities—iron rust, dirt, etc.—which had been collected in the previous breakdown operations.

Purification—For this process a daily charge of 3000 gallons of filtered ammonium nitrate liquor and 80 pounds of Darco (used twice) was used. The equipment consisted of three wooden tanks 10 feet in diameter and 8 feet high lined with brick set in acid-proof cement; two of these tanks were provided with agitators, and one was a simple storage tank; the net capacity was 3000 gallons each. Between the brick lining and the wood tank was a half-inch space, which was filled with asphalt as the bricks were laid. A $1^1/_2$-inch Goulds centrifugal pump was connected to motor.

Procedure. The filtered crude liquor was pumped into the bottom of the agitating tank which contained the charge of once-used Darco from the previous purification. The agitator was started and the Darco stirred in contact with the liquor for 2 to 3 hours. It was then allowed to settle, and the supernatant liquor pumped into the other agitating tank, where it was given a similar treatment of 80 pounds of Darco, but in this case a fresh lot of Darco was added. The time of agitation was likewise from 2 to 3 hours, and was followed by a rest of several hours to permit the Darco to settle to the bottom of the tank. In this way every charge of crude liquor was given two treatments of Darco in a countercurrent fashion. The twice-used Darco was removed from the bottom of the tank to the third 3000-gallon tank, where at the time of the explosion it was being stored awaiting an accumulation of a sufficient quantity to pay to wash out the soluble values. The treatment with Darco was always carried on in the cold since experiments had shown that a 2-hour contact cold was as efficient as a 15-minute contact hot. It was found that the efficiency of the Darco treatment was higher when operating on a factory scale than it had been in the laboratory. In fact, 0.25 per cent of the weight of liquor treated in the factory was more efficient than 0.38 per cent in the laboratory. This was due, however, not only to better contact, but also to the fact that the actual shipments of liquor contained much less benzene extractives than the original sample of liquor.

It had been demonstrated that the coloring matter was removed by the Darco simultaneously with the benzene extractives. Consequently, the daily test that determined the efficiency of the Darco was the degree of removal of the coloring matter, though tests were made at frequent intervals to determine the benzene extractives and also the purity of the finished material. If insufficient Darco had been employed, more was added, but this was rarely necessary. The time for the complete Darco cycle was 4 hours for each treatment.

SAND FILTRATION—For this process also the daily charge of purified ammonium nitrate liquor was 3000 gallons. The same Goulds centrifugal pump used in the purification was employed. Two sand filters consisting of two wooden tanks about 5 feet in diameter and 5 feet high, provided with false bottoms on which were placed a filter sack and 6 inches of sand, were placed above the clear liquor storage tanks, into which they discharged by gravity. One of these sand filters also had a filter bed of Filtros plates, and this was the one usually employed. There were three clean-liquor storage tanks of wood, brick-lined, with a capacity of 3000 gallons each.

Procedure. After most of the Darco had settled out, the supernatant liquor was pumped through one of the two sand filters, the effluent being a liquor of crystal clearness and of a very light lemon color. In designing the plant it had been thought necessary to use a Kelly press to remove most of the Darco prior to sand filtration, but practice had proved this to be unnecessary, as the Darco settled in several hours.

EVAPORATION—The quantity of purified ammonium nitrate liquor evaporated per day was 3000 gallons, or 400 gallons per charge. The equipment consisted of two preheating pots of cast iron 6 feet internal diameter and 4 feet deep, each provided with six aluminum 2-inch pipe U-coils connected to steam; and one vacuum evaporator, Buflokast horizontal type, with 93 square feet of heating surface in the form of $1^1/_4$-inch aluminum tubes.

Procedure. The cold, clear liquor was siphoned into the preheating pots, where the temperature of the 50 per cent liquor was brought up to about 100° C. From there it was sucked continuously into the vacuum evaporator until about 400 gallons had been charged. The evaporation was carried on during the charging but, after the liquor was all in, the concentration was continued until there resulted a liquor containing less than 6 or 7 per cent water, and with a freezing, or so-called "fudging," point of 105–108° C. The temperature of such liquor at the end of the run was usually 110–120° C. This concentrated liquor was then ready for the grainers.

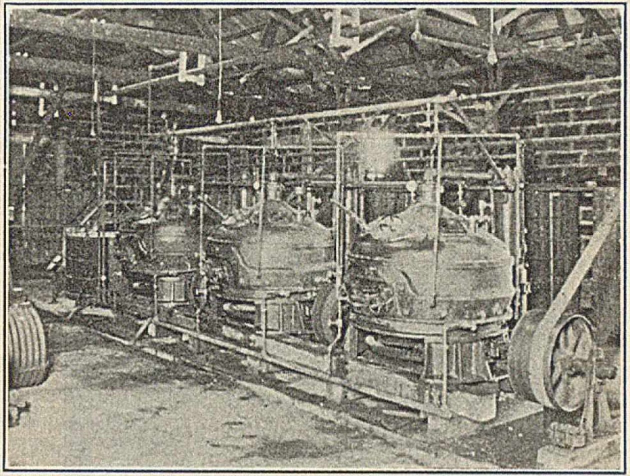

Figure 3—Vacuum Grainers with Agitating Tanks for Darco Treatment in Right Background, and with Sand Filter Above. Purified Liquor Storage in Left Background

Interesting and practical work on the freezing point of ammonium nitrate has been published by Lowry and coworkers (*2*, *3*, *8*), from which the following data are taken:

	FREEZING POINT Uncorrected ° *C.*	FREEZING POINT Corrected ° *C.*
Pure NH_4NO_3	165	169
Pure NH_4NO_3 with 1.05% H_2O	154	157
Pure NH_4NO_3 with 2.01% H_2O	143	146
Pure NH_4NO_3 with 3.20% H_2O	131	133
Pure NH_4NO_3 with 4.39% H_2O	120	122
Pure NH_4NO_3 with 6.24% H_2O	110	112
Pure NH_4NO_3 with 8.76% H_2O	98	99
Commercial NH_4NO_3 with 1.7% $NaNO_3$ and 0.16% NH_4Cl; freezing point taken after drying		164

As commercial ammonium nitrates always contain varying but small amounts of sodium nitrate and ammonium chloride these compounds must be considered in estimating percentage of water from the freezing point. One per cent of sodium nitrate will itself lower the freezing point about 3° C.

The aluminum tubes in the evaporator worked very efficiently and did not corrode. However, in designing the evaporator care was taken to have the tubing plate reamed out sufficiently for the insertion of a heavy rubber gasket, which prevented any contact of the aluminum tube with the cast-iron tube plate. The time of evaporation of one charge was generally about $1^1/_2$ hours. Exhaust steam from the vacuum pump supplemented by live steam reduced to 40 pounds pressure was used in the heating compartment. The safety valve on the steam chest blew at 38 pounds and the pressure was generally considerably lower.

Aluminum tubing was used in this plant for the steam; it worked here very successfully. It has also been used elsewhere with equal success for both vacuum and open atmospheric evaporation of ammonium nitrate solution. Its advantage is excellent heat conductivity with little or no corrosion. However, it has been pointed out that, should evaporation proceed too far, particularly open evaporation, and any organic matter be present, there might result a firing or at least a fuming off of the evaporating pan. In such a case the presence of aluminum might introduce an extra hazard. However, this could not apply to the vacuum evaporators, in which much lower temperatures prevail.

Graining and Coating—From 17,000 to 21,000 pounds of concentrated liquor per day, or 1850 to 2050 pounds per charge, were treated in this plant, and the amount of finished ammonium nitrate produced was 8 to 10 tons per day, or 1800 to 2000 pounds per charge. The equipment consisted of three 6-foot Buflokast vacuum-type crystallizers or grainers; three condensers, each with 28 square feet of cooling surface; one 12 inch by 12 inch belt-driven vacuum pump; one sieve; and one 50-gallon cast-iron jacketed kettle.

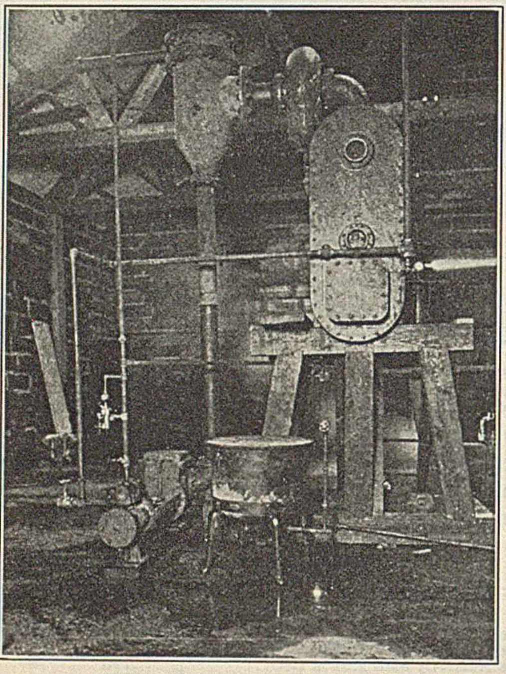

Figure 4—Vacuum Evaporator

Procedure. The concentrated hot liquor was sucked under full vacuum from the bottom of the vacuum evaporator into one of the three grainers. The vacuum was maintained in the grainer with some steam on the jacket, and with the stirrer revolving. Within a few moments after the charge had entered the grainer, it had crystallized and the grains formed. The heat of the liquor, that from the jacket, and the heat of crystallization of the ammonium nitrate itself rapidly removed the moisture, a stream of water appearing through the sight glasses of the condensers immediately after the vacuum was put on a new charge. Generally in 10 or 15 minutes the steam was shut off and water turned into the jacket to begin the cooling; this was done while the grains were still moist, as there was enough heat left in the mass to dry it under the conditions of the vacuum. The charge in the grainer rapidly lost its moisture and the temperature dropped to around 70–80° C. When the crystals appeared, the temperature rose about 10° C. owing to the heat of crystallization. The highest observed temperature in the grainers, even with the heat of crystallization, was 120° C., and this was when the grains were still slightly moist. After about an hour the charge was cooled and it carried from 0.1 to 0.2 per cent of moisture. During the graining operations slow agitation was practiced, the paddle revolving generally at 16 r. p. m., although sometimes half this speed was employed, particularly for the coarser grains.

As is well known, ammonium nitrate is hygroscopic (7). To reduce this property as much as possible, and also to prevent the separate grains from sticking to each other, it is customary to coat the grains. This was done by adding to the material in the grainer, while still warm, 0.3 per cent of a liquefied mixture of paraffin 80 per cent, vaseline 5 per cent, and rosin 15 per cent, followed after a short interval with 1 per cent of a finely divided substance such as kieselguhr or whiting. The charge was then cooled and discharged through the door in the grainer and through an 8-mesh sieve into a box, from which it was shoveled into sugar barrels. The grainers were provided with a large manhole, the cover of which was simply laid on, and would consequently have risen up should a pressure have ever been developed, which as a matter of fact was never observed.

In the atmospheric or open grainers working on ammonium nitrate fires occasionally occur, but in these vacuum grainers there was never the slightest indication of a fire.

From time to time the conditions of evaporation and of handling the crystallization were varied to produce an ammonium nitrate of fine or coarse grain, according to the type of explosive to be made from it. The finer grained material is more liable to harden upon storage. For example, in November, 1923, a coarse and heavier product was made which averaged 345 pounds to a sugar barrel, while in December a finer product was produced which was also lighter and averaged 325 pounds to a barrel. Two weeks before the explosion the factory went back to produce the coarser material and was making this grade when the explosion occurred.

A fine-grained product was one of which at least 80 per cent would pass through a 100-mesh screen and at least 95 per cent through a 40-mesh screen, while a coarse-grained ammonium nitrate would all pass a 10-mesh screen but not more than 5 per cent would go through 60-mesh.

To obtain a coarse grain in an ordinary ammonium nitrate plant with open evaporating pans and open crystallizers, the liquor is evaporated in pans until only about 1 per cent of water remains (freezing point or so-called "fudging point" of 146–153° C.). It is turned into a warm grainer and very little cooling water used, as the object is to cool slowly. After the grains are formed, the steam is turned onto the grainer to dry out the product. When making the finer product, the solution is not concentrated quite so much in the evaporating pan, yet even here there is present only 2 or 3 per cent of water. The fudging point is as low as 127° C. for the finer grades; when run into the grainer, the water is turned on stronger than is the case with the coarse product, the object being to cool more quickly. The finer material is, however, in the grainer longer, as it is more difficult to dry out. It is said in the trade that the presence of a small amount of chloride makes the grain harder, so that less dust is produced in the graining and handling operations.

When manufacturing at the Ammonite plant quite the contrary procedure was necessary for a fine product. The evaporation was carried farther than for the coarse product, but in no case was it carried as high as is common practice with open evaporation and graining. The most concentrated solution practicable from the vacuum concentrator was one with about 5 per cent water and a fudging point of 116° C. The highest temperature observed in the evaporator was 123° C. The steam at the boiler was at 80–85 pounds pressure. The latter pressure corresponds to 164° C., and the difference was lost between the boiler and the solution, which also was somewhat thick and a poor heat absorber and conductor, as can readily be understood when it is realized that this final solution was 95 to 97 per cent ammonium nitrate, which has a specific heat 20 to 25 per cent of that of water. When the more concentrated product was put into the vacuum grainer, the larger amount of cast iron in the vacuum type grainer, in comparison with the open type, quickly absorbed the heat in the ammonium nitrate solution and caused a rapid crystallization to ensue and to result in a fine grain; and this took place notwithstanding prior steam heating of the vacuum crystallizer. The vacuum also caused a rapid evaporation with consequent absorption of heat. On the other hand when solution containing above 5 per cent of water was sucked into the hot vacuum grainer and the concentration finished in the grainer under vacuum, the conditions of crystallization could be retarded so that the coarse grain was obtained. Naturally the once-formed grains dried rapidly in the vacuum grainer or crystallizer.

Finished Material

The finished ammonium nitrate contained from 0.33 to 0.48 per cent of ammonium sulfate and from 1.5 to 2.3 per cent of ammonium chloride. These amounts were conditioned largely by the processes of manufacture of the original ammonium nitrate employed for making the amatol, which was partly by the double decomposition of sodium nitrate and ammonium sulfate and partly neutralization of weak nitric acid with ammonia. The water content was around 0.1 per cent when determined according to the Bureau of Mines method by drying a desiccator for 3 days or at 70° C. for 15 hours. The finished ammonium nitrate gave negative results when subjected to a qualitative test for T.N.T. The ammonium nitrate was shipped in sugar barrels measuring $19^{1}/_{8}$ inches diameter and 30 inches high, and holding from 325 pounds for the finer grains to 350 pounds for the coarser grains. The barrels were lined with paraffined Arkell paper.

Explosion

Figure 2 shows the arrangement of the various pieces of equipment in the building and also the position of the crater left by the explosion. The building was about 200 feet long, 60 feet wide, and 16 feet high, and was constructed of hollow conduit tile with wooden roof trusses extending from wall to wall; it had a corrugated asbestos roof. This building was completely demolished. Figure 5 shows the crater left where this building had stood. The manufacturing operations were conducted at one end, the other end being used for storage of finished product and also for the small works office. The left end as shown in Figure 2 is the north, and the top is the east. The Kelly press, in which the initial filtration of slime containing some T.N.T., etc., was carried on, was blown out of the building a few feet toward the south, and was found to be intact. Also, that portion of the building in which this Kelly press had stood, and where the slime containing T.N.T. was handled, was not so badly shattered as the rest of the building, for the concrete floor remained in place, simply being broken into fragments 3 or 4 feet across. The various tanks used for purification and storage were badly smashed and blown in a general direction away from the crater, and gave not the least indication of having been the seat of any explosion. The storage tank in which the wet used Darco had been kept was blown down, together with the neighboring tanks, but the concrete floor of the tank was intact and also there remained a considerable quantity of spent Darco. Analysis of this spent Darco collected several days after the explosion showed that it was still quite wet, having 26.4 per cent moisture. Figured to a dry basis, this material contained 11 per cent of ammonium nitrate and 2 per cent of benzene extractives.

The preheating pots and the vacuum evaporator were shattered, but very large fragments were recovered, indicating without any doubt that no explosion had occurred in them; furthermore, there was no excavating of the ground under which any of these pieces of equipment had stood. The evaporator was blown to the south and the preheating pots to the southwest.

The general location of the crater was between the line of the three grainers and the track, with the western sloping edge under two of the grainers. The deepest part of the crater was a few feet from where the foundation wall of the building had stood, and roughly paralleled the building wall. Most of the fragments of the grainers resulting from the blow were found toward the west, indicating that some force between the line of the grainers and the wall of the building had blown most of these fragments away from this section. Two of the three bottom bearings and the three bottom shafts of the three grainers were found, also in the same general westerly direction with the majority of the fragments. Buried in the ground underneath where the grainers had stood were found a number of the fragments from one or more grainers. These pieces were much smaller than those of the evaporator and of the preheating pots, but the grainers were located nearer the center of the crater. There is, moreover, a very strong probability that an explosion did occur of the small quantity of ammonium nitrate (1800 to 2000 pounds) in one of the grainers, followed almost simultaneously by the major explosion of the recently made and still warm ammonium nitrate standing between the grainers and the east wall of the building and right over the deepest part of the crater.

There was no equipment between the line of the grainers and the eastern wall of the building where the seat of the explosion was located. However, there were stored here possibly 100 barrels (16 tons) of the finished ammonium nitrate which had been made during the few days preceding the explosion and which had not yet been moved to the storage space at the other end of the building. A few tons of this ammonium nitrate were quite warm, probably 40–60° C., from the batches made the latter part of the night preceding the explosion. Probably none of this ammonium nitrate had cooled completely to room temperature throughout the barrel. Some of these barrels may have been within 4 or 5 feet, or even nearer, of the grainers, though most of it was several times this distance away. The average weight per barrel was 345 pounds. There was a line of steam heating coils hanging on the wall inside of the building a few feet above the floor, but they could not have been in contact with the filled barrels of ammonium nitrate. There is no doubt that the main explosion was caused by the detonation of all or part of this ammonium nitrate temporarily stored in the place where the crater was, and there is a strong prob-

Figure 5—Crater Left Where Building Stood

ability that a detonation of the contents of one of the grainers set off this main explosion.

The reasons for postulating the main explosion as that of the recently finished ammonium nitrate are, first, that only here was there sufficient material to cause such a destructive explosion; secondly, the deepest part of the crater was under the place where this stock was temporarily stored; and finally, the direction throw of the fragments indicated a centering of the main explosion in this area.

If the hypothesis is correct that the initiating explosion was from the contents of one of the grainers, then the question is, what caused it to explode? Furthermore, it has been difficult for some to believe that the exploding of a ton or less of ammonium nitrate in a grainer would detonate the larger amount of recently finished ammonium nitrate that was located a few feet and more from the nearest grainer.

To date, notwithstanding a very careful study and experimentation by a number of experts, we have no clear-cut explanation for any initiating detonation. The presumption would naturally be that some organic matter, such as nitrated products of toluene, accumulated in the grainers, and when mixed with the hot ammonium nitrate caused the contents of one grainer to explode, and to set off all or part of the recently made and still warm barreled ammonium nitrate.

Although this is a thoroughly plausible hypothesis that has survived critical examination, we have very little supporting evidence and considerable contrary evidence. As an example of the latter is the fact that this operation of regaining ammonium nitrate was designed to remove with Darco even the T.N.T.-soluble matter in the strong liquors, which is ordinarily left in with the ammonium nitrate when it has been recovered in other factories. Furthermore, the temperatures in all the operations were lower than normally prevails in ammonium nitrate factories, in fact, the boiler was run with only 85 pounds pressure, the safety valve blowing at 95–100 pounds. A reducing valve was in the line supplying the evaporator and the grainers.

The difference in the equipment of the Ammonite plant from other similar operations was the use of vacuum concentration and of vacuum graining. The concentration had nothing to do with the explosion. The vacuum grainers were kept clean as a regular course of operation, and the men thoroughly brushed out the contents, even cleaning the center block after each charge.

As is known, T.N.T. is volatile and of the traces left in the ammonium nitrate liquor, even after the Darco treatment, some might have been volatilized by the steam and vacuum. Indeed, some time before the explosion, when emptying the condenser of one of the vacuum grainers, a very small amount of T.N.T. was observed in with the water. After this, even more scrupulous cleanliness was observed.

The writer has asked himself whether any T.N.T. could have accumulated in or on the vapor pipe leading from the top of the grainer to the condenser, and by some means have been sucked back into a hot grainer. The presumption is that, even should this have happened, there would have been no danger; furthermore, the men did thoroughly clean these parts. Yet this is a possible explanation. Some precaution must have slipped.

One hypothesis that was carefully studied was that nitrostarch set off the ammonium nitrate. This arose from the fact that it was shown that during the salvaging operation some Trojan powder was worked up with the amatol. This was confirmed by finding traces of nitrostarch in some of the crude, untreated liquors. However, experimentation showed that the Ammonite procedure would remove nitrostarch even more easily than T.N.T. Certain experts studying this procedure have held that hydrolysis products (sugars) of the starch from the nitrostarch would be soluble and might have introduced sufficient organic matter with the ammonium nitrate to sensitize it. However, the concensus of the expert opinion and experimental evidence was against this hypothesis, particularly as it was shown that nitrostarch was more stable when boiled with strong ammonium nitrate solutions than with water. A recently published work by the Bureau of Mines (*11*) states, "The results *** do not indicate that the decomposition of ammonium nitrate at elevated temperatures is affected by the presence of nitrostarch or ammonium picrate." This refers to admixture of 1 per cent nitrostarch. Under confinement in a small cast-iron grainer (6 inches in diameter) an explosion took place when the coated ammonium nitrate containing 1 per cent nitrostarch reached 237° C. With 5 per cent the miniature grainer exploded at 147° C. It is improbable that nitrostarch could have accumulated to any such extent as to cause the explosion. This statement is made even although two months prior to the explosion ammonium nitrate carrying a very small percentage of the nitrates from Trojan powder was processed, but all traces of these were removed a month before the explosion, and could not have influenced the operations as of March 1 (date of explosion) or the ammonium nitrate stored over the crater.

No T.N.T. sludge was ever handled near the explosion crater; furthermore, no T.N.T. sludge was ever dried out even for a sample. The slime from the filter was always handled wet and disposed of, at once, by washing away. The sand filters were cleaned out periodically, and at the time of the explosion several barrels of this impure sand were standing between the sand filters and the Kelly No. 1. This could have had no bearing on the disaster, as this material was too far from the crater; in fact, it was within 10 feet of the south end of the building, where the concrete floor was merely shattered into fragments and no excavation caused.

The primary explosion which destroyed the plant and buildings did not greatly damage the 300 tons of finished (coated) ammonium nitrate stored in the north end of the building. This stock in barrels, arranged two barrels high, was intact after the explosion, but was largely destroyed 5 hours later by the following fire or the water from the fire lines. This fire burned the fragments of wooden roof trusses and the wood barrels, and was set off by wind blowing over embers from a burning building in the vicinity.

The men in immediate charge were killed, but we know that nothing unusual or experimental was going on in the plant at the time of the explosion, as the superintendent and his assistant were both in the works office and not in the factory. Moreover, the foreman had sent a gang of four laborers to the boiler house to eat their lunch at eleven o'clock, saying that a grainer would be ready to be discharged around noon and he wanted them there to handle the barrels.

Although we cannot point to any clearly defined cause for this explosion, the writer would make the following suggestions for handling ammonium nitrate which has or which has had any nitrotoluene substances mixed in with it:

(1) Transfer all barreled goods from the vicinity of the grainers immediately. Keep no stock anywhere near the grainers or evaporators.

(2) Separate the evaporating and graining of ammonium nitrate from other operations, locating these operations preferably in their own building. Immediately remove every single barrel of finished stock from this vicinity.

(3) Keep whatever type of grainers employed and all appurtenances scrupulously clean. Never allow any accumulation of residue or "heel" of one batch to mix in with the next.

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Superiority of the Chemical Industry from the Stock-Market Point of View[1]

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The present world-wide business depression has focused the spotlight upon the status of every branch of industrial activity, throwing into sharp relief inherent weakness and revealing organic strength. In this period of analysis and retrospection the chemical industry has been revealed as better able to withstand depressed conditions than most industries, and examination of its performance under similar conditions during the past decade shows this resiliency to be a characteristic tendency of this industry.

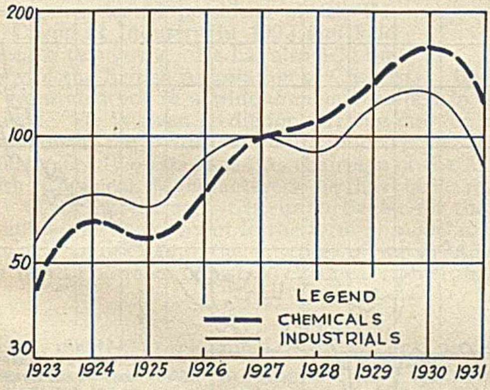

Figure 1—Comparative Earnings of Chemical and Industrial Corporations

Since there are no reliable comparative statistics available, the only possible common denominator is that of common-stock price movements in the New York stock market—not a perfect yardstick by any means, but nevertheless a fairly accurate indicator of the status of an industry.[2] While the trend of security prices over short periods of time may be determined by purely technical market conditions, over a long period it is influenced mainly by actual earnings, prospective earning power, property values, etc., of which the first two items are probably the most important factors. This seems to be clearly demonstrated by Figures 1 and 2, in which are plotted on a semi-logarithmic scale a representative earnings index of chemical and industrial companies and a representative index of chemical and industrial stock prices. Although the advance in stock prices in the later years was more marked than the increase in earnings, in general the stock price movements follow the trend of the earnings curves.

