Friend or Foe?

IT HAS been several years since anything has occurred to stir chemical circles so thoroughly as the formation of the "American I. G. Chemical Corporation," announced in the closing days of April. Suspicions have been aroused, healing wounds have been reopened, and foundations laid for animosities. Naturally it has been difficult to ascertain the facts, and whether the new corporation is to be regarded as a friend or foe of the American chemical industry depends very much upon the interest of the one whose opinion you seek. Is it a well-thought-out effort to promote world peace by inviting the industries of various countries to meet on a common ground, or is it a prime example of the camel whose nose has been thrust under the American tent? A careful consideration of all the obtainable information shows clearly that many have hastily formed opinions based upon rumors and surmises. Whatever our feelings in the case, we prefer to form a critical opinion only after more authentic data are available for study. Perhaps we must await the actual functioning of the new organization before its trends and policies will be sufficiently revealed to enable an unqualified answer to the question, "friend or foe?".

Whatever may be left for the future to decide, it must be said that from the standpoint of those who have continued to strive for the establishment of an American chemical industry one or two criticisms may be made. Manifestly those who chose the name "American I. G. Chemical Corporation" paid little attention to American psychology, although a certain advertising value may be found in it. The very name of the I. G. recalls to thousands the willingness of that corporation to cut off synthetic medicinals from innocent sufferers in America in an effort to force us to break our neutrality. To others it awakens recollections of ruthless policies practiced to prevent competition, days of "dumping," and unfair trade practices in export markets. To many Americans, whether rightfully or not, the I. G. stands not so much for a successful commercial enterprise as for a government-nurtured monopoly which seeks world domination. However successful its business principles, they are believed by many to be in direct conflict with those characterizing American procedure, and the title "American I. G." strikes many as nothing short of sacrilege.

In interviews given out following the announcement, one of the principals is credited with having emphasized the inevitable success which must follow from a "combination of German brains with American capital." This statement would lead one to infer that, while America has money, she is sadly lacking in brain power (at least among the chemists), whereas Germany, though poor in this world's goods, excels in chemical gray matter. This sort of publicity may aid greatly in selling bonds, and when the time comes will doubtless also help in selling stock for, as the *New York Herald Tribune* says editorially, "An idea still not altogether dead was the myth of the mysterious German. No one whose training in chemical science originated more than a hundred leagues

from the Rhine was believed able to compare for an instant— whether in brains, or in magic working in the factory—with the products of that marvelous, if slightly misty school." Without special emphasis from us our readers will be able to recall so considerable a list of research accomplishments which have grown to economic importance in this country as to leave no doubt regarding the ability of the American scientist to cope with his fellows if he is given equal support. Quoting A. D. Little, "The world unquestionably owes a great debt to German science, but the supremacy of German chemistry, of which we have heard so much, is a thing of the past." We are informed that at least one of the corporations controlled by the I. G. in this country has almost completely Germanized its plant. Not only have millions been invested in imported equipment, but hundreds of technicians and chemists have been put into the plant where at present German is the language most frequently heard. It should be remembered that under present immigration laws fifty thousand Germans may enter annually, and when it is recalled how close is the relation between the I. G. and the German authorities it will be seen that it would not be difficult to place particular men in the emigration quota. But we are informed that, notwithstanding enlargements, improvements, and reorganized personnel, large profits have not been made, and perhaps we shall see from experiments conducted close at hand whether, after all, a combination of German brains and American capital is any more potent than American brains as thoroughly backed by American capital. Years ago B. C. Hesse reported that the element of difference between German and American research was the financial backing given the former—a larger supply of educated patient money, as John E. Teeple would say.

We have always maintained that foreign capital seeking investment in America to work under American conditions with due regard for our patent laws, our wage scales, and our trade practices must necessarily be welcome and sincerely wished success. However, if American researchers, technicians, and others are to be displaced, then obviously the enterprise can scarcely be regarded as friendly, nor their policies encouraging to the thousands of youths who have been attracted to a career in chemistry. A considerable number of German enterprises are represented in the United States but in other cases such causes of friction have been avoided and a different reception enjoyed.

Notable among the Interessengemeinschaft interests in the United States are the Agfa-Ansco Corporation, formerly the Ansco Company, engaged in the manufacture of photographic apparatus and supplies, and the General Aniline Works, Inc., which used to be the Grasselli Dyestuff Corporation. The great dye trust doubtless has other interests, and those disposed to be friendly toward the new organization point out that in its formation the Germans have merely taken a leaf from the book of American industry and followed the Yankee practice of establishing strong local corporations in those

foreign lands where they seek to do business. It is pointed out that it is but logical that the Interessengemeinschaft should organize in America a holding corporation over which it could exercise control at all times and the business of which would be to represent German interests here, to receive and dispose of any moneys which may be paid on account of settlements emanating from the Alien Property Custodian's office, and engage in such active expansion of its business as good judgment may dictate. If the German-controlled holding company sees fit to borrow money on American assets by selling bonds to American purchasers and wishes to transfer the proceeds of such a sale to headquarters in Frankfort, then no one is justified in raising an objection. The allegation that the corporation was hurriedly formed to secure money needed in Germany when, because of reparation tangles, a satisfactory loan could not be floated, is stoutly denied. The project is said to have been at least two years in the making.

Colonel Donovan, in his address at the Salesmen's Dinner in New York, reiterated his belief that trusts and organizations such as the German I. G. no longer constitute a menace when they create an American corporation to do their business. This is because they must then obey our laws and we know full well how to deal with monopolistic organizations. There seems to be good ground for this view, but it touches the legal phase only and leaves us with the definite task of safeguarding and building up that which we have already won.

The industries must expand, not curtail, their research programs. Confidence may require demonstration. World domination by one nation through science is only possible if others, by their inaction, make it possible. Our chemists must make every effort to keep abreast of research, and in this they are greatly aided by such publications as *Chemical Abstracts*. American bankers need to be helped to understand and appreciate American capability and opportunity. Our chemical industry would do well to follow Colonel Donovan's suggestion that it organize an inclusive trade association which offers one of the best means of effectively serving the units of an industry under our laws and conditions.

If the American I. G. Chemical Corporation proves to be an entering wedge to disrupt and destroy the American chemical industry, it will meet unyielding opposition.

An Auspicious Meeting

ON NUMEROUS occasions the chemical industry of the United States has been urged to form a federation or a general trade association. The existence of groups organized in special fields of chemical activity would seem to offer the means through which this objective could be attained, but minor discords have interfered. The natural differences between the chemical and other industries, though tending to make the formation of a federation more difficult, would not seem grave enough to defeat such a plan.

Surely there is sufficient common ground for united action and exchange of opinions. The representatives of various associations have harmoniously served on a number of committees, notably the Industrial Advisory Council to the Prohibition Unit of the Treasury Department, and individuals identified with the several branches of the chemical industry have performed valuable service through the Chemical Advisory Committee to the Department of Commerce, which last met April 18, 1929. There is reason to believe that, through the initiation and management of the two conferences of the chemical executives, held in December, 1926, and February, 1928, much was done to promote the better acquaintance

among individuals which underlies successful trade association work. Indeed, the good that has come to the industry and to the Department of Commerce through these conferences of executives has led to the suggestion put forward by Henry Howard, that the plan be adopted by other commodity divisions and that ten representatives of the Department located in the principal foreign countries be brought back for a series of conferences.

An auspicious meeting to be held early in June is the first joint meeting of the Manufacturing Chemists' Association and the Synthetic Organic Chemical Manufacturers Association of the United States. May we not hope that this is but the first of a long series of such meetings, to be enlarged from time to time by bringing in other organized groups, and that ere long some type of federation may be formed? Such a strong association could speak for the chemical industry as a whole, initiate concerted action, and conduct a program of constructive work leading to a realization of trade possibilities, both at home and abroad. The meeting in Wilmington will be watched with unusual interest and on all sides we hear the hope expressed that it may be successful in every particular.

The Cleveland Disaster

EVERYWHERE the deepest sympathy is expressed for those involved in the distressing disaster at the hospital in Cleveland where, from some undetermined cause, x-ray photographic film exploded. George W. Crile, the head of the organization, enjoys a world-wide reputation as one of America's foremost surgeons, a man of kindly sympathies, philanthropic tendencies, technical skill, and constructive imagination. It is ironical that such a catastrophe should overtake an institution to which he and his colleagues have so unselfishly given of their time and their means.

We learn by costly experience. Doubtless there are many other similar potential hazards in the hospitals and laboratories of the country. We do not know what set off the film, but from what we can learn the explosion was somewhat similar to that which has occurred in battleship turrets. When nitrocellulose burns with insufficient air, corrosive and suffocating nitrogen dioxide or its polymer, nitrogen tetroxide—depending on the temperature—is formed and this, red in color, was probably responsible for the early accounts that bromine had done the damage. We are particularly sorry to see certain papers appealing to the misinformation which some still hold with respect to poison gas and failing to distinguish between gas that is poisonous and the war gases which, in many quarters, have been given an undeserved reputation by our newspapers.

On the whole we feel that efforts made during the last decade by many agencies to interest the daily press in true accounts have borne good fruit, but occasionally we despair. Had this calamity befallen some community where competent scientific advice was unobtainable, certain press despatches might more easily be overlooked. In Cleveland there are many sources of information which, if called upon, might have prevented the newspapers from printing the ludicrous statements that have appeared. The press alone is not to blame, however, for some interviews, if correctly quoted, displayed inexcusable carelessness on the part of scientists granting them.

That film stored in any quantity should be placed in a separate building to avoid a repetition of such a disaster seems clear. How it should be stored is known and the information upon the subject is available. Steps should be taken everywhere to make impossible further losses from a similar cause.

Futility in Tariffs

IT IS doubtful whether any tariff bill has produced more adverse comment than H.R. 2667, which is now before the Congress. The bill does not deserve condemnation in every respect, even though it contains some obviously futile provisions. An outstanding example of the latter is the tariff on molasses and sugar sirups, covered in paragraph 502.

The original bill boldly discriminated between inedible molasses to be used for purposes other than the production of alcohol and the same kind of molasses imported for alcohol manufacture. Molasses imported for any purpose other than for human consumption or for distilling would carry a tariff equivalent to one-sixth of one cent per gallon testing 48 per cent total sugars, but if it is to be used for the production of industrial alcohol, the duty becomes equivalent to two cents per gallon. Obviously this is an effort to force the industry to substitute corn for molasses in distilling, and yet minimize the increased cost to the farmers who buy stock feeds containing the same kind of molasses.

Such a provision could bring good to no one. It would force the feed manufacturers to install a series of bonded tanks and to assist in maintaining a staff of inspectors to prevent the diversion of blackstrap, supposedly imported for stock feed, to the production of industrial alcohol. It would not force the distillers to use corn, but it would considerably advance the cost of alcohol, thereby adding to the difficulty of holding the domestic market for goods requiring alcohol in their manufacture and making their export impossible.

Those who would urge the adoption of such a tariff seem to be oblivious of certain well-known facts. Most of the industrial alcohol is now produced in plants near enough the seaboard to benefit from water transportation of their raw material. It would cost upwards of ten million dollars to convert the seaboard plants for the use of corn, and the item of freight on the grain would remain. Freight is such a considerable factor that, if forced to use corn, these plants would need to be moved. More than forty millions of dollars would be involved in moving them into the interior, and under present conditions the business is not sufficiently attractive to warrant such expenditure. Molasses at, say, nine and one-half cents a gallon, plus the proposed duty of two cents, would still give a raw material more attractive than corn, remembering that 2.7 gallons of molasses produce a gallon of alcohol and that one bushel of corn yields 2.5 gallons. Apply these factors to the current price of corn, plus freight to the plant, and the answer is obvious.

Not only is there the constant threat of synthetic ethanol, but we predict that any congressional action resulting in an artificial increase in the cost of a basic raw material will so advance the price of many ultimate products as to bring widespread dissatisfaction. Alcohol enters into so many items of merchandise purchased by all individuals and industries that the adverse effect will be universal, and much more than offset the supposed gain for a single group. As we go to press the bill as revised has been passed by the House. In it the offending discrimination has been deleted and all black strap classed together. The seriousness of the situation is reflected in the record of this measure. A proposal to raise the duty to eight cents per gallon, equivalent on alcohol to twenty-one and six-tenths cents per gallon in the cost of raw materials alone, was actually voted 132 to 130, but fortunately this was reversed in support of the committee recommendation 136 to 116. This illustrates how important industries may become political pawns. Even now final action cannot be forecast since the whole subject may be further reviewed in the Senate.

Another example of unwise tariff proposals is found in the section dealing with vegetable oils. Of the vegetable oil imported, approximately 60 per cent comes from the Philippine Islands, leaving some 280,000,000 pounds to enter from other sources. As against this we export 800,000,000 pounds of lard. So large a proportion of the imported vegetable oil goes into soaps and other products, for the manufacture of which we do not produce suitable oils, that one has difficulty in finding sound reasons for the proposed duties.

If industry would see the fair thing for all concerned accomplished in tariff revision, it should raise its voice not only before congressional committees but in the hearing of the folks back home, most of whom have no appreciation of just how some of the proposals will affect their own economy.

The Exposition

THE Twelfth Exposition of Chemical Industries closed on May 11, and the thirteenth will open May 4, 1931.

It was a splendid exposition and the consensus of opinion is that this year's chemical show was better than its predecessors. The exhibits were more varied, with better display, and altogether more interesting. The exposition management, which placed its facilities at the service of all exhibitors, deserves to be complimented.

From the exhibitors' point of view the attendance was satisfactory and included a smaller percentage of those merely seeking diversion than experienced heretofore. Some would have preferred autumn for in May many engineers are in the field erecting new equipment, but since the decision was reached to hold this exposition biennially, the more desirable fall dates have naturally been given to those exhibits which will use them annually.

Not the exposition, but the manufacturers of chemical products who still absent themselves, deserve such criticism as may be forthcoming. Once more many American chemical manufacturers neglected the great possibilities and the advantages of direct publicity in advertising at home and abroad. While there were a few more chemical products than at the eleventh exposition, yet they comprised a mere 5 per cent of the exhibits and left some with the feeling that, after all, it is more an exposition of chemical equipment than of chemical industries and their products. Chemical manufacturers should realize the importance today, just as much as when the exposition was begun, of showing all and sundry the ability of this country to produce its chemical needs. An occasion of this sort is one upon which the traditional best foot should be put forward, and when, instead, there is inadequate representation of what is being made in the chemical industries, the natural inference is that little is being done or that the makers are ashamed of what they produce. We know the latter is not the case. In the thirteenth exposition chemical products should occupy at least half the exposition space.

On entering the exposition one saw a letter from President Hoover expressing regret at his inability to attend, but asking that this message be conveyed on his behalf:

I sympathize so strongly with the purpose of such expositions that I wish you would kindly convey the following message from me on that occasion:
"The chemical industries are among the foremost of those that ally themselves continuously with workers in pure science and thereby quickly transform discoveries of creative research into practical products for human use. The fact that your exposition equally interests chemists, engineers, and manufacturers symbolizes this close bond, so desirable in all industry. I wish you all success."

The exposition has been a success, but it cannot perform its full service until, in addition to those who have so loyally supported it, there is added an adequate number of the makers of chemical products. With two years to plan, let us do our utmost to see this defect remedied in 1931.
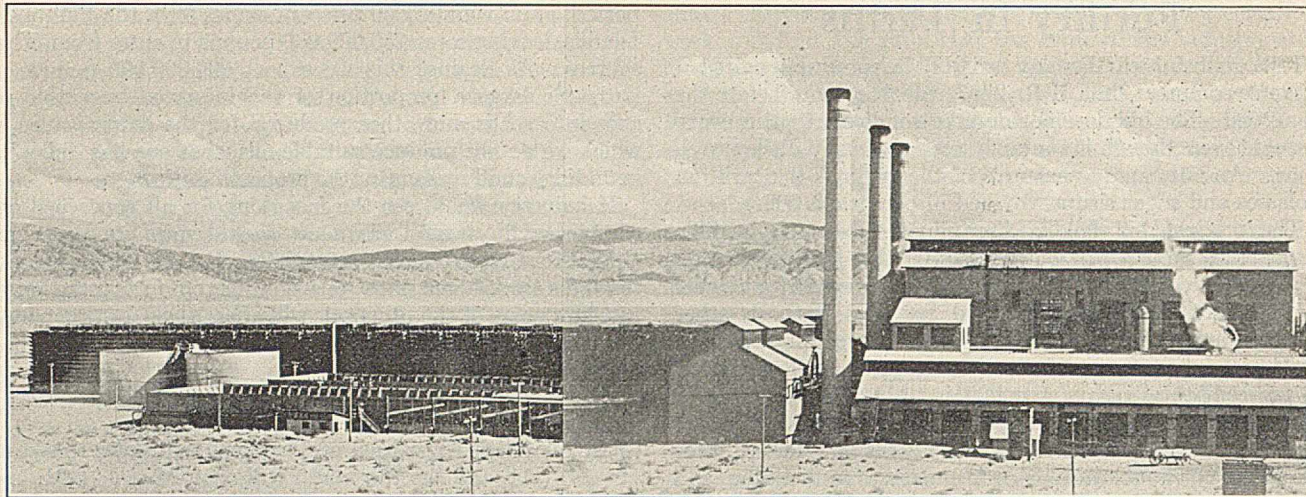
The Trona Enterprise[1]

Plant of the American Potash and Chemical Corporation at Searles Lake

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A VISIT to the remarkable potash-borax plant at Trona, Calif., leads one to suggest an inscription to be carved on its cornerstone—"Dedicated to the memory of Willard Gibbs."

It would be hard to find elsewhere a more striking example of the cash value of the phase rule. Even barring all question of engineering skill and ingenuity, the fact remains that physical chemistry has marked the difference between success and failure in the recovery of California's desert alkalies.

For years various amateurs have stewed and evaporated the bitter waters of Searles Lake, out in the Mohave Desert. In quest of alkali salts they crystallized, filtered, dissolved, and analyzed. Usually they got nowhere. One, the pioneer John Searles himself, coaxed a few hundredweight per year of crude borax out of marginal lake efflorescences. His product of forty years ago, transported with difficulty and sold at fancy prices, could not even find a buyer today under modern purity standards.

In the new industry, however, a research staff revels in thermostats and salt-phase diagrams in two, four, or even six dimensions. The production manager, himself an expert physical chemist, spends the day manipulating phases, components, temperatures, pressures, and concentrations. Of all these he has a-plenty. But when the whistle blows he counts 240 tons of potassium chloride, 130 tons of borax, and 10 tons of boric acid which weren't there the night before. Every pound of this daily output is white and dry as the driven snow in Dakota, and of top purity for its grade.

The cornerstone may belong to the honored Gibbs, but the rest of the plant must be credited to the intelligent and persistent experts who have fought a ten years' battle against a great variety of obstacles. To these men first of all should go the thanks of a nation for demonstrating that there *is* an American potash industry.

Isolated Trona

The town of Trona lies beside Searles Lake in a strange, desert sink about 180 miles in a northerly direction from Los Angeles. It is in a country which Providence seems to have forgotten. Both snowstorms and days at 115° Fahrenheit are to be found in the records. It is a full three hours' trip from the settlements at Searles Lake via the company railway and the connecting Southern Pacific to the nearest human habitation—barring only the lonely station at Searles junction. After one has journeyed through long stretches of sand and creosote bushes, punctuated by a few lizards, it is interesting to come upon a modern town of a thousand souls, with a splendid plant, offices, laboratories, store, school, open-air theater, fine residences, the latest dial-type telephone system, and the latest shade in silk hosiery. It is a little world by itself.

Searles Lake

Extensive geological and analytical reports, dealing with the inland alkali basins of Southern California,[2] are already available. Summarizing briefly the geographical and economic situation:

Apparently the original sources contributing to Searles Lake have run heavily to minerals such as soda and potash feldspars. Upon natural disintegration and carbonation from the air these have long ago thrown out the alkaline earths which would contaminate the normal stream flow. Sodium and potassium are therefore the only cations of importance present.