Examination of earnings figures shows a more rapid growth in those of chemical corporations in the period prior to 1930 and a less severe decline during the recent depression than in those of industrial corporations generally. Starting from a lower base in 1923, chemical corporations' earnings had by 1927 bettered by a considerable margin the general industrial performance. The 1927 recession in business resulted in only a minor decline of the rate of advance in chemical earnings as compared with a fairly sizable setback in industrial earnings as a group. Figures 1 and 2 reveal a surprisingly close degree of correlation between stock price movements and earning trends during the shorter as well as the longer periods, and appear to support the validity of deductions from comparative stock-market action as to possible future performance of chemicals as opposed to industrials, not only

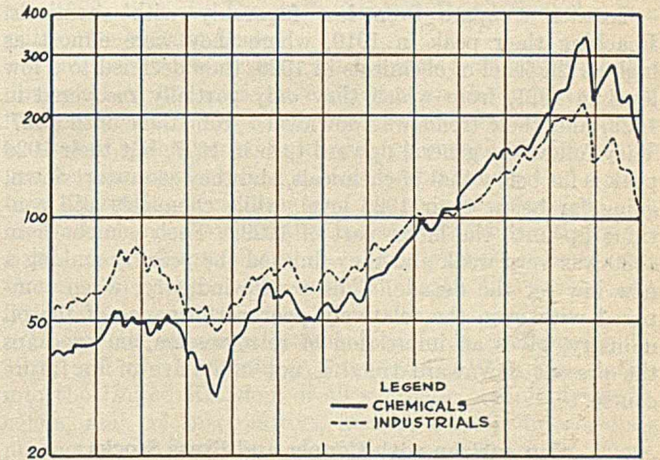

Figure 2—Comparative Price Movements of Chemical and Industrial Stocks

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[1] Received March 4, 1931.

[2] In all computations the figures published by *Standard Statistics* have been used. These are based on 1926 average prices and earnings (equaling 100) and have been adjusted to reflect stock dividends and split-ups.

as a unit, but in its various major subdivisions. In Figures 3 and 4 such a series of comparisons is presented.

Comparison with Oil Stocks

The curve of oil stocks shows less variation than any of the others, never going very far above or below the 1926 level, and showing considerably less recovery after the 1921 depression than chemicals. In 1925 chemicals began a steady upward trend to the 1929 peak; oil stocks rose irregularly and slowly, their high point being far below that of chemicals.

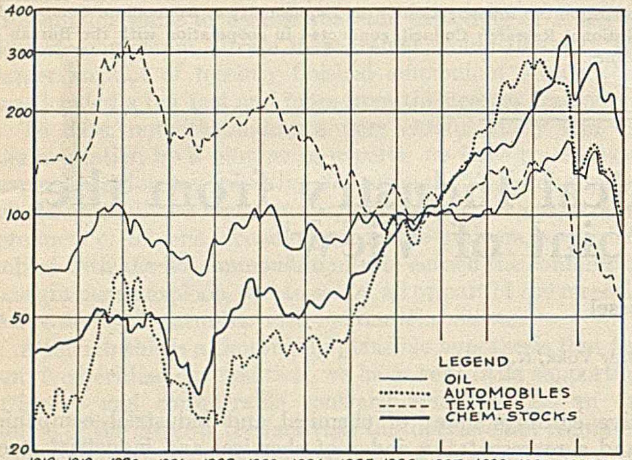

Figure 3—Comparative Price Movement of Chemical, Textile, Oil, and Automobile Stocks

Both followed the general downward trend in the fall of 1929, with a sharp rise in the spring of 1930, and continued to decline to the end of 1930. At that point the chemical stocks were still far above their 1926 level, while the oils were below. Thus, although oil consumption has shown constant progress during the last decade, the earnings of oil companies have not advanced proportionately, and in comparison with chemicals the oil industry appears to have been stationary.

Comparison with Textiles

Textiles compare even less favorably with chemicals. Reaching their peak in 1919, where they were almost as high as the level of chemicals in 1929, they declined to a low level in 1921, from which they only partially recovered in 1923, and their trend was downward from then until 1927. They follow the general upward turn in 1927, but their 1929 peak is far below that of chemicals, and they soon start down, going far below their 1926 level, while chemicals still continue up until the latter part of 1929. Their comeback in 1930 was very weak and they finished the year by making a new low for the decade. The textile industry, when compared with even the relatively poor performance of the oil industry, gives an impression of retrogression, but perhaps the present downward trend is not indicative of its future course.

Comparison with Copper and Brass Stocks

From 1926 through 1929 the curve of the copper and brass industry is not unlike that of chemicals. Its peak, as in the case of chemicals, was reached in 1929, but earlier. The 1930 performance, however, is strikingly different. Copper stock price movements show a steady decline, with only a minor rally during early 1930, and by the end of the year they were back to the 1924 level.

Comparison with Iron and Steel

The iron and steel movement resembles greatly that of copper and brass stocks. Each reaches its peak about the same time as chemicals in 1929, but neither goes so high nor has so much of a comeback in 1930, and at the end of that year both go lower. As compared with both the steel and copper industries, chemicals appear to profit more during periods of prosperity and suffer less acutely during periods of depression.

Comparison with Automobile Industry

When we come to the automobile industry, which has been called "the keystone" of our modern economic structure, we find a stock price curve which resembles more nearly that of chemicals, although it is more irregular. Rising rapidly from 1918 to 1919, it reaches a peak far above that of chemicals in 1919, but the decline in 1921 is also more severe, and it is still low in 1922, when chemicals have already begun their recovery. It is not until 1925 that they pass the level of chemicals, declining again in 1926, as chemicals did, but going lower than chemicals. Automobile stocks then climbed more rapidly than chemicals, but their peak, reached in 1929—earlier than chemicals—is not so high, and they go down faster and further in 1930. Thus, while the automobile industry shows the same steady progress from 1922 to 1929, it seems more subject to change and fluctuation than the chemical industry.

Comparison with Electrical Equipment

It is not until we come to the electrical equipment industry that we find stock price action comparable in extent and pace with that of chemicals. Immediately preceding and subsequent to the 1921 depression, stock price movements in the two groups were generally the same. Even in this case, however, we find a more marked tendency toward recovery in the initial stages of general business pick-up by the chemicals and a less pronounced setback in depression.

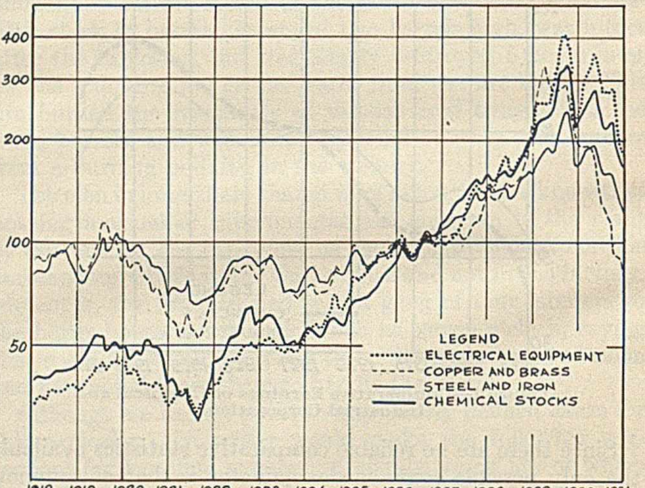

Figure 4—Comparative Price Movement of Chemical, Copper and Brass, Iron and Steel, and Electrical Equipment Stocks

Predictions Based on 1921 Depression

A rather interesting point brought out by the data available in Figures 2, 3, and 4 is the fact that in the 1920–21 depression, while the percentage of decline of chemical and industrial stocks from their high in 1919 to their low in 1921 was approximately the same, the decline of chemical stocks was less gradual, and mostly toward the end of the depression. If we look at the recovery from the lows of 1921 to the highs of 1922, we find that, after the low point had been reached, chemical stocks had a much more rapid comeback than industrials. Industrial stocks had to wait until the beginning of 1925 to touch their 1919 high mark, while chemicals had already done so in 1922. What is true of industrial stocks holds good for those of the individual industries charted, none of them recovering as fast as chemicals.

If its performance after the last depression is indicative of what it will do now, the chemical industry will probably recover more rapidly than industry in general. Notwithstanding temporarily disturbing influences, major developments taking place within the industry itself strengthen the belief that this will happen. Indeed, the inherent character of the industry is such as to insure its recuperative power, for perhaps what most distinguishes the chemical industry from all others is its greater ability to adapt itself to changing conditions.

The Dyestuffs Act in Britain[1]

Ten Years' Progress

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Editor's Note—Edward F. Armstrong is one of the outstanding personalities in England today in industrial chemistry. After studying in England and Germany, he was first connected as chief chemist with Huntley & Palmer. A few years later he became managing director of Joseph Crosfield & Sons at Warrington, as well as of William Gossage & Sons, Ltd., at Widnes and Liverpool. In 1925 he was made managing director of the British Dyestuffs Corporation, in which office he continued even after it became an integral part of the great Imperial Chemical Combine. In 1928 he became an independent chemical consultant, in which capacity he still acts. He holds the degrees of D.Sc. (London), Ph.D. (Berlin), and LL.D. (St. Andrews). He is a Fellow of the Royal Society and of the Institute of Chemistry and is a member of the Institution of Chemical Engineers. He was elected president of the Society of Chemical Industry in 1922 and held that office for two years. He has also held the presidency of the British Association of Chemists. He has done original research work in a wide domain recorded in numerous publications. He is given credit for carrying out the necessary reconstruction in the British dyestuffs industry and for setting that industry firmly on its feet. As chairman of the Association of British Chemical Manufacturers he has been responsible for many of its present activities, in particular for the drawing up of a miniature Factory Act in the form of model safety rules for chemical factories and the creation of an organization to establish British national industrial chemical standards.


Claude Harris

E. F. Armstrong

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IT IS a matter of chemical history that aniline dyes were first discovered in England by William Henry Perkin, but that from prosperous and promising beginnings the industry slowly declined or failed to develop. The continental industry, however, in Germany and Switzerland, prospered greatly and grew to large dimensions. At the outbreak of the war there was not only a lack of many of the dyestuffs required by the textile trade which had never been manufactured in England, but, owing to the further fact that practically none of the intermediates was being made in the country, there was great difficulty in making even those dyes which England had been producing.

In 1914 the country had a dyestuff industry small in magnitude, struggling under great difficulties but in some cases understanding and endeavoring to remedy the errors of the past. This formed a nucleus for the extensions which were to come. There was available also, though in limited amount, both technical experience and scientific knowledge of dyes.

The Government Aids Dyestuff Industry

We are not concerned here to describe the swift resuscitation of the industry other than to chronicle that the Government took a hand in it and that a new company, British Dyes, Ltd., was brought into existence in March, 1915, which in 1919 linked up with the older and more virile organization of Levinstein, Ltd., to form the British Dyestuffs Corporation. Several others, small at first, were enlarged and new ones came into existence.

In May, 1918, the British Government gave a pledge that the importations of all foreign dyestuffs should be controlled by a system of licenses for a period of not less than ten years after the war; this was followed in February, 1919, by a Prohibition of Imports Proclamation. The dyestuff makers set busily to work to build an industry on the insecure foundations of their war work, but their plans were seriously upset by a judgment of Mr. Justice Sankey that the prohibition was invalid, and it was not until December, 1920, that the Dyestuffs (Import Regulation) Act was put on the statute book.

There was, therefore, a period of a little over twelve months during which there was no restriction on the importation of foreign dyestuffs. Naturally, the fullest possible advantage was taken of this period to bring large quantities of dyestuffs to this country, including a considerable amount of reparation dyestuffs. Unfortunately, the period coincided with the trade slump, which further increased the difficulties of the British dyestuff manufacturers. The dyestuffs industry was thereby threatened with extinction until the act became law.

Under the act, which came into force on January 15, 1921, and which expired on January 14, 1931, importation into the United Kingdom of all synthetic organic dyestuffs, colors, and coloring matters, and all organic intermediate products used in the manufacture of such dyestuffs, colors, or coloring matters, is prohibited except under license granted by the Board of Trade on the recommendation of the Dyestuffs Advisory Licensing Committee. This licensing Committee consists of five representatives of the color-using industries; three representatives of the dye-manufacturing industries; together with three independent persons, one of whom is the chairman. It thus affords ample protection to the consuming interests.

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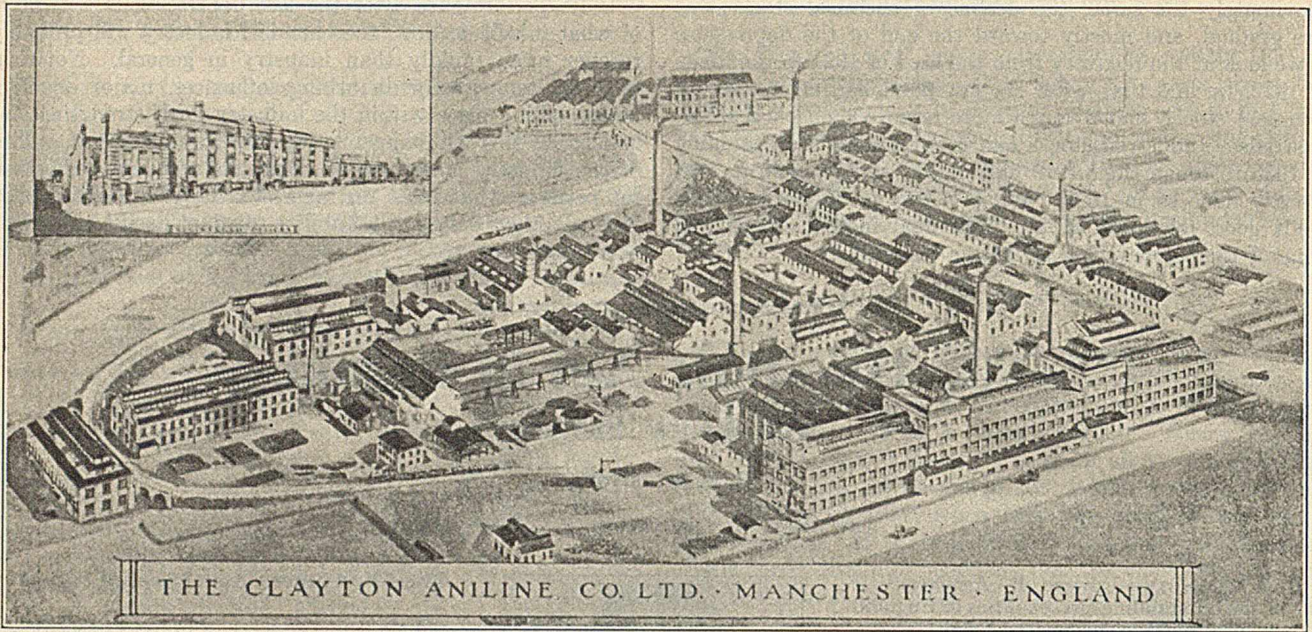
[1] Received March 6, 1931.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Broadly, two sets of circumstances constitute grounds for the granting of licenses—viz., (1) the lack of a British equivalent; (2) price; i. e., where there is a British equivalent but the price is higher than the foreign color, but with adequate safeguards for the British makers.

Achievements under the Act

It is universally agreed that the main object of the act has been achieved and a substantial dye-making industry built up in Great Britain. The dyestuffs produced now represent about 93 per cent of the quantity consumed in the country, and about 81 per cent of their sale value. A very wide range of dyestuffs not previously made has been placed on the market, and their quality is fully equal to that of any foreign manufacture, though many important dyestuffs have not yet been domestically produced.

Vat colors were not made in Great Britain in 1913, whereas in 1928 the production of this series alone, exclusive of indigo, was 64 per cent of the country's requirements.

On the technical side, it is true that, compared with prewar periods, there has been very little production of an original character in dyes either on the Continent or in Great Britain or throughout the world. Thus not many new colors, in the sense that they have not been manufactured anywhere else in the world, have been included in the British products, with the exception of colors for the dyeing of various types of artificial silk. The latter is undoubtedly the outstanding achievement of British makers, and the foreign dyestuffs makers have followed the British in the manufacture of these products. Indeed it may be claimed that the performance chronicled in the following paragraphs is highly meritorious.

Ionamine dyes. This range of entirely new products was discovered and elaborated by the British Dyestuffs Corporation, Ltd., in 1922, being a series which temporarily possess the character of soluble products but have no dyeing affinity for cotton. During the dyeing process they are changed into soluble products and have a direct affinity for cellulose acetate but not for any of the other textile fibers.

Duranol colors. The same firm marketed a range of basic anthraquinone derivatives under the above description which are primarily intended for the dyeing of acetate silk. All these products are characterized by their generally excellent fastness to the usual agencies, light, washing, etc.

Closely related to the above are the *Celatene colors*, introduced by Scottish Dyes, Ltd., possessing the same affinity for acetate silk and equal properties.

S. R. A. products were put on the market by the British Celanese, Ltd., and are mainly insoluble azo dyes in a finely divided state which are primarily intended for, and used in, the dyeing of cellulose acetate silk.

The dispersol colors are products of similar properties and characteristics to the afore-mentioned but introduced by the British Dyestuffs Corporation, Ltd., for the dyeing of acetate silk.

Caledon jade green G, introduced by Scottish Dyes, Ltd., is by far the most important addition to the series of vat colors during the last ten years, and is an outstanding feature in a range of colors especially noted for their brilliance of tone and excellent fastness.

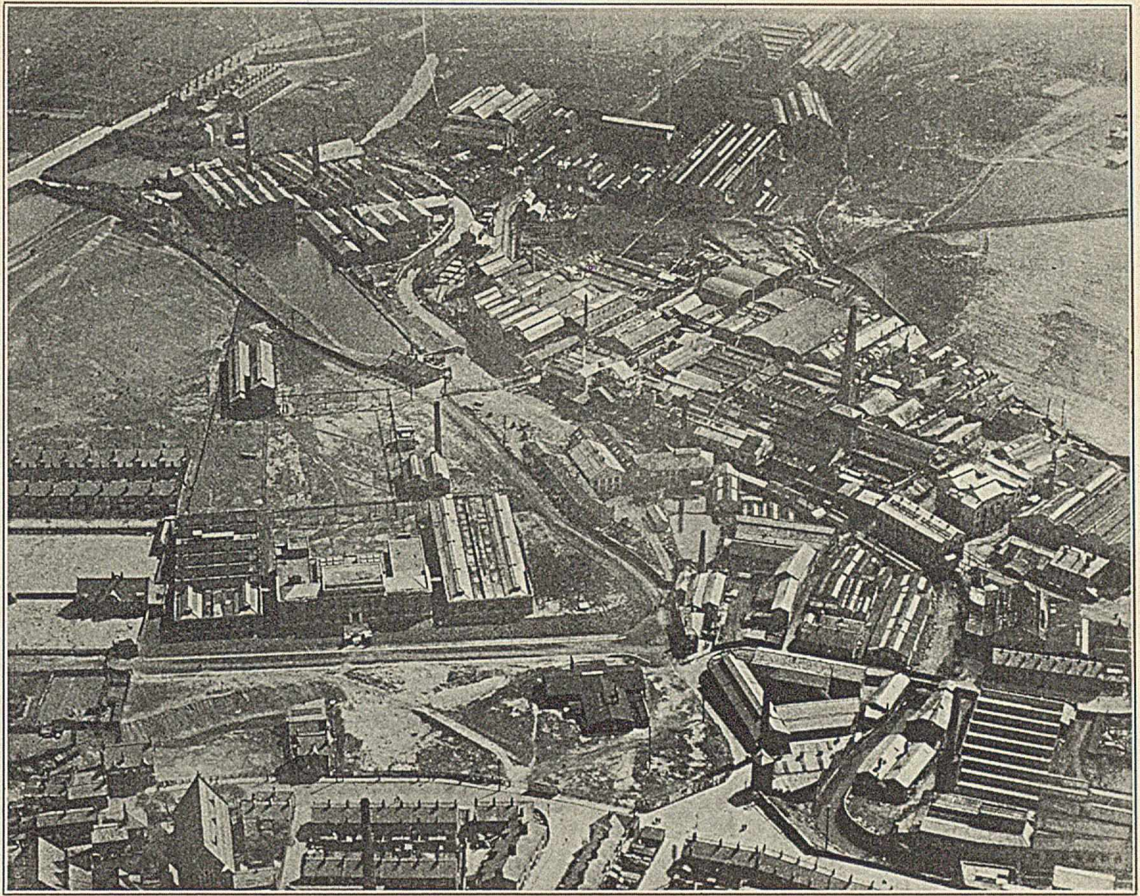
The icyl colors represent a special type of azo dyes which possess the great feature of dyeing level shades on uneven viscose.

The chromazol colors are a new series of dyestuffs specially suitable for calico printing and possessing a special feature in that the alteration in shade, which takes place when the product is fixed with the mordant, is only very slight, which is contrary to the usual development of chrome colors under similar circumstances.

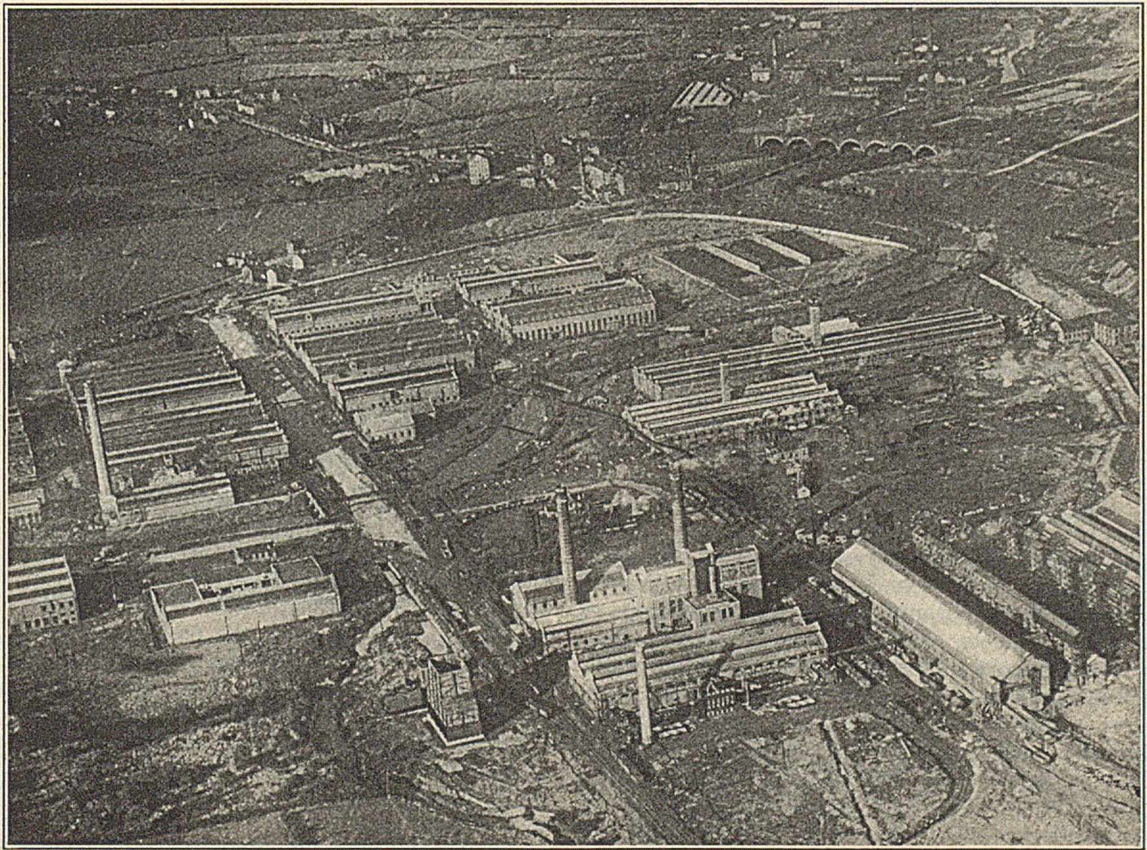
Among other notable features may be included the manufacture, on a large scale, of a series of pigment yellows, oranges, and reds, largely used in the manufacture of paints and colors for lithographic printing; an extensive range of vat dyestuffs (anthraquinone colors) of all shades; a complete range of chrome colors for the dyeing of fast shades on woolen material; developments in the manufacture of accelerators and antioxidants for use in the rubber industry; and new processes for the application and discharging of colors.

According to the report of the Development Committee, in the last ten years there have been introduced 80 new British colors in the chrome and mordant group; 30 basic; over 40 sulfur; 74 vat; 26 lake; 20 oil, spirit, and wax colors; and 20 new colors for acetate silk.

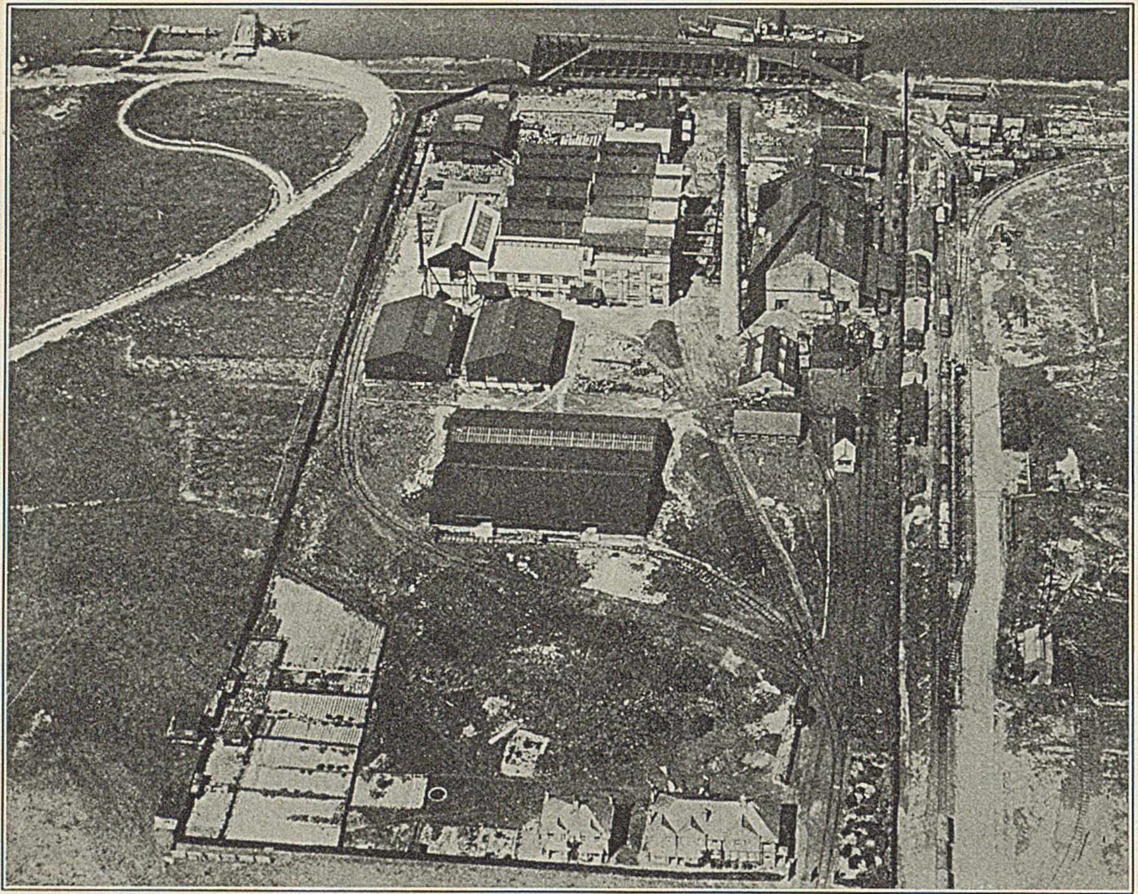
The problem confronting the dye maker has been much the same in England as in America. In 1913 practically no intermediates were made, and it was necessary in the first place to find out how to make these of sufficient purity and



Blackley Works and Hexagon House, British Dyestuffs Corporation



Dalton Works, British Dyestuffs Corporation, Huddersfield



Ellesmere Port Works, British Dyestuffs Corporation

regularity to give dyes which satisfied the ever more rigorous standards of the consumer.

The success obtained has been due in no small part to the helpful coöperation of the color-using industries. In the early days color users were often called upon to use dyes of British manufacture which were either not entirely satisfactory in quality or were higher in price than those which might have been obtained from abroad, in order to give the British dye maker the experience in production so essential to successful manufacture.

It is also due to the joint labors of the chemist and chemical engineer. The successful preparation of these complicated organic chemicals in the research laboratories has been followed by expensive, but vitally important, trials on a semi-works scale and then on a factory scale. Special plant has had to be devised and older apparatus modified to meet the increasingly stringent demands of modern color production.

Bearing on Training of Chemists

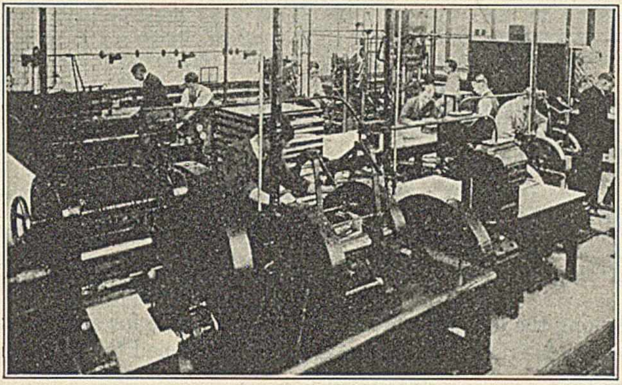
Technical efficiency is very largely dependent upon the employment of chemists of sound training and wide experience in the highly complicated technic of manufacture of organic chemical products. During the past ten years a large number of chemists have gone out from universities and other educational institutions to the various dyestuffs-manufacturing concerns in this country to apply and adapt their academic knowledge and training to the needs of the industry. Many of the works chemists, however, are as yet too young in experience fully to have explored all the intricacies of efficient production, even in connection with products the manufacture of which is long established. From the point of view of developing and cultivating this experience, which will be of material assistance in the expansion of the export trade, the retention of the act for a further period would be of invaluable service to the industry, which probably employs a larger proportion of technically trained men than any other manufacturing industry in the country.

The national importance of the dyestuffs industry as an outlet for British brains and a field of employment for trained chemists and chemical technologists cannot be too strongly stressed. Any restriction of this field would lead to a diminution in the numbers trained with a repercussive effect on the facilities for instruction and research in organic chemistry. This would have an adverse influence, not only on other branches of the organic chemical industry, such as those engaged in the manufacture of medicinal products and other fine chemicals of vital national importance, but on many industries outside the purely chemical field, the progress of which requires the services of highly trained organic chemists.

Prices

Prices were regulated under the act by a factor which the Dyestuffs Advisory Licensing Committee imposed upon the industry, whereby prices of dyestuffs were established bearing a definite ratio to the pre-war prices. The factor, originally fixed at three times pre-war, has by successive stages been reduced to 1.75. It must be borne in mind that this factor price is by no means the average price, but rather a maximum price, and is therefore unsuitable for purposes of comparison. It is calculated that 80 per cent by weight of the British sales of home manufacture are at prices below this factor. For several years British prices have compared so favorably with those of foreign competitors that requests to import products for price reasons have been very few.

The service rendered by the British dyestuffs industry, as a competitive instrument for reducing prices alone, is abundantly evident from a study of the downward trend of prices of foreign dyestuffs consequent upon the appearance of British equivalents on the market.

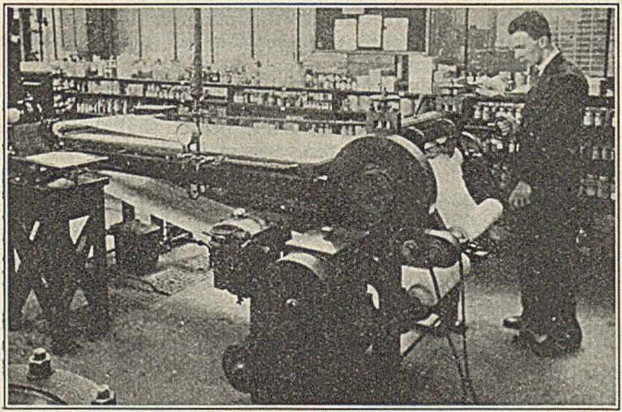


Rubber Service Laboratory, British Dyestuffs Corporation

Import Producers

The making of dyes has been in the hands of the British Dyestuffs Corporation, of Scottish Dyes, Ltd., both merged in Imperial Chemical Industries, Ltd., since 1926; of the British Alizarine Company, L. B. Holliday & Company, Brotherton & Company, Hickson & Partners, Williams Brothers, and others; and in addition the Clayton Aniline Company, Swiss-owned since 1911, which is the second largest producer and manufactures at Clayton a very large range of colors of all types. All of these have made great technical progress and played their part in the advance recorded.

The factory at Ellesmere Port built by Meister, Lucius & Brüning and employed to convert phenylglycine into indigo, which had been closed on the outbreak of war, was purchased by Levinstein in 1916 and the manufacture of indigo resumed within three months. A product of the highest quality was produced able to satisfy the home demands and maintain a large export business.



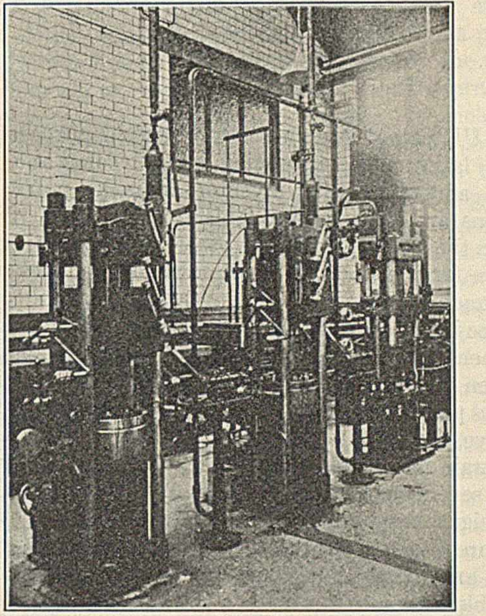
Spreading Machine, Rubber Service Laboratory, British Dyestuffs Corporation

Alizarin had always been manufactured by the British Alizarine Company, who later extended their operations to vat dyes. The vat colors were primarily the concern of Scottish Dyes, who were associated with large consumers of these dyes in Morton's Sundour Fabrics, Ltd. Mr. Morton has told his own story of the achievement in graphic language in the *Journal of the Society of Arts* for April 12, 1929.

Vat dyes have been successfully made also by Claus, subsequently merged into the British Dyestuffs Corporation.

Other Products of Industry

The operations of a dyestuff industry cannot be confined to the production of colors alone. The primary organic raw materials and the intermediates produced from them are available for the production of such substances as accelerators for the vulcanization of rubber, wetting out and other reagents for the textile industry, synthetic resins, and many others. The English industry has not neglected these fields, and in rubber questions in particular it has taken a lead.



Curing Presses, Rubber Service Laboratory, British Dyestuffs Corporation

Conclusion

We have told our story in formal language, since it is a record of a serious attempt to solve a technical and economic problem under government protection of an entirely novel type in Britain, which necessarily has drawn upon itself the closest scrutiny and much criticism.

It is agreed by all fair-minded persons that the experiment has been a success, that a dyestuffs industry, and that no weakling but a lusty forceful adolescent, has been established during the ten years of the act. That the time has been too short for its development to a stage when those responsible for it consider it fit to stand alone to experience the buffeting of a competitive world, confronted by new and undreamed of economic problems of overproduction and underconsumption, is not to be wondered; unexpected and unforeseen happenings have reduced the effective value of the ten years' period. Hence the almost universal pressure for the renewal of the act which, though abandoned by the Government, was inserted by the House of Lords in the Expiring Laws Continuation Act and is consequently renewed until January 15, 1932.

We can conclude in the words of the widely circulated statement of the Association of British Chemical Manufacturers:

> The Dyestuffs Industry is a Key Industry of vital importance to the national prosperity and safety. We have, in the past, paid heavily for the neglect of this branch of applied chemistry. The Dyestuffs Act was passed to enable this handicap to be overcome. The present trend of industrial development shows indisputably that a nation's prosperity will in future depend

more and more on chemical science and its applications. No branch of chemical activity, least of all the organic side, can be allowed to languish if Great Britain is to maintain her position as an industrial power.

This is not the place to write of the future of dyestuffs. It is at least certain that supremacy in the organic chemical industries will largely lie with that country which has the right men—directors with sound chemical knowledge and commercial ability coupled with breadth of outlook and enterprise, and chemical investigators having the heaven-born gift of scientific discovery and a love of research for its own sake.

What's Patentable in Industrial and Chemical Engineering[1]

Charles W. Rivise

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OUR patent system has the twofold purpose of stimulating and encouraging inventiveness and ingenuity and of inducing inventors to make public their inventions and discoveries. This it does by offering the inventor the right to exclude others from practicing his invention for a period of years, provided he makes such a full and exact disclosure of his invention that the public can practice it at the expiration of the inventor's monopoly. The document giving the inventor this right is a binding contract between the Government and the inventor and is termed "letters patent" or simply "patent." To render his monopoly effective, the patentee is allowed the use of the federal courts to restrain infringers. The period of the monopoly has been set at seventeen years in the case of all patents except those for designs, because this length of time was thought sufficient to secure to inventors a reasonable compensation for the time, effort, and money that they may have expended in making available their contributions to the arts and sciences.

A patent does not confer upon its owner the right to use his own invention. All it gives him is the right to exclude others from doing so. Hence it follows that there are situations in which the patentee may be restricted in the use of his invention or even entirely precluded. Thus it has been decided that inventors of butter substitutes, patent medicines, adulterated foods, and gambling devices cannot vend these articles in states prohibiting their sale. And the inventor of an improvement on a prior dominating patent cannot use the improvement until the dominating patent expires. He can, however, prevent the owner of the dominating patent from using the improvement. In this way he may induce the prior patentee to exchange licenses with him and thus put both patents to work over a much larger field. An exchange of licenses also strengthens both patents by the admission of validity.

PREREQUISITES FOR OBTAINING A VALID PATENT

The inventor, in order to take advantage of the protection afforded by the patent statutes, must comply with certain requirements. Furthermore, the alleged invention or discovery must fulfil certain essential conditions. These requirements and conditions will be defined and explained by means of examples taken from litigated patents. Wherever possible the examples will be limited to industries involving industrial and chemical engineering.

Right to Patent

In the first place, the inventor must not have abandoned his invention or otherwise forfeited his right to a patent. Among the many ways in which it is possible for an inventor to lose his right to a patent may be mentioned the following:

(*a*) Suppression of the invention until after it is independently rediscovered by another.

Mere delay in applying for a patent is not a bar to a patent, and a person may conceal his invention as long as he wants to. But when the inventor deliberately suppresses his discovery, he takes the risk that some one else may rediscover or stumble across the invention and make it available to the public. In such case the first inventor may lose his right to a patent. Hence, few inventors resort to suppressing the invention unless they are in very adverse circumstances or feel that their contributions are so far ahead of the art that the seventeen-year monopoly of a patent would be insufficient to secure to them an adequate reward.

(*b*) Practice of the invention as a trade secret for two years without in the meantime having applied for a patent.

Chemical compositions and processes lend themselves readily to protection by means of trade secrets. Hence it is often possible to secure by this means a monopoly more enduring than that given by the patent laws. The disadvantage of this method of protecting an invention is the difficulty of keeping the secret from enterprising or dishonest competitors. Employees must be enjoined to secrecy, visitors barred from the plant, and in many cases it is even necessary to adopt such subterfuges as marking measuring instruments with false scales.

Any one who comes upon the secret honestly or rediscovers it by analysis or experimentation may use it freely or make it public. Those who use dishonest means to acquire the secret can be stopped from availing themselves of it. But it often happens that the public also learns the secret, in which case it becomes public property unless the inventor had taken the precaution of filing a patent application before the secret had been used for two years.

A notable case illustrating this principle of law is that of Macbeth-Evans Glass Company *vs.* General Electric Company (246 Fed. Rep. 695). In that case it appeared that the Macbeth Company had for a period of ten years made glass under a secret process until the secret was stolen by a competitor through a dishonest employee. Suit was brought against the competitor and he was enjoined from making use of the stolen information. The details of the process, however, leaked out and the Macbeth Company, to protect its rights against other competitors, applied for and secured a patent. Suit was then brought against the General Electric Company, one of the competitors, to stop it from infringing the patent, but the Court held the patent invalid on the ground that by practicing the invention secretly for more than two years the Macbeth Company had abandoned its right to patent protection.

(*c*) Public use of the invention for two years prior to filing and application.

This bar operates without reference to the intent of inventor, and if once proved cannot be mitigated or excused. However, the Courts will in a worthy case allow an inventor a wide latitude in proving that an apparent public use was merely for the purpose of experimentation. Thus, in the celebrated case of Elizabeth *vs.* American Nicholson Paving Company (97 U. S. Rep. 135), the Supreme Court saved a valuable patent for an improved paving by holding that an alleged public use in a public highway for a period of seven years was but an experimental use to test the wear and tear of the paving. However, it must be emphasized that if an inventor makes a device and gives or

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[1] Received January 12, 1931. Copyright 1931 by Charles W. Rivise. All rights reserved by the author.

sells it to another to be used without limitation or restriction or injunction of secrecy, and it is so used, it is a public use, even if confined to one person. And it is not necessary to public use that the article could have been seen by the public eye, if the ordinary use of such articles is veiled from view.

(*d*) Placing the invention on sale for two years prior to filing an application. It is immaterial whether or not the device of the invention was actually sold, provided it was placed on sale.

(*e*) The securing of a patent in a foreign country by the inventor or his agent, without filing a corresponding application in this country within twelve months after the filing of the foreign application.

(*f*) Allowing two years to elapse after the grant of a patent or the publication of an article disclosing the invention, before filing an application.

It is immaterial whether the use, sale, or description occurs with or without the knowledge or permission of the inventor.

(*g*) Failing to appeal from a final decision of the Patent Office refusing a patent. This is so, whether or not the Patent Office is correct in its decision. If the applicant is of the opinion that the Patent Office has erred, it is up to him to appeal to the proper tribunals.

Patent Application

In the second place, the inventor must file an application in the United States Patent Office adequately describing and clearly defining the subject matter of the invention and prosecute it to allowance.

The application must be made by the inventor only. If more than one person contribute mutual suggestions which result in a unitary invention, they are joint inventors and all must join in making the application. If any of them neglect to join, the patent will be held invalid; similarly if a person who had no part in making the invention files the application or joins with the true inventor in filing the papers. In this connection it must be emphasized that one who makes a financial contribution and nothing more is not a joint inventor. The only way he can acquire an interest in the patent is by assignment from the true inventor.

The mere fact that one who conceives an invention avails himself of the constructive skill and ingenuity of another to reduce the inventive idea to practice does not make the second person a joint inventor. And this is so, even if the second person makes valuable discoveries ancillary to the plan and preconceived design of his employer. But if the second person makes suggestions which modify and make the main idea operative or contributes an independent part of the entire invention which combines with the part produced by the other to create the whole, he is entitled to be considered a joint inventor and must join in filing the application. Furthermore, if the second person is merely given a problem in very general terms or finds it necessary to discard or depart radically from the plans of his employer, he is a sole inventor and the application must be filed by him alone. Under proper circumstances, however, the patent, when issued, may belong to the employer or he may be given a shop right therein.

THE SPECIFICATION—The part of the application describing the invention is called the specification and must be in such full, clear, concise, and exact terms as to enable any person skilled in the art or science to which the invention or discovery appertains to make, construct, compound, and use the same. The withholding of any information essential to the working of the invention is sufficient to invalidate the patent. In the case of devices that can be illustrated, the specification must be supplemented by a drawing.

Since the description is directed to those skilled in the art, it is unnecessary for the applicant to point out the relationship between his particular improvement and the prior art devices. In the language of the Supreme Court, the patentee need only "begin at the point where his invention begins, and describe what he has made that is new and what it replaces of the old. That which is common and well known is as if it were written out in the patent and delineated in the drawings."

Neither is the inventor required to state all the advantages and functions of his invention or all the uses to which it may be put. Likewise, he may omit from his application the scientific principles or theory underlying his invention or the causes which produce the desirable result. And if he does state what he believes to be the principles governing his discovery, it is wholly immaterial to the validity of the patent whether or not the statement is correct, so long as he has so set forth the thing to be done that it can be reproduced by one skilled in the art.

THE CLAIMS—At the end of the specification are one or more short statements called claims. The claims are the vital part of the patent and define the scope of the patent. Great skill is required in drafting them. Usually the patent examiner does not agree with the inventor that the presented claims represent his contribution to the art. In such cases the inventor may amend the rejected claims or try to persuade the examiner to his own way of thinking. When the inventor and the examiner finally agree, the patent is granted with the claims agreed upon. If they cannot agree, the inventor may appeal to a higher tribunal in the Patent Office and then to the courts. But if the inventor acquiesces in the rejection of a claim and the patent is granted with a narrower claim, he is forever estopped from contending that he was entitled to the broader claim.

Each claim in a patent is considered a separate and independent invention. One may be valid, all the rest invalid. But the claim that is good remains good and is unaffected by the presence of those that are bad. Likewise, one claim may be infringed and the others not. In other words, the patent does not stand or fall as a unity—each claim is in effect a separate patent. However, if some of the claims of a patent are finally held invalid, the patentee must within a reasonable time file a disclaimer in the Patent Office as to the claims held invalid. Otherwise he will not be allowed to bring an infringement suit on the claims held valid.

Patentable Subject Matter

In the third place, the invention or discovery must be directed to patentable subject matter; i. e., it must be capable of being expressed in one or more of the following ways: (1) an art; (2) a machine; (3) a manufacture; (4) a composition of matter; (5) an improvement on an already existing art, machine, manufacture, or composition of matter; (6) the asexual reproduction of a newly created species of plant or tree; (7) a design for an article of manufacture.

ART OR PROCESS—The term "art" is commonly considered synonymous with "process" and may be best defined as "an operation performed by rule to produce a desired result."

A patentable process may consist of one or more steps. An excellent example of a one-step process is that defined in a claim of Weston's Reissue Patent 13,730, which reads as follows:

> The method herein described of manufacturing paper having a thinned portion, which consists in removing from the web at the portion to be thinned along a definite line some of the material by the application of air pressure thereto.

This claim was held valid in the decision of the Weston Company *vs.* L. L. Brown Company (20 Fed. Rep. [2nd] 183).

Splendid examples of processes of more than one step are disclosed in Patent 762,880 to Chambers, held valid in the case of Consolidated Window Glass Company *vs.* Window Glass Company (261 Fed. Rep. 362), in Patent 483,646 to Dyer, held valid in the case of Mica Insulator Company *vs.*

Union Mica Company (137 Fed. Rep. 928) and in Bowes Patent 1,489,477, held valid in the case of Knick *vs.* Bowes (25 Fed. Rep. [2nd] 443).

A representative claim of the Chambers patent reads as follows:

> The method of shaping glass articles, consisting in drawing them from a glass bath and gradually increasing the speed of drawing through the drawing operation, substantially as described.

A claim of the Dyer patent reads as follows:

> The herein described method of building up electrically insulating mica sheets, consisting in varnishing a foundation plate, placing mica scales thereon while the varnish is still wet or soft with their edges overlapping, varnishing the mica sheet, thus forming a second and a third, etc., layer of mica in a similar manner until the required thickness of mica sheets is obtained and chilling the sheet while rigidly held in a curved position.

The Bowes patent discloses a method of patching rubber articles including the following steps:

> (1) Buffing the surface to which the patch is to be applied in the presence of a rubber softener and solvent.
> (2) Rubbing the softener and solvent into the pores.
> (3) Scraping and thoroughly removing the softener to leave the surface clean and dry.
> (4) Applying a soft clean rubber patch.

It will be noted that in the Weston patent the mechanism for carrying out the process was old. There was certainly nothing new in the paper-making machine or in the air hose utilized in creating the air pressure for removing some of the stock along the desired line. In fact, anyone skilled in the particular art can, without exercising any inventive ingenuity, devise other mechanisms capable of carrying out the steps of the process. Some of the operations can even be performed by means of simple tools or by hand. This is particularly true in the Dyer and Bowes patents cited above.

Hence, it may be stated as a general rule that the tools or apparatus utilized in carrying out a process are of minor importance as far as the patentability of the process is concerned. In fact, the steps or operations themselves should be as far as is possible independent of the form or kind of tools used.

If the steps of the process are not independent of the form or kind of tools or apparatus utilized in performing them, the Courts will hold a claim covering the process invalid, as being for the mere function or mode of operating the machine. The usual test to determine whether a so-called method is a true process or the mere function or mode of operation of a machine, is whether the process can be carried out by more than one form of machine or tool. If it can, it is a true process; otherwise, not.

It is conceivable that a process may be invented that can be carried out by means of a newly invented machine. In that case both the method and the machine may be patented, either in the same or different patents.

This was the situation in the case of Hammerschlag *vs.* Scamoni (7 Fed. Rep. 585) involving a patent covering both a method and a machine for making waxed paper for wrapping butter, cheese, etc. The method consisted in spreading wax on one surface of the paper, heating the paper from the opposite side to spread and fuse the wax into the fabric of the paper, removing the surplus wax, and polishing the wax upon the paper. The Court held that both the method and the machine utilized for carrying out the steps of the process were new and entitled to patent protection.

Obviously a method of doing something by machine that had previously been done by hand is not patentable, if the hand and machine methods are essentially the same. Nor is an old method performed by means of a tool patentable as a method. In both cases, however, the machine or tool may be patentable.

In the case of Thropp Sons' Company *vs.* Seiberling (264 U. S. 320) involving Patent 941,962 to State for making tires by machinery, the patentee claimed that he had been the first to successfully build tire carcasses by machinery. The Supreme Court held that the method used by State consisted of the same succession of steps as had been previously performed by hand. Patentability was therefore denied to his method. The machine claims were also held invalid on the ground that the transfer from hand to power was by the usual appliances used before State's alleged invention.

MACHINE—A machine has been defined as "an instrument composed of one or more mechanical powers and capable, when set in motion, of producing by its own operation, certain predetermined effects."

A claim for a machine held valid in the case of Keasbey & Mattison Company *vs.* American Magnesia Company (143 Fed. Rep. 490) reads:

> A machine or apparatus for making plastic tubes, having a press with a mold therein, a reservoir, a supply pipe leading from said reservoir to said mold, a pumping device for forcing tube material from said reservoir to said mold, an air chamber communicating with said supply pipe and between the pumping device and the mold, said parts being combined substantially as described.

MANUFACTURE AND COMPOSITION OF MATTER—The term "manufacture" is synonymous with article of manufacture and is best defined as "whatever is made by the art or industry of man, not being a machine, a composition of matter or a design."