Centuries of evaporation without drainage have caused so much crystalline precipitation in the lake that the crystal bed now stands a trifle above the level of the briny mother liquor. The occasional flooding and drying of the lake following a rainstorm have caused a cement-like crust to coat the surface, largely preventing evaporation of the brine

[2] Gale, U. S. Geol. Survey, *Bull.* 580-L (1914).
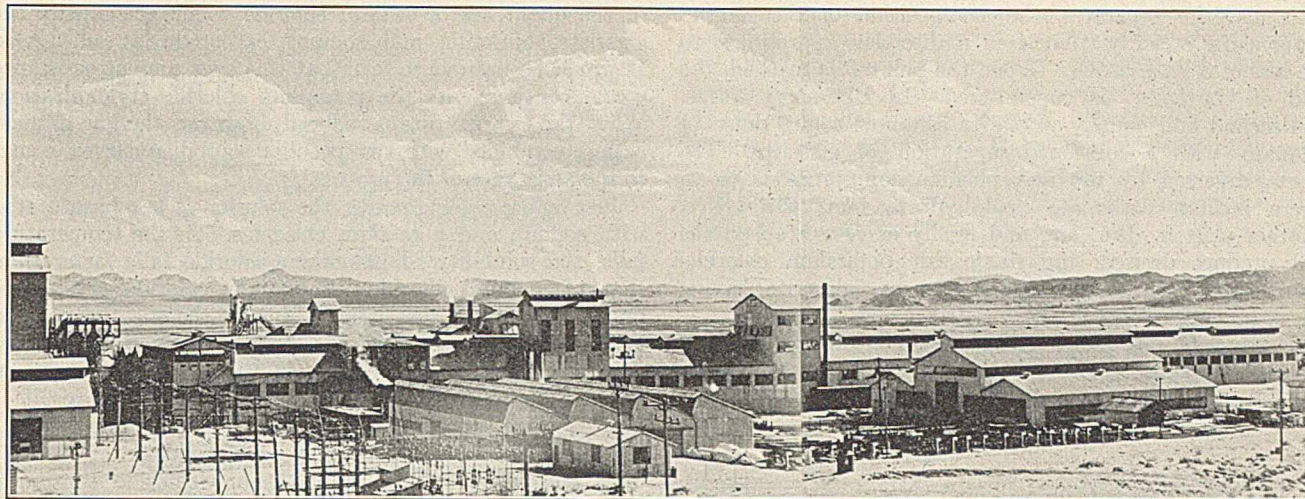
Corporation, Trona, California

beneath. The solid material at the surface is almost wholly common salt, but in submerged layers there is a queer series of little-known double salts, precipitated from complex brines at various stages in recent geological history. So smooth, so level, and so compact is the crystal mass that a 2-ton automobile speeds with impunity at 60 miles per hour over its 12 square miles of glittering surface. The crystal bed is practically valueless; but the brine, itself of enormous volume, is the basis of the present industry.

The latest analysis of Searles Lake brine is suggestive of complications:

	Per cent by weight		Per cent by weight
NaCl	16.35	CaO	0.0022
Na₂SO₄	6.96	Fe₂O₃ + Al₂O₃	0.0020
KCl	4.75	NH₃	0.0018
Na₂CO₃	4.74	NaI	0.0014
Na₂B₄O₇	1.51	Sb₂O₃	0.0006
Na₃PO₄	0.155	Organic	0.006
NaBr	0.109		
LiCl	0.021	Total solids approx.	34.65
Na₂S	0.020	Water by difference	65.35
As₂O₃	0.019		

These analytical values, with ion pairs coupled in conventional fashion, warrant a slight modification in the light of hydrogen-ion concentration. The pH of the brine is 9.48. Under such a condition it is seen that bicarbonate, metaborate, and monohydrogen-phosphate ions exist in appreciable quantity, thus adding to the complexity.

The total quantity of raw material in Searles Lake is stupendous. The industry removes nearly 400 tons of product daily, and throws back into the selfsame lake the rejected residue of 1500 tons of worthless salts. Owing to the low level of the plant site relative to the surrounding country, there is no drainage to the outer world. There simply isn't anything else to do with the refuse. Despite the wholesale throwback, analysts have been unable in ten years to measure a change in composition of the lake brine as great as the probable error of their determination. So why worry?

Solar Evaporation

The blazing sun of the Mohave Desert was the natural and obvious tool of most of the ill-fated amateurs who dabbled in Searles Lake. It looked like good economy to throw up a few dikes, pen in a lot of brine, and let Old Sol drink up the water. Unfortunately the phase-solubility diagram for this brine does not permit the separation of any single salt of value at natural outdoor temperatures. Moreover, it is difficult to construct a solar pond which will not

leak. It is also expensive to harvest and leach a solar, crystalline precipitate.

Failure was the inevitable result. Much to the credit of Doctor Teeple[3] and his technical staff, the "obvious" has been rejected. The sun has been discharged from the job, and fuel oil hired. Mathematics has been substituted for hunches. Details of the early phases of the enterprise may be seen in the papers of Teeple[3,4] and De Ropp.[5]

Why the Sunshine Failed

The fundamental principle which revolutionized the mode of attack on Searles Lake is best illustrated in phase diagrams. Of the hundreds constructed by the Trona research staff, two, shown in slightly abbreviated form in Figures 1 and 2, will suffice to show what is perhaps the most important feature of the process.

Figure 1 is a solubility-composition diagram for the principal components of interest in Searles Lake brine. The temperature is 20° C., taken roughly as a mean of desert lake temperatures, summer and winter, day and night. It therefore may be applied to a solar evaporation pond. For simplicity minor constituents are ignored. Moreover, since sodium chloride is present in gross excess in all such evaporations, the further assumption is made that the solution is always saturated with that compound.

By such tricks the physical chemist gets rid of a threatening fourth or fifth dimension, and confines his geometry to three critical components, K^+, CO_3^{--}, and SO_4^{--}, without great error. Following conventional phase-rule practice, any point within the equilateral triangle, such as A, marks the three equivalent concentrations of the ions in question; the nearness of the point to either vertex is the measure of the relative concentration of that component.

The point A represents Searles Lake brine—(approx.) 5 equivalents K^+, 7 equivalents CO_3^{--}, and 8 equivalents SO_4^{--} per unit quantity. The point is located in a pentagonal geometric field marked "glaserite." Using customary phase-rule interpretation, this means that a brine of A composition evaporated at 20° C. will begin deposition of that particular double salt. The product is of course worthless. Nobody has commercial use for both sodium and potassium sulfate in one preparation, especially if mixed with sodium chloride. At the same time, nevertheless, the brine is being robbed of valuable potash.

[3] Teeple, IND. ENG. CHEM., 19, 318 (1927).
[4] Teeple, Ibid., 13, 249 (1921); 14, 787 (1922); 14, 904 (1922).
[5] De Ropp, Chem. Met. Eng., 19, 425 (1918).

As glaserite separates, the composition of the mother liquor shifts steadily from A in a direction appropriate to the loss of $3 K + 2 SO_4$. When the point B is reached, the field of "burkeite" is encountered. In laboratory terms, this second and equally worthless salt now comes down in company with a continued separation of glaserite. The arrow, diverted by the new phenomenon, proceeds to C, where sodium carbonate heptahydrate joins the mêlée. Another shift in direction, and finally at D is reached the real product desired, the single salt potassium chloride. Unfortunately the brine is nearly gone, glaserite having

Figure 1—Evaporation of Searles Lake Brine at 20° C.
Dotted triangle indicates field of hanksite, $KCl.2Na_2CO_3.9Na_2SO_4$, which does not appear in rapid evaporation and may be ignored

taken most of the potash. D being the end point of crystallization, the system becomes monovariant and a mixed product of constant composition, consisting of four salts, runs out to the end. The process is a complete failure.

Phase Manipulation

Figure 2 shows the same components at 100° C. Point A again marks the composition of the lake brine. The fields, while identical in composition and general arrangement, are widely different in size, owing to variations in the slopes of solubility curves.

Plainly burkeite is the first salt to crystallize this time. Worthless, but a good riddance at the outset. Its quantity is large—the larger the better. After a gross deposition of burkeite has taken place along the line of the downward arrow, at E this salt is joined by sodium carbonate monohydrate. More good riddance. Deposition of the two salts occurs up to F, where potassium chloride is then about to join the mixture. Failure is again imminent, but at this strategic moment the physical chemist administers the *coup de grace*. He suddenly lowers the temperature to 20° C.

Graphically this move of course means a shift at once back to Figure 1, where point F is found far out in the field of pure potassium chloride. One substance and one alone may separate; and it does separate in quantity aided by the fall in temperature. As potassium chloride is being precipitated, the glaserite field will again be reached; but just before that misfortune occurs, the sludge of potassium chloride is filtered and the mother liquor sent back in cyclic flow to the start of the process. Thus we get pure potash; but the change from Figure 1 to Figure 2 has tremendous significance in the engineering application to follow.

In the above discussion no formal notice has been taken

of the quantities of sodium chloride which accompany the glaserite, burkeite, and sodium carbonate at all times. It would be natural to fear that this ever present substance would continue into the potassium chloride crystallization. When the temperature is reduced, however, the law of mass action, combined with two peculiar solubility curves, comes to the assistance of the process.

Just before cooling starts, the solution is barely saturated with sodium and potassium chlorides. As the temperature falls, the solubility of potassium chloride falls faster than that of sodium chloride. Potassium chloride crystallizes first. The instant this happens, just so the effective concentration of chloride ion falls. Sodium chloride becomes more soluble, not less soluble, in the remaining liquor, in spite of falling temperature. The all-important result is that no more sodium chloride comes out in a place where it would contaminate the finished potash product.

As the crystallization of potassium chloride continues, the solubility of sodium sulfate—a possible product—rises according to its well-known reversed solubility curve. It is accordingly not to be feared as a contaminating impurity. Thus the crystallization of potassium chloride may be prolonged for an extended period with large yield. Eventually, of course, at a certain concentration the process must stop, and the brine go back to the start.

Construction of Graphs

The preparation of even so simple a diagram as that of Figure 1 comes only after long and patient laboratory research. Synthetic mixtures approximating Searles Lake brine had to be made, components entering one by one. The identity of each double salt must be detected at the
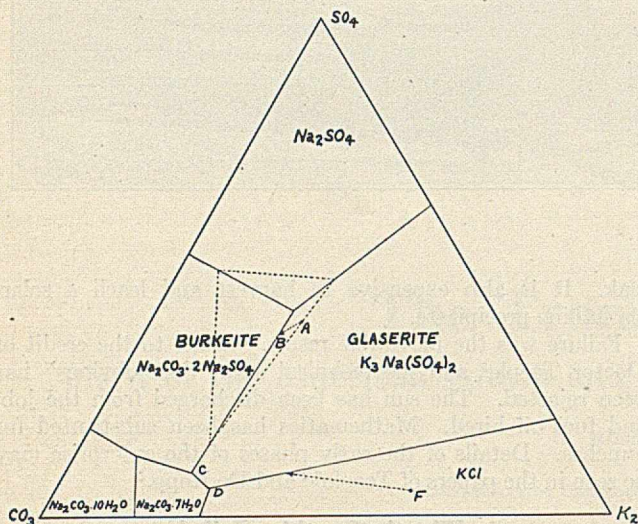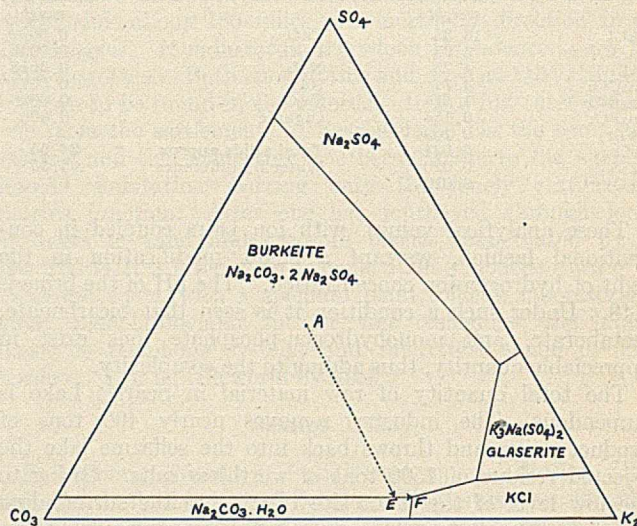

Figure 2—Evaporation of Searles Lake Brine at 100° C.

instant of appearance, a difficult task when the mixture was continually agitated in a thermostat. New double salts were occasionally discovered, and in some cases named after members of the Trona family. It seems queer that so worthless a crystal as the carbonate-sulfate should be named after a really useful executive, Assistant Manager W. E. Burke.

Space forbids more than mere mention of further graphic problems. Each single variation in temperature involves a complete repetition of one of the tasks. The manipulation of tetraborate and metaborate ions, carbonate and bicarbonate ions, as components has alone given the staff plenty to do.

Rate of Crystallization

Most troublesome is the problem occasionally arising when a salt is due according to solubility rules but hangs back in supersaturation. The Trona laboratory is still nursing one solution which has been working toward equilibrium for two years and still yields crystals. In fact, rate of crystallization promises to be a feature of critical importance in the development of new methods now in prospect.

Plant Practice

The Searles Lake plant at the outset follows in modified technic the program cited with Figure 2. First the brine is pumped through emergency storage to two colossal triple-effect evaporators, which are the feature exhibit of the whole enterprise. In these evaporators, following the continuous cyclic process, the brine is joined by other brine which has already run the gauntlet of the plant, and has returned for another treatment.

The evaporators, receiving steam from the power-house turbines, operate in three stages of reduced pressure. Thermal efficiency is attained by introducing the brine to the low-temperature, high-vacuum evaporator first, then in turn to the others. An efficiency of 2.2 pounds of evaporated water to 1 pound of steam is attained. In this system the pipe removing vapor from the low-pressure evaporator is 6 feet in diameter—a sizable caliber for a steam pipe.

In the daily run of these evaporators over 1500 tons of burkeite and allied salts settle out in concentrated sludge and are sluiced back into the lake. Enough liquor is steadily wasted here to keep down the percentage of minor components, which would otherwise accumulate in a cyclic, closed system. At just the proper concentration the liquor, free from waste salts, is ready to yield both potassium chloride and borax upon cooling.

Were one to judge by the solubility diagrams, the process shortly to follow would seem hopeless. Unfortunately potassium chloride and borax, the two products to come, have solubility curves of roughly similar slopes. Fortunately, on the other hand, the rate of crystallization of the chloride at certain moderate temperatures is very much greater than that of borax. In fact, borax under these conditions readily forms a supersaturated solution. Thus the crystallization of actual borax in the normal hydrated form is held back, though but for a few minutes.

The plant now loses no time. Vacuum cooling brings down the potassium chloride rapidly. The ebullition incident to the vacuum process prevents incrustation and permits prompt and effective treatment in the centrifuges and driers which immediately follow. Finally a bone-dry, pure white product is loaded into box cars as though it were wheat from an elevator. Its final analysis, following the latest technic of manufacture, shows approximately 97.5 per cent KCl; the remainder almost entirely common salt, with borax, the impurity most feared, now entirely negligible.

Borax

The stage is set for the crystallization of borax. The liquor, passing into tall cylindrical crystallizers, is cooled in the presence of a charge of crystalline seed. The resulting crystals, already pure enough for technical use, are then recrystallized to give a product of exceptionally high degree of purity. A continuous time and temperature control regulates the crystal size neatly to suit commercial demand. The isolation, washing, and drying follow immediately.

Just at present the entire borax output of the world is coming from a small area adjacent to the Kern-San Bernardino County line, stretching from Trona to Amargo. Death Valley, the Funeral Range, and its famed colemanite reserves, off to the east, have gone into retirement. The discovery of rasorite (sodium tetraborate tetrahydrate) and allied water-soluble minerals, combined with the Trona operations, has put the Mohave Desert in full control of the international borax market. About 400 tons daily is the estimated output from the several operating companies. All of this comes solely by crystallization of natural borax from solution, or recrystallization and hydration of natural solid sodium borates.

Boric Acid

A limited portion of the Trona borax is treated at the plant with sulfuric acid, yielding high-grade boric acid and, with recrystallization, U. S. P. boric acid in extreme purity. As yet the production is not sufficient to warrant the manufacture of sulfuric acid on the ground.
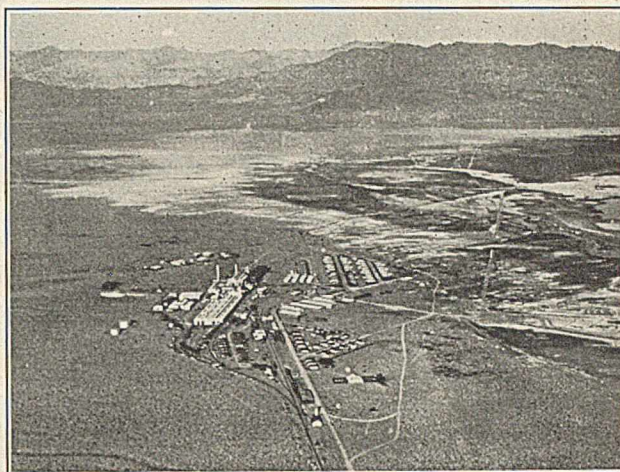
Plant of American Potash and Chemical Corporation, Showing Searles Lake in Background

Other Products

Common salt is almost scorned at the Trona plant. It is hardly worth hauling to Los Angeles, although enormous quantities are to be had a few rods from the railway terminus. The rise of mechanical refrigeration, and to a slight extent the use of solid carbon dioxide, has depressed the western market in salt.

The research department has its eye on the great waste of carbonates in the present process. Several hundred tons of potential soda ash escape daily down the sewer, largely in the complex of impure burkeite. Under present conditions in the West soda ash is nearly as valuable as borax, particularly in view of freight relations.

A Wartime Resource

The Trona project is now long past the purely experimental and promotion stage. It stands as the Verdun fortress of the American potash industry—the only real potash plant to survive the post-war deflation.

America need fear no longer a war blockade against German and French potash. If the Federal Government will furnish 30 to 40 millions—a couple of days' outlay in a modern war—Trona will build a plant to supply the entire country continuously without restriction.

Supply Problems

Thanks partly to the thermodynamics of turbines and evaporators connected in tandem, Trona is able to generate electric power much more cheaply than it can buy hydro-

electric power at high-tension lines a few miles to the west. Incidentally, it may be noted that the California hydro-electric companies are not at present in danger of bankruptcy. The Trona plant operates a 440-volt motor service, using fuel oil. Despite the long desert haul of fuel, costs are reasonable.

Drinking water is a treasure. Usually there is an adequate supply, curtailed slightly in dry seasons, for human consumption. This is obtained from springs high up in the Argus mountains at some distance from the town. From wells near the plant a slightly brackish supply is available and finds technical use in the plant. It also serves the company swimming pool, a popular feature.

Triple-Effect Evaporators at Trona

is hauled that can be sluiced; nothing is shoveled that can be dissolved, sucked, or blown in some manner suggestive of a fluid. As a result the company employs a minimum of muckers and a maximum of intelligent young fellows with hands on valves and eyes on chronometric recorders.

Filter presses are avoided where possible. Instead, the separation of crystalline matter is carried out in conical settling chambers, which are washed by countercurrent brine. The wash waters, or rather wash brines, after doing duty, pass on through the elaborate pipe system to such part of the plant as may be appropriate to receive them and continue the cycle. On account of limited water supply, saline solutions are employed to the limit for washing purposes before fresh water is expended.

The problem of the cooling of liquids is solved in various ways, in spite of torrid weather, from the spraying of exposed piping to vacuum evaporation and standard compressed-ammonia refrigeration.
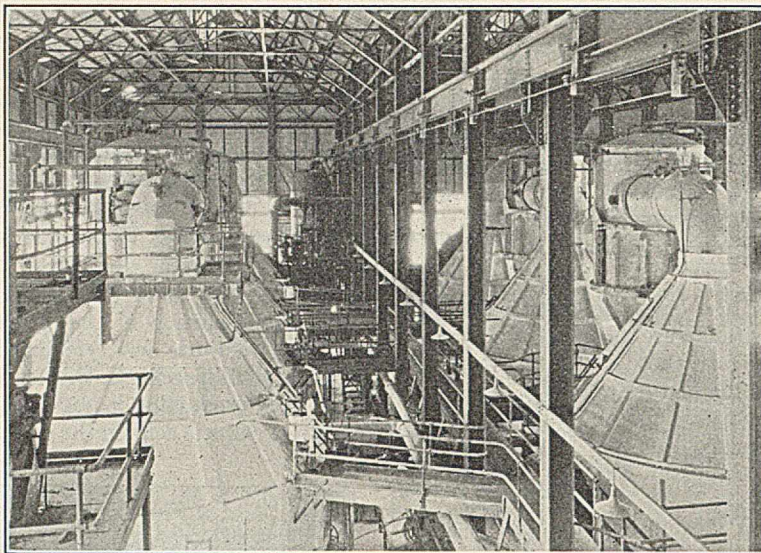
Living Conditions

The human element in the desert industry remains very much of a problem. The weather is undeniably hot at times. Wages run from 10 to 30 per cent higher than in Los Angeles. Sliding scales are arranged to encourage employees to stay a second and third year on the job. Mechanics have the advantage of steady work in contrast to the lay-offs common in adjacent coast cities. Employees receive all company supply store profits.