A composition of matter may be defined as that which is formed by the intermixing of two or more substances whether it be by chemical union, mechanical mixture, or both, and whether the ingredients be fluids, solids, or gases.

The difference between a machine and an article of manufacture is that a machine has a law of operation inherent within itself, while an article of manufacture has no law but depends entirely upon external forces. The difference between an article of manufacture and a composition of matter is that in a composition the patentable quality resides in the novel combination of ingredients, while the patentability of an article depends upon the inherent characteristics of the article itself. It follows, therefore, that an article may be composed in whole or in part of a composition of matter, which in itself may be novel and form the subject matter of a patent.

It must be emphasized that the product of a process is not an article of manufacture in a patent sense unless it has been transformed from raw or prepared materials in such a manner as to acquire a new or distinctive form, quality, or property. It has been held that the products of the following processes are not manufactures: (1) adding borax to the rind of a fruit to prevent decay; (2) cleaning and ginning of cotton; (3) washing or scouring of wool; (4) grinding off of the top layers of a shell to expose the inner or brilliant surface.

Likewise, a patent cannot be obtained for an intermediate product of a process unless it is in commercial form. Thus, valid patents have been granted on gear blanks and on intermediate resinous condensation products suitable for varnishes and molding compositions, but a patent was refused on a gob of glass in its temporary condition while being transformed into something else.

An article is entirely independent of the machine or method by which it is made. Many articles are still made by old hand processes. If the machine or method by which the new article is made is also novel, it may be protected in the same or a separate patent. In fact, it is possible to secure patent protection on a machine, method, article, and composition, if the composition is new and can be made into a new article of manufacture by performing a new series of steps by means of a new machine. Usually the invention of a new composition is followed almost immediately by many new methods of making the composition as well as new uses and applications of the new composition, many of which form the basis for valid patents for compositions, articles, methods, and machines.

As a general rule an old composition in a different state or condition may be patentable as a new composition. As illustrations may be mentioned calcium carbide in the form of aggregated crystals, Union Carbide Company *vs.* American Carbide Company (181 Fed. Rep. 104), and a synthetic resin in a solvent for use as a varnish or mixed with a filler for use as a molding composition, General Bakelite Company *vs.* Nikolas (225 Fed. Rep. 539) involving Patents 954,666; 1,018,385; and 1,037,719.

IMPROVEMENT—An improvement is an addition to or an alteration in some already existing art, machine, manufacture, or composition. It need not be better in all respects than the thing upon which it purports to be an improvement. At the present state of the arts most of the patents for which applications are made are but improvements on some basic patent. However, the day of generic or basic patents is not yet past.

DESIGN—A design may be defined as that which gives a peculiar or distinctive appearance to an article of manufacture. The appearance may be the result of peculiarity of configuration, or of ornament alone, or of both conjointly, but, in whatever way produced, the new thing is the subject of a design patent. However, if the main purpose of the configuration is for mechanical utility, it cannot form the basis for a design patent. Nor can a valid design patent be obtained for a machine, no matter how much its appearance appeals to the esthetic senses. The Courts have recently relaxed the rule, however, and allowed a design patent on a concrete mixer.

Unpatentable Discoveries

It follows from what has already been said that many inventions and discoveries fall outside the pale of patent protection for lack of patentable subject matter. In this category may be placed abstract forces of nature, causes, and effects. Thus, in the case of M'Ewan Brothers *vs.* M'Ewan (91 Fed. Rep. 787), it was held that the mere discovery that a board already on the market had inherent strength did not entitle to a patent the first person to observe this fact.

The discovery that ether would produce insensibility to pain in animals and human beings was held not a proper subject matter for a patent in the celebrated case of Morton *vs.* New York Eye Infirmary Company (5 Blatchford 116).

In the case of *In re* Kemper (Fed. 7687), the facts were these: The alleged inventor discovered that blocks of ice placed on edge, owing to the peculiar action of air currents within the ice, melted less rapidly than when laid flat. The Court held this discovery to be unpatentable.

In the case of Wall *vs.* Lech (66 Fed. Rep. 553), it appeared that the old process of fumigating plants and trees by hydrocyanic gas, after covering them with an oiled tent, was more effective in the absence of actinic rays of the sun. The Court held that the idea of carrying out the process at night or in foggy weather was not patentable. And in the leading case of O'Reilly *vs.* Morse (15 Howard 62), the Supreme Court held that Morse could not claim the exclusive right to his discovery that electromagnetism can be utilized as a motive power for making intelligible marks at a distance, on the ground that it would amount to giving him a monopoly on one of the forces of nature for a particular purpose.

In all the decided cases the Courts have taken great pains to point out the fact that, though neither the cause nor its effect is patentable by itself, the means by which the cause is applied to produce the effect is patentable. Likewise, a new property discovered in matter, when practically applied in the making of a new manufacture or composition, may be the basis of a valid patent. In other words, the principle of nature itself is not patentable, but its utilization by means of an art, machine, manufacture, or composition of matter, when properly expressed in one of these forms, is patentable.

Thus, the Supreme Court allowed Morse patent protection on his telegraph apparatus. And in the case of American Box Machine Company *vs.* Wilson Paper Machine Company (71 Fed. Rep. 884), the Court held that the patentee of Patent 244,919 had discovered that paper moistened with paste must be in the air a few moments before being laid on the box and that he had invented mechanical means to adapt the discovery to actual use. He was, therefore, held entitled to protection on his machine but not on his discovery.

On the whole, the policy of the patent law to protect the utilization of the forces and principles of nature rather than the abstract discoveries themselves has reacted very beneficially upon industry. This is reflected in the large number of patented inventions consisting either partially or wholly in the utilization of forces or powers of nature such as chemical reaction, heat, magnetism, electricity, hydraulics, light, pneumatics, etc. As an example of a process utilizing an elementary principle of pneumatics may be mentioned the Weston method for forming a thinned portion along a web of paper. Among the many employing chemical and physical forces may be mentioned the tanning process disclosed in Patents 291,784 and 291,785 held valid in the Tannage Patent Cases 70 Fed. Rep. 1003 and 93 Fed. Rep. 811.

Utility

In the fourth place, the invention must be useful. This requirement has been interpreted by the Courts to mean that the device must be operative to perform a purpose not against public morals. If a thing is only capable of an illegal use, it is not patentable. The device need not, however, be either practical or a commercial success.

Novelty

In the fifth place, the alleged invention must be new. In other words, it must not have been known or used by others prior to the time of the alleged invention. However, prior knowledge or use in a foreign country is not sufficient to defeat a patent granted in this country, provided the patentee, at the time he completed the inventive act, believed himself to be the first and original inventor, unless the thing patented had been described in a prior patent or printed publication.

To determine the question of novelty the Patent Office institutes a search through its files. These files contain all the patents granted in most of the countries of the world that grant patents and considerable technical and scientific publications. The inventor, in order to avoid disappointment, should make an unofficial preliminary search before filing his application. The results of such preliminary investigation also give the inventor an idea of the scope of his invention and enable him more intelligently to prepare and prosecute the application.

Invention

In the sixth place, inventive ingenuity must have been exercised in producing the new thing. The fact that it is different from what was done before is in itself insufficient to sustain a patent, for it has never been the object of the law to grant a monopoly for every shadow of a shade of an idea which would naturally occur to anyone working in the art, or for every trifling device which could be produced by a skilled mechanic whenever required.

Presence of invention is always determined from the result and never from the mental process of the inventor. It is immaterial how small may be the actual effort involved—how easily, or how quickly the idea may have come to the inventor. It may have been the result of deliberation, conscious or unconscious, or of intuition, or of any other exercise of the reasoning faculty. It may even have been the result of a happy thought or of what is usually termed an "accidental discovery."

One Court even went so far as to make the following statement:

> Invention is not always the offspring of genius; more frequently it is the product of plain hard work; not infrequently it arises from accident or carelessness; occasionally it is a happy thought of an ordinary mind; and there have been instances where it is the result of sheer stupidity. It is with the inventive concept, the thing achieved, not with the manner of its achievement or the quality of the mind that gave it birth, that the Patent law concerns itself.—Radiator Specialty Company *vs.* H. W. Buhot (39 Fed. Rep. [2nd] 373).

Simplicity does not necessarily imply the lack of invention. As a matter of fact and of law, the highest trait of genius is to obtain simplicity. Thus, in the case of Emerson & Morris Company *vs.* Simpson Brothers (202 Fed. Rep. 747) involving Patent 624,653 to Stevens, it was held that the molding of an artificial stone compound in a mold of dry sand, which absorbs the excess moisture from the stone and hastens the setting, constituted invention of a high order. Similarly, in the case of U. S. Mitis Company *vs.* Midvale Steel Company (135 Fed. Rep. 103), it was held to involve invention to add a small piece of aluminum to the iron or steel after it has fully melted and just as soon as it is about to be poured into the mold, for the purpose of making the casting free of "blow holes."

Simplicity must not be confused with obviousness. They are far from being synonymous terms in the patent law. As has already been pointed out, simplicity is not evidence of lack of invention. Obviousness, on the other hand, is such evidence. But it must be strongly emphasized that if the advance in the art, however slight, appears obvious only after it has been made, this is no evidence of the lack of invention; furthermore, that, no matter how obvious the change over the prior art appears to be, a valid patent can be secured if the modification is accompanied by an unobvious or unexpected change in the result produced and provided that the invention is of sufficient importance.

For, as has been authoritatively stated by the Supreme Court in the case of Diamond Rubber Company *vs.* Consolidated Tire Company (220 U. S. 428):

> Knowledge after the event is always easy, and problems once solved present no difficulties, indeed, may be represented as never having had any, and expert witnesses may be brought forward to show that the new thing which seemed to have eluded the search of the world was always ready at hand and easy to be seen by a merely skilful attention. But the law has other tests of invention than subtle conjectures of what might have been seen and yet was not.

And, as stated by the District of Columbia Court of Appeals, in the case of *In re* Huff (1919 C. D. [Commissioner's Decisions] 152):

> Many things appear easy after they have been explained, and doubtless many a man has wondered why he failed to think of some apparently simple device or improvement that yielded a fortune to the one who did and revolutionized an industry. The simple fact is that the average person sees things as they are, and he who has originality of vision enabling him to visualize defects and the means of overcoming them should receive adequate reward.

Invention sometimes resides in the discovery or appreciation of the difficulty with an existing device or art, even though the solution readily becomes apparent after the difficulty is understood. This was the situation in the case of *ex parte* Phair (1928 C. D. 76) involving an application which matured into Patent 1,708,519 for a method of laundering textile fabrics. It appeared that Phair had discovered that the holes in laundered fabrics were caused by the corrosive action of sulfur compounds absorbed from the air during the drying. The rather obvious expedient then occurred to him to add a protective agent or neutralizing substance to the rinse water to counteract the effects of the sulfur compounds. This idea had previously been applied to tire fabrics before incorporating them into tires. The Commissioner of Patents, on this state of facts, decided that Phair was entitled to a patent, stating that this was a case where the mechanical or chemical change over the prior art was the minor part of the invention. Of course it is clear that, had Phair stopped at the discovery of the problem and had not completed the inventive act by suggesting the solution, obvious though it was admitted to be, he would not have received the patent. For, as pointed out previously, the discovery of a principle of nature by itself is not patentable.

NEGATIVE RULES BY WHICH PATENTABILITY IS DETERMINED

The Courts have found it impossible to determine the presence of invention by applying the test of any general definition to the device under consideration. In one case it is possible to say that invention of a high order is present. In another case it is possible to say that there is lacking that intangible something which distinguishes invention from non-invention. The intangible something, however, cannot be segregated and defined so as to aid in the determination of the majority of cases, which lie in between the two extremes. Hence, the Courts have contented themselves by deciding individual cases on their own merits by means of a process of exclusion. As a result of the many adjudicated cases in which this process has been utilized, there has grown up a set of negative rules, which are to be applied in given situations to determine whether certain variations in old devices and processes do or do not arise to the dignity of invention.

Mechanical and Chemical Skill

The first of these rules is that it is not invention to produce a device or process which any skilful mechanic or chemist could produce whenever required. Any advance in the arts that results from this skill the public is entitled to avail itself of as a fruit of mechanical growth and advance.

The test is whether an ordinary person skilled in that particular art would spontaneously make the change represented by the invention. If he would do so, there is no patentability. A person skilled in the art is a fictitious person supposed to know all that has been done in that field.

Examples of changes that have been held to involve nothing more than mechanical skill, and hence to be unpatentable, are as follows:

(1) Selections from a large number of previously used substances, those that give the best results. Thus, in the case of Welling *vs.* Crane (14 Fed. Rep. 570), Patent 98,727 to Welling for an artificial horn made from finely divided cotton or wool and powdered shellac mixed dry was held invalid on the ground that the ingredients of the patent had been judiciously selected from the many previously mentioned in the literature.

(2) Weighting knife bar of a roll paper cutter so as to obviate the necessity of pressing it down by hand when cutting off a sheet of paper. American Roll Paper Company *vs.* Weston (59 Fed. Rep. 147).

(3) Placing two sheets of fly paper together with their sticky surfaces face to face, for convenience in handling and packing. Andrews *vs.* Thum (67 Fed. Rep. 917).

(4) Making knife of leather skiving machine removable so that it can be sharpened without removing the knife holder. Apple *vs.* American Shoe Machinery & Tool Company (232 Fed. Rep. 603).

(5) In the case of Window Glass Machinery Company *vs.* Pittsburgh Plate Glass Company (284 Fed. Rep. 645), the Court found that prior to the Speer and Harvey Patent 828,147, commonly known as the "shawling patent," it had been the practice to divide the cylinder of glass into small sections and crack each section from end to end along a single line. The section was then placed on the flattening stone with the cracked line uppermost so that, as the cylinder softened under the heat, each side fell away from the crack and opening gradually sank upon the flattening stone. The patent in suit suggested cutting or cracking the cylinder longitudinally along two or more lines instead of one. The Court held that an increase in the size of the cylinders had made it impossible to flatten the cylinder in an oven of ordinary size and that "to cut the cylinder to fit the oven just as the tailor cuts the cloth to the garment" constitutes mere mechanical skill.

In the case of Corona Cord Tire Company *vs.* Dovan Chemical Company (273 U. S. 692), the defendant contended that, since triphenylguanidine had been used as a vulcanization accelerator, it involved nothing more than chemical skill to suggest the use of diphenylguanidine for the same purpose since both compounds are closely related chemically. The Supreme Court, however, dismissed this argument with the statement that "the catalytic action of an accelerator cannot be forecast by its chemical composition, for such action is not understood and is not known except by actual test." The Weiss patent covering diphenylguanidine as an accelerator was, however, held invalid on other grounds.

Change of Size or Degree

The second rule is that a mere carrying forward of the original thought, a change only in form, proportions, or degree, doing the same thing in the same way by substantially the same means, with better results, does not constitute patentable invention. Exceptions to the rule are made when the results are disproportionate or unexpected.

As examples of unpatentable changes falling within this rule may be mentioned:

(1) Increasing the size of a machine or some of its parts. Thus, in the case of Murray Rubber Company *vs.* De Laski & Thropp Circular Woven Tire Company (21 Fed. Rep. [2nd] 823), Patent 1,119,316 for a machine for building tires was held invalid on the ground that the only real change over the prior art was an increase in the size of the spinning rollers.

(2) Increase of strength or rigidity of a mechanical part. Thus, in the Walker Mfg. Company *vs.* Illinois Brass Company (265 Fed. Rep. 279) it was held that the strengthening of a radius rod by means of a brace could have been thought of by a layman.

(3) Operating a paper machine at higher pressure to produce a greater vacuum in the paper. Guardian Trust Company and Paper & Textile Machine Company *vs.* Downington Mfg. Company (29 Fed. [2nd] 887), in which Patent 1,025,822 to Wm. H. Millspaugh, dated May 7, 1912, was held invalid.

(4) Doing something more thoroughly. Thus, in the case of Continental Fibre Company *vs.* Formica Insulation Company (287 Fed. 455), the Court had this to say about a patent for laminated board *uniformly* saturated with a phenolic condensation product to form a *homogeneous* product: "Neither skilful selection of material, nor thoroughness of workmanship, nor superiority of product constitutes in itself and without change of method or novelty of use patentable invention."

(5) Increasing the elasticity of a fabric by knitting more tightly and placing the rubber cords more closely together. Smith *vs.* Nichols (21 Wallace 112), in which the Supreme Court has this to say: "Many textile fabrics, especially those of cotton or wool, are constantly improved. Sometimes the improvement is due to the skill of the workman, and sometimes to the perfection of the machinery employed. The results are higher finish, greater beauty of surface and increased commercial value. A patent for the better fabric, would, we apprehend, be unprecedented."

(6) Changing the shape of the cross section of a balloon tire from an ellipse, as shown by Hawley in Patent 1,433,008, to a circle, as claimed by Putnam in Patent 1,537,879. The Putnam "balloon tire" patent was, therefore, held invalid in the case of Steel Wheel Company *vs.* Goodrich Rubber Company (27 Fed. [2nd] 427).

(7) Changing proportions of ingredients. Thus, in Brady Brass Company *vs.* Ajax Metal Company (160 Fed. Rep. 84) a mere difference in the proportions of the constituents of an alloy was held not to involve invention.

In the case of Spill *vs.* Celluloid Manufacturing Company (21 Fed. Rep. 630) it was shown to be old to dissolve celluloid in camphor and alcohol. Patent 97,454, which suggested using alcohol of less strength than had previously been used but still of sufficient strength for the purpose, was therefore held invalid.

The following examples illustrate the exceptions to the rule:

In the case of Kuehmusted *vs.* Farbenfabriken of Elberfeld Company (179 Fed. 701), the Court held that the reduction of the amount of impurities in aspirin, which in its impure form had long been known to chemists, whereby a deleterious substance was converted into a valuable medicine, was not merely a change in degree, but a change of kind, producing a new substance.

Another notable exception to the rule was made in the case of Eibel Process Company *vs.* Minnesota & Ontario Company (261 U. S. 45). The evidence showed that the Fourdrinier machine for making paper for many years had been well known and most widely used for making newsprint paper. By improving the stock and by strengthening the parts, the speed of the machine had been brought up to between 500 and 600 feet per minute. But when this speed was attained and maintained for any length of time, the operation showed defects in the paper, described as waves and ripples, which were only overcome by a reduction of speed to less than 500 feet per minute. Eibel's invention was to enable the paper maker to increase the speed to 600 or 700 feet and even more and still produce a good product. To do this he increased the pitch of the wire at the initial point from 15 to 24 inches, giving the stock the added force of the downhill flow, and increased the speed of the machine to correspond, so that the speed of the stock and the speed of the machine were increased coöperatively to 600 or 700 feet, reaching this efficiency by experiment and actual trial.

An exception was also made in the case of Edison Electric Light Company *vs.* U. S. Electric Lighting Company (52 Fed. Rep. 300), involving Edison's carbon filament patent. It appeared that Edison's carbon filament differed from the carbon burners of Sawyer and Man in being $^1/_{64}$ inch in diameter instead of $^1/_{32}$. This reduction in diameter by 2 was held to be more than a change in degree since it increased the resistance of the burner by 4, decreased the radiating surface by 2 and thus increased by 8 its ratio of resistance to radiating surface.

Similarly in the case of Bakelite Company *vs.* Brunswick-Balke-Collender Company (7 Fed. Rep. [2nd] 694), it was held that Baekeland in his patent 942,809 had exercised inventive ingenuity of a high order in reducing the amount of basic catalyst in the preparation of a phenolic condensation product to less than one-fifth of the equimolecular proportion of the phenol used. The change in amount of basic catalyst made it possible for the first time to control the condensation reaction and stop it at any one of three stages.

Substitution of Material

The third negative rule is that it does not involve invention to substitute superior for inferior materials in making one or more parts of a thing, unless the substitution involves a new mode of construction or develops new uses and properties of the article not obvious from the change, or where superiority of the substituted article is shown to consist, not only in greater cheapness and durability, but also in more efficient action.

Among the many illustrations of this rule may be mentioned:

(1) Gauze fabric instead of glass for name plate on casket. National Casket Company *vs.* Stolz (204 Fed. Rep. 983).

(2) Bakelite micarta instead of hard fiber for noiseless gears. Westinghouse *vs.* Formica (270 Fed. Rep. 632).

(3) Elastic cord instead of tape for sweat band. *In re* Taylor (1913 C. D. 418).

(4) Parchment paper instead of cloth or linen for collars. Collar Company *vs.* Van Dusen (23 Wall. 530).

(5) Celluloid instead of glass for watch crystal. Ingraham *vs.* Silver (297 Fed. Rep. 194).

The following examples illustrate the exceptions to the rule:

(1) Substitution of wooden blocks for iron blocks, resting in oil for supporting rim of saw carriage. The wooden blocks, by capillarity, supply oil to the bearing surfaces, whereas in the case of iron an independent means was necessary to supply the oil. Perkins *vs.* Interior Lumber Company (51 Fed. Rep. 286).

(2) Use of muslin stiffened with shellac for shoe-lace tips. Shuter *vs.* Davis (16 Fed. Rep. 564).

(3) Substitution of an old and well-known multiply interwoven fabric for the materials formerly used in semi-soft collars. Van Heusen Products Company *vs.* Earl & Wilson (300 Fed. Rep. 922). The Court was evidently persuaded that invention existed by the phenomenal commercial success of the new collar.

(4) Substitution of thin, highly porous sheets of Yoshino paper coated with paraffin for ordinary paper coated with hard wax for stencil or mimeograph paper. The Yoshino paper has sufficient porosity to permit transmission of the ink, while the soft paraffin is easily displaced by a writing instrument, as a result of which perfect reproduction of the loop letters was made possible for the first time. A. B. Dick Company *vs.* Fuerth (57 Fed. Rep. 834).

(5) Use of rubber for artificial gums and teeth, where it appeared that the change in material resulted in a structure wherein the false teeth were firmly and inseparably fitted into the plate in such a manner that no spaces were left between the plate and points of the teeth into which acids or food could be introduced. Smith *vs.* Goodyear Dental Vulcanite Company (93 U. S. 86).

(6) Substitution of rubber for the cork, leather, and soft metal previously used in steam-gage gaskets. This invention was based upon the discovery that rubber is less corrosive than the previously used materials.

(7) Making the button of the Boston type of garter of rubber instead of metal. The rubber held the hosiery without slipping and tearing. George Frost Company *vs.* Cohn (119 Fed. Rep. 505).

(8) Substitution of tungsten for carbon in lamp filament. General Electric *vs.* Laco Phillips (233 Fed. Rep. 96).

Duplication of Parts

The fourth rule is that it does not constitute patentable invention to duplicate one or more parts of a device. Thus, in the case of Slawson *vs.* Grand Central Railroad Company (107 U. S. 649), it was held unpatentable to place two glass panes in a fare box so that both the conductor and passenger could see the amount, for the change produces merely a duplication of the old result.

An exception to this rule is made when the duplication of parts modifies the old result in an entirely unexpected manner or produces a new result. Thus, in the case of Goss-Printing Press Company *vs.* Scott (108 Fed. Rep. 253), it was held patentable to bank one printing press upon the other, since the two, when so combined, and in their new relation, so coacted as to dispense with angle bars, as well as with a web-deflected course, and made possible a straight-line duplex press.

Omission of Elements

The fifth rule is that it is not invention to omit one or more parts of an existing thing, unless the omission causes a new mode of operation of the parts retained, or results in a substantial simplification of construction or rearrangement of the remaining elements, whereby the same or a better result is obtained by a less number of parts. Obviously, if a man discovers that he can eliminate one or more parts of a machine or process and still get the old result, he is entitled to patent protection. But, if the omission of the element also eliminates the function of the omitted element and does nothing more, no patentable invention is present. An example of the exception to the rule is the case of Lawther *vs.* Hamilton (124 U. S. 6) upholding Patent 168,164 for a method of treating flaxseed. The method differed from the prior art by omitting the grinding and mixing of the flaxseed under muller stones and instead, mixing in the mixing machine by means of steam.

Making Device Portable

The sixth rule is that it does not constitute patentable invention to make an old device portable. The advantage and convenience arising from making a device portable are usually so obvious that their perception and appreciation cannot be held to involve an exercise of the inventive faculty. However, in a very small percentage of cases it happens that the change brings about new and unexpected results. In such a case the change may be patentable.

Substitution of Equivalents

The seventh rule is that no invention is involved in substituting equivalents in an old device or thing. An equivalent is usually defined as an element that performs the same function, in substantially the same way, to produce substantially the same result as that produced by the element replaced. Terms and nomenclature do not determine the question; neither does form nor shape.

(1) Calcined plaster and dissolved bone as ingredients of a bone phosphate fertilizer were held equivalent to ground plaster and ground bone. Boykin *vs.* Baker (9 Fed. Rep. 699).

(2) Porcelain, argillaceous earth, etc., were held equivalents of kaolin, in a plastic composition, containing kaolin, shellac, and coloring matter. Welling *vs.* Crane (21 Fed. Rep. 707).

(3) Copper sulfate was held to be the equivalent of previously used metal-salt hardening agents in plastic paving compositions containing a finely divided filler, a mineral asphaltic binder, and a hardening agent. Western Willite Company *vs.* Trinidad (16 Fed. Rep. [2nd] 446).

(4) Boric acid and borax were held by the Supreme Court in a recent decision to be equivalents in a method of treating citrus fruits to prevent decay due to blue mold. It is immaterial that one of the substances is a weak acid and that the other has an alkaline reaction, since the antiseptic quality in both cases is due to the presence of the boric acid radical. American Fruit Growers *vs.* Brogdex (*U. S. Daily* of March 3, 1931).

(5) A bolt and a screw are usually held equivalent.

(6) Ball bearings and roller bearings are equivalent.

(7) A crank is usually held equivalent to a cam or an eccentric.

(8) A spring and a weight are equivalent for pulling down, but not for absorbing vibrations owing to the difference in the manner of producing the result.

Change of Location

The eighth rule is that no invention is involved in merely changing the relative location of parts of an old device.

As examples of changes of location that were held unpatentable may be mentioned:

(1) Changing the angularity of two shafts which are operatively connected by gearing.

(2) Location of reënforcing members in a bridge. *Ex parte* Luten (1917 C. D. 34).

(3) Reversal of parts such as placing cutting knife behind instead of in front of moistener. National Binding Machine Company *vs.* Harper Paper Company (242 Fed. Rep. 939).

(4) Reversal of parts such as making the type bed stationary under traveling cylinders, instead of making the cylinder stationary and the type bed movable under it. Duner Company *vs.* Grand Rapids R. Company (171 Fed. Rep. 863).

If the change in location is not merely arbitrary, but is accompanied by some unexpected or unobvious result, the Courts will uphold the patent. Thus, in the case of Hoyt *vs.* Horne (145 U. S. 302), it appeared that, prior to Hoyt's patent 303,374, dated August 12, 1884, rag engines were usually constructed with a vertical midfeather. Hoyt found that by placing the beater roll in one end of the vat and providing a horizontal midfeather extending from the beater roll to the other end of the vat, an unexpected increase in beating action was obtained, in that the fibrous material and liquid were carried from the lower section between the knives and delivered over the top of the beater roll into the upper section. This change was therefore held patentable.

Making an Element Adjustable

Rule nine is that it is not patentable to make an element adjustable, if no unexpected new result is produced by the change. Thus, in the case of Houser *vs.* Starr (203 Fed. Rep. 264), it was held not to constitute invention to make a tool adjustable in four directions instead of two.

Making Parts Integral or Separate

The tenth rule is that there is no invention in making two parts integral that had previously been separate and vice versa, unless the new integral part, or the separate parts, perform some new or additional function that is unobvious from the change. It has been held that an increase in strength is not such an additional function as to create an exception.

Double Use

The eleventh rule is that the application of an old device or process to a similar or analogous subject, with no material change in the manner of applying it, is not patentable even if the new form of result has never before been contemplated.

This rule, often called the rule of double use, is tied up with the question of analogous art. A man is expected to know of a solution in his own and analogous arts, but not in remote arts. Hence, it may involve invention of a high degree to take over a device from an entirely unrelated art and apply it to produce a different result, even if no material change is made in the construction.

Illustrations of cases in which the adaptations were held to be mere double uses are as follows:

(1) Punching metal and punching paper. Conley *vs.* King Bridge Company (175 Fed. Rep. 79), in which the Court said that a man would naturally consider machines in other arts adapted for punching materials of like form.

(2) A method of cleaning rubber and a method for cleaning clay. In both processes the steps were the same—namely, reducing the material to a plastic state and forcing it through a strainer. Patent 642,814 in the case of Gowen *vs.* Boston Woven Hose & Rubber Company (214 Fed. Rep. 806).

(3) Blind stitching sewing machine and machine for sewing curved wire upon hats. Lewis Blind Stitching Machine Company *vs.* Premium Manufacturing Company (163 Fed. Rep. 950).

(4) Lifting pills by suction when it was old to lift buttons, nail heads and sheets of paper in that manner. F. R. Stearns Company *vs.* Russel (85 Fed. Rep. 218).

(5) Applying process of coating paper, metal, fabric, glass, etc., to shoes, since the operation was merely coating. *In re* Braselton (273 Fed. Rep. 759).

(6) Transfer and adaptation of a machine for coating glass and emery paper to the art of coating paper with gelatin emulsion for photographic use. Eastman Company *vs.* Getz (84 Fed. Rep. 458).

Some cases in which the new adaptation was held to be more than a double or analogous use, and hence patentable, are as follows:

(1) Cylinder for polishing wood and cylinder for disintegrating clay. Potts *vs.* Creager (155 U. S. 597).

(2) Tanning leather and dyeing fabric. In both the dyeing and the tanning processes the material was treated with an acid which was then reduced to oxide by chemical reduction. Tannage Patent Cases (70 Fed. Rep. 1003 and 93 Fed. 811).

(3) Grinding buttons and grinding lenses. Bisight Focal Company *vs.* One-Piece Bifocal Lens Company (259 Fed. Rep. 275).

(4) In the case of Dodge *vs.* Porter (98 Fed. Rep. 625) Patent 497,971 to Tillinghast for a bicycle tire was held valid, although rubber hose and gaskets had been made substantially of the same materials and in the same way. The Court held that Tillinghast had been the first to produce a single-tube pneumatic tire for bicycles and was therefore entitled to a patent.

(5) In the Yablow case (21 Fed. [2nd] 885) a patent on a gas mask containing granulated hydrated copper sulfate to absorb ammonia was held not to be anticipated by a process for removing ammonia from illuminating gas during its manufacture by the use of the same material.

In many cases it has been held that the necessity of considerable change in the old device to adapt it for its new purpose is evidence of invention. Thus, in the case of Potts *vs.* Creager *supra*, the fact that the wood-polishing machine had a series of peripherally extending glass strips or bars which had to be replaced by steel bars to produce an operative clay disintegrator was the decisive point.

The argument that considerable change was necessary to adapt the old device to its new use was relied upon in the case of Eastman Company *vs.* Gentz mentioned above. In this case it appeared that to adapt the glass-coating machine to coat paper it was necessary to increase the distance between the coating and driven rolls to give more time for the drying and setting of the gelatin emulsion. The Court, however, held this change to be one that would naturally occur to a skilled mechanic when confronted with the problem of applying an emulsion of a different consistency from that formerly employed.

Combination and Aggregation

The twelfth and last negative rule is that aggregation or lack of combination is not patentable. Restated in nontechnical language, the component parts or elements of a device or process must co-act with each other in such a manner as to produce a unitary result which is not merely the aggregative effects of the individual elements.

When operations or devices are brought together and united, one or the other of two results must follow. Either each element remains unchanged in function or effect, or each one performs additional functions and produces additional effects due to their action upon each other or their joint action upon the common object. The former union is an aggregation or a mere collocation of elements and is not patentable.

As examples of aggregations may be cited the following cases:

(1) Eraser and lead in a lead pencil. Reckendorfer *vs.* Faber (92 U. S. 347).

(2) Two machines on a single bed plate for performing successive operations in a single piece.

(3) Plurality of tools on a turret head of lathe for tire making. Thropp Sons *vs.* Seiberling (264 U. S. 320).

(4) Adding a second lock to bag already having one lock. Wertheim *vs.* Lefkowitz (232 Fed. Rep. 474).

(5) Washing machine and wringer both operated by same motor. Grinnel Washing Machine Company *vs.* Johnson Company (247 U. S. 426).

(6) An apparatus for making inner tubes, including various mechanisms for performing independent and unrelated operations on a tube with conveyers to carry the tube from one mechanism to another, each of which performs its function without regard to the presence or absence of the others. *Ex parte* Pade (1928 C. D. 42).

(7) Library-paste jar divided into compartments, one for paste and one for water.

If several elements are brought together so that additional functions are performed and additional effects are produced, the union is a true patentable combination. In such a combination the final result is unitary and due to the joint coaction of all the elements. It is not, however, necessary that all the elements operate simultaneously so long as every one of them contributes to the unitary result. They may operate successively. Nor is it necessary that all the elements coact or coöperate with each other all the time, as long as they do so part of the time to produce a new and useful result or an old result in an improved and modified manner. In any event, the result must be more than that of the separate elements, and the combination of elements in correlation must produce a different force, or effect, or result, from the sum of that which is produced by their separate parts.

An excellent example of a true combination is the process described and claimed in Patent 1,316,120 to Sutherland, which was held valid in the decision of Michigan Carton Company *vs.* Sutherland Paper Company (29 Fed. Rep. [2nd] 179). The method calls for sealing waxed cartons by dewaxing, gluing, and pressing the surfaces together. This process was held patentable though each one of the steps was individually old. The invention resided in bringing them together so that they coöperated to produce a new and unitary result.

A new and patentable combination may also be created by rearranging the elements of an old combination. This was the case in the Hoyt patent already cited, in which the patentee rearranged the beater roll and the midfeather in the vat to produce a new rag engine.

It often happens that the elements themselves are new and patentable. In such case patent protection may be secured on both the combination and on each of the new elements. However, it must be emphasized that, if a new element is introduced into an old combination, a patent cannot be secured for the combination unless the new element coacts with the remaining elements in a different manner than did the replaced element to produce a modified or different effect. In other words, improving merely one element of a combination does not ordinarily create a new combination in a patentable sense.

COMMERCIAL SUCCESS

If, after applying all the tests of invention, the Court is doubtful whether invention exists in a particular instance, the doubt will usually be resolved in favor of the patentee. This is especially so if he can show that his invention satisfied a long-felt need and solved a problem that existed for years in spite of all that prior workers claimed to have accomplished. It also helps to show that the teachings of the patent were regarded with skepticism when first disclosed to workers in the art and that, after its utility was demonstrated, the invention went into immediate use and achieved great commercial success. However, if there is no doubt in the mind of the Court, commercial success is irrelevant and will not be considered. This is because the Courts utilize commercial success to resolve a doubt in favor of invention and patentability, not to raise a doubt when none exists.

Cartels and Consolidations[1]

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QUITE definitely the World War initiated a new era in chemical industry. It forced enormous expansions in practically every line of chemical production. It stimulated research, introduced new processes, brought new products to the commercial markets, dislocated old established channels of chemical trade; and finally it transferred from one country to another some of the world's chief sources of chemical supply.

To these revolutionary changes must be added certain psychological factors which certainly helped shape the course which the development of the industry has taken since 1920. The war impressed statesmen and industrialists alike with the fundamental importance of chemicals in modern life. Even Mr. and Mrs. John Doe became for the first time conscious of the chemistry involved in their food and clothing, their newspapers and books, their home and motor car. Thus a background of friendly sympathy, if not remarkably clear understanding, was created which has been most helpful in the banker's private office and the editor's sanctum, in legislative halls, and in the court room.

This broad interest in chemical industry had important effects. The war's nitrogen lesson, learned at such cost, prompted practically every nation of any industrial importance, or any military pretentions, to install its own air-nitrogen plant and won from several governments preferred treatment for other branches of the chemical industry. In Germany, France, and Italy there was deliberate, official promotion of the cartel movement, with the view of strengthening the essential industries by combining resources and eliminating direct, domestic competition. Many of the smaller nations granted subsidies for plant construction and authorized various forms of tax remission, preferential freight rates, and export bounties. All over the world, along almost every national boundary line, a series of chemical tariff walls sprang up. Even Great Britian forsook her proverbial free-trade position and passed a protective schedule of duties, known as the Safeguarding of Industries Act, among which chemical items occupied a leading place. In our own country Schedule One of the Fordney-McComber tariff law of 1922, especially paragraphs 26 and 27 covering coal-tar products, was adopted on the frank plea of the military and industrial importance of chemicals, and these favorable rates were continued in the Hawley-Smoot law of 1930.

Repercussions of this official recognition of the chemical industries were felt most strongly in Germany. The transformation of the old Dye Cartel into the Chemical Trust shifted the center of interest from coal-tar to nitrogen products. This change was doubtless prompted by war experience. The Germans apparently calculated to regain their dominating position in world chemical trade by means of their great, war-built ammonia fixation plants and their war-won experience in the technic of handling gas reactions under high pressure and at high temperature. They recognized that their dyestuffs monopoly was a thing of the past. They banked for the future upon nitrogen products (notably fertilizers), synthetic methanol, and synthetic motor fuels.

The magnitude of the task to which they boldly set themselves may be appreciated by the estimate of the Economic Section of the League of Nations. At the international chemical conference of 1927 comparative figures were presented that showed Germany's proportion of the world's chemical production was 24 per cent in 1914 and 17 per cent in 1924. For the same years Germany's share of world's total of chemical exports had shrunk from 28.4 per cent to 17 per cent. The well-laid plan of the Germans was severely disarranged by the desire for chemical self-sufficiency among the nations, a prominent symptom of which was the world surplus of fixed nitrogen which became a fact in 1930.

In the United States this new chemical consciousness changed the public's attitude toward the industry from indifference or suspicion to a rather fulsome, patriotic appreciation. The chemical industry, long regarded as the producer of cheap and nasty substitutes, became suddenly the creator of "new values." Manufacturers in other fields shook off ancient prejudices against chemicals and chemical processes.

[1] Received March 25, 1931.

In financial circles, where scientific discoveries had traditionally been viewed with distrust as destroyer of invested capital and disturber of industrial *status quo*, research became almost a fetish, blindly worshipped as a sort of protective charm in the competitive battle between industries.

These psychological factors undoubtedly helped pave the way for lacquers, rayon, plastics, mechanical refrigeration, and other chemical products and chemical processes. They encouraged much research in non-chemical fields that discovered new uses and so widened the chemical sphere in industry. They suggested to our financial interests that the chemical industries offered a field for investment or speculation, and so helped raise in Wall Street the additional capital needed for the expansions and consolidations which marked this period.

American chemical industrialists were not untouched by these psychological influences. The war experience had given them mass production on a huge scale. It had also given them a taste of the operating economy and the commercial power which it brings. Government control and their own coöperation for the common, patriotic cause, had demonstrated the practical advantages of centralized direction and pooled resources. Working shoulder to shoulder, personal contacts were established during the war between competitors who thus came to know each other as men and to test each other's business capabilities in a new way, not as bitter rivals, but as eager associates. For many the war opened up new vistas of a vastly extended chemical horizon.

In 1920 the post-war boom collapsed all over the world. Chemical producers stood face to face with falling commodity prices, while behind them was piling up the surplus output of their expanded plants, and the leaders of the industry quite naturally turned to consolidation as a way out of the dilemma. In the United States the antitrust laws blocked this avenue of escape which was being eagerly sought in Europe.

It was not until the new idea of vertical combination had been successfully demonstrated abroad and a practical method of accomplishing it under our laws had been evolved that the merger movement gained real headway in America. This was in the late twenties, several years after the important chemical consolidations of Germany, England, France, and Italy. In these countries the friendly attitude of the Governments toward such consolidations overcame the handicaps of restricted domestic markets, lack of the apparatus, ignorance of the technic of mass production in the American sense, and a positive dearth of working capital.

Germany

In Germany out of the old Dye Cartel, a purely voluntary association of dye manufacturers which allocated markets and correlated research, there grew the I. G. Farbenindustrie, A. G. As far back as 1904 the six leading dye companies had begun quite informally to gather in two distinct groups. Badische, Bayer, and Agfa formed a "community of interest" to run for fifty years, by which they divided world markets, exchanged basic patents, and shared profits. On the other side, Hochst acquired 99 per cent of the stock of Kalle and a 75 per cent stock interest in Cassella. Thus as far back as the opening years of the century we find these two distinct types of association—the voluntary agreement of the cartel and the outright purchase or exchange of stock ownership.

These two dye groups very shortly reached a working understanding of the cartel type on the important subjects of patents and markets. Owing not a little to the united front they presented to the world, they were able to dominate the international coal-tar chemical market till 1914, when the war shut down their export business.

The war, however, opened new fields. It transformed their dye plants into munitions factories. It expanded their heavy and medicinal chemical operations. Most important of all, it opened up the new field of nitrogen fixation. Enormous profits were made and ploughed back into expansions and new plants.

In 1916 the two groups drew up a much more closely knit cartel agreement, and at the same time took in one of the two most important outsiders, Weiler-ter-Meer. The next year the sole remaining important outsider, Greisheim Elektron, was brought into the fold. At this stage their cartel agreement consisted of a contract with severe penalities for violation, to act uniformly in the market, although every item was to be produced in at least two different companies' plants; to exchange the results of research and patent rights; to pay out of the common cartel funds specified bonuses to executives and chemists as an incentive to general progress and the efficiency of the individual member firms; and to pool profits. An even closer coöperation by depositing their stock in a voting trust was discussed at the time, but this proposal was rejected.

Operations under this cartel agreement were extremely profitable. No more financial information than was required by the German law was made public; but at different times several of the companies increased their capitalization by large sums, and in 1919 the members of the group raised 500 million marks (at that time but little depreciated) for the building of the Oppau-Merseburg synthetic ammonia plant. In 1923, at the time of the stabilization of the currency and the publication of the new gold-mark balance sheets, this great plant, employing about 30,000 workmen, did not appear in the statements of a single one of the member companies of the cartel, but was absorbed in the general investment account.

Early in the twenties signs of a still closer consolidation began to appear within the Dye Cartel. Agfa and Greisheim organized a company in 1924 to sell the products of both. On April 1, 1925, Agfa turned over to Bayer the sale of all pharmaceuticals, undertaking, in return, to market all photographic chemicals and specialties. The middle of September in that same year, the associated companies made a joint statement to the press in which, while protesting their extreme reluctance to lose their corporate individuality, they declared that they had at length come to complete agreement upon the principle of actual consolidation. This merger, so they said, was forced upon them in spite of themselves by competition in markets and by the imperative necessity of reducing to the minimum all costs of administration and manufacture. Thus the way was prepared for the formal announcement of the combination on November 28, 1925.

This consolidation was accomplished by substantially the same legal and financial methods that later became typical of the American chemical mergers. The capitalization of the Badische company was increased to 461,600,000 gold marks of common stock and 4,400,000 gold marks of preferred. Share for share and class for class these new securities were issued for the outstanding stocks of Elberfelder, Hochst, Agfa, Weiler-ter-Meer, and Greisheim Elektron. Thus, at the time of organization, there was no change in the stock capitalization of the companies. Badische changed its name to the Interessen Gemeinschaft Farbenindustrie Aktiengesellschaft (the Community of Interest of the Dye Industry Corporation) familiarly abbreviated to the "I. G.," and the headquarters were moved from Ludwigshafen to Frankfurt.

The I. G. at once consolidated its internal organization. In order to preserve the good will of the individual companies, these remained in nominal existence as branches; but the selling staffs were largely combined and reorganized into five grand sales divisions—dyes, nitrogen, pharmaceuticals, cellulose (rayon and photographic), and heavy chemicals.

Every duplication in production, formerly so cherished, was decisively eliminated. The elaborate interlocking management committees of the various companies of the old cartel were ruthlessly telescoped into a single managing committee of the supervising board, and although executive control was much less concentrated than is common in American corporations, nevertheless the revised organization was a long step toward simplification. Rationalization and mass production were the objectives sought by the executives through a drastic lowering of manufacturing and distributing costs, the liberation of capital frozen in inventories and duplicate plant investment, a comprehensive research campaign, and aggressive selling policies.

Simultaneously an ambitious program of expansion into new fields was launched. Its ways and means are interesting in comparison with American methods of diversification through consolidation.

To provide working funds the capitalization was increased from 646 million to 1100 million gold marks. The rayon field was invaded peacefully by an alliance with the Glanzstoff-Bemberg interests, the terms of which provided that the two groups should share in the financing and control of a new company to manufacture acetate silk. At the same time the Koln-Rottweil firm, with its own rayon process and plants, was absorbed. A working agreement with the large dynamite makers had been in effect for several years, which made it easy for the I. G. successfully to negotiate control of the Nobel and Rheinisch-Westphfalische interests, a combination into which in 1925 they allowed both the British Nobels and the American du Ponts to acquire a 750,000-gold-mark share.

In the petroluem field an alliance, cemented by a 25 per cent stock ownership, was entered into with the Reibecksche Montanwerke, a 50-million-gold-mark corporation; and the oil business was split off to form the Deutsche Gasolin, of whose stock the I. G. owns a half. The other half is owned equally by the Dutch Shell and the Standard Oil (New Jersey) interests. By the end of 1926 the I. G. owned all the stock of the company controlling the Bergius process for the liquefaction of coal and the manufacture of synthetic motor fuels in Germany, as well as a half interest in the international company, with headquarters at The Hague, which controls the foreign rights to these patents. A financial interest with the control over the sales organization of the lithopone cartel, with extensive ramifications in the paint field, was also consummated.

Numerous similar excursions into many other fields were made, and within five years the I. G. had so successfully carried out this policy of diversification that it embraced every important branch of chemical enterprise. It produced over 95 per cent of the German-made coal-tar dyes and, in spite of the war set-back, controlled about 25 per cent of the world's dye trade. It combined some 750,000 tons of nitrogen in the form of ammonia by the Haber-Bosch process and fixed 80,000 tons in cyanamid by the arc process. At this time (1930) the total fixation of nitrogen from the air of the seven American plants was about 100,000 tons. It owned its coal, lignite, and gypsum properties. It held a dominating position in the German production of heavy chemicals, pharmaceuticals, photographic supplies, synthetic perfume materials, lacquers, rayon, cellophane, explosives, synthetic resins and other plastics, synthetic camphor, synthetic methanol, synthetic motor fuel, fertilizers, paints, linoleum, artificial jewels, and light metal alloys. It employed in plants and mines over 97,750 workmen and on its various technical staffs were more than 3000 chemists. It exported annually more than 150 million dollars' worth of chemical products and in 1929 earned net profits, after depreciation, taxes, and interest, of 104,597,746 gold marks.

So vigorously and skilfully had the program of expansion through consolidation been pushed that during these first five years after its formation the I. G. could announce, "among other items," holdings of shares and participations in the following companies:

COMPANY	I. G. SHARE	TOTAL CAPITALIZATION	PRINCIPAL PRODUCTS
	Gold marks	*Gold marks*	
Ammoniakwerk Merseburg	101,250,000	135,000,000	Nitrogen, gasoline
Rheinische Stahlwerke	67,078,000	150,000,000	Coal, coke, and byproducts
Leopold Cassella & Co.	49,480,000	60,880,000	Dyestuffs
Gewerkschaft Auguste Viktoria	16,880,500	18,550,000	Coal, coke, and byproducts
A. Riebeck'sche Montanwerke A. G.	15,757,200	50,000,000	Lignite, briquets, tar, oil, paraffin
Aktiengesellschaft für Stickstoffdunger	7,928,000	8,000,000	Calcium carbide, acetic acid, sodium, calcium cyanamide
Kalle & Co.	5,959,000	6,000,000	Cellophane, Ozalid
Duisburger Kupferhütte	5,431,200	6,000,000	Pig iron, agglomerate, copper, zinc oxide, Glauber's salt, sulfate
Gewerkschaft Elise II	5,000,000	5,000,000	Lignite
Dr. Alexander Wacker	3,750,000	7,500,000	Caustic soda, trichloroethylene, calcium carbide, acetic acid, and derivatives
Chemische Werke "Lothringen"	3,000,000	6,000,000	Nitrogenous compounds
Deutsche Celluloid-Fabrik	2,714,000	5,000,000	Nitrocellulose, collodion wool, sera, celluloid
Zuckerfabrik Korbisdorf	2,453,400	2,700,000	Lignite
Grube Auguste bei Bitterfeld	2,280,000	2,400,000	Lignite
Deutsche Grube bei Bitterfeld	2,275,000	2,500,000	Lignite
Ford Motor Co. (Berlin)	2,250,000	15,000,000	Motor cars, tractors, etc.
Consolidiertes Braunkohlenbergwerk "Caroline"	2,216,400	2,407,800	Lignite
Behringwerke, Marburg	1,736,400	1,800,000	Sera
Holkenseide	1,500,000	3,000,000	Artificial silk
Wachtberg-Gruppe	1,003,500	1,070,000	Lignite and briquets
Aceta	1,000,000	2,000,000	Artificial silk

Details of these numerous consolidations and associations were naturally not made public, but sufficient has been indicated to show that, in lieu of capital investments or the exchange of securities, the I. G. management like to employ their own vast purchasing powers and producing capacities in reciprocity agreements and further to strengthen their alliances by the exchange of patents, sales agreements, and other concessions. In this way they can use their present investments in plants, in scientific personnel and sales organization, in patents and contracts, to assure control over widely diversified interests. They are obviously willing to forego financial control, provided management, especially of sales or of production, is in their hands. There is probably more of expediency than indifference behind this policy. It is a method not dissimilar in theory to the original form of the American trust and, like it, allows in practice a maximum of executive control with a minimum of financial responsibility.

Great Britain

In Great Britain the course of industrial consolidation has been different, slower, and less certain. Historically one might expect that England would be a leader in this movement. She had been the first European country to free her industries from the fetters of guild regulation, which on the Continent continued to check the growth of modern industrialism long after the decay of the feudal system. Moreover, England had early experience with "big business." Monopolies granted by the Crown—a number, like soap, glass, salt, and alum, distinctly chemical in character—were common in the sixteenth and seventeenth centuries. Share companies, usually trading ventures like the East India and the Hudson's Bay companies, were the direct ancestors of our modern corporations. Furthermore, England was the home of the Industrial Revolution and of the corporate form of business organization which it called into being.

Yet with all this background of experience and initiative, Britain was not a leader in the post-war consolidations. Compared with the Governments of Germany, France, and Italy, Great Britain was backward in fostering rationalization of her industries during the reconstruction period. The same sturdy independence of action which broke up the guilds and forbade the granting of crown monopolies fosters a spirit of free competition in British business. The Government was not afraid of industrial combinations, nor was it zealous to protect the consumer from the dangers of restricted competition; but British industrial leaders were themselves suspicious of consolidation.

The situation was almost directly opposite to that which obtained in the United States where Congress makes a political practice of being suspicious of big business. It was quite different, too, from the anxious parentalism displayed by many European cabinets in promoting chemical consolidations and financing chemical expansions designed to assure military and industrial independence of foreign chemical supplies. The British Government neither helped nor hindered the consolidation movement; but in sharp distinction to the acts of other governments, they turned over the coal-tar and nitrogen properties, which they had built or acquired as a war measure, to private operation as promptly and with as little assistance or interference as was practical.