Although the thermometer runs up to 115° F. once in a while, the low humidity gives compensation. A man may dry up more or less, but at least he will not be prostrated by the heat. Ample porches surround business offices and stores, and the numerous company dwellings are designed with an eye to good ventilation, particularly during sleeping hours. While the summer climate leaves something to be desired, fall, spring, and winter are delightful.

Modern Plant Economies

The phase-rule chemist is not the only one at Trona who looks askance at solar evaporation. Sun-dried salts would have to be loosened, shoveled up into vehicles, and laboriously carried to storage or dump. Wherefore the engineering staff has adopted a gospel of pipe lines and pumps. Nothing

German Practice

In spite of the obvious advantage of the Stassfurt potash industry from the wage standpoint, a comparison with Trona bears closer analysis. The Stassfurt beds, deep beneath the earth, constitute a mining problem, not amenable to handling with a collection of pumps, evaporators, and pipe lines alone. The desert operators, after having weathered the drop in the price of potassium chloride from $155 per ton, ten years ago, to $34.50 today, are now confident that the Searles Lake industry can hold its own indefinitely against any such competition.

Chemically the Stassfurt problems do not compare with those of Searles Lake. The German supply consists of segregates of individual double salts which can be dissolved by themselves and treated with relative simplicity. Ages ago Nature went through a complex sequence of solid-phase depositions, roughly analogous to the processes which Trona must now do in a manufacturing plant. The components are to be sure in a different assortment. At Stassfurt, therefore, separate veins or beds lie ready for selection. In contrast with Searles Lake, for illustration, it is a simple matter to obtain potassium chloride from the single, ready-made mineral carnallite, $KCl.MgCl_2.6H_2O$. Trona's polyglot solution is another story. We can therefore take our choice—engineering brains, pumps, and pipe lines, or pick, shovel, and hoist. And the desert industry is quite sure of its answer.

Helium Plant Makes Initial Shipment—Shipments of helium from the Government's new helium production plant, near Amarillo, Texas, started May 6, with the dispatching of a tank car filled with about 200,000 cubic feet of helium, to Langley Field, Va. The new plant, which has been designated as the Amarillo helium plant, was built and is operated by the Bureau of Mines at Soncy, on the Rock Island Railroad about 7 miles west of Amarillo. The helium is extracted from natural gas having a helium content of 1.75 per cent, produced from the Cliffside structure lying northwest of Amarillo. Gas from 26,000 acres of land is available to the plant through a contract between the Department of Commerce and the Amarillo Oil Company.

The car in which this first shipment was made is one of two specially built helium tank cars owned by the Air Corps, U. S. Army. It carries helium under a pressure of 2000 pounds per square inch. When the car reaches Langley Field the helium will be discharged into other containers for use in the Army's lighter-than-air craft and the tank car will be returned to the Amarillo plant for reloading.

Electrical Heating by the Container-Resistance Method[1]

Articles of Process Equipment Become Their Own Heating Systems

R. A. Carleton

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HEATING by electricity possesses the inherent industrial advantages of high efficiency, simplicity, close automatic temperature control, safety, and cleanliness. It has been successfully applied on a large scale to such metallurgical equipment as steel heat-treating and forging furnaces; it has been utilized in driers for many types of products; and, in the form of small units of the immersion, cartridge, or clamp-on type, has served for everything from making candles to sticking labels on tin cans.

Electrical heating has not, however, made much headway in the process industries until recently. In many cases it has been considered too costly. In other instances heating units have been applied to existing apparatus with unfortunate results, due to local overheating of sensitive materials. The most fundamental objection, however, has been the small capacity of the heating units available for process equipment, and the corresponding necessity of using a large number of individual units which take up space and complicate maintenance.

It is the purpose of this article to describe a new method of applying electrical heating which seems to have many possibilities for the chemical engineer. This new method is called the container resistance method, and has been developed for use in a number of industries.

Description of Method

As its name implies, the container-resistance method of electrical heating depends upon the production of heat directly in the walls of a containing vessel as the result of the resistance to the flow of electric current in the walls themselves. Since practically all ordinary engineering materials used in the fabrication of equipment for the process industries have high electrical conductivities, and since the cross sections of articles of equipment are generally large, it is obvious that the total electrical resistance is, on the average, quite low. It is therefore necessary to use a large current under a low potential drop for the production of heat by container resistance. From the standpoint of safety this necessity is an advantage, as it eliminates the difficulty and danger of handling electrical energy at high potentials in connection with process equipment. The actual voltage drop across different installations varies, of course, with the dimensions of the equipment, the material from which it is constructed, and the rate of heat input desired, but these values do not exceed 8 volts for most units, and are generally lower. For example, an 8 by 8 foot drying drum requiring 100 kilowatts energy input will take current at a potential of approximately 2.5 volts.

Current at low voltage for use in container-resistance heating is usually obtained by means of stepdown transformers. The characteristics of these transformers vary with the requirements of the systems for which they are designed but, owing to patented features covering the arrangement of the heating circuits, the power factor of the entire layout may be made better than 90 per cent. Direct current or single or polyphase alternating current may be used. Temperature

regulation in the apparatus being heated is obtained by a thermostatic control which automatically controls the heat input by regulation of the voltage. This is done by automatic switching equipment, or, in the case of large apparatus, by induction voltage regulators.

In some instances in which the dimensions of the apparatus and the rate of heat input permit, relatively high potentials may be used directly, thus reducing the weight and cost of equipment. In other instances where the power requirements are relatively large, the heating transformer and control equipment are arranged for operation directly on the power transmission line of 2300 or 4000 volts, eliminating the customary service transformer. In all cases special regard is had for safety, and the electrical circuits are so arranged that all parts of the apparatus with which the operator might come in contact are at ground potential.

The distinctive difference between heating by container resistance and heating by any other means, electrical or non-electrical, is that by using the containing vessel as the element within which heat is generated very even distribution of this heat may be obtained. The temperature variation in different parts of equipment heated directly by coke, oil, or gas may be very great, and is never negligible. Portions of the equipment exposed to radiation receive heat at a much higher rate than those exposed only to heat transfer by convection and conduction from hot gases. Electrical heating by the use of a number of small immersion or clamp-on units is open to the same objection of uneven heating, with possible injury both to materials being heated and to heater units, but careful design of equipment for heating by container resistance allows the practically uniform distribution of heat over the entire surface of the kettle or tank or other piece of apparatus.

An additional advantage of container-resistance heating over electrical heating by the use of a number of small applied units is the tremendous range of heat-energy input rates which may be obtained with a simple installation. The usual limit for the application of clamp-on units is a heat input rate of 15 to 20 watts per square inch of surface, while with a container-resistance installation it is possible to increase this to as high a value as the material being heated will stand. With very efficient agitation of the contents of a kettle, it is possible to put in heat energy at the rate of 125 watts per square inch, or 61,500 B. t. u. per square foot per hour.

In many heating processes high working temperatures are necessary, and at the same time rather close temperature control is a prime requisite. Heating by steam allows close temperature control, but necessitates heavy, expensive, and dangerous equipment to stand high pressures, while direct firing is not possible because of poor heat regulation, and heating by hot gases necessitates large heat-transfer surfaces. In such cases container-resistance heating finds a field for which it is particularly adapted, since any desired temperature may be attained with high efficiency, close temperature control, simplicity and compactness of design, and without the necessity of building equipment to stand pressures higher than those developed by the material being heated.

Types of Equipment Heated

Since the only fundamental limitation in the application of this method of electrical heating is that the equipment to be heated must be at least a fair conductor of electricity, it finds wide application. For example, it may be used for heating drums, rolls, rotary roasters, ovens, tables, benches, kettles, tanks, drying trays; and it may be applied to pipe or tubing for a multitude of purposes, including the high-temperature cracking of oils, the heating of fluids during transfer, the transfer in the liquid state of materials which are solid or very viscous at ordinary temperatures, evaporation in film-type apparatus, and fractional distillation where accurate temperature control is of great importance.
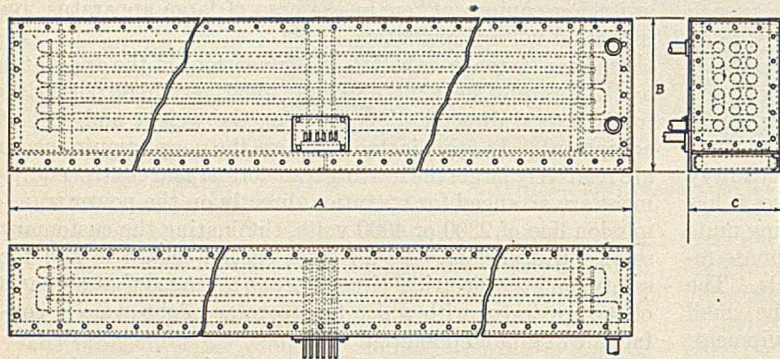

Figure 1—Tubular Heater Utilizing Electrical Energy by the Container-Resistance Method

Heaters of this type are built for high liquor velocity, high rates of heat transfer, and minimum time of contact of liquor with heating surfaces. Automatic thermostatic control actuated by exit liquor controls the temperature within 2 per cent. Note electrical connections made through heat-insulating shell to middle of length of tubes.

Equipment may be constructed of steel, nickel, copper, aluminum, lead, high-silicon or ordinary cast iron, chrome-iron or chrome-nickel-iron alloys or monel metal or other special non-ferrous alloys to satisfy unusual conditions. Where desired, equipment may of course be plated internally, or may even be enameled for use with relatively low rates of heat transfer.

A few specific types of equipment heated by container resistance are described in the following sections.

Tubular heaters ranging in capacity from 50 to 1000 or more gallons per hour are built ordinarily for operation at temperatures up to approximately 425° C. or 800° F., and may be designed for still higher temperatures if desired, and for pressures up to 1500 pounds per square inch. These heaters are designed to operate with a high liquor velocity, with a correspondingly high rate of heat transfer from metal to fluid, and minimum time of contact of the liquid with the heater surface. In most cases the time of travel through the heater is of the order of 50 to 60 seconds, so that materials which would be damaged by continued exposure to a given temperature may still be safely heated to that temperature.

Temperature control is automatically maintained by a thermostat actuated by the exit liquor from the heater. The thermostatic control holds this exit liquor temperature constant within 2 per cent, and is arranged to cut off the power supply whenever the flow of fluid stops.

The over-all efficiency of energy utilization in heaters of this type is very good. The efficiency of the heating transformer may safely be taken as 98 per cent, that of the conversion of electrical energy into heat energy is 100 per cent, and the utilization of heat energy in the equipment may be maintained at 90 to 95 per cent by careful heat insulation. An over-all efficiency from electrical power supply to heat in the product will therefore approximate 90 per cent.

Figure 1 shows a drawing of a tubular heater arranged for container-resistance heating. The tubing is supported within an insulating shell, and the electrical connections are made to the tubes midway of the length of the heater.

In heaters of this type vegetable oils may be brought to a desired temperature rapidly, without the discoloration produced by extended heating, while sugar, sirup, milk, or other food products may be flash-evaporated in a system using such electrically heated units in connection with a spray chamber.

Tubular heaters of this sort are also built for strenuous duty at 1500 pounds pressure and temperatures up to 540° C. or 1000° F. in oil-cracking work. By placing the heater tubes in a container under a balancing pressure, relatively thin-walled tubes may be used. For a 4000-barrel-per-day cracking still such a heater has a diameter of 30 inches and a length of 45 feet. A heat transfer rate of 75,000 B. t. u. per square foot per hour is claimed for this equipment, which may be installed underground, if desired, in order to economize on space.

An electrically heated *forced-circulation evaporator* is shown in Figure 2. Such evaporators have a particularly high rate of heat transfer, and have an especially important application in the treatment of solutions which show a high elevation of the boiling point upon concentration, such as caustic soda. In order to eliminate overheating at any point due to possible incomplete wetting of the tube surfaces, oil is circulated through the shell around the tubes to act as a heat equalizer. The upper and lower halves of the evaporator shell are separated by an insulating gasket, on each side of which the current leads are brought in.

Kettles of all types may also be heated by this modern electrical method. The customary round and horizontal types are built in capacities of from 50 to 600 gallons or larger, and may be designed with sufficient heating capacity to raise the temperature of their contents at any desired rate up to approximately 10° C. or 18° F. per minute. With such kettles varnish oils and gums in 100- to 600-gallon batches may safely be heated from room temperature to 400° C. or 750° F. in from 30 to 45 minutes.

One design of kettle heated by container resistance has a diameter relatively small with respect to its height, thus increasing the heating surface for a given volume and providing a high-speed piece of heating equipment. This type of kettle is well adapted to the handling of very thick or viscous materials when it is equipped with a power agitator of the screw or turbine type.

Tanks for dipping pipe or other articles with asphalt, pitch, or similar substances constitute another application of container-resistance heating. Evaporation and fume loss are reduced and the consistency of the coating material is easily maintained by automatic temperature control at the point which allows most efficient application.

In the ordinary construction of kettles and tanks heated by methods other than container resistance, the heating zone is relatively low in order to prevent overheating of the sides of the equipment should the liquid level be lowered by evaporation or leakage. This practice substantially reduces the heating surface available. With container-resistance heating the whole surface is heating surface, but the area above the liquid level is protected from overheating by the circulation of oil in an external jacket. Special construction can also be provided in which the upper parts of the equipment are electrically insulated from the lower section, and automatic control is provided to cut off the power from the upper sections if the liquid level drops below a predetermined level.

Pipe lines may be heated simply and effectively by container resistance. In cases where materials such as asphalt, gums, oil, and rosin are ordinarily transferred from process to process in
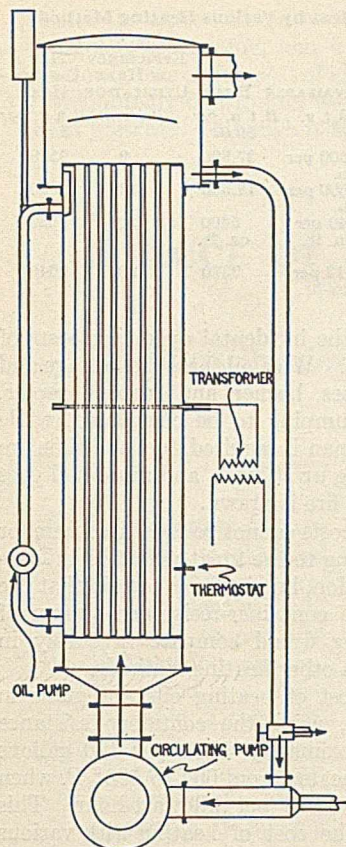
Figure 2—Forced Circulation Evaporator Arranged for Heating of Tubes by the Container-Resistance Method

Positive high liquor velocity through tubes is combined with closely controlled temperature of heating surfaces. Temperatures for the evaporation of liquids with high elevation of the boiling point are easily obtained without construction necessary to stand pressures attendant on use of high-pressure steam for this type of work. Note electrical connections made to upper and lower halves of evaporator shell, which are insulated from each other by a gasket.

Figure 3 shows two arrangements for the electrical heating of pipe lines. In the more elaborate system, designated *A*, the inner pipe conveys the fluid and offers the greater part of the resistance to the flow of electric current, while the outer casing, preferably made of some material with a high electrical conductivity, serves to enclose a heat-insulating space around the inner pipe and to conduct the current. The electric circuit is arranged so that one side of the line is connected directly to the inner pipe, the current flowing along this pipe in both directions to the first flanged pipe joint, where contact is made with the outer casing, through which the current returns to the leads of the other side of the line.

Drums or cylindrical heaters for drying or roasting materials offer another field for heating by container resistance, especially in cases where sensitive materials are to be handled and close temperature control is therefore a prime requisite. An electrically heated drum is shown in Figure 4, with the heating transformer mounted within the shell and connected with the power circuit through contactor rings, as is also the thermostatic control circuit which operates the magnetic switches for power regulation. Owing to the absence of large masses of material, heating and cooling take place quickly and the temperature may be held within 1 per cent at any value up to 425° C. or 800° F.

Present Applications in Industry

One field of application of container-resistance heating is in the varnish industry, where archaic methods have persisted

batch lots, frequently by manual labor, this method offers the alternative of moving these materials in the fluid state in pipes electrically heated. When these materials must be heated anyway before processing, as is generally the case, the pipe line then becomes an attenuated tubular heater combined with a transfer system. This method should also be interesting to operations such as the Solvay process, where a highly concentrated salt solution must not be allowed to cool in the lines because of the plugging which would result from crystallization of the dissolved substances. With the pipe lines equipped as heating units in themselves by the application of the container-resistance system, an accidental freezing of the material in transit could be melted out with but a few minutes' delay. An interesting installation of electrically heated piping is being made at the present time to convey melted lead used in lead-coating work, the temperature of the line to be maintained at 415° C. or 780° F.

long beyond their time. The traditional method of varnish manufacture involves: (1) the melting of gums in a cumbersome kettle, which is wheeled by hand into a brick setting, where it is exposed to the uneven and inefficiently utilized heat from an open flame; (2) the removal of the kettle for addition of oils; (3) its return to the fire; and (4) its ultimate removal to cool in the air. This does not compare advantageously with the efficient system using electrical heating, where the equipment is stationary and all materials except the original gums are handled in the fluid state, and where heating is rapid and closely controlled and heat recovery from the hot made varnish is practiced.

Figure 5 shows a typical layout for varnish manufacture with heating by container resistance. Three stationary kettles heated by this method and equipped with mechanical agitators are used for running the gums. These kettles are operated in rotation as batch processes. As the contents of a kettle reach the proper consistency, oil, heated to the proper temperature in a tubular heater using the container-resistance method and delivered continuously to a storage and measuring tank, is added to the kettle. The oil and gum are thoroughly mixed and are then delivered to one of a battery of insulated bodying and thinning tanks, where the mixture is held during the time necessary for bodying and is then thinned to the correct consistency. These tanks may also be heated by container resistance, but this is not necessary unless the contents are to be held longer than three hours. The hot varnish from the bodying and thinning tank is finally passed through a heat exchanger, where it gives up its sensible heat to fresh oil on the way to the heater, thus cutting the electrical energy requirements for heating to approximately 50 per cent of the amount necessary without this recovery.

In this system temperature control is automatic throughout; fume loss, spillage, and danger of fire are greatly reduced or eliminated by the use of stationary closed kettles; and labor cost is cut to 25 per cent of that required by the old method. The elimination of open fires reduces fire and liability insurance rates approximately 50 per cent, and the uniformity of the product is controlled with ease.

It is possible to use kettles heated by container resistance in an intermittent cycle similar to the old method, but such an arrangement does not allow continuous use of the more expensive equipment. By the arrangements shown in Figure 5, where bodying is done in relatively cheap

Figure 3—Two Arrangements of Pipe-Line Heating by Container Resistance

A—Double pipe construction with insulating space between concentric pipes, showing details of electric circuit connections. *B*—Simple arrangement for heating pipe line from three-phase circuit, with electrical connections to pipe flanges.

unheated tanks, almost continuous use of the melting kettles and completely continuous use of the oil heater are possible. One continuous heater will supply three or more kettles through the storage and measuring tank, and batches may be put through each kettle at the rate of three per hour.

Other current applications of container-resistance heating are in the paper and textile industries, where electrically heated drying rolls are maintained uniformly at the optimum
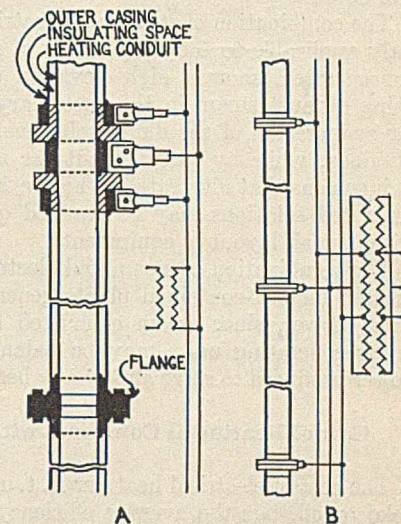
temperature; in the food industries where vegetable oils are bleached, deodorized, and bodied in electrically heated equipment, coffee and cocoa beans are roasted in electrically heated rotary drums, and milk is heated in continuous heaters as a preliminary to spray drying; and in various industries where drying processes utilizing large areas must be maintained under carefully controlled temperatures, as in the drying of leather, explosives, and photographic films.

Container-Resistance Heating in Conjunction with Other Heating Methods

In cases where high temperatures are required in process heating, but where steam or hot gases are available from other
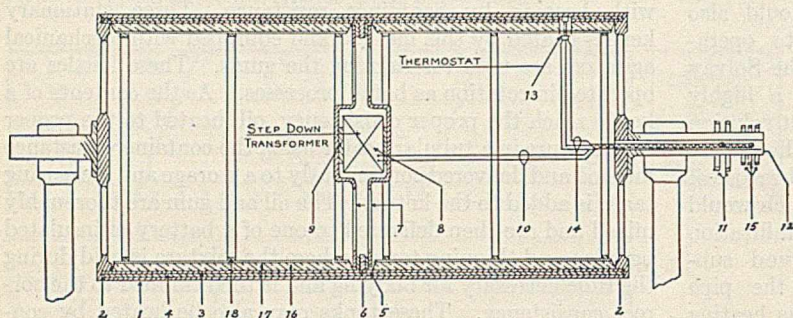

Figure 4—Drying Drum Heated by Electricity, Using the Container-Resistance Method

The temperature of the drying surface is automatically controlled within 1 per cent at any temperature up to 425° C.

processes and should be utilized for economy, it is possible to obtain both economy and efficiency by utilizing the steam or hot gases as a first step, followed by container-resistance heating to the desired temperature. Even in cases where as little as 5 per cent of the heat is supplied electrically, the use of the second step is justifiable on the basis of the close control obtainable.

The combination of steam and electrical heating is particularly applicable to the evaporation of solutions which, when concentrated, show a high elevation of boiling point. By using exhaust steam in the customary multiple-effect units for evaporation of the dilute solutions, excellent economy is obtained, while by carrying out the final evaporation in a unit such as that illustrated in Figure 2, the high-boiling concentrated solutions may be handled quickly and efficiently with a small layout of equipment.

The combination of steam and electrical heating is also indicated for self-contained plants generating their own electrical power, since steam exhausted at low pressure from power-generating units may be balanced against electrical power produced to solve almost any heating problem.

Cost of Heating as Compared with Other Methods

The cost of electrical heat per B. t. u. is many times that of coke or oil, but the average efficiency of utilization of the former is ten times that of the latter, so that the apparent disparity in cost is largely canceled. In addition, many secondary factors enter in to favor the use of electrical heat; close automatic temperature control, rapidity and uniformity of heating, reduction in space requirements, labor costs, fire hazards, and insurance rates, and increased uniformity of product have previously been mentioned. Many of these factors can only be evaluated individually in each case under consideration, and no attempt will be made to treat them here.

The actual cost of the heat energy alone has been calculated for several methods of industrial heating, and is shown in the accompanying table. Average values of fuel cost and efficiency of utilization have been taken.

Comparison of Net Cost of Heat by Various Heating Methods

Fuel	Fuel Cost	Available Heat		Over-All Efficiency of Heat Utilization	Net Cost of Heat
		B. t. u.	B. t. u. per $0.01	Per cent	B. t. u. per $0.01
Coke	$9.00 per ton	12,500 per lb.	27,800	9	2500
Oil	0.075 per gallon	18,500 per lb.	18,500	12	2220
Gas	0.001 per cu. ft.	540 per cu. ft.	5400 cu. ft.	20	1080
Electricity (container resistance)	0.015 per kw-hr.	3412 per kw-hr.	2270	90	2040

These data do not include the incidental operating costs of the various fuels. With oil there are leakage and evaporation losses, burner and furnace repair, and power for pumping to be considered, while with coke a fireman is required, fuel and time are wasted in coming up to heat, and more fuel goes to waste when a fire is drawn.

Maintenance costs cannot be estimated here for comparison, owing to the great variation in conditions of operation, but it seems certain that the simplicity of the container-resistance system of electrical heating would compare favorably in this respect with other heating methods.

The actual cost of heating oils and gums in varnish making, using the container-resistance method, is approximately $0.81 per 100 gallons of oil and gum heated from 60° to 580° F. when the electric power rate is $0.015 per kilowatt-hour. This value compares well with the cost of heating with various fuels.
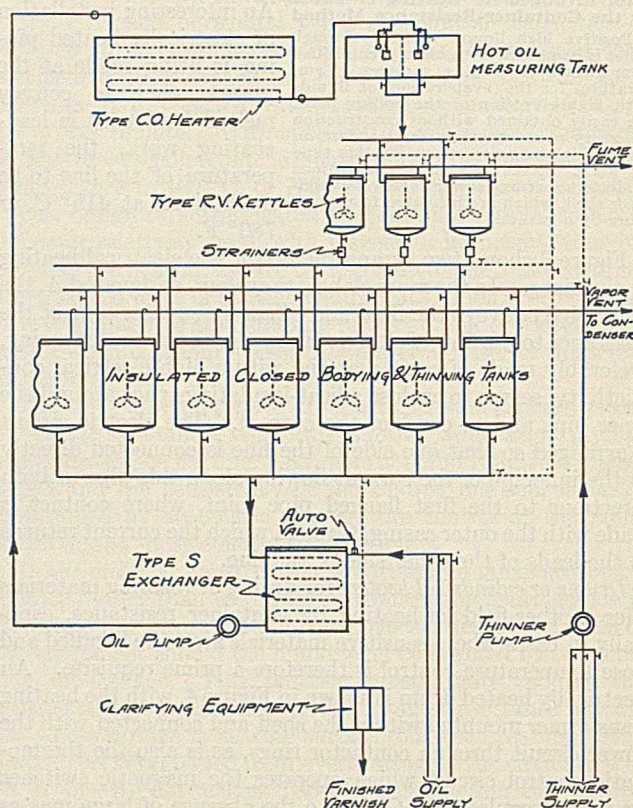
Figure 5—Equipment Layout for Varnish Plant Utilizing Tubular Oil Heaters and Kettles Heated by Container Resistance

Semi-continuous process designed to replace old batch process using direct-fired kettles. Oil is heated continuously in tubular heater, is taken from measuring tank to electrically heated kettles in which gums have been run. The mixture is run to bodying and thinning tanks, from which the hot made varnish passes to storage through a heat exchanger in which it gives up its sensible heat to fresh oil on its way to the heater.

With the current trend of industrial development showing no signs of slackening, and with the increasing availability and slowly decreasing cost of electric power, electrical heating is undoubtedly due to find wider fields of application than it has at present. Although it is not the purpose of this article to suggest that electrical heating is the solution of even a majority of the process heating problems of the chemical engineer, it is evident that the container-resistance method offers him a new and flexible means of heating rapidly under close automatic control.

Effect of Cathode Rays on Hydrocarbon Oils and on Paper[1]

A Contribution to the Study of the Mechanism of Cable Deterioration

C. S. Schoepfle and L. H. Connell

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THE underground transmission of electrical power at high voltages is accomplished by the use of impregnated, paper-insulated, lead-covered cables. The cross section of a three-conductor cable of this type is shown in Figure 1.

The impregnating compound formerly used was generally a mixture of mineral oil and rosin or rosin oil, but this material when used for this purpose had a high dielectric loss due, it is now believed, to the impurities in the rosin employed at that time. Moreover, the dielectric loss showed a rapid increase with rise in temperature, an inherent characteristic of the rosin itself. In order to eliminate these undesirable properties, the rosin mixture has often been replaced, in recent years, by pure mineral oil or petrolatum. The dielectric loss of cable impregnated with a pure petroleum oil has an initially low value, but when the cable is placed in service the loss increases at an alarming rate and after a period of years may become as high or higher than that of the older cable impregnated with the rosin mixture. This deterioration of cable constitutes a serious problem in power transmission, since the use of "high-loss" cables greatly restricts the energy-carrying capacity of conduit runs, owing to the limited heat-dissipating ability of the conduit.

The most marked visual evidence of a chemical change having occurred in cable is the formation, apparently from the impregnating compound, of an insoluble, flaky, wax-like deposit. This material, called "X" or "wax," is not uniformly distributed within the cable, but is found in largest amounts at those points subjected to the strongest electric field, and in spaces having sufficient length to permit cumulative ionization, such as the spaces between the abutting edges of consecutive turns of the paper tape. This wax appears to be a good dielectric and its presence does not seem to be harmful. Cable containing large amounts of wax may and does give satisfactory service. But although wax is not the cause of deterioration or failure, the impression has prevailed that it is in some manner associated with failure

About two years ago the Detroit Edison Company became so alarmed at the apparently rapid deterioration of some of its newer cable, that an investigation into cable deterioration was instituted. This paper deals with some of the chemical phases of that investigation.

A review of the literature is given for the polymerization and condensation of hydrocarbons and mineral oils by means of the silent electric discharge and alpha particles. Cathode rays are shown to produce the same effect and a method is described which is suitable for an exact comparison of various oils. Large amounts of gases, mainly hydrogen, are obtained from the condensation of saturated oils, and only small amounts with highly unsaturated oils. Paper subjected to the action of cathode rays or the silent electric discharge gives moisture, hydrogen, and carbon dioxide as the principal volatile products. The importance of the reaction of oils and paper under the influence of the silent electric discharge is discussed in connection with the deterioration of impregnated, paper-insulated cable during use.

and that its presence indicates that an action has occurred within the cable which is detrimental. Our original problem, then, was the study of the reaction resulting in the formation of wax from oils. It was shown by Farmer[1],* that this wax, or a substance resembling it in every way, can be prepared experimentally by placing a sample of the oil between glass plates and subjecting it to a high electric stress for several days. Later Willman[2] and also Del Mar[3] stated that wax cannot be produced by stress alone, but that a gaseous electric discharge is essential for its formation. From analysis of the wax, Del Mar assigned to it the formula $(C_{12}H_{28}O)_n$, although subsequently he admitted that oxygen probably does not enter into its formation since wax can be produced *in vacuo*.

Preliminary laboratory experiments led the present writers independently to the same general conclusions. An apparatus similar to that described by Farmer was set up, except that an oil film between concentric glass tubes was used. The following samples were subjected to stress in this apparatus:

(a) A sample of vaseline taken directly from the jar.
(b) A sample as in (a) except that it was very carefully vacuum-dried in the tubes in which it was to be tested and exposed to air only after it had cooled.
(c) A sample as in (b) except that the tubes were separated and replaced, thus exposing the oil to the air.

Samples (a) and (c), which contained air and therefore were subjected to a gaseous discharge, became masses of wax after $2\frac{1}{2}$ days. Sample (b), which was air-free and consequently not subjected to such a discharge, was unchanged in appearance after more than 2 weeks. These results indicate that stresses of the order of those encountered in cable work cannot of themselves cause any deterioration and that all changes come about as a result of bombardment of insulation by a gaseous electric discharge. Transformers, for instance, have been in service for many years with paper and oil exposed to much higher stresses than in cables, with no deterio-

* Numbers in text refer to bibliography at end of article.

ration other than the "sludging" which is recognized as being simply an oxidation phenomenon.

In order to determine the effect of oxygen, a run similar to those described above was made with a petroleum oil through which a continuous stream of oxygen was bubbled. Within 24 hours the oil had changed in color, had become rancid, and was generally ruined. However, no solid similar to wax was formed and there was no indication that the deterioration corresponded in any way with that found in cables. In other words, oxidation (from atmospheric oxygen) does
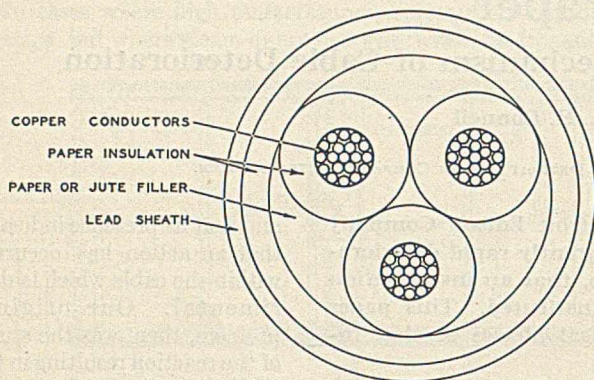

Figure 1—Cross Section of 24,000-Volt, Three-Conductor Cable

not enter into the problem of wax formation, and therefore oxygen must be definitely excluded in experimental work. As there is no reason to suppose that the lead sheath of a cable is permeable to oxygen, this seems altogether logical. These general conclusions concerning wax formation have also been accepted by other workers.[4,5]

Reaction of Hydrocarbons under Influence of Electric Discharge

Inasmuch as it appeared evident that wax is formed as an effect of bombardment of oil by a gaseous electric discharge, the literature on this subject was carefully reviewed. The investigation of the action of the silent electric discharge upon hydrocarbons was begun by Thenard[6] in 1873 and has been continued by Wilde,[7] Berthelot,[8] and many others.[9 to 21] Practically the same type of apparatus has been used in all cases—namely, two concentric glass tubes which were attached to the poles of an induction coil or a transformer, the gas or liquid being introduced into the space between the tubes. The results are generally in satisfactory agreement and are summarized in the following paragraphs:

All hydrocarbons which have been studied react under the influence of the silent electric discharge to give colorless or slightly colored liquid and solid products, the latter being usually of a resinous nature. These products are unsaturated and they absorb oxygen on exposure to air. The reaction may consist either of (1) polymerization, in which no gaseous products are evolved, or (2) condensation in which hydrogen and other gaseous products are produced; or, as is often the case, the two reactions may proceed simultaneously.

Acetylene polymerizes without loss of hydrogen to give a yellow oil, which when heated or allowed to stand changes to an insoluble solid. Kaufmann[17] found the molecular weight of the freshly prepared liquid to be 226, while after 12 hours the value had increased to 266; after 24 hours the compound was no longer soluble. An analysis of a sample of oil that had not been exposed to air gave the empirical formula of acetylene, showing that polymerization alone had taken place.

Ethylene reacts with the evolution of considerable amounts of hydrogen, Berthelot[8c] obtaining 25 cc. of hydrogen from

100 cc. of ethylene and Collie[13] 40 cc. of hydrogen from 210 cc. of ethylene. The liquid product varies widely in solubility, boiling point range, and molecular weight, depending upon the extent to which the reaction has been carried. The liquid obtained by Collie had a boiling point of below 100° C. to above 250° C. with about 40 per cent of the material remaining in the flask as a resin. The analysis of the volatile fractions gave a formula corresponding to C_nH_{2n}— i. e., a polymer of ethylene—while the resin gave the approximate formula $(C_{10}H_{17})_n$, which represents a condensation product at least in part. Collie[13] and also Losanitsch[11e] are of the opinion that the initial reaction is polymerization, followed by condensation of the polymerized product with the liberation of hydrogen. Other members of the olefin series of hydrocarbons have been investigated with similar results.

Methane and ethane condense under the influence of the electric discharge, and according to Berthelot[8c] liberate hydrogen in amounts equivalent to the original volume of hydrocarbon in each case. Losanitsch[11d] found that the gaseous products obtained from isopentane and n-hexane contained methane in addition to hydrogen, while Lind and Glockler[21] found with ethane that, although hydrogen was the principal gaseous product, methane and propane were also present in appreciable amounts and butane and pentane in smaller amounts. The molecular weight of the liquid reaction product varied from 105 to 467, depending upon the length of time the first reaction product was further exposed to the discharge. The analyses of the liquid or resinous products show that they are condensation products of the original hydrocarbons. Although there is no polymerization of the original hydrocarbons in this case, there is the possibility that polymerization of the unsaturated condensation products may play an important part in the reaction.

The aromatic hydrocarbons—toluene, xylene, naphthalene, etc.—polymerize without loss of hydrogen. Losanitsch[11e] finds that benzene is an exception, since diphenyl is obtained as one of the products; however, the hydrogen resulting from the condensation hydrogenates the polymerized reaction products and is not liberated as gas. Berthelot[8b] had previously shown that benzene will absorb hydrogen. Aromatic hydrocarbons with branched side chains also undergo condensation as well as polymerization.

The action of the silent electric discharge on vegetable and mineral oils has also been investigated.[22 to 28] DeHemptinne found a marked increase in the viscosity of the oil as a result of the reaction and patented the process which has proved of commercial application for the manufacture of lubricating oils from cheap vegetable or fish oils of low viscosity or from mixtures of these oils with pure mineral oil. The treated oil, which is given the trade name "Voltol," has a desirable characteristic in that the viscosity varies less with temperature than that of mineral oil. The increase in viscosity has been shown to be due to the condensation of the oil and the consequent building up of larger molecules, the condensation being accompanied by the liberation of hydrogen.

The action of alpha particles from radon (radium emanation) upon hydrocarbons has been studied by Mund and Koch[29] and by Lind, Bardwell, and Perry,[30a] and found to be similar to the action of the silent electric discharge. Acetylene is polymerized to a light yellow powder, no methane being liberated and less than 1 per cent of hydrogen if the solid polymer is protected from further radiation. Ethylene condenses to a colorless liquid with the evolution of hydrogen; in the initial stages of the reaction the volume of hydrogen is equivalent to about 16 per cent of the volume of ethylene which has disappeared, but this value rises to about 30 per

cent at the end of the reaction, owing to further condensation of the liquid products formed.

In the case of the saturated hydrocarbons Lind and Bardwell[30b] found that (1) ethane, propane, and butane condense with the elimination of hydrogen and methane to give higher hydrocarbons, gaseous, liquid, or solid, saturated and unsaturated; methane eliminates hydrogen only; (2) the higher the initial hydrocarbon, the more readily the liquid or solid phase is attained; (3) analysis of the gaseous products shows the presence of all saturated members either higher or lower than the original one. Unsaturated compounds are absent in the gaseous phase, which indicates immediate polymerization of a freshly formed (nascent) unsaturated hydrocarbon to form liquid. The resulting liquid has an empirical formula close to or slightly less saturated than the olefins, C_nH_{2n}. Richards[31] has shown that the reaction is not confined to gaseous hydrocarbons, since liquid and solid paraffin behave similarly.

Coolidge[32a] found that still a third method could be used for the polymerization of acetylene in large amounts to a yellow, insoluble powder—namely, the action of high-velocity electrons or cathode rays.

It appeared, therefore, that the same reactions with hydrocarbons were produced by the silent electric discharge and the alpha particle, and presumably also by the cathode ray.

Experimental Method

As mentioned previously, the first problem was the study of the reaction involved in the formation of wax from oil. In view of the results with hydrocarbons, it was evident that the wax was probably a condensation product of the oil and that its formation should be accompanied by the liberation of considerable amounts of gas, principally hydrogen, which would be particularly objectionable in cable. It was desired, therefore, to measure quantitatively the amount of gas given off by different oils under the same electrical conditions. No simple means could be found, however, for obtaining even semi-quantitative results with the silent electric discharge, since the amount of energy used up in the reaction could not be measured, and would necessarily differ with oils of different electrical properties even if the same apparatus and the same experimental conditions were used. On the other hand, the Coolidge cathode-ray tube is a dependable source of energy, since by operating at the same voltage and by holding the filament amperage at a value giving a specified discharge current the amount of energy at a given distance from the window would always be the same, and by standardizing the procedure at least a quantitative comparison of various oils could be obtained even though the actual energy input in the reaction was not known. For this reason the writers decided to use the cathode-ray tube in their experiments.

Apparatus and Procedure

The design and operation of the cathode-ray tube has been described in detail by Coolidge.[32b] The tube used in this work was set up with its long axis vertical and the window at the bottom, the window being grounded. Voltage was supplied by an a. c. transformer, the tube acting as a self-rectifier; the inverse was kept less than the useful voltage by means of tungar rectifiers in the primary circuit.

Although the tube was capable of operating at several milliamperes and 350,000 volts, 0.3 milliampere and 170,000 volts were used in these experiments. This not only insured complete freedom of voltage troubles, but permitted continuous raying without undue heating of the window, and thus precluded the possibility of pyrogenic cracking of the oil vapor.