However, those same economic forces, especially potent in chemical industries, which have prompted combination in all industrial countries had been at work in England. As elsewhere in Europe, these culminated in the formation of an all-embracing, nation-wide British chemical trust shortly after the World War.

As early as 1890 forty-eight British manufacturers of caustic soda, who all employed the old Leblanc process, combined in the United Alkali Company, welding into a single unit virtually the whole of the Leblanc industry in Great Britain. This move was highly expedient in view of severe competition with the newer soda-ammonia process of the Solvays and the serious curtailment of British alkali exports due directly to the development of domestic alkali industries in the United States and in the more important industrial countries in Europe. At home their chief competitor was the Brunner, Mond & Company, Ltd., operating the Solvay process under the energetic leadership of Ludwig Mond.

As in the United States, the war tremendously stimulated the explosives and chemical industries of Great Britain and revealed the embarrassing dependence upon Germany for coal-tar intermediates and finished products. During this period the Brunner-Mond interests naturally expanded their own operations. Rather than pay war taxes, they employed war profits to acquire several smaller chemical companies, notably the Castner-Kellner alkali concern. Their resources, technical experience, and aggressive spirit made them quite logically the associate of the Government in the building of a synthetic-ammonia plant at Billingham-on-Tees in order to make good the munitions demands for nitrogen. In this undertaking their position was parallel to the association of the American Cyanamid Company with our own Government for a similar purpose at Muscle Shoals. But there were two vital differences. The Muscle Shoals plant was designed to fix nitrogen by the cyanamide process: the Billingham operation, to employ the synthetic-ammonia process; and in violent contrast to the years of delay Congress has wasted in disposing of Muscle Shoals, the British Minister of Munitions sold Billingham to the Brunner-Monds in May, 1920. Accordingly, the close of the war found this company dominating in the British heavy-chemical industry and with a firm foothold in synthetic ammonia, which was to play so important a role on the international stage of the post-war chemical drama.

Nobel Industries, Ltd., the leading British explosives manufacturers, naturally expanded largely during the war. As the Brunner-Mond's ammonia experience almost thrust upon them leadership in air-nitrogen developments, so the Nobel experience in cellulose shoved them into a similar leadership in airplane dopes, artificial leather, lacquers, and rayon.

At the very beginning of hostilities, in August, 1914, the British Government organized the Chemical Supplies Committee to ration raw materials and coördinate a national production program. As the struggle progressed the control of this official committee over chemical operations became more and more complete, and its activities were furthered by the voluntary teamwork of the industry which resulted in the organization of the Association of British Chemical Manufacturers in 1916. These agencies, like our own War Industries Board and Chemical Alliance, not only made possible the abnormal chemical output of the war years, but also indicated with unmistakable emphasis the solution which consolidation offers for the problems arising out of normal chemical production and competition.

Moreover, the British Government stepped even further into chemical manufacturing. In March, 1915, in order to relieve the plight of their important textile industries, threatened with a dye famine, they organized and financed the British Dyes, Ltd. Immediately after the war, this war-born dyestuff enterprise of the government was merged into the British Dyestuffs Corporation, Ltd. Initially this semi-official trust was able to establish almost a monopoly of British dye production; but it was handicapped by a divided control and restricted financing. It was also subjected to severe criticisms from the powerful textile interests, who claimed that its prices were exorbitant and the quality of its products unsatisfactory, so that it threatened to cost England her valuable supremacy in the world's textile markets. Accordingly, the trust agreement was broken in 1925. The very year following, however, these scattered dyestuffs interests were in a great measure reassembled, and British Dyes, Levinstein, Read & Halliday, Blackey & Clayton, and Scottish Dyes were all consolidated in the British Dyestuffs Corporation, which in turn was incorporated into the Imperial Chemical Industries, Ltd.

This most important chemical consolidation amalgamated four great chemical interests—the Brunner-Monds, Nobel, the United Alkali, and British Dyestuffs. Each of these participants, as we have seen, had previously built itself up by means of consolidations; and the ultimate combination, effected in December, 1926, resulted in a single corporation commanding control over all the important branches of chemical industry in Great Britain.

Like Doctor Bosch in Germany, Lord Melchett (then Sir Alfred Mond) led his company into the fields of synthetic ammonia, selecting fertilizers as the best means of increasing nitrogen consumption. To his restless energy and positive genius for organization the Imperial Chemical Industries not only owned its initial formation, but also to a great measure the success of its early, especially critical years. A publicist by inclination and naturally internationally minded, the gifted son of Ludwig Mond was receptive to foreign chemical alliances. At the same time he shrewdly emphasized the military and economic values of a chemically self-contained British Empire and the importance of chemicals to agriculture. He also supported research generously and actively advocated scientific and commercial causes. Within his own organization he introduced welfare work and bonus systems for plant laborers and the clerical and technical staffs. These enlightened policies brought the amalgamated company a deserved popularity and veiled with patriotic sentiments its monopolistic character.

The British *modus operandi* of chemical consolidation is interesting in comparison with German and American methods. The Imperial Chemical Industries, Ltd., was an entirely new corporation, registered December 7, 1926, for the express purpose of acquiring, by exchange of shares, the four principal constituent companies. In this it resembled the original set-up of the German I. G. and is contrary to common American financial practice, which is to increase the capitalization of a going company which subsequently purchases, with stock or cash or various combinations of each, the property of the companies to be amalgamated. Unlike the I. G., however, the stock exchange was not upon the flat basis of 100 per cent exchange share for share. The British company aimed only at control, not full ownership. Accordingly, a particular basis of shares exchange was agreed upon with each of the four companies. In fact, although the Nobel company was completely liquidated in 1928, the other three maintained their corporate existence and the minority stockholders of the Brunner-Mond concern even questioned in the courts the equity of the consolidation terms.

The original capital structure of the Imperial Chemical Industries, Ltd., consisted of 16,200,000 preferred shares, par value £1, 7 per cent interest, preferred as to assets and dividends, and entitled to one vote for ten shares: 31,800,000 common shares, par value £1, one vote per share; and 4,825,000 deferred shares, par 10 shillings, carrying a vote for each share.

The shares exchange of the original consolidation was upon the basis of share for share of Imperial Chemical Industries preferred for the preference stocks of Nobel and United Alkali, and five for four of the preference shares of Brunner-Mond; three shares of common with two deferred for either two common shares or four deferred shares of Nobel; three for two common shares of United Alkali; three of common with two deferred for two of Brunner-Mond common. The British Dyestuffs Corporation had but a single issue, that of common stock, forty shares of which were exchanged for sixteen each of preferred and of common and one of deferred of the I. C. I. To provide for expansions this original capitalization has been increased from time to time; for example, the deferred shares were increased by an additional 40 million 10-shilling shares in April, 1929.

Like the German I. G., the Imperial Chemical Industries has energetically extended the scope of its operations. The very first year of its existence it acquired control of the Cassel Cyanide Company, the Union Acid Company, Oliver Watkins & Company, and Casebourne & Company. The following year (1928) it took over the Teas Salt Company, Elliott's Metal Company, British Copper Manufacturers, Ltd., and Allen Everett & Sons, Ltd.; and it shortly afterward added to the list of its subsidiary and associated companies Canadian Industries, Ltd., Scottish Agricultural Industries, Ltd., and the International Nickel Company. In 1928 it organized, with the Chase Securities Company of New York, the Finance Company of Great Britain and America.

France

These gigantic, dominant chemical consolidations in Germany and Great Britain have their peers in the other industrial countries of Europe. In France, in 1928, the Établissments Kuhlmann, with an industrial pedigree that traces straight back to a modest sulfuric acid factory which began operations in 1825, effected an amalgamation of the four chief factors in four distinct branches of the French chemical industry. These four themselves represent in turn consolidations of some forty smaller chemical producers. The Kuhlmann activities are roughly parallel to the du Pont chemical interests—explosives, dyes, rayon, lacquers, etc.—but they are also large manufacturers of superphosphate fertilizers. Their associates in the French trust are St. Gobain (heavy chemicals, alkalies, fertilizers, glass) Pechinoy (electrochemicals), and the Usine d' Ammoniaque Synthétique (synthetic ammonia, etc.) This quartet operates under a trust agreement, more rigidly controlled than the ordinary cartel, and has working agreements, especially on dyes and fertilizers, with the German, Swiss, and Italian industries.

Italy

In Italy the chemical situation is dominated by a powerful holding company, the Societá Generale Montecatini per l'Industria, mineraria ed agricola. Through a group of more than thirty subsidiaries this company operates, usually as a holding company in most branches of industrial chemistry. It produces a practically full line of heavy chemicals, rather specializing in acids and in copper sulfate for which there is a large insecticide demand in the Italian vineyards, and in synthetic ammonia, solvents, explosives, aluminum, and other metals. Like its compeers in other countries, Montecatini has, since the war, gone in strongly for fertilizers, rayons, and plastics.

Chemical operations in Italy must leap peculiar economic obstacles. The country is quite dependent upon imported coal. With the exception of crude brimstone, sodium chloride, alumina, and the organic waste materials for the manufacture of tartaric and citric acids, Italy is deficient in chemical raw materials. The domestic industrial consumption of chemicals has been limited, although since 1920 there has been a very great expansion, most remarkable in synthetic fibers and fertilizers. Rayon has created a new market for cautic soda, hydrochloric acid, and carbon disulfide, while the fertilizer production has, as elsewhere, been correlated with the development of synthetic ammonia and nitric acid. A chemical economy that imports not only coal but limestone also, and that regularly employs hemp stalks, straw, and esparto grass as a commercial source of cellulose, necessitates clever juggling of orthodox chemical processes. As a very simple example, the shipment of caustic soda in solution, introduced to the American market a few years ago as a consumer's convenience, is a necessity in Italy in order to conserve the fuel necessary to carry on the evaporation process. This fuel problem is the critical point of Italian chemical enterprise. Coal processing, with its accompanying use of gas for fuel and the salvage of chemical by-products, is carried on extensively; and there is assiduous cultivation of hydroelectric power. It is significant that Montecatini consumes one-tenth of all the electric current produced in Italy.

Belgium

In Belgium, although the home and headquarters of the Solvay process group which has long exerted a world-wide influence in alkalies, the chemical industry is virtually a post-war development. Here the Union Chimique Bélge, a holding and operating corporation of the general type of Imperial Chemical Industries and Montecatini, occupies a similar position and has adopted similar tactics to diversify its operations by consolidations. During 1929 it increased its capitalization from 175,000,000 francs to 192,000,000 francs and, having consolidated its position at home as strongly as practical, began investment in foreign chemical companies. The domestic strength of the Union is tempered somewhat by the power of the metallurgical interests whose by-product coke output it has not been able to amalgamate, and also by the presence in Belgium of a number of branch plants of foreign chemical interests with whom consolidation is obviously impractical. Furthermore, a strong cooperative association of farmers, the Boerenbond, is an active, efficient, incompatible competitor in the production of chemical fertilizers. However, through the controlling influence of the leading Belgian financial interests, a benign alliance with the metallurgical works is in effect and sales agreements with foreign competitors make possible a staple and uniform marketing policy.

In Czechoslovakia, to draw a final example of European chemical consolidation from one of the smaller countries, the Verein für Chemische und Metallurgische Produktion vom Aussig (commonly known as the Aussiger Verein) is estimated to produce more than 60 per cent of the country's industrial chemicals, with virtual monopolies in soda ash, caustic soda, liquid chlorine, potassium, dyes, zinc salts, synthetic ammonia, and lithopone, and even an important European position in tin salts and activated carbon. The Aussiger Verein operates three of its own plants in Czechoslovakia at Aussig-on-the-Elbe, at Hruschau, and near the great lignite fields at Falkenov.

The company was organized in 1857 to operate, at Aussig, a refinery for potash salts imported from the Stassfurt mines. A Leblanc soda plant was shortly added, but this was abandoned in 1907. Dyes and a general line of heavy chemicals then became the chief products. Aussig introduced alizarine red and today enjoys patent and sales agreements with the I. G. The extension of the chemical lines has been continuous, and as far back as 1911 the firm acquired rights to the Goldschmidt process for the recovery of tin from scrap and the manufacture of the chloride. A full line of mineral acids and electrochemical products is produced. In 1911 Aussig bought Sodafabrik von Miller von Aichholz at Hruschau, originally a Leblanc process operation but now manufacturing mineral acids, lithopone, dry colors, and activated carbon. The Falkenov plant is a post-war expansion into the carbide and cyanamide fields, which came into production in 1918, and which has been expanded by the addition of a new lignite distillation and tar-cracking unit.

The Aussiger Verein furnishes a fine example of those international chemical alliances which in the late twenties began to assume a new importance in chemical economics. Their connection with the Solvays dates back to 1905, when the two interests combined in the erection of the soda ash plant at Nestomitz-on-the-Elbe; but it includes participation in similar enterprises in Austria, Roumania, Poland, and Yugoslavia. Aussiger Verein is in the international cartel on activated carbon with the Urbain Corporation, the German Dye Trust, and the Metallbank of Frankfurt. They share in the Bohemian rayon factory; in pharmaceutical chemical manufactories in Yugoslavia and Hungary; in the heavy chemical plant of the Zorka company in Subotia, Yugoslavia; and in the electrochemical works of the German Salzbergwerk Niew-Stassfurt, near Bitterfeld in central Germany.

International Agreements

Such international participation in chemical operations and a wide variety of agreements on patent rights and sales territories are a natural development. They logically follow the unification of the most important chemical interests within each of the national boundaries.

International alliances of this sort obviously strengthen the participating companies and tend increasingly to concentrate chemical resources. Already they have woven a highly complicated web of mutual self-interest among the leading chemical factors in different countries.

The German, French, and Swiss dye interests in 1928 reached a close, amicable cartel agreement. This was widely heralded at the time as the forerunner of a thorough-going European chemical trust. By 1930 the ramifications of these alliances included—to mention but a few of the more important—an agreement between all the synthetic-nitrogen producers of Europe and with the natural nitrate producers of Chile; the I. G. and Montecatini on patent rights for phosphatic-nitrogenous fertilizers; the I. G. with Courtaulds (British) and Enka (Dutch) on rayon; Kuhlmann with the German Potash Syndikat on marketing mixed fertilizers; the I. G., Standard Oil of New Jersey, and Shell on synthetic motor fuel; Kuhlmann and du Pont on the Claude ammonia process; Nobel (I. C. I.), du Pont, and the I. G. on explosives.

Even more complex, less obvious, but not less potent, are the indirect connections through banks and large financial intrests, while the interlocking directorates and investments among chemical interests form naturally a most powerful bond of mutual interest. The Imperial Chemical Industries and the German Dye Trust have both organized American financial companies in alliance with New York banks. The Solvay interests have very substantial holdings in the Imperial Chemical Industries, the Allied Chemical and Dye Corporation, and other important chemical companies. Their American investment trust corporation is an important factor in a strategic position to swing the balance of power in important, international chemical negotiations.

Two decades before the consolidation era in the chemical industries, back in 1900, it was the active head of these same Solvay interests, Ernest Solvay, who first envisioned the possibilities of the international chemical trust. By patent rights to the Solvay process licensed to companies in different countries, tangibly supported by substantial investments in those same operating companies, the Belgian firm had already penetrated close to the very core of this ambitious idea. The organization of the United Alkali Company in England furnished at once inspiration and opportunity, and an effort was made to materialize a heavy-chemical cartel. It failed. It did, however, bring the scattered soda ash producers closer together and established some trade agreements, notably between the Brunner-Monds and the Germans, which were extremely valuable. It is more than a coincidence that the realization of Ernest Solvay's international chemical vision is being realized by his successors and the successors of his direct associates.

Standard Samples of Medium Manganese Steel Available

The U. S. Bureau of Standards has prepared a standard sample of medium manganese steel of the following composition:

	%
Carbon	0.618
Manganese	1.39
Phosphorus	0.023
Sulfur	0.021
Silicon	0.192
Copper	0.123
Nickel	0.151
Chromium	0.180
Vanadium	0.012

This standard is No. 100 in the series and costs $2.00 per sample of 150 grams. The sample may be paid for in advance with the order or be sent parcel post, C. O. D., in the United States and its possessions. All foreign shipments require prepayment, together with 20 cents additional postage.

A complete list of standard samples, analyses, fees, etc., is given in Bureau of Standards Supplement to *Circular* 25, which may be obtained free of charge upon application to the Bureau of Standards, Washington, D. C.

AMERICAN CONTEMPORARIES

Harley James Morrison

H. J. Morrison

If MOST of the readers of Industrial and Engineering Chemistry do not know of H. J. Morrison, it is neither to their discredit nor to his. He is one of those technical workers who have allowed their well-timed contributions to add to the progress of an already advancing industry without ever drawing attention to themselves.

Even among those hundreds of men whose method of earning a living has been determined by chemical developments for which Mr. Morrison was primarily responsible, very few have any concept of the part which he has indirectly played in their lives. Some of these developments have affected practices in the laundries and kitchens of millions of homes; yet very likely Mr. Morrison's closest friend outside of business associations has no idea of this far-reaching effect of his work. Being one of the quietest and most unpretentious of men, Mr. Morrison is satisfied to have the recognition of his own achievements blended into the impersonal recognition of the growth and progress of the company which he has served.

Harley James Morrison was born in Cincinnati, February 15, 1866. He was one of five brothers who attended Yale University, where he studied chemistry and graduated with the class of 1887. Following graduation, he entered the employ of Procter & Gamble, then a partnership with only one factory, at Cincinnati.

Starting work in the Alkali Department, he was subsequently shifted so as to become familiar with the various departments of the factory. Although he was not working as a chemist, he could not escape his chemical background and soon became recognized as an intermediary whose unofficial duty was to secure better team work between laboratory and plant.

He left Procter & Gamble in 1892 and became vice president of Lytle Safe & Lock Company, where he was chiefly concerned with supervisory sales work. Being still a chemist at heart he introduced improvements which increased the speed of setting and decreased the "sweating" of the cement used as a filler between the inner and outer metal walls of the safe.

Subsequently Mr. Morrison, with his brother, W. P. Morrison, organized the Arcanium Process Company for the manufacture of alkalies in Cincinnati, but was induced to rejoin Procter & Gamble early in 1897.

He was given the job of developing a formula and process for manufacturing soap powder. This was successfully done, but news of a new entry into this field brought on a price war by competitors. Procter & Gamble discreetly withdrew for the time being, and sold the improved packaging equipment developed by Mr. Morrison to a competitor.

Next Mr. Morrison assumed supervision of cottonseed-oil refining. Procter & Gamble was then the least important among vegetable-oil refiners. Mr. Morrison promptly laid the foundation of a growth which led the company to become finally the most important among vegetable-oil refiners in the country. Within a few years he planned and completed a refinery which is today the most important unit in the company's chain of refineries.

Following about two years' service as superintendent of the company's new Kansas City soap plant, Mr. Morrison returned to Cincinnati in 1907 and undertook the problem of developing a satisfactory formula for white soap for household laundry use. The idea of a white laundry soap was by no means new, but its actual manufacture had led to considerable grief. It continued to lead to grief while Mr. Morrison tried in his experimental work to do justice to various ideas carried over from previous experience. Finally he gently suggested that he be given a free hand in the matter, and the granting of this request proved the most successful experiment of all. In a short time important changes in the manufacturing technic overcame the earlier difficulties. The use of white laundry soap rapidly increased and finally reduced yellow laundry soap to a position of secondary importance in the American trade.

As soon as the manufacture of white laundry soap was put on a satisfactory basis, Mr. Morrison gave his principal attention to the hydrogenation development which had already been started by E. C. Kayser. There is a tendency in scientific circles not to give any great credit to the Procter & Gamble organization for this development, and Mr. Morrison would be the last to wish to contest the point. Nevertheless, there was a great deal of effective hard work by Kayser, Morrison, Burchenal, and others, and the results were revolutionary. Hydrogenated edible oils were produced and sold for the first time and their importance has steadily increased.

Meanwhile incidental contacts had made Mr. Morrison's interests as broad as those of the company itself and he became the recognized technical leader. In 1912 he was made chemical superintendent, which position he held until 1919, when he retired from active administrative responsibility to be special and consulting chemist. In 1921 circumstances made it advisable for him to resume administrative control of the Chemical Division, but he retained the title of special and consulting chemist. Less than two years later he was relieved of active administrative responsibility by his own request, and R. K. Brodie was made chemical superintendent. On this occasion he said to the Chemical Division staff: "I do not consider myself a good administrator, but I believe that I have exercised good judgment in choosing the man to whom I have already been delegating a large proportion of my administrative duties." Some of us think it a mark of administrative talent to make the proper choice of the man to whom duties are delegated.

Another trait stamped Mr. Morrison as a fine administrator—a simple, direct way of giving instructions, such as to avoid all possibility of misunderstanding.

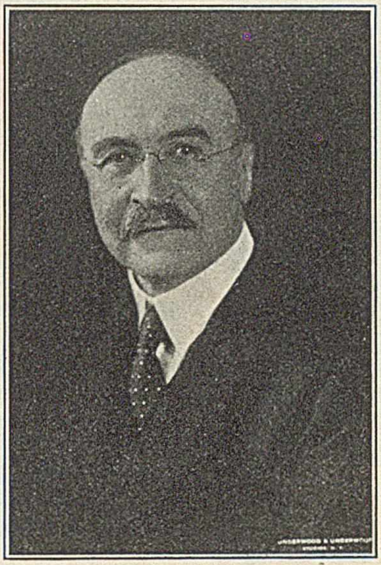
In preparation for writing this sketch, I have talked with a number of men who have known Mr. Morrison a long time. They comment in different language, but through it all runs a common theme. Above everything, Mr. Morrison is clear and direct in his dealings with other men. No one has ever gone away from a conversation with Mr. Morrison wondering what he said.

A. S. Richardson

AMERICAN CHEMICAL INDUSTRIES

The Bakelite Corporation

THE Bakelite Corporation was formed in 1922, when the General Bakelite Company, the Condensite Company of America, and the Redmanol Chemical Products Company decided to combine their interests. Chemically speaking, it had its origin in the researches on the phenol-aldehyde reaction conducted between 1905 and 1909 by L. H. Baekeland. The story of this brilliant work is familiar to every student of chemistry. As in his earlier work leading to the production of gas-light photographic papers, Baekeland displayed his rare gift for picking the winner. In photography he pinned his faith to the sluggish silver chloride emulsion prepared without the usual ripening or even washing; in phenol resins he chose the insoluble, infusible, porous mass of Kleeberg studiously avoided by previous workers; with what industrial success in each case two trade-marked names of world-wide significance bear witness—"Velox" and "Bakelite." Seldom has it been the lot of one man to revolutionize two such important industries.

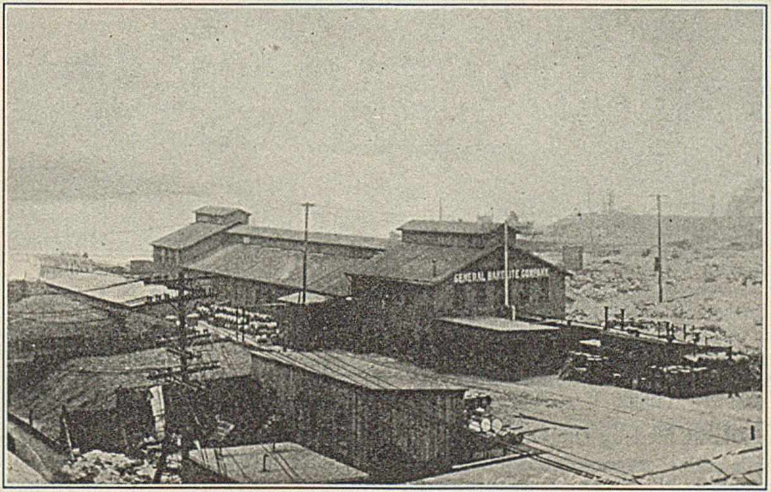


L. H. Baekeland, President and Founder

At the February, 1909, meeting of the New York Section of the AMERICAN CHEMICAL SOCIETY, Doctor Baekeland announced his discoveries which gave to the world new and superior plastic materials, the phenol-aldehyde resinous condensation products. He had previously applied for patents on his inventions and a trade-mark on "Bakelite," the name proposed by his patent attorney, C. P. Townsend, for the new synthetic products.

The announcement was everywhere received with enthusiastic interest. J. W. Aylsworth, of East Orange, N. J., chemical consultant for Thomas Edison and, as such, interested in a superior material for phonograph records, turned his attention to the phenol-formaldehyde reaction as a promising source of such material.

Out in Chicago Adolph Karpen, of S. Karpen Brothers, makers of fine furniture, attracted by the popular science writings of Robert Kennedy Duncan, became interested in having a research fellowship established under Duncan at the University of Kansas looking to the production of a superior varnish for furniture. Also L. V. Redman, just out of the University of Toronto, who had been selected for the fellowship, became impressed with the possibilities of the phenolic resins for such use.



The First Bakelite Plant

Thus are accounted for the beginnings of Condensite and Redmanol—the Condensite Company organized, with Kirk Brown as president, to exploit the inventions of Aylsworth, and the Redmanol Company to exploit the inventions of Redman and his two associates, A. J. Weith and F. P. Brock, who early joined him in the work.