Since it was desired to determine both the volume and the composition of the gas given off in the reaction, a round-bottom glass reaction chamber approximately 75 mm. in diameter and 80 mm. in length was sealed to the bottom of the tube by means of a brass collar. This reaction chamber was connected by means of a side arm with a vacuum pump and McLeod gage and also with the apparatus shown in Figure 2. The gas obtained in the raying experiment was transferred by means of the Toepler pump, A, to a buret, B, where the volume was measured, and then to the bulb, C, which was immersed in liquid air. The volatile fraction, consisting principally of hydrogen and methane (and carbon monoxide if present), was separated from the non-volatile fraction consisting of the higher hydrocarbons (and carbon dioxide) by means of the Toepler pump, A', and was collected in the buret B', where the volume was measured. The gas was then analyzed by means of the Henderson-Haldane type of apparatus described by Novy, Roehm, and Soule,[33] which had been further modified as shown in Figure 3. The buret, A, has a volume of 10 cc., the stem and tip being graduated in 0.01-cc. divisions; the absorption pipets, B, C, and D may be used for the absorption of carbon dioxide, acetylene, etc., or for storing nitrogen
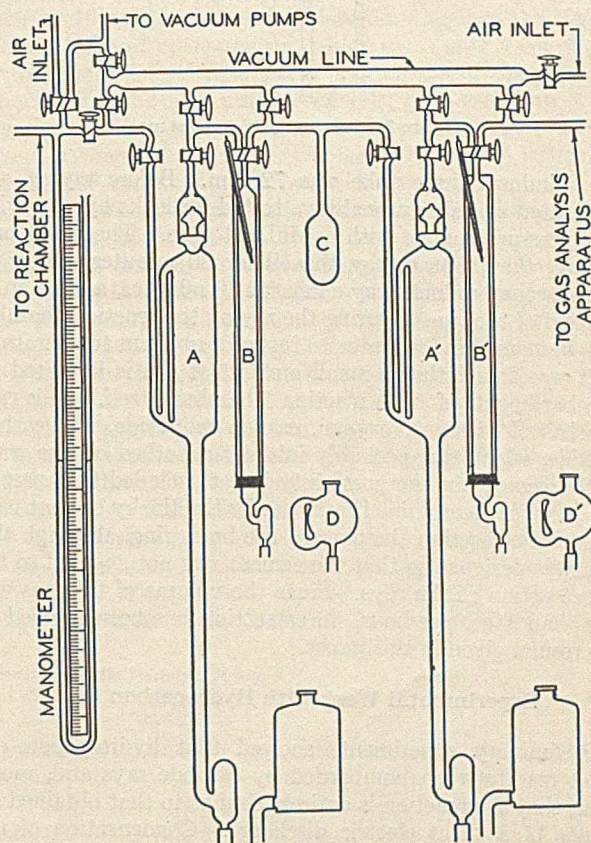
Figure 2—Apparatus for the Transference and Fractionation of Gas

or oxygen; the inverted U-tube, F, contains copper oxide which may be heated to any desired temperature by an electric heating unit, and E is a combustion pipet. Hydrogen and carbon monoxide were determined by combustion with copper oxide, and then methane by combustion with a heated platinum spiral.

A sample of oil in a flat-bottom crystallizing dish of 70 mm. diameter was dried and degassed by heating in a boiling water bath in vacuo, after which it was allowed to cool in vacuo. The dish was then transferred to the reaction chamber, which was immediately sealed to the tube and

evacuated, thus keeping the exposure to air at a minimum. Although it was found that about 5 cc. of oil gave a layer of sufficient thickness to absorb all of the cathode rays, a sample of approximately 10 cc. was used to afford a safe margin. The actual distance of the surface of the oil from
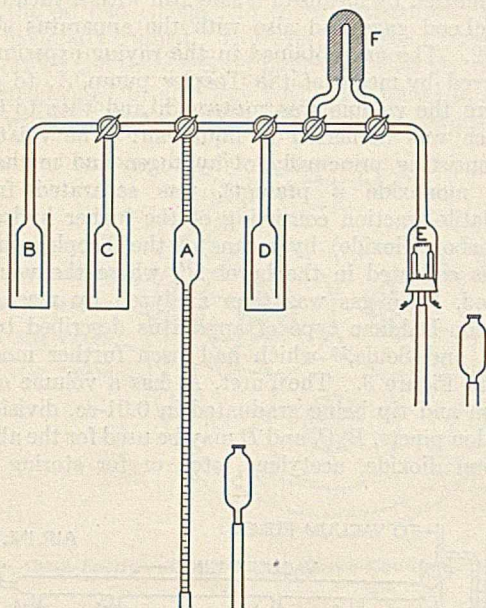

Figure 3—Gas Analysis Apparatus

the window of the tube was 72 mm. Before raying, the evacuated chamber was always tested for leaks by observing any pressure change with a McLeod gage. The usual procedure, then, was to ray the oil for 30 minutes, pump off the gaseous products, ray again for 30 minutes, and so on to the end of the run. During the raying the reaction chamber was immersed in ice water to insure a uniform temperature.

It was found that a small amount of gas is liberated by bombardment of the reaction chamber itself. This gas consists of nitrogen, oxygen, carbon monoxide, and carbon dioxide, which was probably initially adsorbed on the walls of the vessel, but the possibility is not excluded that part of the gas may be obtained from the DeKhotinsky cement used to seal the reaction chamber to the brass ring, although this ring was designed so that the cement was not exposed to the direct action of the rays. Since the volume of this gas was less than 1 cc. per hour, no correction has been applied to the results given in this paper.

Experimental Work with Hydrocarbon Oils

Preliminary experiments showed that hydrocarbon oils react readily when bombarded by cathode rays and, moreover, that the reaction is entirely similar to that obtained by means of a silent electric discharge. Condensation of the oil takes place with the evolution of gaseous products—namely, hydrogen and saturated hydrocarbons—and with the formation of an insoluble product resembling wax from cable both in appearance and in physical properties. In order to determine the rate of formation of the wax and the amount of gas obtained, a sample of a typical rosin-free cable compound was rayed *in vacuo* for prolonged periods.

In the first experiment a sample of 6.4 grams was rayed for 20 hours, the gas being pumped off at 2-hour intervals, measured, and analyzed. The volume of gas obtained during each period is given in Table I and the data are plotted in curve 1, Figure 4. The average analysis of the gas from various periods was hydrogen, 90.4 per cent; methane, 3.2 per cent; and higher hydrocarbons (C_nH_{2n+2}), 5.5 per

cent. There was no marked variation in composition during the run. A second sample of 2.9 grams was rayed for 15 hours, but in this case the gas was allowed to remain in the reaction chamber and the pressure read at intervals. The total volume of gas measured after completion of the run was 178.8 cc. (corrected). The volumes of gas for intermediate periods were computed from the pressure data and are given in Table II and plotted in curve 2, Figure 4.

Table I—Volume of Gas Obtained in Raying Cable Compound *in Vacuo*

TIME	INCREASE IN VOLUME (N. T. P.)	TOTAL VOLUME OF GAS (N. T. P.)
Hours	Cc. per hour	Cc.
2	19.9	39.8
4	22.4	84.5
6	18.9	122.3
8	17.2	156.7
10	14.0	184.7
12	13.8	212.2
14	11.8	235.7
16	11.3[a]	258.2
18	10.8	279.8
20	9.4	298.5

[a] This volume is estimated, owing to loss of sample.

Table II—Observed Increase in Pressure and Calculated Volumes of Gas Obtained in Raying Cable Compound

TIME	GAS PRESSURE	CALCD. INCREASE IN VOLUME (N. T. P.)	CALCD. TOTAL VOLUME (N. T. P.)
Hours	Mm. Hg	Cc. per hour	Cc.
1	60	23.2	23.2
2	110	19.4	42.6
4	187	15.0	72.5
6	263.5	14.8	102.1
8	315.3	10.0	122.1
10	360.5	8.8	139.6
12	404.5	8.5	156.6
14	441.5	7.2	170.9
15	461.9	7.9	178.8

A comparison of the two curves shows that the volume of gas liberated in the first experiment, in which the gas was pumped off frequently, is greater than the volume liberated in the second experiment, in which the gas was allowed to accumulate in the reaction chamber. This difference may be due to the fact that in the latter case the increasing quantities of gas absorb an appreciable amount of energy which would otherwise be available for the reaction. In both cases the volume of gas evolved in a given length of time decreases as the reaction proceeds. The reaction takes place principally at the surface, and as the condensation proceeds a film of highly condensed product or wax forms, which probably gives off less gas than the original oil.
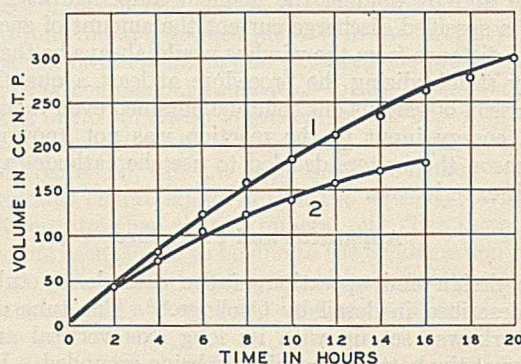
Figure 4—Volume of Gas Obtained in Raying Cable Compound

Curve 1, when gas is pumped off. Curve 2, when gas is not pumped off.

In the first experiment 1.16 grams of insoluble wax were obtained by extracting the rayed oil with ether, and in the second experiment about 0.75 gram was obtained. The wax showed a much higher carbon-to-hydrogen ratio than the original cable compound, as should be the case if it is a condensation product of the oil.

	CARBON	HYDROGEN	RATIO
	Per cent	Per cent	C:H
Original cable compound	86.50	12.71	6.81
Wax from cable compound:			
Sample A	85.96	11.16	7.70
Sample B	86.85	11.62	7.47

The wax readily absorbs oxygen from the air; a sample on drying in air at 100° C. gained in weight and on analysis was found to contain approximately 10 per cent of oxygen.

After having shown that cathode rays have an effect on oils similar to that of the silent electrical discharge, the next step was to ascertain whether or not oils of different types would show any marked difference in behavior. Therefore a large number of oils of known history were investigated. These samples, with a few exceptions, were furnished by the technical division and the research laboratory of the Standard Oil Company of Indiana, for whose generous coöperation the writers wish to express their fullest appreciation. Table III gives the results obtained with a series of products that were carefully selected in order to determine in what manner the reaction is influenced by factors such as viscosity, degree of refinement, etc. Data on a number of miscellaneous oils are given in Table IV.

In these experiments the oil was rayed for three periods of 30 minutes each, and the gas pumped off and measured after each period; in a few cases, when the volume of gas was quite small, the sample was rayed for a single period of 90 minutes. The gas from each period was fractionated by means of liquid air and the volatile portion analyzed. In addition to hydrogen and methane, carbon monoxide was often found in this fraction, but the amount was usually less than 1 per cent. The non-volatile fraction, consisting of ethane, propane, etc., was shown to be practically free from unsaturated components, but was not investigated further.

As a rule, the volumes of gas obtained in the three periods did not vary more than about 1 cc., and with oils that give but small amounts of gas the variation was even less. The results with duplicate runs which were made in many cases were also found to check usually within about 1 cc. Since the variations both in the volume and in the composition of the gas during the course of a run were apparently without significance, only the average of all the results obtained in each run is given in the tables. However, in order to show the limit of accuracy attained, the data for the three periods for two different cable compounds are given in Table IV. The results with oil No. 43 are typical of most of the runs, while those with oil No. 44 constitute one of the least satisfactory of the runs.

The consideration of the data given in Table III leads to the following conclusions:

(1) If midcontinent and naphthenic oils of the same viscosity and the same degree of refinement are compared (Samples 6 and 7 with 12 and 13, respectively), the naphthenic oils are found to give somewhat less gas than the midcontinent oils, but the difference is too slight to be significant.

(2) In either series, if the degree of refinement is the same, the oils of low viscosity give more gas than those of about medium viscosity (Samples 6, 7, and 8, also 12 and 13); in the midcontinent series the oils of high viscosity also give more gas than those of medium viscosity (Samples 7, 8, and 9), but the difference is not so great as in the previous case and is probably due to a slight difference in the degree of refinement of the oils.

(3) Except in the case of the high-viscosity midcontinent oils, there is a marked difference in the amount of gas obtained from oils of the same base and viscosity when one is highly refined and the other is not (Samples 1 and 2, 3 and 4, 5 and 6, 13 and 14, 15 and 16).

The degree of refinement is a good index to the degree of unsaturation of the oil, since the unsaturated portion of the oil is more or less completely removed during the refining process. It follows, therefore, that the oils which give the least amount of gas are those which contain the greatest fraction of unsaturated constituents. The two extremes are shown by the highly saturated waxes and oils which give as much as 40 cc. of gas per half-hour, as against the highly unsaturated and untreated oil, which gives only 4 cc. of gas per half-hour. In Table IV it will be noted that several mineral oils, and also anthracene oils, give less than 3 cc. of gas per half-hour, while three cable compounds in use at present average about 20 cc. per half-hour. This difference in behavior cannot be attributed to impurities in the oil, since the same difference is found with pure saturated and unsaturated hydrocarbons which are now being investigated. The amount of gas obtained with the unsaturated oils does not increase appreciably with longer periods of raying. For example, a sample of oil No. 24 was rayed for 10 hours and gave 24.3 cc. of gas, the rate of evolution of gas being uniform throughout the run.

The decreased amount of gas obtained with unsaturated mineral oils can be explained in either of two ways—namely, (1) that the unsaturated oils do not suffer condensation with consequent liberation of hydrogen; or (2) that some condensation does take place but that the liberated hydrogen adds itself to the double or triple bonds in the molecule, as in the case of benzene, which absorbs hydrogen under the influence of the silent electric discharge.[8b,11e] The second explanation seemed to be the more reasonable, since even a

Table III—Data from Raying Experiments with Mineral Oils

No.	TYPE OF OIL	DEGREE OF REFINEMENT	SAYBOLT VISCOSITY	GAS PER 30-MINUTE PERIOD[a] (N. T. P.)	$H_2 + CH_4$	C_nH_{2n+2}	H_2	CH_4
			Seconds	Cc.	%	%	%	%
1	Saturated wax (m. p. 74° C.)	Undistilled		27.7	94.6	5.4	93.0	1.3
2	Unsaturated (m. p. 50–52° C.)	Distilled and refined		34.0	93.2	6.8	90.9	1.9
3	Wax and oil	Moderate		18.6	92.0	8.0	88.5	2.2
4	Wax and oil (m. p. 48° C.)	High		40.4	93.7	6.3	90.5	1.8
			(At 38° C.)					
5	Midcontinent	High	Low, 80	29.7	92.5	7.5	88.8	2.9
6	Midcontinent	Moderate	Low, 55	24.0	91.3	8.7	86.0	4.0
7	Midcontinent	Moderate	Below medium, 180	12.7	92.0	8.0	88.3	2.9
8	Midcontinent	Moderate	Medium, 300	13.4	93.3	6.7	88.4	3.7
			(At 99° C.)					
9	Midcontinent	Moderate	High, 165	19.4	91.7	8.3	87.7	2.8
10	Midcontinent	High	High, 160	19.5	92.5	7.5	88.6	3.0
11	Midcontinent	Very high	High, 150	21.0	90.8	9.2	86.2	4.4
			(At 38° C.)					
12	Naphthenic	Moderate	Low, 50	20.8	90.2	9.8	86.0	4.2
13	Naphthenic	Moderate	Below medium, 100	10.0	90.0	10.0	85.8	3.8
14	Naphthenic	High	Below medium, 180	35.8	93.6	6.4	91.0	2.2
15	Naphthenic	Moderate	Medium, 300	10.9	93.5	6.5	89.3	3.6
16	Naphthenic	High	Medium, 300	33.6	95.1	4.9	92.7	2.4
17	Highly unsaturated oil	Untreated		3.9	91.5	8.5	90.7	0.5

[a] The volumes and also the analyses represent the average of three periods.

highly unsaturated oil must contain appreciable amounts of saturated components; the extent of the condensation would, of course, vary with the nature of the oil. Evidence in support of this view was obtained by raying a mixture (Sample 33) of 25 per cent of a saturated oil (Sample 16), which gave 33.6 cc. of gas, and 75 per cent of an unsaturated oil (Sample 24), which gave 2.0 cc. of gas per half-hour period. This mixture gave 4.2 cc. of gas per half-hour period instead of about 10 cc. which might have been expected. However, the same unsaturated oil when rayed in 0.5 atmosphere of hydrogen for 5 hours showed no noticeable absorption. These results indicate, therefore, that hydrogen can be absorbed in appreciable amounts by the unsaturated molecules only when it is in the nascent or in an activated state and in intimate contact with the oil, which conditions are fulfilled at the moment at which the hydrogen is liberated in the oil.

The electrical properties of the unsaturated oils that have been investigated up to the present time have been unsatisfactory. Nevertheless, it does not seem unreasonable to believe that oils of this type can be obtained which will prove satisfactory for cable impregnation, and work in this direction is being continued.

Table IV—Data from Raying Experiments with Miscellaneous Oils

No.	Type of Oil	Gas per 30-Minute Period (N.T.P.) Cc.	$H_2 + CH_4$ %	C_nH_{2n+2} %	H_2 %	CH_4 %
18	Highly unsaturated, untreated oil of same history as No. 17	3.6	92.4	7.6	87.2	3.2
19	No. 18 contacted with fuller's earth	3.2	92.4	7.6	88.5	3.0
20	Last cut from coking distillation of midcontinent crude oil	11.1	85.6	14.4		4.2
21	No. 20 contacted with fuller's earth	6.7	92.8	7.2	89.3	2.7
22	Same as No. 20, but refined by distillation	9.2	92.5	7.5	87.5	2.7
23	Cut obtained during redistillation of No. 22	9.3	94.4	5.6	90.6	2.5
24	Same history as No. 20	2.0	83.1	16.9	77.4	3.2
25	No. 24 contacted with fuller's earth	3.2	90.3	9.7	84.6	4.7
26	Cut obtained during distillation of No. 24	2.7	93.4	6.6	90.6	2.5
27	Same history as No. 20	2.7	87.1	12.9	78.4	8.5
28	Distillate recovered from acid sludge from treatment of lubricating oil	3.3	86.6	13.4	80.8	4.4
29	Hexane soluble from pressure-still product	5.0	79.9	20.1		
30	Hexane insoluble from pressure-still product dissolved in naphthenic white oil	36.1	95.3	4.7	90.2	3.1
31	Cut from redistillation of pressure-still product	6.2	85.5	14.5	77.2	5.2
32	Overhead product derived from No. 18	1.5				
33	Mixture of 75% No. 24 and 25% No. 16	4.1	87.9	12.1	82.2	2.5
34	Pennsylvania oil	21.7	93.9	6.1	88.6	2.8
35	Rosin oil	22.6	39.1	60.9		
36	Rosin oil	20.6	42.8	57.2	37.4	1.7
37	No. 13 + 25% rosin oil	18.5	58.2	41.8		
38	No. 13 + 2% antioxidant (Age-Rite)	14.8	90.6	9.4	84.3	3.9
39	Last cut from distillation of low-temperature coal tar	5.1	87.6	12.4	79.7	4.7
40	Anthracene oil	0.8	78.6	21.4	64.8	12.2
41	Anthracene oil	1.5				
42	Typical cable compound containing rosin	24.1	70.7	29.3	61.5	5.7
43	Typical cable compound (rosin-free)	18.7	93.3	6.7	90.0	2.9
		17.4	92.8	7.2	89.5	3.1
		17.4	92.2	7.8	88.9	2.9
44	Typical cable compound (rosin-free)	21.4	95.6	4.4	91.7	5.6
		20.1	94.4	5.6	91.6	2.3
		23.7	97.2	2.8	91.5	4.9

DISCUSSION OF RESULTS—From the results obtained with typical cable oils, it is evident that in order to explain the presence of wax in cable we must conclude that condensation of the oil has taken place with the liberation of a large amount of hydrogen within the cable. In dissecting a large number of cables that had been removed from service, 66 in all, wax was found in nearly all cases and varied in amount from 0.0 to 4.5 grams per foot of cable, the average of all samples being 1.7 grams per foot. In the experiment described earlier in this paper, in which a sample of cable compound was rayed 20 hours, 1.16 grams of wax and 298.5 cc. of gas were obtained. Therefore we should expect that 1.7 grams of wax would correspond to the liberation of 1.7/1.16 × 298.5, or 437 cc. of gas of which about 90 per cent or 393 cc. is hydrogen. This is a rough approximation, to be sure, since the analysis of wax from raying experiments and wax from cables indicates that the condensation has been carried further in the former case than in the latter. On the other hand, owing to the difficulty in removing wax from used cable, the amount recovered is probably considerably less than that actually present, so that the two factors may tend to compensate each other.

The fact that such appreciable amounts of gas are formed within the cable during use lends support to the theory that deterioration, and possibly ultimate breakdown, is due to gaseous electric discharge. However, there are certain objections to this theory. For example, attempts to collect the gas from an oil-fed cable in operation gave volumes far below what were to be expected. Moreover, the gas contained only about 2 per cent of hydrogen; the remainder was largely nitrogen and oxygen and probably came from the gas dissolved in the oil used for feeding the cable. The disappearance of hydrogen can be explained in several ways. For example, it may diffuse through any imperfections in the lead sheath of the cable or it may enter into some secondary reaction.

Further disturbing observations were made during an investigation of the electrical characteristics of a number of new and used cables, which indicated that factors other than gaseous ionization may be involved in the deterioration of cable. The curves given in Figure 5 show the variation in power factor with temperature and with voltage for a sample of cable when new and after 11 months' service. This sample was admittedly of poor manufacture, and consequently the differences are greater than with the average sample studied. The shape of the curve of power factor against temperature is that which is generally associated with electrolytic conduction. (It should be noted that these measurements were made on 10-foot (3-meter) lengths with no pressure-tight seals on the ends, so that the conditions are somewhat different from those encountered in service where the ends are sealed.) The absolute value of the dielectric loss at 60° C. and operating voltage was 1.05 watts per foot (30.5 cm.), sufficiently high to be alarming from an operating standpoint, as has been previously noted.

This deterioration of cable in service might reasonably be ascribed to electrolytic conduction, which could be due to overoxidation of the oil, the presence of water in the oil, or degradation products of paper dissolved in oil or water. The method of manufacture and the electrical properties of new cable give satisfactory evidence that overoxidation of the oil has not taken place and that water is not initially present in harmful amounts, but the possibility exists that water may be formed within the cable during its operation. The hydrogen obtained from condensation of the oil might react with oxygen-containing compounds under the influence of the electric discharge. The hydrocarbon oils used for cable impregnation may be regarded as substantially oxygen-free, if they have been properly protected from oxygen during shipping, storing, and cable manufacture. The paper is therefore the most likely source of oxygen present in the cable. The possibilities which present themselves are either that the activated hydrogen reacts with the paper or that the paper itself is decomposed by the electric discharge and yields products which will be reduced by the hydrogen. (Clark[4] found that paper is disintegrated when exposed to a corona discharge in an atmosphere of hydrogen.) The

Table V—Data from Raying Experiments with Paper *in Vacuo*

No.	Type of Sample	Gas per 2-Hour Period (N. T. P.) Cc.	Fraction Volatile in Liquid Air %	Fraction Non-Volatile in Liquid Air %	H₂ %	CO %	CH₄ %	CO₂ %	C₂H₂ %	Water Calcd. from Volume of C₂H₂ Mg.
1	Unimpregnated cable paper	15.7	58.6	41.4	...	...	...	10.3	31.5	8.6
		12.5	46.8	53.2	36.5	2.2	1.1	20.3	32.9	7.2
2	Partially purified cellulose from cotton	21.6	67.1	32.9	56.6	1.8	1.2	....	...	...
3	Cable paper impregnated with mineral oil	18.3	68.4	31.6	66.1	0.2	2.1	9.6	18.4	5.9
4	Same	16.8	74.6	25.4	69.9	2.2	1.7	13.0	12.0	3.5
5	Same	17.6	69.8	30.2	64.6	2.1	1.6	12.6	16.6	5.1
6	Same	18.1	77.8	22.2	71.8	4.1	1.9	7.8	14.3	4.5
7	Cable paper impregnated with mineral oil and rosin	17.3	66.1	33.9	60.8	3.3	1.4	18.3	16.3	4.9
8	Same	18.5	66.3	33.7	60.1	4.0	2.0	20.2	12.8	4.1
9	Same	17.0	65.9	34.1	59.8	4.2	1.6	17.1	15.7	4.6
10	Same	17.6	69.9	30.1	63.6	4.2	1.6	18.2	11.1	3.4
11	Unimpregnated cable paper subjected to silent electric discharge for 44 hours	10.3	37.4	62.6	32.0	2.3	0.6	11.6	50.4	9.0

second possibility seemed the more plausible, and consequently it was decided to investigate the action of paper under electrical bombardment.

Experimental Work with Paper

The procedure for raying paper was, in general, quite similar to that used for oils. In this case, though, it was necessary to determine the amount of water present in the reaction products. Therefore, a large U-tube filled with small pieces of calcium carbide was inserted in the line connecting the reaction chamber with the first Toepler pump, so that any moisture in the gas would react with the calcium carbide to
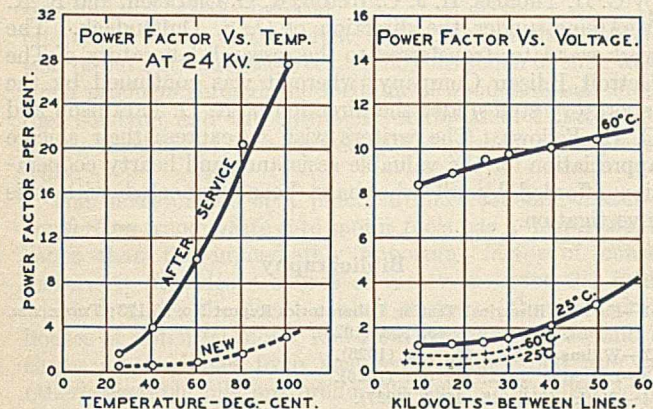

Figure 5—Effect of Service on Characteristics of Cable

give acetylene. It was found by test that, with the grade of carbide used, the volume of the acetylene liberated amounted to about 0.575 cc. (corrected to standard conditions) per milligram of water, which value checked well with that of 0.580 cc. found by Masson[34] and was used in subsequent calculations. After measuring the volume of gas obtained in the raying experiment, the gas was fractionated with liquid air and the volatile fraction analyzed by the methods previously described; the non-volatile fraction consisted principally of carbon dioxide and acetylene, which were absorbed in sodium hydroxide solution and ammoniacal cuprous chloride solution, respectively.

A reaction chamber approximately 195 mm. in length was used in these experiments, so that the paper could be dried directly in the chamber. The sample was placed in a crystallizing dish 70 mm. in diameter, three or four layers or strips being used to insure complete absorption of the rays. The dish was placed in the chamber, which was then sealed to the tube and evacuated. The lower half of the chamber was then immersed in boiling salt water for two hours to remove as much of the moisture as possible; after raying for a period, usually of 2 hours, the reaction chamber was again immersed in boiling salt water and the gas pumped off. Since the drying conditions were duplicated, it was assumed

that the same amount of moisture would be retained by the paper before and after the raying.

The intensity of the cathode rays is necessarily less in the experiments with paper than in those with oils, owing to the greater distance of the sample from the tube window. In order to obtain a comparison of the intensity in the two cases, a sample of the same oil was rayed for 30 minutes in both the short and long reaction chambers, 9.2 cc. of gas being obtained in the former case and 4.0 cc. in the latter. Therefore, somewhat less than half the energy utilized in the reaction with oils is available for the reaction with paper.

The results with paper and partially purified cellulose from cotton are given in Tables V and VI. About 2 to 3 grams of sample were used, this quantity being sufficient to absorb all of the cathode rays; the exact weight is of no importance, since only that part of the sample which is exposed to the rays enters into the reaction. The preliminary experiments 1 and 2, Table V, showed that paper and partially purified cellulose react to give water as one of the products; the other principal volatile products are hydrogen and carbon dioxide, with carbon monoxide and methane present in smaller amounts. It should be noted that the acetylene mentioned in the tables is not a primary product of the reaction, but is formed by the action of the water with calcium carbide.

Table VI—Data from Raying Experiments with Paper in Hydrogen and Nitrogen

No.	Type of Sample	Gas Non-Volatile in Liquid Air per 2-Hour Period (N. T. P.) Cc.	CO₂ %	C₂H₂ %	Water (Calcd. from Volume of C₂H₂) Mg.
1	Unimpregnated cable paper in hydrogen	4.5	16	84	6.6
		6.3	28	73	8.0
2	Same	3.6	60	42	2.6
		7.4	50	50	6.4
3	Same	7.2	19	83	10.0
		3.6	50	51	3.2
4	Partially purified cellulose from cotton in hydrogen	6.7	25	75	8.7
5	Unimpregnated cable paper in nitrogen	5.1	46	54	4.8
		4.8	45	53	4.4

It was thought that more water might be produced in excess of hydrogen, and indeed this condition must exist within the cable where the condensation of oil liberates hydrogen. To test this point, paper was rayed in hydrogen and in nitrogen at one-half atmospheric pressure. The results, given in Table VI, do not check very well, and since there is no marked difference in the amount of moisture obtained in the two cases no definite conclusions can be drawn.

Experiments 3 to 10, Table V, were made to determine the effect of rosin on the reaction. Paper impregnated with pure mineral oil and with mineral oil containing rosin was rayed *in vacuo*, but practically the same amount of moisture was obtained in each case.

Unimpregnated paper after raying showed no marked change in color, but the fibrous structure was completely

destroyed, the material becoming so brittle that it powdered readily. The copper number was utilized in order to obtain an indication of the extent of the degradation of the cellulose. Paper with an initial copper number of 1.13 gave values after raying which ranged from 12.4 to 43.1. The rayed paper also showed distinctly acid properties, although the original paper was neutral. In one case a sample weighing 1.1557 grams after raying for 4 hours in hydrogen required 1.6 cc. of 0.1 N potassium hydroxide for neutralization. A sample of partially purified cellulose weighing 1.4234 grams after raying for 2 hours *in vacuo* required about 8 cc. of 0.1 N potassium hydroxide for neutralization.

The paper in used cable, however, showed no great change in physical properties, such as was found in the raying experiments. Moreover, the copper number of paper from used cable was never unduly high, values varying from 1.3 to 2.8 being obtained. These values, of course, could not be checked with the initial values, since samples of the original paper used in the cables were not available, but at least it was evident that any decomposition of the paper in cable was not of the same order as that obtained in the raying experiments. In other words, the reaction produced by cathode rays was very much more pronounced and perhaps was even of a different nature than that produced by the silent electric discharge. Paper was therefore subjected to a corona discharge in order to determine to what extent the two reactions could be correlated.

The apparatus was of the usual type and consisted of a $^1/_8$-inch (3-mm.) brass rod running through the center of a glass cylinder, $1^1/_2$ inches (38 mm.) in diameter, which was sealed at both ends; the cylinder was connected by means of a side arm to the vacuum pump and to the analysis apparatus. The paper, which was placed adjacent to the inner wall of the cylinder, was dried before the run by immersing the vessel in boiling salt water and evacuating thoroughly; later this bath served as the outer electrode. The power was supplied by a transformer operating on a 110-volt, 60-cycle circuit; in this experiment 7500 volts were used, although it is believed that the reaction can be produced by lower voltages. The run was continued for 44 hours, after which the volatile products were pumped off and analyzed by the procedure used in the experiment with the Coolidge tube. The results are given in experiment 11, Table V.

The amount of gas obtained with the corona discharge in 44 hours is somewhat less than that obtained with cathode rays in 2 hours (experiment 1, Table V), which allows a rough comparison of the rates of reaction with the two sources of energy. The composition of the gas obtained in the two reactions is approximately the same except that the moisture content is higher in the corona discharge experiment. The paper, however, did not show any marked change in structure in the latter case and, moreover, the copper number increased only to a slight extent, the initial value being 2.0 and the final value 2.3. The conclusion may be drawn, therefore, that although the volatile products are approximately the same in the two reactions, the degradation of the paper itself is carried much further by cathode rays than by the corona discharge.

Some of the water which is produced in the reaction with paper in the corona discharge or with cathode rays probably results from the secondary reaction between carbon dioxide and hydrogen. However, although carbon monoxide and methane are always present in the reaction product, the amounts of these gases are small and can account for only a portion of the amount of water which is produced. The remainder of the water then must come from the paper itself. The water may be obtained from paper by the actual decomposition of the material or it is possible that water

absorbed on the paper may be liberated as a result of the electrical bombardment. At present no conclusions can be drawn as to which explanation is correct.

Summary of Results

The wax found in cable is formed by condensation of the impregnating compound due to the action of the silent electric discharge and is accompanied by the liberation of hydrogen. Paper under the influence of the silent electric discharge produces appreciable amounts of moisture as well as gaseous products, hydrogen, carbon dioxide, etc. The formation of gases and of moisture within cable during use are two very important factors in causing deterioration of cable. Improvement in cable can, therefore, be expected if the silent electric discharge can be eliminated by satisfactory changes in design, or if an impregnating compound and a paper or suitable substitute can be found which will not produce gaseous products and moisture when subjected to such a discharge.

Acknowledgment

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Motor Fuels and Other Products from the Cracking of Wood Tars[1]

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The possibilities of the utilization of waste wood products, particularly tars from the destructive distillation of wood, by conversion into motor fuels and other products by the cracking process are pointed out by means of data obtained by cracking three types of wood tar. These data indicate that, in general, the products obtained from the pine tar are most suitable for solvents and paint thinners, the hardwood tar may be utilized for the manufacture of low-boiling tar acids and phenols, and the Douglas fir tar produces a highly antiknock motor fuel.

O NE of the purposes of the present work is to point the way to the utilization of some of the tremendous quantity of material that is wasted by the lumber industry, in addition to a wider utilization of one of the present principal products of wood distillation—namely, the tars. Conversion of this waste material into useful products is of great importance in the conservation of our national resources. The conversion of such waste wood products through the medium of wood tars into motor fuel, solvents, and turpentine-like material or flotation oils by the cracking process has been accomplished in the present work.

The development of a practical and economic means of converting wood waste into motor fuels has a deeper significance than the immediately important factor of conservation—it provides a source of motor fuels for the future which is under the direct control of man. Our great store houses of potential motor fuel from petroleum, coal, and oil shales are heritages from past ages, while wood tars and other vegetable oils are producible under controlled conditions.

According to statistics given by the Forest Service of the United States Department of Agriculture, approximately 24 per cent of the standing tree—i. e., the total wood in the forest—is converted into useful products, while 76 per cent is wasted. About 31 per cent of the wood used for making lumber based on the log is available for carbonization for the production of charcoal, tar, and other products. The factory waste in working up the lumber represents another 20 per cent based on the log, making a total of over 50 per cent, not including the bark, of the total log available at the mill and factory.

As an example of the possibilities of the utilization of this waste, from an average annual yield of 7.5 billion board feet (Bureau of Census) of Douglas fir the equivalent of 2.5 million cords, or 4.2 million tons, is available for destructive distillation, yielding the following products:

	Gallons
Turpentine and light oils	8,500,000
Tar	70,000,000
Wood alcohol	9,780,000
	Pounds
Acetate of lime	187,500,000
Charcoal	2,440,000,000

A large yield of gas for fuel is also obtained.

The 70,000,000 gallons of tar will produce by cracking, according to present research, 23,300,000 gallons of motor fuel equal in antiknock properties to benzene, in addition to approximately 6,000,000 gallons of low-boiling tar acids or phenols for antiseptic, disinfectant, and other uses. Further, approximately 125,000 tons of high-grade coke and 1,830,000,000 cubic feet of gas will be made in the cracking operation.

The above is representative of only one kind of wood. For the other kinds the yields of other products may be similarly shown. Yellow pine heads the list in production with over 12.5 billion board feet (in 1924), and Douglas fir is second with over 7.5 billion board feet. The yellow pine and Douglas fir are both softwoods of the coniferous group. A hardwood tar made from oak and hickory woods was also selected.

Products of Wood Distillation

The products of wood distillation may be divided into four groups—pyroligneous acid, tar, gas, and charcoal. These four products vary in amount depending on the species of wood and the conditions of distillation, but the average yields from hardwood body wood at atmospheric pressure and 350° to 400° C. maximum temperature are as follows:

	Per cent
Pyroligneous acid	45
Total tars	7
Gases	19
Charcoal	29

A great many chemical individuals have been identified among the products of wood distillation.[2] The chief commercial products obtained aside from charcoal are acetic acid, acetone, methanol, and the wood tar. Beechwood creosote is an important medicinal product manufactured from the destructive distillation of any of the hardwoods, but preferably beech. It is derived mostly from the soluble tars recovered by the refining of the pyroligneous acid. Turpentine and rosin are among the most important of the products obtained from the distillation of resinous wood. Pine oil is another important product. Their uses are numerous and well known.

The recovery of by-products from resinous wood is carried on by one of two methods—destructive distillation and the

[2] Hawley and Wise, "The Chemistry of Wood," p. 199, Chemical Catalog Co.

steam and solvent process. The material used is old stumps from the long-leaf pine; the ordinary saw-mill waste or green timber does not contain sufficient pitch to make the process profitable as practiced at present. Douglas fir and Norway pine have been used to some extent, but in neither case can commercial quantities of wood be collected equal in quality to the long-leaf pine wood. Processes and equipment for handling this long-leaf pine wood or, in fact, any of the soft-woods have not been standardized. This, of course, is a handicap to the industry owing to difference in the products.

Ordinary unselected saw-mill waste and green timber from long-leaf pine produces about 27 gallons of black tar per ton of wood, while the light wood will produce from 50 to 80 gallons of oily or tarry material per ton of drywood. The weight of ordinary long-leaf pine wood with about 15 per cent moisture and 5 per cent rosin is about 42.5 pounds per cubic foot, which gives an average of about 3700 pounds per cord, and for 15 per cent rosin content will yield 75 gallons of oil or tar oil; for 30 per cent rosin content the weight will go up to approximately 4100 pounds per cord and will yield 152 gallons of total oily products.

Benson and Darrin[3] show the following yields of products from Douglas fir and western yellow pine:

Material	Weight per Cord Lbs.[a]	Turpentine and Light Oil Gal.[d]	Tar Gal.[d]	Wood Alcohol Gal.[d]	Acetate of Lime Lbs.	Charcoal Lbs.
Douglas fir, commercial mill waste	3330[a]	3.40	27.80	3.90	75.0	977
Douglas fir, selected resinous waste	4250[b]	10.86	46.37	3.71	74.3	900
Douglas fir, stump wood	3260[b]	5.59	19.88	2.60	55.8	675
Western yellow pine mill waste	2840[b]	4.91	24.80	3.25	73.4	478
Western yellow pine stump wood	2620[b]	6.06	23.05	1.83	60.8	520
Western hemlock mill waste	3270[c]	2.76	21.60	5.00	94.0	938

[a] Based on 15 half-cords.
[b] Based on 4 half-cords.
[c] Based on 5 half-cords.
[d] U. S. gallons.

Cracking of Douglas Fir Wood Tar

A wood tar derived from the thermal decomposition of Douglas fir was subjected to the cracking process under pressures of 75, 100, and 120 pounds per square inch and temperatures ranging from 393° to 405° C. The yield of tar-acid-free motor fuel based upon the dry wood tar was approximately 26 per cent. The antiknock properties of the motor fuel were better than the aromatic hydrocarbon, benzene.

An automotive engine test rated the motor fuel as 100+ per cent benzene equivalent.

Analysis of the Douglas fir wood tar used in the cracking test is shown in Table I.

Table I—Distillation Analysis of Douglas Fir Wood Tar (A. S. T. M.)

Specific gravity... 1.061
A. P. I. gravity... 1.7
Initial boiling point:
  ° F... 240
  ° C... 116

Per cent over	° F.	° C.	Per cent over	° F.	° C.
10	342	172	60	630	332
20	443	228	70	651	344
30	506	263	80	655	346
40	550	288	85	655	346
50	597	314			

Coke, per cent by weight........................... 14.4

	Per cent	Acidity Per cent
Aqueous distillate	15.5	0.4
Oil	61.5	...
Coke, gas, and loss	23.0	...

[3] Benson and Darrin, J. Soc. Chem. Ind., 34, 1201 (1915); J. Ind. Eng. Chem., 7, 916 (1915).

A summary of the cracking tests and yields of products is shown in Table II.