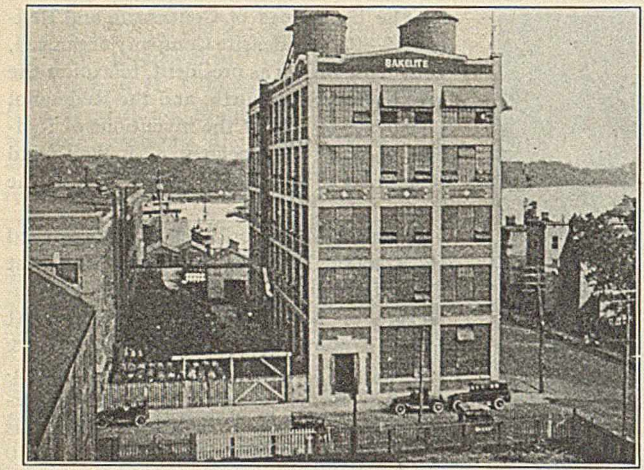
Meanwhile Doctor Baekeland organized the General Bakelite Company, and cast about for a suitable location to begin manufacture of Bakelite in a large way. At Perth Amboy, N. J., was the Roessler & Hasslacher Chemical Company who manufactured formaldehyde, one of the important raw materials of Bakelite. From this company a building was leased in 1910 and manufacture of Bakelite transferred from Yonkers to Perth Amboy. To Perth Amboy with the new industry went Nathaniel Thurlow, who had been associated with Doctor Baekeland almost from the first of his researches. L. M. Rossi was in charge of formaldehyde manufacture for the Roessler & Hasslacher Chemical Company, and he soon gave much of his time, and later his full time, to the new industry. Hylton Swan, who had been with the industry from its beginning, was sales engineer.

In 1913 the General Bakelite Company, having purchased an adjacent site, erected a three-story reënforced-concrete building and moved into it. This building was increased to five stories and its length doubled in 1917, when the leased building was abandoned.

In 1914, the Condensite Company, which in 1910 had begun operations in Edison's plant at Glen Ridge, N. J., moved into new quarters in the neighboring town of Bloomfield.

In 1913, preliminary work at the University of Kansas having been completed, Redman, Weith, and Brock moved to the Chicago plant of S. Karpen Brothers and began development of their processes.

Doctor Baekeland's first customer was Edward Weston, one of the earliest and most successful pioneers in the electrical industry. Doctor Weston molded, from Bakelite, bushings the size of mustard seeds for his now celebrated electric measuring instruments. Though the tonnage was small, the encouragement was great. Soon the demand by the rapidly growing electrical industry became general and insistent. This industry was in great need of dependable insulating material, one which not only had good electrical properties, but which could stand abuse. Charles F. Kettering had recently brought out his new starting, lighting, and ignition system for the automobile, to the successful operation of which the new insulating material was practically a necessity. It withstood the heat of the engine and its oil as well. Added to its enduring character was the ease with which it could be molded into accurately dimensioned, replaceable parts. The labor-saving effected, particularly when metal inserts were required, made the cost of the material a matter of secondary importance.



The Perth Amboy Plant

Then came the war with its increased demand for the new material—also its demand for phenol. All the companies had large supplies of this important raw material, the price of which rose rapidly from eight cents to a maximum of a dollar and eighty-eight cents a pound. But the production of phenolic condensation products had become an essential industry. The phenol was retained and did service in the ignition systems of trucks and airplanes, and even in airplane propellers, with little increase in the price of the condensation products made from it. The three companies preferred to get along with small profits and thus encourage the growing demand for their products, now needed in war as well as in peace. The supply of pre-war phenol having become exhausted, cresol, with its slower reacting resins, had to be substituted. Formaldehyde also became scarce through increased demand, which added to the difficulties of the industry. Its price fluctuated from a pre-war ten cents a pound, or under, to eighty cents a pound. After the war came radio and its rapid development, replacing war demand.

Bakelite Research and Development Plant at Bloomfield, N. J.
View shows about 40 per cent of plant

Before the war a bill of complaint filed by the General Bakelite Company against the Condensite Company, charging patent infringement, led to the licensing of Condensite under Bakelite patents. After the war suit against a customer of the Redmanol Chemical Products Company was successfully prosecuted by the General Bakelite Company. Negotiations which followed brought about, in 1922, consolidation of the three companies.

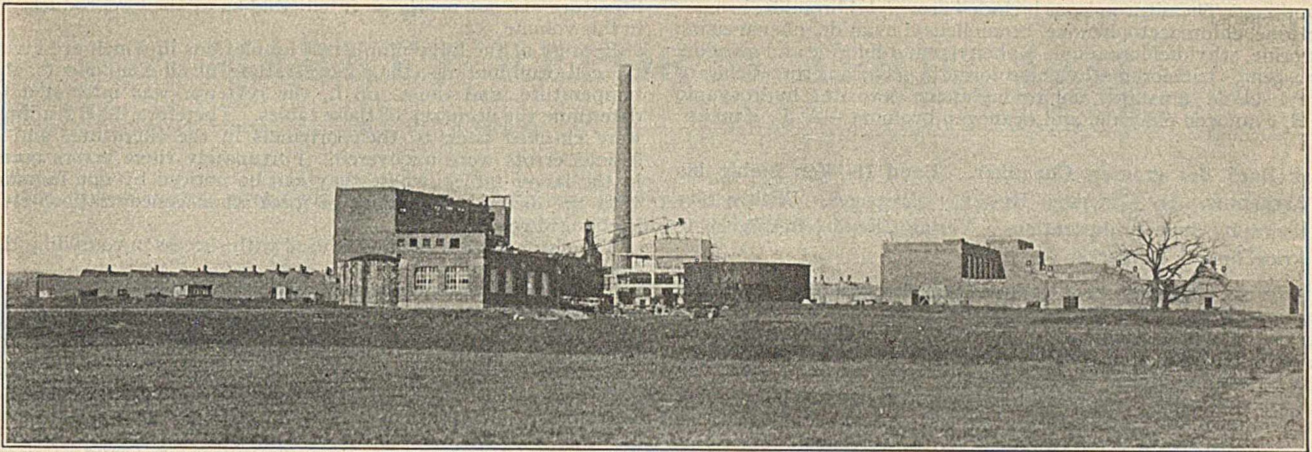
The after-war supply of phenol nearing exhaustion and an increased tariff threatening a radical rise in prices, the corporation erected at Painesville, near Cleveland, Ohio, a plant for the synthesis of its full requirement of this important raw material. Moreover, pressure of business required re-occupancy, in 1921, of the original factory building, which had been abandoned in 1917. The corporation's New York office, which was first opened at 8 West Fortieth Street, was moved, in 1923, to its present location, 247 Park Avenue. About this time and later, affiliations were established in several foreign countries.

For a time after the consolidation manufacture of Bakelite was continued at all three of the original plants—at Perth Amboy, Bloomfield, and Chicago. In 1924 a building for research was erected at the Bloomfield plant, and centralization of research and development at Bloomfield was begun. Since then the whole plant has been taken over and buildings have been added as required. The latest and largest single addition is a three-story building of brick and concrete, 50 by 150 feet, erected in 1930.

Not only was the Bakelite Corporation founded on research, but the control of its policies has remained largely in the hands of men of scientific training and achievement. Doctor Baekeland, its president, still maintains active leadership. Associated with him are Adolph Karpen, vice president; George Baekeland, vice president and secretary; L. M. Rossi, vice president and director of manufacture; L. V. Redman, vice president and director of research and development; and C. Lansing Hays, treasurer. Hylton Swan is now manager of service and sales. Sanford Brown, associated from the early days of the Condensite Company with his father, Kirk Brown, now retired, is president of the Halowax Corporation, a subsidiary having its origin in the early researches of J. W. Aylsworth on the chlorination of naphthalene. Aylsworth, who was a man of rare ability, died in 1916, still tireless in research and invention. A. J. Weith, early associate of Redman, is in charge of development at Bloomfield. F. P. Brock, his other associate of the days at the University of Kansas, is manager of the Chicago plant. C. P. Townsend, the man who christened "Bakelite," and incidentally the inventor of the electrolytic cell that bears his name, was an early associate of Doctor Baekeland. He has remained through the years as technical consultant and consultant in patent matters.

In every division of the corporation the great majority of those in positions of responsibility are men of scientific training. The corporation at present employs sixty-three chemists and physicists in scientific work. Of these, forty-four are at Bloomfield, with a hundred twenty-three other workers engaged in research and development.

It is to research that the industry must look for its future growth, just as it was in research that it had its origin. The present, relatively large research organization is still young, but it has already justified its existence. The outlook is for



New Bakelite Manufacturing Plant, at Bound Brook, N. J., Now in Process of Erection

increased justification. One of the latest, and by no means least, of its achievements is the development of a series of new and superior synthetic varnish resins. In fact, it begins to look as if another important industry, that of paints and varnishes, were about to be revolutionized—as if a dream of twenty years ago were to come true.

As for the synthetic resin industry, only a beginning would appear to have been made. Its products are finding increasing opportunity for service in mechanical and structural application, the possible extension of which seems almost unlimited.

As a next step in meeting the growing demand for synthetic resin products, the Bakelite Corporation is now erecting at Bound Brook, N. J., a central plant which will provide considerably enlarged manufacturing facilities and will have plenty of room for future expansion.

L. V. Redman
A. V. H. Mory

BOOK REVIEWS

Carburanti e carburazione. By Umberto Re and E. Vareton. xvi + 516 pages. 316 illustrations. Ulrico Hoepli, Milan, 1931. Price, 50 lire.

According to the authors, this book is intended to acquaint automotive engineers with the physical and chemical characteristics of the materials which are or may be used as motor fuels, while giving the chemists an outline of the workings of combustion motors.

The book is divided into twenty chapters. The first chapters deal with the mechanism and operation of motors, carburetion, and compressors and superfuelizers. Then follow chapters on the mechanism of combustion, knocking and antiknock materials, and gasoline substitutes. Lubricating systems, lubricant dilution, and carbon deposition are also discussed. A final chapter deals with carburetion using natural gas, hydrogen, cracked gases, and Blau gas.

American practice is given extensive consideration and the results of numerous workers in the various fields are noted, although references to the original literature might well be more frequent.

Volume II, dealing with the preparation and evaluation of various fuels, is to follow.—A. W. Contieri

Die Schlämnanalyse. By Hermann Gessner. **Band X, Kolloidforschung in Einzeldarstellungen,** founded by Richard Zsigmondy. 244 pages. Akademische Verlagsgesellschaft m. b. H., Leipzig, 1931. Price, bound, 18 marks; paper, 16.50 marks.

The methods of analyses described in this volume are all based upon the general principle that small particles fall through water with a constant velocity, and mathematical calculations and formulas are collected from different sources, mostly from soil chemists and soil physicists, together with experimental data to show that the velocity of particles of a definite size (soil) falling through water is constant. The effect of coagulation, together with the theory of floc formation, is discussed.

The bulk of the work is concerned with a description of methods to determine the size of particles; processes of sedimentation; and methods to determine the amount and rate of sedimentation; methods of decantation, plasticity, and sifting; and methods of separation of larger particles from fine material by air. The selection of proper methods is discussed and emphasized, together with the necessary preparation of the materials to be analyzed. Practical hints are supplied for the exercise of the usual methods employed, and finally the methods of calculating results and the presentation in graphical forms are discussed and illustrated. The methods described are of particular interest to soil chemists and soil physicists, and are of use in ceramics, analyses of building and road materials, mining, dyestuffs, and paper and rubber, where in many instances the production could be guided by one or more of the methods given.

The book is profusely illustrated and the set of analyses, brought together in a handy form, is undoubtedly an important contribution.—Willem Rudolfs

Anleitung zur Herstellung von Ultragiften. By Hugo Stoltzenberg. 70 pages. 34 illustrations. Norwi-Druck, Hamburg, Germany, 1930. Price, 20 marks.

The author uses the appropriate name "Ultragifte" to designate those extremely poisonous substances which have become known throughout the world by reason of their use in the World War as war gases or chemical warfare agents. Many of them are finding ever widening application for peacetime uses and the term "ultra-poisons" removes from them the opprobrium of their wartime origin.

The book describes in an unusually clear and concise manner the methods for the laboratory preparation of ultra-poisons. The description includes the equations involved, lists of equipment required, photographs of laboratory set-up, details of manipulation, yields for each step of the process, properties of the product, precautions to be observed, and the treatment to be used in case of injury by the chemicals. Several different methods of preparation are given for a number of the substances described.

The ultra-poisons are classified into eye irritants or lacrimators, nose irritants, respiratory poisons, blistering agents or vesicants, and blood and nerve poisons. These are arranged in the ascending order of the danger attending their preparation and handling. The ultra-poisons included are: xylyl bromide, bromoacetone, chloroacetophenone, bromobenzyl cyanide, phenarsazine chloride, ethyldichloroarsine, diphenylarsine chloride and cyanide, phosgene, trichloromethylchloroformate, chloropicrin, dichloroethyl sulfide (mustard), chlorovinylarsine (lewisite), hydrocyanic acid, cyanogen chloride, and cyanogen bromide.—A. L. KIBLER

Das Buch der grossen Chemiker. Band II—Von Liebig bis Arrhenius. BY GUNTHER BUGGE. 559 pages. With a bibliography and 78 illustrations. Verlag Chemie, Berlin, 1930. Price, bound, 32 marks.

This is a continuation of Volume I, which appeared in 1929 and was reviewed in IND. ENG. CHEM., **21**, 1150. Volume II continues the same high standards of interest and accuracy, the articles being written by men not only familiar with their subjects but able to write in a pleasant and effective style.

Thirty chemists have been chosen for portrayal, all born before the sixties of the last century. No list of thirty men could be chosen upon which there could be perfect agreement (one notes possibly an overweighting on the German side, and questions why, for instance, W. H. Perkin and Moissan should not have been included), but after all one could ill spare any of these elect. Organic chemists seem to predominate, but that is owing to the great development of that phase of chemistry in the last century, and the other fields have their due measure of publicity. In the list one finds the great masters, Liebig, Wöhler, Kékulé, A. W. von Hofmann, Emil Fischer, and Adolph von Bayer, who is pictured by his successor, Willstätter. Due respect is paid to the sharp-tongued and conservative Kolbe, to Peter Griess, who emerged with azo compounds after his twelve "bummel" semesters, and to the brilliant Victor Meyer.

France has a notable group in Dumas, Wurtz, the unhappy Gerhardt and his friend Laurent, and Berthelot, an organic and physical chemist and publicist. His son, who has just passed away, was a general in the French Army.

Richard Koch has written of Pasteur and Ehrlich, whose discoveries in bacteriology and chemotherapy have accomplished so much in medicine.

The Italian Cannizzaro, who brought order out of the chaos of equivalents and molar weight, is delineated by Vanzetti and Speter.

In the inorganic field comes "Papa" Bunsen and Clemens Winkler, of whom a most interesting and personal account has appeared by Professor McCay of Princeton in his "Student days in Germany" [*J. Chem. Education*, 7, 1081 (1930)].

Following chapters include Graham and Crookes; then one on Lothar Meyer, Mendelejeff, and Ramsay, by Paul Walden, and finally an account of two of the great triumvirate in physical chemistry, Van't Hoff and Arrhenius.

Doctor Bugge brings in the industrial side of chemistry when he lists von Brunck, the founder of the Anilin und Soda Fabrik, Caro and the dyestuff industry, Frank and his relation to the "Kaliindustrie," cyanamide, etc.; and George Lunge, the teacher and writer on technical chemistry.

The value of the book is much increased by a fifty-page biographical bibliography of general and specific sources of data regarding the sixty-eight chemists in Volumes I and II.

The perspective and knowledge of students in America will be greatly enhanced by reading this unusual account of chemistry's greatest century as set forth in the personal accomplishments of these chemists whose names are so synonymous with progress.—F. B. DAINS

Elektromotorische Kräfte. BY R. KREMANN AND ROBERT MÜLLER. **Erste Teil, Band VIII of Handbuch der allgemeinen Chemie,** compiled by PAUL WALDEN and CARL DRUCKER. xvi + 891 pages. Akademische Verlagsgesellschaft m. b. H., Leipzig, 1930. Price, paper, 81 marks; bound, 85 marks.

In this volume are maintained the remarkable high standards for completeness and excellence which have characterized the previous seven volumes of this famous handbook. It is really a monumental work on the subject of electromotive force measurements, for not only are there discussions of the theoretical phases, but the measurements of electrode potentials are reproduced in 379 tables and 95 figures, the transcription of which from the literature must have been a gigantic task.

The completeness of the work is shown by the fact that the potentials of hydrogen on platinum in the many solutions which have been investigated require 57 pages of tables. Many calculations were necessary to obtain the uniformity of tabulation which is used throughout the book. Many of the measurements were originally made for the determination of activity and in the literature are not nearly so intelligible as in their reproductions in this volume.

Because of the large number of tabulations in which are given the cell combinations, the concentrations of all components, the temperature, and the e. m. f., the reviewer was interested to determine the accuracy of these tables. Therefore, 1000 readings were checked back to their originals in the literature, and 8 serious errors were uncovered. Fortunately these errors occur in the larger tables, where they can be noticed by one familiar with the drift in electromotive force when concentration, etc., is changed regularly.

The chronological method is used with success in compiling the tables.

There are some obvious typographical errors. It is rather disconcerting to check a reference, say, from Conant's work on page 741 to the author index and to find it spelled "Konant." Some initials are inverted here and there.

Any fair-minded reader of this huge volume is forced to admit that everything worth while on the subject of electromotive force has been included in a manner which is useful and readily accessible. The discussions are clear-cut, logically presented, and the sentences are not too "germanically" long.

The publishers have done an extraordinarily fine job of printing and binding, which makes the handling of the volume a distinct pleasure.—C. J. BROCKMAN

Vom Wasser. Ein Jahrbuch für Wasserchemie und Wasserreinigungstechnik. Band IV—1930. Published under the direction of the Division of Water Chemists of the Verein deutscher Chemiker. 192 pages. Two portraits, 10 tables, 20 cuts. Verlag Chemie, G. m. b. H., Berlin, 1930. Price, paper, 15 marks; bound, 17 marks.

Volume IV of this yearbook contains sixteen papers dealing with treatment of acid waters; aspects of surface and ground waters in relation to use, hygiene, and treatment; effect of chlorination on corrosiveness of water; physical-chemical changes in foaming of boiler waters; brittleness of boiler pipes; Crystalit, a new zeolith for water softening; a summary of the present sewage-disposal technic; and a discussion of the gas production from sewage sludge.—WILLEM RUDOLFS

Die natürlichen und künstlichen Asphalte. Ihre Gewinnung, Verwendung, Zusammensetzung, und Untersuchung. BY J. MARCUSSON, WITH H. BURCHARTZ AND P. WILKE. 2nd improved edition. 253 pages. Wilhelm Engelmann, Leipzig, 1931. Price, paper, 17 marks; bound, 19 marks.

This book is concerned chiefly with laboratory methods for the examination of asphalts, tars, and pitches, as well as some of the more common fabricated articles made from these materials, such as mastics, roofing paper, emulsions, and paints. It is written almost entirely from the standpoint of German practice, and there is only occasional fragmentary mention of British or American methods.

Unfortunately, however, the laboratory methods of examination are not always described in sufficient detail to enable an operator, previously unfamiliar with them, to utilize them with any degree of certainty as to the results obtained. The figures and drawings, as well as the text, in many cases lack some of the exact dimensions of equipment, etc., which are so necessary when applying proximate tests of this type, where each variable may make a decided difference in the result. Tolerances for the variables such as given in our own A. S. T. M. methods for similar purposes are entirely lacking. From the German standpoint it is fair to state that such tolerances are not always necessary, since the equipment is built by some specific manufacturer who maintains his own standard of tolerances. However, the chemist in the United States has no easy way of securing such apparatus here, in case he desires to duplicate the foreign results.

The book also contains general matter on the classification of bitumens and on the methods of their preparation and use. The portion dealing with practical applications is a matter of mention, rather than any attempt at description. It is only fair to state, however, that, had these subjects been covered in detail, the book would necessarily have been many times its size.

The book as a whole is of little use to the great majority of the American workers in the field of bitumens. Only in unusual cases are there imports or exports of these products where the testing methods given might be applied; and its use as a reference text would therefore be infrequent.

The paper and printing are excellent and the illustrations show a high grade of workmanship. The subject index is complete and well arranged.—J. M. WEISS

MARKET REPORT—APRIL, 1931

THESE PRICES UNLESS OTHERWISE SPECIFIED ARE THOSE PREVAILING IN THE NEW YORK MARKET, APRIL 15, FOR COMMERCIAL GRADES IN CARLOAD QUANTITIES

Newer Chemicals

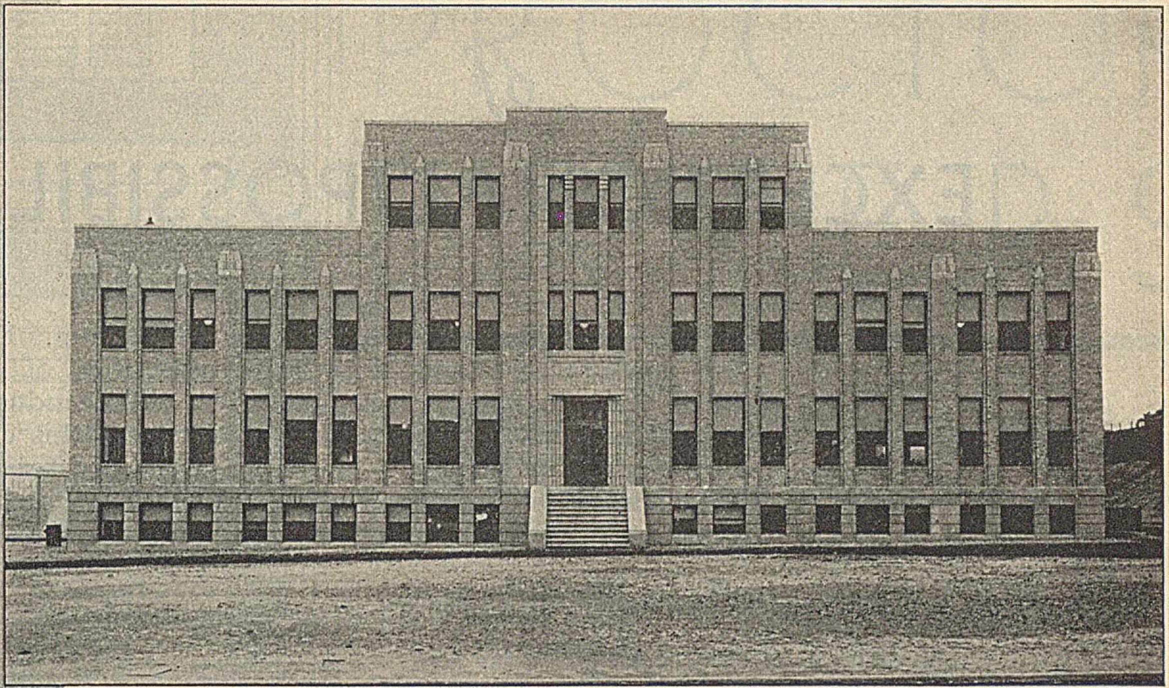
Acetaldehyde, drums, lc-l., wks.	lb.	.18½
Acetaldol, 50-gal. drums	lb.	.27
Acetylene tetrachloride, *see* Tetrachloroethane		
Ammonium linoleate, drums	lb.	.15
Amyl furoate, 1-lb. tins	lb.	5.00
Aroclors	lb.	.40
Butyl carbitol, *see* Diethylene glycol monobutyl ether		
Cellosolve, *see* Ethylene glycol monobutyl ether		
Furoate, tech., 50-gal. drums	lb.	.50
Carbitol, *see* Diethylene glycol monoethyl ether		
Cellosolve, *see* Ethylene glycol monoethyl ether		
Acetate, *see* Ethylene glycol monoethyl ether acetate		
Crotonaldehyde, 50-gal. drums	lb.	.32
Dichloroethyl ether, 50-gal. drums	lb.	.06
Diethylene glycol, drums	lb.	.14
Monobutyl ether, drums	lb.	.24
Monoethyl ether, drums	lb.	.15
Diethylene oxide, 50-gal. drums	lb.	.50
Dioxan, *see* Diethylene oxide		
Diphenyl	lb.	.30
Ethyl acetoacetate, 50-gal. drums	lb.	.65
Carbonate, 90%, 50-gal. drums	gal.	1.85
Chlorocarbonate, carboys	lb.	.30
Ether, absolute, 50-gal. drums	lb.	.50
Furoate, 1-lb. tins	lb.	5.00
Ethylene chlorhydrin, 40%, 10-gal. cbys	lb.	.75
Dichloride, 50-gal. drums	lb.	.05
Glycol, 50-gal. drums	lb.	.25
Monobutyl ether, drums, wks.	lb.	.24
Monoethyl ether, drums, wks.	lb.	.17
Monoethyl ether acetate, drums, wks.	lb.	.19½
Monomethyl ether, drums	lb.	.21
Oxide, cyl.	lb.	2.00
Furfuramide (tech.), 100-lb. drums	lb.	.30
Furfuryl acetate, 1-lb. tins	lb.	5.00
Alcohol, tech., 100-lb. drums	lb.	.50
Furoic acid (tech.), 100-lb. drums	lb.	.50
Isopropyl ether, drums	lb.	.10
Lead dithiofuroate, 100-lb. drums	lb.	1.00
Magnesium peroxide, 100-lb. cs.	lb.	1.15
Methyl acetate, drums	gal.	1.20
Cellosolve, *see* Ethylene glycol monomethyl ether		
Furoate, tech., 50-gal. drums	lb.	.50
Paraldehyde, 110–55 gal. drums	lb.	.20½
Phosphorus oxychloride, 175 cyl.	lb.	.20
Propyl furoate, 1-lb. tins	lb.	5.00
Strontium peroxide, 100-lb. drums	lb.	1.25
Sulfuryl chloride, 600-lb. drums, crude	lb.	.15
Distilled	lb.	.40
Tetrachloroethane, 50-gal. drums	lb.	.09
Trichloroethylene, 50-gal. drums	lb.	.10
Triethanolamine, 50-gal. drums	lb.	.40
Trihydroxyethylamine stearate	lb.	.35
Vinyl chloride, 16-lb. cyl.	lb.	1.00
Zinc dithiofuroate, 100-lb. drums	lb.	1.00
Perborate, 100-lb. drums	lb.	1.25
Peroxide, 100-lb. drums	lb.	1.25

Chemicals Previously Quoted

Acetanilide, U. S. P., powd., bbls.	lb.	.24
Acetic anhydride, 92–95%, cbys.	lb.	.21
Acetone, drums, wks.	lb.	.10
Acetphenetidin, bbls.	lb.	1.25
Acid, acetic, 28%, c/l., bbls.	100 lbs.	2.60
56%, c/l., bbls.	100 lbs.	4.85
Glacial, c/l., bbls.	100 lbs.	9.23
Glacial, U. S. P., c/l., carboys	100 lbs.	9.73
Acetylsalicylic, bbls.	lb.	.85
Anthranilic, 99–100%, drums	lb.	.85
Benzoic, tech., bbls.	lb.	.40
Boric, bbls.	lb.	.06⅛
Butyric, 100% basis, cbys	lb.	.80
Chloroacetic, mono-, bbls., wks.	lb.	.18
Di-, cbys	lb.	1.00
Tri-, bbls.	lb.	2.50
Chlorosulfonic, drums, wks.	lb.	.04½
Chromic, 99%, drums	lb.	.15
Cinnamic, bottles	lb.	3.25
Citric, U. S. P., cryst., bbls.	lb.	.37
Cresylic, pale, drums	gal.	.58
Formic, 90%, cbys., N. Y.	lb.	.10¼
Gallic, U. S. P., bbls.	lb.	.74
Glycerophosphoric, 25%, 1-lb. bot.	lb.	1.40
H, bbls., wks.	lb.	.65
Hydriodic, 10%, U. S. P., 5-lb. bot.	lb.	.67
Hydrobromic, 48%, cbys., wks.	lb.	.45
Hydrochloric, 20°, tanks, wks.	100 lbs.	1.35
Hydrofluoric, 30%, bbls., wks.	lb.	.06
60%, bbls., wks.	lb.	.13
Hydrofluosilicic, 35%, bbls., wks.	lb.	.11
Hypophosphorus, 30%, U. S. P., 5-gal. demis	lb.	.85
Lactic, 22%, dark, bbls.	lb.	.04
48%, light, bbls., wks.	lb.	.11
Mixed, tanks, wks.	N unit	.07
	S unit	.08
Molybdic, 85%, kegs	lb.	1.25
Naphthionic, tech., bbls.	lb.	nom.
Nitric, C. P., cbys.	lb.	.11
Nitric, 36°, c/l., cbys., wks.	100 lbs.	5.00
Oxalic, bbls., wks.	lb.	.11
Phosphoric, 50%, U. S. P.	lb.	.14
Picramic, bbls.	lb.	.65
Picric, bbls., c/l.	lb.	.30
Pyrogallic	lb.	1.50
Salicylic, tech., bbls.	lb.	.33
Stearic, d. p., bbls., c/l.	lb.	.13½
Sulfanilic, 250-lb. bbls.	lb.	.15
Sulfuric, 66°, c/l., cbys., wks.	100 lbs.	1.60
66°, tanks, wks.	ton	15.00
60°, tanks, wks.	ton	10.50
Oleum, 20%, tanks, wks.	ton	18.50
40%, tanks, wks.	ton	42.00
Sulfurous, U. S. P., 6%, cbys.	lb.	.05
Tannic, tech., bbls.	lb.	.23
Tartaric, U. S. P., cryst., bbls.	lb.	.31½
Tungstic, kegs	lb.	1.40
Valeric, C. P., 10-lb. bot.	lb.	2.50
Alcohol, U. S. P., 190 proof, bbls.	gal.	2.37
Amyl, from pentane, tanks	lb.	.236
Amyl, Imp. drums	gal.	1.75
Butyl, drums, c/l., wks.	lb.	.15½
Cologne spirit, bbls.	gal.	2.69
Denatured, No. 5, comp. denat., c/l., drums	gal.	.27
No. 1, comp. denat., drums	gal.	.27
Isoamyl, drums	gal.	4.00
Isobutyl, ref., drums	lb.	1.00
Isopropyl, ref., drums	gal.	.60
Propyl, ref., drums	lb.	1.00
Wood, *see* Methanol		
Alpha-naphthol, bbls.	lb.	.73
Alpha-naphthylamine, bbls.	lb.	.32
Alum, ammonia, lump, bbls., wks.	100 lbs.	3.30
Chrome, casks, wks.	100 lbs.	5.00
Potash, lump, bbls., wks.	100 lbs.	3.35
Soda, bbls., wks.	100 lbs.	3.45
Aluminum, metal, N. Y.	ton	22.90
Aluminum chloride, anhyd., commercial, wks., drums extra, c/l.	lb.	.05
Aluminum stearate, 100-lb. bbl.	lb.	.18
Aluminum sulfate, comm'l, bags, wks.	100 lbs.	1.25
Iron-free, bags, wks.	100 lbs.	1.90
Aminoazobenzene, 100-lb. kegs	lb.	1.15
Ammonia, anhydrous, cyl., wks.	lb.	.15½
50,000-lb. tanks, wks	lb.	.05625
Ammonia, aqua, 26°, tanks, wks. contained NH_3	lb.	.05½
Ammonium acetate, kegs	lb.	.33
Bifluoride, bbls.	lb.	.21
Bromide, 50-lb. boxes	lb.	.38
Carbonate, tech., casks	lb.	.10½
Chloride, gray, bbls.	100 lbs.	5.40
Lump, casks	lb.	.10½
Iodide, 25-lb. jars	lb.	5.20
Nitrate, tech., cryst., bbls.	lb.	.08½
Oxalate, kegs	lb.	.22
Persulfate, cases	lb.	.26
Phosphate, dibasic, tech., bbls.	lb.	.11½
Sulfate, bulk, wks.	100 lbs.	1.80
Amyl acetate, tech., from pentane, drums	lb.	.22
Aniline oil, drums	lb.	.15
Anthracene, 80–85%, casks, wks.	lb.	.60
Anthraquinone, subl., bbls.	lb.	.50
Antimony, metal	lb.	.07⅛
Antimony chloride, drums	lb.	.13
Oxide, bbls.	lb.	.10
Salt, dom., bbls.	lb.	.22
Sulfide, crimson, bbls.	lb.	.25
Golden, bbls.	lb.	.16
Vermilion, bbls.	lb.	.38
Argols, red powder, bbls.	lb.	.07½
Arsenic, metal, kegs	lb.	.30
Red, kegs, cases	lb.	.09¾
White, c/l., kegs	lb.	.04
Asbestine, bulk, c/l.	ton	15.00
Barium carbonate, bbls., bags, wks.	ton	56.50
Chloride, bbls., wks.	ton	63.00
Dioxide, drs., wks.	lb.	.12
Hydroxide, bbls.	lb.	.05¼
Nitrate, casks	lb.	.07½
Barium thiocyanate, 400-lb. bbls.	lb.	.27
Barytes, floated, 350-lb. bbls., wks.	ton	23.00
Benzaldehyde, tech., drums	lb.	.60
F. F. C., cbys	lb.	1.40
U. S. P., cbys	lb.	1.15
Benzidine base, bbls.	lb.	.65
Benzol, tanks, wks.	gal.	.19
Benzoyl chloride, cbys	lb.	1.00
Benzyl acetate, F. F. C., bottles	lb.	.75
Alcohol, 5-liter bot.	lb.	1.20
Chloride, tech., drums	lb.	.30
Beta-naphthol, bbls.	lb.	.22
Beta-naphthylamine, bbls.	lb.	.58
Bismuth, metal, cases	lb.	1.50
Bismuth, nitrate, 25-lb. jars	lb.	1.25
Oxychloride, boxes	lb.	2.95
Subnitrate, U. S. P., 25-lb. jars	lb.	1.50
Blanc fixe, dry, bbls.	ton	70.00
Bleaching powder, drums, wks.	100 lbs.	2.00
Bone ash, kegs	lb.	.06
Bone black, bbls.	lb.	.08¼
Borax, bags	lb.	.02½
Bordeaux mixture, bbls.	lb.	.11½
Bromine, bot.	lb.	.36
Bromobenzene, drums	lb.	.50
Bromoform, jars	lb.	1.80
Butylacetate, drums, c/l.	lb.	.17
Cadmium bromide, 50-lb. jars	lb.	1.40
Cadmium, metal, cases	lb.	.55
Cadmium sulfide, boxes	lb.	.60
Caffeine, U. S. P., 5-lb. cans	lb.	2.40
Calcium acetate, bags	100 lbs.	2.00
Arsenate, bbls.	lb.	.06
Carbide, drums	lb.	.05½
Chloride, drums, wks., flake	ton	22.75

Cyanide, 100-lb. drums	lb.	.30
Nitrate, bbls	ton	40.00
Phosphate, monobas., bbls	lb.	.08
Tribas., bbls	lb.	.11
Calcium carbonate, tech., bgs.	100 lbs.	1.00
U. S. P., precip., 175-lb. bbl	lb.	.06½
Camphor, Jap., cases	lb.	.55
Carbazole, bbls	lb.	.75
Carbon, activated, drums	lb.	.08
Carbon bisulfide, drums	lb.	.05½
Carbon black, cases	lb.	.06
Carbon dioxide, liq., cyl	lb.	.06
Carbon tetrachloride, drums	lb.	.06¼
Casein, stand. gr., bbls	lb.	.09
Cellulose acetate, bbls	lb.	.80
Cerium oxalate, kegs	lb.	.32
Charcoal, willow, powd., bbls	lb.	.06
China clay, bulk	ton	8.00
Chloral hydrate, drums	lb.	.70
Chlorine, liq., c/l., cyl	lb.	.04
Chlorine, tanks	100 lbs.	1.75
Chlorobenzene, mono-, drums	lb.	.10
Chloroform, tech., drums	lb.	.15
Chromium acetate, 20° soln., bbls.	lb.	.05
Coal tar, bbls., wks	gal.	.10
Cobalt, metal, kegs	lb.	2.50
Cobalt oxide, bbls	lb.	2.10
Cod-liver oil, bbls	bbl.	30.00
Copperas, c/l., bulk	ton	13.00
Copper, metal, elec	100 lbs.	9.75
Copper carbonate, bbls	lb.	.08½
Chloride, bbls	lb.	.22
Cyanide, drums	lb.	.41
Oxide, red, bbls	lb.	.15½
Sulfate, c/l., bbls	100 lbs.	4.25
Cotton, soluble, bbls	lb.	.40
Cream tartar, bbls	lb.	.23¾
Cyanamide, bulk, N. Y.	Nitrogen unit	1.39
Diaminophenol, kegs	lb.	3.80
Dianisidine, bbls	lb.	2.35
Dibutylphthalate, drums, wks	lb.	.24½
Diethylaniline, drums	lb.	.55
Diethylene glycol, drums	lb.	.14
Diethyl phthalate, drums	lb.	.23
Diethyl sulfate, tech., drums	lb.	.30
Dimethylaniline, drums	lb.	.26
Dimethylsulfate, drums	lb.	.45
Dinitrobenzene, drums	lb.	.15½
Dinitrochlorobenzene, bbls	lb.	.13
Dinitronaphthalene, bbls	lb.	.34
Dinitrophenol, bbls	lb.	.29
Diphenylamine, bbls	lb.	.37
Diphenylguanidine, bbls	lb.	.30
Epsom salt, tech., bbls., c/l., N. Y.	100 lbs.	1.70
Ether, nitrous, bot	lb.	.80
Ether, U. S. P., drums	lb.	.13
Ethyl acetate, tanks c/l	lb.	.075
Bromide, drums	lb.	.50
Chloride, drums	lb.	.22
Methyl ketone, drums	lb.	.30
Ethylbenzylaniline, 300-lb. drums	lb.	.88
Ethylene dichloride	lb.	.05
Chlorohydrin, anhyd., drums	lb.	.75
Glycol, c/l.,wks	lb.	.25
Feldspar, bulk	ton	7.50
Ferric chloride, tech., bbls	lb.	.05
Ferrous chloride, cryst., bbls	lb.	.06
Ferrous sulfide, bbls	100 lbs.	2.50
Fluorspar, 98%, bags	ton	41.00
Formaldehyde, bbls	lb.	.06
Formaniline, drums	lb.	.37½
Fuller's earth, bags, c/l., mines	ton	15.00
Furfural, drums, tech., contract, works	lb.	.10
Glauber's salt, bbls	100 lbs.	1.00
Glucose, 70°, bags, dry	100 lbs.	3.14
Glycerine, C. P., drums	lb.	.12½
G salt, bbls	lb.	.42
Hexamethylenetetramine, tech., drums	lb.	.46
Hydrogen peroxide, 25 vol., bbls.	lb.	.05½
Hydroquinone, kegs	lb.	1.20
Indigo, 20%, paste, bbls	lb.	.12
Iodine, crude, 200-lb. kgs	lb.	4.20
Iodine, resubl., jars	lb.	4.65
Iodoform, bot	lb.	6.00
Iridium, metal	oz.	160.00
Kieselguhr, bags	ton	60.00
Lead, metal, N. Y	100 lbs.	4.50
Lead acetate, bbls., white	lb.	.11½
Arsenate, bbls	lb.	.11
Oxide, litharge, bbls	lb.	.08¾
Peroxide, drums	lb.	.20
Red, bbls	lb.	.103
Sulfate, bbls	lb.	.06¾
White, basic carb., bbls	lb.	.07¼
Lime, hydrated, bbls	100 lbs.	.85
Lime, live, chemical, bbls., wks.	100 lbs.	1.05
Limestone, ground, bags, wks	ton	4.50
Lithopone, bbls	lb.	.04½
Magnesite, crude	ton	36.00
Calcined, 500-lb. bbls., wks	ton	50.00
Magnesium, metal sticks, wks	lb.	.85
Magnesium carbonate, bags	lb.	.06
Chloride, drums	ton	36.00
Fluosilicate, cryst., bbls	lb.	.10
Oxide, U. S. P., light, bbls	lb.	.42
Manganese chloride, casks	lb.	.07½
Dioxide, 80%, bbls	ton	80.00
Sulfate, casks	lb.	.07
Mercury bichloride, cryst., 25 lbs.	lb.	1.63
Mercury, flasks, 76 lbs	flask	102.00
Meta-nitroaniline, bbls	lb.	.67
Meta-phenylenediamine, bbls	lb.	.80
Meta-toluylenediamine, bbls	lb.	.67
Methanol, pure, synthetic, drums, wks.	gal.	.42
Tanks, wks	gal.	.40
Methyl acetone, drums	gal.	.50
Salicylate, cases	lb.	.42
Methyl chloride, cylinders	lb.	.45
Michler's ketone, bbls	lb.	3.00
Naphtha, solvent, tanks	gal.	.35
Naphthalene, flake, bbls	lb.	.04½
Nickel, metal	lb.	.35
Nickel salt, single, bbls	lb.	.10½
Double, bbls	lb.	.10½
Niter cake, bulk	ton	12.50
Nitrobenzene, drums	lb.	.09
Oil, castor, No. 1	lb.	.11½
China wood, bbls	lb.	.07
Coconut, Ceylon, tanks	lb.	.05½
Cod, N. F., tanks	gal.	.44
Corn, crude, tanks, mills	lb.	.07⅜
Cottonseed, crude, tanks	lb.	.06⅛
Lard, edible, bbls	lb.	.13¼
Linseed, bbls	lb.	.094
Menhaden, crude, tanks	gal.	.21
Neat's-foot, pure, bbls	lb.	.11
Oleo, No. 1, bbls	lb.	.07½
Olive oil, denat., bbls	gal.	.82
Foots, bbls	lb.	.06½
Palm, Lagos, casks	lb.	.05⅛
Peanut, crude, bbls	lb.	nom.
Perilla, bbls	lb.	.10
Rapeseed, bbls., English	gal.	.71
Red, bbls	lb.	.08⅜
Soy bean, crude, bbls	lb.	.07
Sperm, 38°, bbls	gal.	.84
Whale, bbls., natural, winter	gal.	.72
Ortho-aminophenol, kegs	lb.	2.15
Ortho-dichlorobenzene, drums	lb.	.08
Ortho-nitrochlorobenzene, drums	lb.	.28
Ortho-nitrophenol, bbls	lb.	.85
Ortho-nitrotoluene, drums	lb.	.16
Ortho-toluidine, bbls	lb.	.27
Palladium, metal	oz.	20.00
Para-aminophenol, kegs	lb.	.84
Para-dichlorobenzene	lb.	.17
Para-formaldehyde, cases	lb.	.38
Paraldehyde, tech., drums	lb.	.20½
Para-nitroaniline, drums	lb.	.48
Para-nitrochlorobenzene, drums	lb.	.25
Para-nitrophenol, bbls	lb.	.45
Para-nitrosodimethylaniline, bbls.	lb.	.92
Para-nitrotoluene, bbls	lb.	.29
Para-phenylenediamine, bbls	lb.	1.15
Para-toluidine, bbls	lb.	.44
Paris Green, 250-lb. kegs	lb.	.25
Phenol, drums	lb.	.14¼
Phenolphthalein, drums	lb.	1.10
Phenylethyl alcohol, 1-lb. bot	lb.	7.00
Phosphorus, red, cases	ib.	.42
Phosphorus trichloride, cyl	lb.	.35
Phthalic anhydride, bbls	lb.	15
Platinum, metal	oz.	30.00
Potash, caustic, drums	lb.	.06⅛
Potassium acetate, kegs	lb.	.28
Bicarbonate, casks	lb.	.09½
Bichromate, casks	lb.	.09
Binoxalate, bbls	lb	.14
Bromate, cs	lb.	.35
Carbonate, 80–85%, calc., casks.	lb.	.05¼
Chlorate, kegs	lb.	.08
Chloride	ton	34.55
Cyanide, cases	lb.	.55
Meta-bisulfite, bbls	lb.	.11
Permanganate, drums	lb.	.16
Prussiate, red, casks	lb.	.38
Yellow, casks	lb.	.18½
Titanium oxalate, bbls	lb.	.21
Pyridine, drums	gal.	1.50
Resorcinol, tech., kegs	lb.	.90
Rochelle salt, bbls., U. S. P	lb.	.19
R salt, bbls	lb.	.42
Saccharin, cans	lb.	1.70
Salt cake, bulk	ton	18.00
Saltpeter, gran., bbls	lb.	.06⅛
Silica, ref., bags	ton	22.00
Silver nitrate, 16-oz. bot	oz.	.21⅞
Soda ash, 58%, light, bags, contract, wks	100 lbs.	1.15
Soda, caustic, 76%, solid, drums, contract, wks	100 lbs.	2.50
Sodium acetate, bbls	lb.	.04½
Benzoate, bbls	lb.	.42
Bicarbonate, bbls	100 lbs.	2.00
Bichromate, casks	lb.	.07
Bisulfite, bbls	lb.	.04
Bromide, bbls., U. S. P	lb.	.34
Chlorate, kegs	lb.	.05¾
Chloride, bags	ton	12.00
Cyanide, cases	lb.	.15½
Fluoride, bbls	lb.	.08
Metallic, drums, 12¼-lb. bricks	lb.	.19½
Naphthionate, bbls	lb.	.52
Nitrate, crude, bags, N. Y.	100 lbs.	2.05
Nitrite, bbls	lb.	.07¼
Perborate, bbls	lb.	.18
Peroxide, cases	lb.	.21
Phosphate, trisodium	100 lbs.	3.05
Picramate, kegs	lb.	.69
Prussiate, bbls	lb.	.11½
Silicate, drums, tanks, 40°	100 lbs.	.75
Silicofluoride, bbls	lb.	.04
Stannate, drums	lb.	.23½
Sulfate, anhyd., bbls	lb.	.02
Sulfide, cryst., bbls	lb.	.02½
Solid, 60 %	lb.	.03½
Sulfocyanide, bbls	lb.	.28
Thiosulfate, reg., cryst., bbls	lb.	.02½
Tungstate, kegs	lb.	.81
Strontium carbonate, tech., bbls	lb.	.07¼
Nitrate, bbls	lb.	.09
Sulfur, bulk, mines, wks	ton	18.00
Sulfur chloride, red, drums	lb.	.05
Yellow, drums	lb.	.03½
Sulfur dioxide, commercial. cyl	lb.	.07
Sulfuryl chloride, drums	lb.	.10
Thiocarbanilid, bbls	lb.	.26½
Tin	lb.	.26
Tin tetrachloride, anhydrous, drums, bbls	lb.	.19¼
Oxide, bbls	lb.	.26
Titanium dioxide, bbls., wks	lb.	.21
Toluene, tanks	gal.	.29
Tribromophenol, cases	lb.	1 10
Triphenylguanidine, drums	lb.	.58
Triphenyl phosphate, bbls	lb.	.60
Tungsten, powder	lb.	1.65
Urea, pure, cases	lb.	.11
Whiting, bags	100 lbs.	1.00
Xylene, 10°, tanks, wks	gal.	.28
Xylidine, drums	lb.	.36
Zinc, metal, N. Y	100 lbs.	4.30
Zinc ammonium chloride, bbls	lb.	.05½
Chloride, granulated, drums	lb.	.05¾
Oxide, Amer., bbls	lb.	.06½
Stearate, bbls	lb.	.19
Zinc dust, bbls., c/l	lb.	.06

INDUSTRIAL PROGRESS DEPENDS ON THE SCIENTIST



Values are weighed *carefully* in lean years

COMPANIES with sufficient foresight to erect laboratories during 1930 could be depended on to select their equipment also with an eye to the future. Initial cost was considered, of course, but performance for the life of the structure was the yardstick of measurement.

The prominent laboratories built during 1930, listed at the left, all are equipped with Alberene Stone Table-tops, Fume Hoods, Sinks, Drain-boards, etc. Conclusive evidence of the fitness of this Virginia Soapstone equipment for all surfaces exposed to the action of corrosive acids, alkalis, fumes and heat.

- Aluminum Co. of America, New Kensington, Pa.
- Bakelite Company, Bloomfield, N. J.
- Barber Asphalt Company, Maurer, N. J.
- Calco Chemical Company, Bound Brook, N. J.
- Dearborn Chemical Company, Chicago, Ill.
- Gulf Refining Company, Pittsburgh, Pa.
- International Nickel Co., Bayonne, N. J.
- John A. Roebling Company, Trenton, N. J.
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METHYL CHLORIDE	Refrigerant for household, commercial and industrial units.

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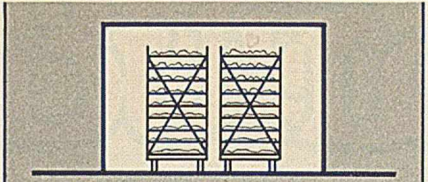
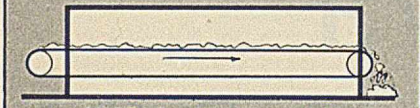
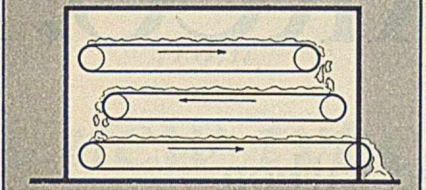


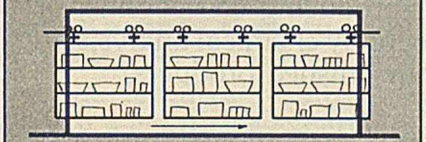
TRUCK SYSTEM DRYER



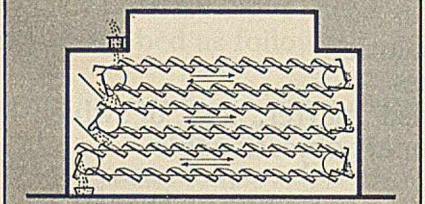
SINGLE APRON DRYER



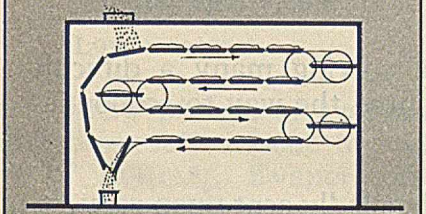
MULTIPLE APRON DRYER



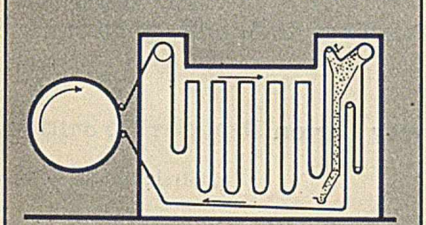
MONORAIL SYSTEM DRYER



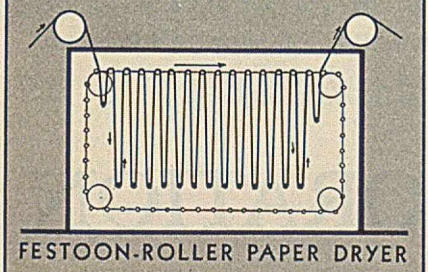
REVERSING PAN DRYER



CONTINUOUS FLAT PAN DRYER



CONTINUOUS FILTER & DRYER



FESTOON-ROLLER PAPER DRYER

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