Table II—Summarized Data on Cracking of Douglas Fir Wood Tar

OPERATING CONDITIONS

Temperature:			
° F.	740	760	770
° C.	393	404	410
Pressure, lbs. per sq. in.	75	100	120

SUMMARY OF RESULTS
(Per cent based on charge)

Pressure distillate, per cent	48.6	46.5	44.5
A. P. I. gravity	19.3	21.1	21.8
Specific gravity	0.9383	0.9273	0.9230
Residuum	None	None	None
Water, per cent	19.3	20.5	21.4
Coke, lbs. per bbl.	...	84	98
Gas, cu. ft. per bbl.	627	750	955
Motor fuel, fraction per cent	26.3	27.1	27.2
Tar-acid-free motor fuel, per cent	21.2	21.9	22.0
Gas oil (recycle stock)	21.4	18.2	16.3
Coke, gas, and loss, per cent	32.1	33.0	34.1

MOTOR FUEL AND GAS OIL
(Per cent based on dry wood tar)

Motor fuel, fraction per cent	31.0	32.1	32.2
A. P. I. gravity	27.7	30.2	29.2
Specific gravity	0.8888	0.8751	0.8805
Initial boiling point to end point, ° F.	146–440	137–436	137–434
Tar-acid-free motor fuel, per cent	25.0	25.8	25.9
Gas oil (recycle stock)	25.0	21.8	19.5
A. P. I. gravity	9.5	10.1	10.3
Specific gravity	1.003	0.9993	0.9979
Coke, lbs. per bbl.	127	97	115
Gas, cu. ft. per bbl.	735	880	1120

Approximately 30 per cent of tar-acid-free motor fuel can be made from the gas oil by recycling, thus bringing up the yield of tar-acid-free motor fuel to a maximum of 33 per cent.

The pressure distillate oil derived from the cracking reaction was subjected to Hempel distillation analysis and fractionated into motor fuel and gas oil bottoms. (Table III)

Table III—Analysis of Pressure Distillate Oil Derived from Cracking Douglas Fir Wood Tar

A. P. I. gravity	19.3	21.1	21.8
Specific gravity	0.9383	0.9273	0.9230
Initial boiling point:			
° F.	93	88	102
° C.	34	31	39
End point:			
° F.	420	420	425
° C.	216	216	218
Unsaturates, per cent	48	...	...

Per cent over	° F.	° C.	° F.	° C.	° F.	° C.
10	284	140	166	74	232	111
20	315	157	324	162	314	157
30	338	170	342	172	340	171
40	377	192	364	184	372	189
48.3	410	210				
50	...	...	396	202	391	199
53.9	420	216				
54.6	...	...	410	210		
55.3	...	...			410	210
58.2	...	...	420	216		
61.0	...	...			425	218

Aldehydes, Trace

Distillation analysis of the motor fuel is given in Table IV.

The gum present in the motor fuel was determined by the U. S. Bureau of Mines method and showed 140 mg. per 100 cc.

The tar acids in the motor fuel were determined and found to average 19 per cent. These tar acids are suitable for antiseptic, disinfectant, and other uses. To produce a finished motor fuel the tar acids should be removed by caustic soda treatment.

A chemical analysis of the motor fuels showed the content of aromatic and unsaturated hydrocarbons to be 97.2 per cent, whereas the paraffin and naphthenes showed a total of only 2.8 per cent. The motor fuels produced from cracking wood tars show a high benzene equivalent (100+ per cent) when tested in an automotive engine—far higher than the usual cracked gasoline obtainable from petroleum, coal, or shale oil.

Distillation analyses of the gas oil or bottoms from the pressure-distillate oil are given in Table V.

Table IV—Distillation Analyses of Motor Fuel from Douglas Fir Wood Tar (A. S. T. M.)

A. P. I. gravity	27.7		30.2		29.2	
Specific gravity	0.8888		0.8751		0.8805	
Initial boiling point:						
° F.	146		137		137	
° C.	63		58		58	
End point:						
° F.	440		436		434	
° C.	227		224		223	
Unsaturates, per cent	38		...		...	

Per cent over	° F.	° C.	° F.	° C.	° F.	° C.
5	184	84	177	81	178	81
10	257	125	258	126	251	122
15	294	146	281	138	285	141
20	308	153	295	146	301	149
25	317	158	309	154	313	156
30	327	164	319	159	322	161
35	332	167	326	163	329	165
40	336	169	332	167	335	168
45	342	172	336	169	341	172
50	348	176	344	173	347	175
55	352	178	349	176	351	177
60	358	181	354	179	356	180
65	362	183	360	182	362	183
70	369	187	366	186	366	186
75	377	192	374	190	372	189
80	384	196	382	194	381	194
85	392	200	392	200	389	198
90	404	207	404	207	400	204
95	419	215	429	221	418	214
97	...	...	436	224	...	...
98	...	...	...	...	434	223
99	440	227	...	...	...	...

Table V—Distillation Analyses of Pressure-Distillate Bottoms from Douglas Fir Wood Tar (A. S. T. M.)

A. P. I. gravity	9.5		10.1		10.3	
Specific gravity	1.003		0.9993		0.9979	
Initial boiling point:						
° F.	455		448		440	
° C.	235		231		227	
End point:						
° F.	835		740		760	
° C.	446		393		404	

Per cent over	° F.	° C.	° F.	° C.	° F.	° C.
5	470	243	456	236	452	233
10	473	245	462	239	474	246
15	480	249	473	245	476	247
20	487	253	475	246	478	248
25	498	259	480	249	488	253
30	508	265	490	254	496	258
35	518	270	502	261	502	261
40	530	277	508	264	510	266
45	545	285	518	270	516	269
50	560	293	540	282	526	274
55	575	302	550	288	540	282
60	598	315	560	293	544	284
65	617	325	584	307	563	295
70	645	341	590	310	582	306
75	672	356	642	339	624	329
80	700	371	660	349	646	341
85	733	390	680	360	668	353
90	775	413	690	365	690	365
95	800	427	720	382	748	398
98	835	446	...	...	760	404
99	...	...	740	393	...	...

Table VI—Comparison of Douglas Fir Wood Tar and Cracked Pressure Distillate

	Based on Distillate from Dehydrated Charging Stock	Based on Dehydrated Charging Stock	Pressure Distillate
	Per cent	Per cent	Per cent
Tar acids	33.35	24.15	22.35
Tar bases	0.80	0.59	0.25
Unsaturated hydrocarbons	62.70	45.34	15.10
Aromatic hydrocarbons	...	...	60.00
Paraffins and naphthenes (by diff.)	...	...	2.30
Aromatics, paraffins, and naphthenes (by diff.)	3.15	2.31	...
Coke and pitch	...	27.61	...

The gas oil or pressure-distillate bottoms make excellent recycle or blending stock for recracking.

A comparison of the composition of wood tar and the cracked pressure-distillate oil was made relative to their content of tar acids, tar bases, and the hydrocarbon groups. The dehydrated wood-tar charging stock was distilled to coke to obtain a clean distillate on which to make the analysis. The percentages were calculated on the basis of the dehydrated wood tar and distillate from dehydrated wood tar. The pressure distillate contained 2.4 per cent water. The percentages were calculated on the basis of anhydrous pressure distillate. The results are summarized in Table VI.

The fraction obtained under dehydrated charging stock and the distillate from it designated as aromatic, paraffin, and naphthene hydrocarbons was too small to make an accurate analysis for the determination of these components. The analysis for hydrocarbon groups was made by the method of Egloff and Morrell.[4] Traces of aldehydes were found in both charging stock and pressure distillate.

Table VII—Products Other than Motor Fuel Derivable from Pressure Distillate from Douglas Fir Wood Tar

Fraction		
	° C.	Per cent
Light solvents	To 154	4.7
Turpentine substitute	154–190	17.0
Pine oil equivalent	190–230	20.0
Pressure-distillate bottoms		36.0
Tar acids		22.3

Analysis of Turpentine Substitute

	Cut containing tar acids	Tar-acid-free
	Per cent	Per cent
Tar acids	12.5	..
Bases	2.0	...
Unsaturated hydrocarbons	23.5	27.5
Aromatics	48.0	57.0
Paraffins and naphthenes	14.0	15.5

Table VIII—Distillation Analyses of Pine Tar Oils

	Pine Tar		Medium Pine Tar	
Specific gravity	1.026		1.072	
A. P. I. gravity	6.3		0.2	
Initial boiling point:				
° F.	271		416	
° C.	133		213	
End point:				
° F.	706		718	
° C.	374		381	

Per cent over	° F.	° C.	° F.	° C.
5	330	165	462	239
10	354	179	470	243
15	377	192	514	268
20	400	204	529	276
25	431	221	572	300
30	465	241	613	323
35	500	260	635	335
40	543	284	652	344
45	583	306	662	350
50	615	324	670	354
55	634	334	675	357
60	652	344	675	357
65	662	350	700	371
70	668	353	708	376
75	683	362	710	377
80	690	365	714	379
85	695	368	718	381
90	702	372	718	381
95	706	374	...	...
96	...	...	700	371
Coke, per cent by weight	4.7		4.5	

Table IX—Cracking of Pine Tars

Operating Conditions

	Pine tar	Medium pine tar
Temperature:		
° F.	815	830
° C.	435	443
Pressure, lbs. per sq. in.	100	80

Summary of Products (Per cent based on tar oil)

Pressure distillate, per cent	60.4	54.0
A. P. I. gravity	21.3	14.9
Specific gravity	0.926	0.9665
Residuum	None	None
Water, per cent	4.2	4.8
Coke, lbs. per bbl.	69	75
Gas, cu. ft. per bbl.	822	940

Distillate within Motor Fuel Boiling Range

Per cent of tar oil	40.9	21.6

Gas Oil

Per cent of tar oil	31.7	59.1

It may be that products derivable from the cracking of Douglas fir tar have greater economic value for other purposes than their utilization for motor fuel and gas oil. Hence the pressure-distillate oil was subjected also to Hempel distillation and fractionated into light solvent, turpentine substitute, pine oil equivalent, and pressure-distillate oil bottoms. A chemical analysis was also made of the turpentine substitute fraction. The results are given in Table VII.

The gum formation in the motor fuel by the usual A.S.T.M.

⁴ Egloff and Morrell, Ind. Eng. Chem., **18**, 354 (1926).

test is approximately 350 mg. per 100 cc. by ordinary refining and can be reduced greatly by special refining.

Table X—Distillation Analyses of Pressure Distillate from Pine Tar Oils (A. S. T. M.)

	PINE TAR	MEDIUM PINE TAR
A. P. I. gravity	21.3	14.9
Specific gravity	0.926	0.9665
Initial boiling point:		
°F.	86	108
°C.	30	42.2
End point:		
°F.	435	420
°C.	224	216

Per cent over	°F.	°C.	°F.	°C.
10	267	131	274	134
20	303	151	324	162
30	328	164	367	186
38	...	...	410	210
40	337	169	420	216
50	348	176	...	...
60	399	204	...	...
63.8	410	210	...	...
67.7	435	224	...	...

Cracking of Pine Tars

Pine tar oils from the destructive distillation of lightwood were subjected to the cracking process. The yields of distillate oil boiling within motor fuel range were approximately 22 and 41 per cent. In the event that the economic situation does not justify motor fuel production from the cracking of pine tar, the cracked products may be fractionated into solvent oil, turpentine substitute, and pine oil equivalent for flotation oils. The distillation of pine tar and medium pine tar which were used in the two cracking tests are given in Table VIII.

The summary of the operating conditions and yields of pressure-distillate oil, coke, gas, and motor fuel boiling-range material and gas oil is shown in Table IX.

The pressure-distillate oils produced from the cracking process were subjected to distillation analysis to determine their motor fuel content. Analyses are given in Table X.

Depending upon the products desired, the pressure-distillate oil may be distilled into motor fuel and gas oil, or solvent oil, turpentine substitute, and pine oil equivalent. The distillation analyses with the percentage yield and properties of these substances are given in Table XI.

A composite sample of the light solvent, turpentine substitute, and pine oil corresponding to motor fuel of U. S. motor fuel specifications was tested for its gum-forming properties by the usual Bureau of Mines method. The determination upon the refined and redistilled product showed 1.193 grams for 100 cc., which is far too high to permit the use of this distillate for motor fuel. It is therefore believed that the cracking of pine tars will be directed towards the manufacture of solvent oils, turpentine substitutes, flotation oils, paint thinners, etc., rather than for the production of motor fuels.

In order to compare the solvent properties of the light distillate (indicated as solvent oil) with other usual solvents, a series of tests was made upon crude rubber. The order of the dispersive power for crude rubber is as follows for the distillates tested: light solvent distillate, turpentine substitute from cracking, wood turpentine (known as spirits of wood turpentine) from the destructive distillation of lightwood, and petroleum ether. It is concluded from this that the light solvent would have wide use as a solvent for crude

Table XI—Distillation Analyses of Products from Pressure Distillate from Pine Tars (A. S. T. M.)

DISTILLATE WITHIN MOTOR FUEL BOILING RANGE			PRESSURE-DISTILLATE BOTTOMS		
	Pine tar	Medium pine tar		Pine tar	Medium pine tar
A. P. I. gravity	31.2	29.6	A. P. I. gravity	6.2	6.5
Specific gravity	0.8697	0.8783	Specific gravity	1.027	1.025
Initial boiling point:			Initial boiling point:		
°F.	158	154	°F.	455	424
°C.	70	68	°C.	235	218
End point:			End point:		
°F.	433	438	°F.	745	735
°C.	223	226	°C.	396	391

Per cent over	°F.	°C.	°F.	°C.	Per cent over	°F.	°C.	°F.	°C.
5	229	109	196	91	5	480	249	448	231
10	272	133	246	119	10	490	254	460	238
15	283	139	268	131	15	500	260	476	247
20	297	147	279	137	20	510	266	492	256
25	304	151	290	143	25	525	274	502	261
30	308	153	299	148	30	545	285	520	271
35	316	158	309	154	35	565	296	538	281
40	321	161	316	158	40	580	304	556	291
45	328	164	324	162	45	600	316	576	302
50	332	167	330	166	50	615	324	594	312
55	336	169	335	168	55	630	332	615	324
60	340	171	343	173	60	650	343	630	332
65	344	173	349	176	65	660	349	647	342
70	347	175	356	180	70	675	357	662	350
75	353	178	362	183	75	682	361	675	357
80	360	182	370	188	80	690	365	686	363
85	367	186	382	194	85	700	371	696	369
90	382	194	393	201	90	710	377	709	376
95	415	213	419	215	95	735	391	724	384
98	...	...	438	226	98	745	396	735	391
99	433	223	...	...					

PRODUCTS DERIVABLE FROM PRESSURE DISTILLATE OTHER THAN MOTOR FUEL AND GAS OIL					
Fraction °C.	Product	Pine tar	Medium pine tar	Pine tar Per cent	Medium pine tar Per cent
To 154	Solvent oil			12.8	8.7
	A. P. I. gravity	41.4	42.0		
	Specific gravity	0.8184	0.8155		
	Initial boiling point	123° F., 51° C.	134° F., 57° C.		
	End point	371° F., 188° C.	393° F., 201° C.		
154–190	Turpentine substitute			21.9	6.2
	A. P. I. gravity	30.1	27.7		
	Specific gravity	0.8756	0.8888		
	Initial boiling point	202° F., 94° C.	208° F., 98° C.		
	End point	396° F., 202° C.	413° F., 212° C.		
190–230	Pine oil equivalent			7.7	10.6
	A. P. I. gravity	18.4	16.0		
	Specific gravity	0.9440	0.9593		
	Initial boiling point	331° F., 166° C.	316° F., 158° C.		
	End point	474° F., 246° C.	495° F., 257° C.		
	Gas oil			17.9	27.0
	A. P. I. gravity	....	....		
	Specific gravity	1.039	1.014		
	Loss			0.1	1.5

rubber, especially as the odor and color are favorable to such use.

In cracking pine tar it must be remembered that the charging stock is so costly as to prohibit cracking the raw material down to coke and distillate. Hence the guiding factor is to crack so that the residue remains suitable for the uses to which the original pine tar is applied. Under these conditions the following distribution of products can be expected from each 100 gallons of charging stock:

	Gallons
Solvent distillate	10
Turpentine substitute	10
Pine oil equivalent	12
Residual pine tar	65
Coke, gas, and loss	3

Cracking of Hardwood Tars

A mixture of tar derived from the thermal decomposition of hickory and oak was subjected to cracking conditions of 90 pounds per square inch pressure and 720° F. (382° C.). A yield of approximately 24 per cent of high antiknock motor fuel was produced. The cracking stock of hardwood tar was subjected to distillation analysis and the percentage of tar acids, tar bases, and neutral oil present were determined by several methods. The data are given in Table XII.

A creosote cut (240° C.) was taken from each of these oils and this cut was extracted for tar acids and bases. (Table XIII)

A summary of the cracking of hardwood tar with the products of pressure-distillate oil, coke and gas, motor fuel, and gas oil is given in Table XIV.

The gas oil or recycle stock may be used directly as a disinfectant or wood preservative, or may be recycled in the cracking process for additional yields of products.

Analysis of the pressure-distillate oil derived from the pressure distillation of the wood tar is given in Table XV.

Analysis of the 420° F. (216° C.) fraction derived from the pressure-distillate oil by Hempel distillation is given in Table XVI.

The distillate boiling within the motor fuel range contained 52 per cent of tar acids and 6 per cent of tar bases.

An analysis of the pressure-distillate bottoms or gas oil derived from the Hempel distillation of the cracked oil is shown in Table XVII.

It is apparent that the tar acid content of cracked distillates from hardwood tar is too high to make it economically profitable to crack the hardwood tars for motor fuels alone. In the thermal decomposition of tar acids, the products are lower molecular weight and lower boiling tar acids, coke, gas, water, and a small percentage of hydrocarbons. From an economic viewpoint, it is believed that it will be most profitable to crack hardwood tars for the simultaneous production of motor fuel and low-boiling tar acids with the manufacture of antiknock motor fuel as a secondary object. The lower boiling tar acids possess higher toxicity than the higher boiling tar acids. In this way the cracking process increases the commercial value of the tars.

Refining of Cracked Distillates from Wood Tars

The refining of cracked distillates from wood tars is similar to the refining of cracked distillates from low-temperature coal tars and shale oils. Where a high percentage of tar acids is present, the tar acids are removed first by treatment with a 20 to 25 per cent solution of sodium hydroxide. Treatment in several steps is desirable for complete removal of the tar acids.

The cracked distillate is then water-washed and treated with dilute sulfuric acid. If the amount of bases present exceeds several per cent, treatment with first a 10 per cent and then a 95 per cent solution of sulfuric acid is desirable. An alternative treatment is the use of 60 to 85 per cent sulfuric acid with no concentrated acid following, and is applied when the percentage of bases is low. The sludge from the acid treatment is withdrawn and the distillate is water-washed and neutralized with sodium hydroxide. The strength of the sodium hydroxide solution may vary from 5 per cent upward—usually 5 to 10 per cent.

Table XII—Data on Hardwood Tar Cracking Stock

DISTILLATION ANALYSIS

	A. S. T. M.	Hempel method
Specific gravity	1.1119	1.1119
Initial boiling point:		
° F.	210	195
° C.	99	91
End point:		
° F.	610	
° C.	321	

Per cent over	° F.	° C.	° F.	° C.	A. P. I. gravity	Specific gravity
5	347	175				
10	405	207	388	198	10.6	0.9958
15	433	223				
20	455	235	440	227	5.5	1.0336
25	465	241				
30	483	251	458	237	1.9	1.0598
35	502	261				
40	515	268	480	249	0.7	1.0692
45	527	275				
50	538	281	517	270	0.1	1.0758
55	545	285				
60	552	289	565	296	..	1.0812
65	562	295				
70	610	321				
75	606	319				
81	570	299				

Coke, per cent by weight, 19.1

TAR ACIDS, BASES, AND NEUTRAL OIL PRESENT IN TAR (Per cent based on tar)

	Tar acids			Tar bases			Neutral oil	
Tar at 240° C.	240° C. cut	Raw oil		240° C. cut	Raw oil		240° C. cut	Raw oil
%	%	%		%	%		%	%
24.5	57.7	14.1		12.7	3.1		29.6	7.3

Table XIII—Distillation of Hardwood Tar

			TAR ACIDS		TAR BASES	
			Cut	Raw oil	Cut	Raw oil
	Grams	Per cent	%	%	%	%
	FIRE AND STEAM DISTILLATION					
Charge	540					
Pyroligneous acid	5	0.9				
Cut, 420° F. (216° C.)	170	32.0	66.4	20.9	3.2	1.0
Cut, pitch	43	8.0	67.6	5.4	2.0	0.6
Bottoms	245	45.2				
Water	14	2.5				
Loss	63	11.4				
Total	540	100.0		26.3		1.6
	VACUUM DISTILLATION					
Charge	594					
Pyroligneous acid	5	0.8				
Cut, 350° F. (177° C.) 6 cm. Hg.	175	29.5	68.0	20.4	1.6	0.5
Cut, pitch	42	7.1	67.0	4.8	1.3	0.3
Bottoms	333	56.0				
Water	10	1.7				
Loss	29	4.9				
Total	594	100.0		25.2		0.8

Table XIV—Cracking of Hardwood Tar

(Mixture of tar from hickory and oak)

OPERATING CONDITIONS

Temperature:	
° F.	720
° C.	382
Pressure, lbs. per sq. in.	90

SUMMARY OF RESULTS (Per cent based on charge)

Pressure distillate, per cent	34.0
A. P. I. gravity	12.4
Specific gravity	0.9833
Water, per cent	2.1
Residuum	None
Coke, lbs. per bbl.	127
Gas, cu. ft. per bbl.	329
Coke, gas, and loss, per cent	65.0
Motor fuel, per cent (tar-acid and tar-base free)	9.9
Tar acids to 450° F. (232° C.)	12.4
Tar bases to 450° F. (232° C.)	1.4
Gas oil or recycle stock	8.0

The distillate is finally distilled in the presence of steam. With some types it is desirable to stabilize the overhead product from the distillation by using a small amount of fuller's earth or activated clay in the still. Distillation over alkaline solutions and mild polymerizing agents also assists in stabilizing the final distillate and lowering the gum content.

Table XV—Pressure-Distillate Oil Derived from Cracking Hardwood Tars (A. S. T. M.)

A. P. I. gravity 12.4
Specific gravity 0.9833
Initial boiling point:
  ° F. 127
  ° C. 53
End point:
  ° F. 420
  ° C. 216

Per cent over	° F.	° C.	H_2O Cc.
10	177	81	22
20	190	88	32
30	228	109	36
40	331	166	
50	378	192	
60	391	199	
70	406	208	
73.1	410	210	
79.8	420	216	
Water, per cent		11.2	

The final product may be treated with a dilute solution of sodium hydroxide, which improves the odor. Final contact with a small percentage of fuller's earth also assists in the stabilization.

As an example of the treatment of a cracked distillate from wood tars, the following is shown for pine tar distillate. The cracked distillate is treated with 10 to 15 pounds of 60 per cent concentration sulfuric acid per barrel of distillate. The sludge is withdrawn. The distillate is then water-washed and neutralized with about 2 per cent of a 10 per cent solution of sodium hydroxide alone or containing litharge dissolved in it. The treated cracked distillate is distilled over about 1 pound of fuller's earth per barrel, using top steam and maintaining the temperature just above that required

to prevent condensation of the steam. A temperature of 121° to 135° C. is satisfactory. The final product may be further stabilized by treatment with a small amount of fuller's earth and is improved in odor by subsequent washing with a dilute solution of sodium hydroxide. After a final water-washing the treatment is complete.

Table XVI—Distillation Analysis of Distillate from Hardwood Tars with Motor Fuel Boiling Range (A. S. T. M.)

A. P. I. gravity 15.4
Specific gravity 0.9632
Initial boiling point:
  ° F. 147
  ° C. 64
End point:
  ° F. 437
  ° C. 225

Per cent over	° F.	° C.	Per cent over	° F.	° C.
5	166	74	55	366	186
10	173	78	60	375	191
15	180	82	65	381	194
20	187	86	70	388	198
25	203	95	75	391	199
30	245	118	80	395	202
35	293	145	85	402	206
40	318	159	90	411	211
45	345	174	95	431	222
50	357	181	98	437	225

Table XVII—Distillation Analysis of Gas Oil (A. S. T. M.)

A. P. I. gravity 1.0
Specific gravity 1.066
Initial boiling point:
  ° F. 432
  ° C. 222
End point:
  ° F. 556
  ° C. 291

Per cent over	° F.	° C.	Per cent over	° F.	° C.
5	435	224	55	462	239
10	437	225	60	468	242
15	439	226	65	473	245
20	441	227	70	479	248
25	444	229	75	486	252
30	447	231	80	497	258
35	450	232	85	514	268
40	453	234	90	539	282
45	456	236	95	549	287
50	458	237	98	556	291

Trace of coke

Sulfonated Oxidation Products of Petroleum as Insecticide Activators[1]

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THE continuous search for cheaper and more effective methods of controlling insect pests has given the chemists a very enticing problem. To a chemist not in intimate contact with entomological problems a general spray mixture for all troubles—a cure-all—would seem to be the product to develop. Upon close study of the variables in spraying the many species of destructive insects, a product that would increase markedly the efficiency of any specific control would be well worth while.

In view of this fact a thorough study of the application of the oxidation products of petroleum to the insecticide field has been conducted for the past four years in coöperation with state entomologists and the Crop Protection Institute. As a result of this work a definite procedure in attacking soft-bodied sucking insects, such as aphis and leaf hoppers, was developed. By the addition of chemically treated oxidation products of Pennsylvania gas oil to a solution of nicotine sulfate, the efficiency of the poison was strikingly increased. For example, where these oxidation products have been

added, at the rate of 1 to 200, to nicotine sulfate spraying solutions, a satisfactory kill has been obtained with only one-third to one-fifth of the nicotine commonly employed when soap is used as a spreader.

The underlying principle is, briefly, the increase of the efficiency, or the activation, of an insecticide by bringing about certain physical changes in the resultant spray mixture. This group of chemically treated oxidation products of Pennsylvania gas oil has been termed "activator" in explanation of its performance in the insecticide field.

Properties Desirable in a Contact Spray

A spray intended for sucking insects should be:

(1) Safe to foliage under all climatic conditions at all effective dilutions with allowance for ample margin of safety.
(2) Easily measured and handled.
(3) Readily miscible with a variety of natural waters.
(4) Toxic to the most resistant individuals of the species of insect sprayed. The final kill may be affected by the following properties: (*a*) absolute lethal effect, (*b*) coverage on the

foliage, (c) adhesion to the insect's body, (d) penetration into an insect's body, (e) service as a carrier of other spray materials.

The Activator Principle

The exact function of spreading and wetting has not been clearly defined. One thing certain is that a material causing death of insects will work the more quickly and surely if it is able to make a definite close contact with the vital organs. Picturing, therefore, the waxy body of an aphis, what is the best method of introducing the insecticide? The spray mixture holding the toxic material must be of such chemical and physical structure as to reach and enter the tracheae of the insect and thence gain access to its vital cells. Whatever may be the mechanism by which the poison thus conveyed is able to bring about the insect's death, the fact remains that the performance of the insecticide is profoundly influenced by the physical nature of the spray liquid. The function of the activator is to bring about precisely such desirable effects. The principle that it serves may be summed up as follows: (1) To wet the foliage and the insect's body effectively; (2) to carry the insecticide; (3) to penetrate to vital cells; and (4) to exhibit in itself strong toxic qualities against the insect.

Entomological Technic

In studying the effects of activators and the toxic substances combined with them, every care has been taken to secure maximum accuracy. Such factors as temperature, humidity, and the like have been recorded in detail throughout. In the laboratory experiments many duplications have been made, using thousands of insects. In all cases laboratory studies have been followed by long series of field experiments under different climatic and geographical conditions. These results have been repeatedly checked and counterchecked. A complete entomological report of this extensive research will be published shortly by the Crop Protection Institute.

Process

A great number of samples have been made for field tests in this research. Emulsions of oxidation products of various boiling-point ranges and the addition of chemical groups have given a great variety of results. Although several of these have been encouraging, the product formed by the following process has given most satisfactory and consistent results in field tests:

OXIDATION—A straight distillate of Pennsylvania crude of 38° Bé. was reacted with oxygen by the James catalytic vapor phase oxidation process.[2] The oil was vaporized and passed over a catalyst with a definite volume of air after

[2] James, *Trans. Am. Inst. Chem. Eng.*, **14**, 189, 201 (1922); Bitler and James, *Chem. Met. Eng.*, **35**, 156 (1928).

which the oxidation products were condensed. This condensate consists of a mixture of alcohols, aldehydes, ketones, and acids, saturated and unsaturated, both simple and complex, together with unaltered hydrocarbons.

The proportion in which these constituents were formed in the mixture can be controlled quite accurately by the screen temperature and oil and air flow. In the final product about 75 per cent of the hydrocarbons have reacted.

SULFONATION—Sulfuric acid was added slowly to the oxidized gas oil, the mixture being cooled by means of a water jacket. The reaction mixture was then decomposed with water. This step removed the excess of sulfuric acid and hydrolized a great percentage of the sulfonates and all the sulfates. After settling, the dilute acid was drawn off. The product was then neutralized with sodium hydroxide and allowed to settle to remove the salt solution.

Chemical and Physical Properties

The product contains about 40 per cent oxygen, analyzed by the combustion method, and about 1.5 per cent sulfur by bomb and Eshka's mixture. Empirical chemical tests have been found quite satisfactory for control and assurance of a uniform product. The product has been held at 50° and −18° C. for varying lengths of time with no evidence of chemical change.

The physical properties, with particular reference to insect control, have been studied quite thoroughly. The activator is a clear maroon-colored liquid. It is easily miscible with water, forming an opalescent emulsion. The wetting, spreading, and other allied entomological properties have been outlined above. In this regard a 1 per cent solution of the product is of itself toxic to various aphids, leaf hoppers, and red mites.

The greatest field for service of this material is as an activator. For example, nicotine sulfate, not fully effective alone, is commonly used in the proportion of 1 to 800 with soap added as spreader. By omitting soap and using 0.5 per cent of the activator instead, the necessary concentration of nicotine is reduced as low as 1 to 4000.

Future Possibilities

Tests indicate that other materials of a high order of toxicity, such as pyrethrum, can be made more efficient by using an activator, although data in hand are not so extensive as those referring to the nicotine combinations.

It is difficult at this time to predict the extent to which the principle of activating insecticides will affect the control of other insects and the development of other spray materials. Its numerous applications should provide many interesting problems.

Termite Investigations Committee

The extensive damage done by the termite, or white ant, has led to the formation of the Termite Investigations Committee, which will be supported in its investigations by a large number of Pacific Coast corporations. The general plan is to combine all the data relating to termites and termite damage on the Pacific Coast through the coöperation of these contributing organizations. A large number of scientific investigations will be furthered and directed by an advisory council consisting of members of the faculty appointed by the president of the University of California.

A three-year program is planned under eleven subcommittees chosen with respect to special phases of the investigation. The chairman of the subcommittee on chemistry is Merle Randall, University of California, Berkeley, Calif., and under this committee a laboratory has been established at the university, with T. C. Doody as chemical engineer. This laboratory will study the

relative merits of chemical methods of termite control and the effectiveness of wood preservatives against these pests. The California State Insecticide Laboratory, directed by Firman Thompson, is in coöperation.

Since the problem is of general interest, some of the tests will be conducted under the severe conditions of the Panama Canal Zone by T. E. Snyder, senior entomologist of the Bureau of Entomology, Department of Agriculture.

The subcommittee on chemistry is anxious to gather the fullest possible information relative to preparations or methods for termite control. The names, addresses, and claims of manufacturers or agents for such preparations, and any service records available on their products as applied to termites are especially desired. Any information on termites will be gratefully received and put in the hands of the proper subcommittee.

A Study of Auto-Ignition Temperatures

III—(a) Mixtures of Pure Substances, (b) Gasolines[1,2]

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A S THIS study is concerned primarily with an investigation of the relationship of auto-ignition temperature to knock or other characteristics of motor fuels, a brief review of this application may be presented.

To Constam and Schläpfer[1,*] and later Moore[2] are due credit for attempting to associate auto-ignition temperatures with the suitability of a fuel for use in the internal-combustion engine, especially of the Diesel type. Whereas the direct test in the engine gave information as to the suitability of the fuel for that particular type of engine, it was unsatisfactory from the standpoint of time required, ease of manipulation, cost, and control of the variables entering the test. Since ignition in the Diesel engine takes place as a result of the high temperature developed through adiabatic compression, it was evident that if the temperature attained was too low rapid combustion would take place when the liquid fuel was injected into the hot, highly compressed air in the cylinder. The important factor under consideration was the temperature necessary to ignite the fuel. From the equation

$$T_2 = T_1 \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}$$

knowing the initial temperature, T_1, and the initial and terminal pressures, P_1 and P_2, the terminal temperature, T_2, could be calculated for any particular engine. If the temperature at which a given combustible liquid would ignite were known, then it could be readily determined, by applying the above formula to a given engine, whether or not a given liquid fuel would ignite properly in the engine. However, no data being available on the ignition temperature of such liquid fuels as were used in the Diesel engine, it was necessary to develop apparatus for a comparative test which would give the desired information. With the apparatus of Holm[3] for guidance, Moore[2] evolved a form of apparatus and technic suitable to his purpose, which has been followed more or less closely by all subsequent investigators except the authors. By means of his "ignition meter" Moore[2] determined the auto-ignition temperatures of a number of substances and from these temperatures estimated their suitability for use in the Diesel engine. The results so obtained were not di-

The auto-ignition temperatures of a number of mixtures of pure substances and gasolines of known knock rating have been measured. The mixtures selected represented a wide range of fuel characteristics and were chosen for their value in working toward the more complex mixtures represented by the gasolines. Three general types of curves showing the relationship between composition and auto-ignition temperature were obtained—one showing a minimum, another showing a maximum, and a third showing both a maximum and minimum. Straight-run gasolines show a regular relationship between knock rating and auto-ignition temperature, the auto-ignition temperature changing toward an optimum with improved knock rating. Cracked gasolines do not show a distinct relationship, but give a characteristic curve. The effect of lead tetraethyl is to raise or lower the auto-ignition temperature toward the optimum. A working hypothesis to correlate auto-ignition temperatures and knock is advanced.

ship between the auto-ignition temperature of a gasoline for use in an engine operating on the Otto cycle and its tendency to knock directed attention to the determination of the auto-ignition temperature of gasolines of known knock rating. That such a suspicion was not unfounded and had been conceived by others was shown by an examination of the literature. For example, Ricardo[4] states that one of the factors determining the tendency of a fuel to knock is the "self-ignition" temperature of the fuel-air mixture. Brown[5] has shown that

$$\frac{\text{Rate of pressure rise}}{\text{Absolute auto-ignition temperature}} = \frac{1}{\text{H. U. C. R.} \times \text{constant}}$$

The relationship of auto-ignition temperature to knock has also been discussed by Egerton and Gates,[6] Tanaka and Nagai,[7] Guiselin,[8] Ormandy and Craven,[9] Weerman,[10] and others. No data are available, however, on the auto-ignition temperature of gasolines whose knock ratings have been determined on an experimental engine according to some generally accepted procedure.

The study of the mechanism of combustion of gasolines and their peculiar behavior in the internal-combustion engine has always been confronted with difficulties of considerable magnitude. One can hardly hope to arrive at a satisfactory understanding of the complex reactions which take place when the characteristics of the raw material are so little known. When the exact composition of a given gasoline under investigation is not known, the experimental results will be difficult to interpret and more qualitative than quantitative. Obviously investigations should begin back among fundamentals by a study of pure substances, then known mixtures of pure substances, and thence to the more complicated mixtures as represented by gasolines. With that principle and in that spirit these researches have been undertaken. Previous papers[11] give the results of a study of the auto-ignition temperatures of a wide range of pure substances of practical or structural organic interest. Additions are constantly being made to this list, but sufficient data have been gathered to justify proceeding to the study of mixtures of

rectly comparable with performance in a given engine, but might be equated by means of a constant for each set of engine conditions. This, however, is disputed by Tausz and Schulte.[22] The work of Moore,[2] carried out less than twelve years ago, was the first positive attempt to determine the suitability of a fuel for use in the internal-combustion engine through a measurement of its auto-ignition temperature.

Although the authors originally undertook a study of auto-ignition temperatures for their abstract value, the suspicion or subconscious urging that there might be a relation-

varying degrees of complexity. The results of a study of some of these mixtures are here presented.

Experimental Procedure

The apparatus and procedure used are those previously described by the authors[11a] except that it was not found necessary to use auxiliary alternating current as a means of obtaining delicate temperature control.[11b]

Study of Simple Mixtures

A study of the auto-ignition temperature of simple mixtures is related not only to fuels such as are used in the internal-combustion engine but to many other fields as well. The widespread use of certain chemicals, such as carbon tetrachloride, to extinguish fires or to reduce the inflammability of various solvents has suggested the study of the effect of carbon tetrachloride upon the auto-ignition temperature of various inflammable liquids such as benzene. Egerton and Gates[12] found a lowering of 30° to 40° C. of the auto-ignition temperature of gasoline on the addition of carbon tetrachloride. According to this observation, gasoline (vapor-air mixture) might become more inflammable instead of less inflammable when carbon tetrachloride is added to it. The effect of knock inducers and suppressors is a question which has not been definitely decided. The consensus of opinion, among previous observers, is that in general knock inducers lower and knock suppressors raise the ignition temperature of a fuel,[13] but this statement is not without contradictions.[14] Egerton and Gates[6] state that the ignition temperatures of mixtures are usually closer to those of the lower igniting component. This statement is only partially confirmed.

The curves of Figure 1 indicate the effect of adding carbon tetrachloride and diethyl ether in varying amounts by volume to benzene. The addition of carbon tetrachloride to benzene gives results similar to those reported by Egerton and Gates[12] for gasoline. Carbon tetrachloride itself could not be caused to ignite in the apparatus at any temperature available (1000° C.). If it can be ignited at all, its auto-ignition temperature is well above 1000° C. The presence of 5 per cent by volume of benzene does not render it ignitible. However, when the concentration of benzene reaches 10
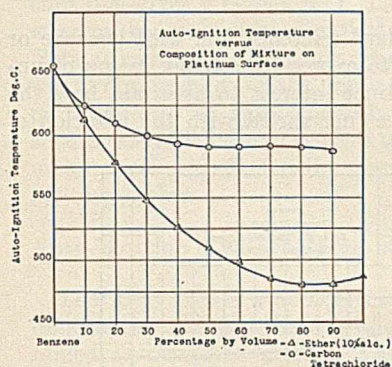
Figure 1

per cent by volume, the mixture ignites readily with a sharp flash at a temperature (68° C.) below the auto-ignition temperature of pure benzene. Based upon the properties of carbon tetrachloride, it is natural to assume that when added in increasing amounts there would be a rapid rise in the auto-ignition temperature and that the addition of a comparatively small amount would render the mixture non-ignitible.

The fact that carbon tetrachloride containing 10 per cent of benzene has a lower ignition temperature than benzene is of significance in connection with the use of carbon tetrachloride in fire extinguishers, dry cleaners, etc., for such a mixture may be more inflammable than the pure substance even though it contains 90 per cent carbon tetrachloride. The addition of diethyl ether to benzene produces a similar, but much more marked, effect. At a concentration of approximately 85 per cent by volume of ether and 15 per cent

by volume of benzene a minimum auto-ignition temperature is obtained. Although carbon tetrachloride and diethyl ether have quite different properties, they both have the same general effect on benzene, both exhibiting a minimum auto-ignition temperature although the minimum in the case of benzene–carbon tetrachloride is not so pronounced. To what this minimum is due and its significance are at present matters of conjecture.

Figure 2 shows another type of auto-ignition temperature vs. composition curve. Both a maximum and a minimum are exhibited when acetic acid or p-xylene is added to absolute alcohol in increasing amounts. It is believed that this is the first time this type of curve has been observed.

Figure 2

The fact that both a maximum and a minimum are obtained would seem to preclude any simple explanation. This cannot be due to any vapor pressure effect, as neither curve bears any relation to the vapor pressure curves of either mixture; nor can it be due to compound formation, solubility, or any other factor usually considered in the case of curves which exhibit abnormalities in properties which should otherwise be additive.
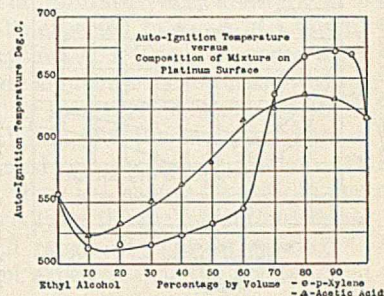
Edgar[15] has suggested the use of mixtures of normal heptane and isoöctane (2,2,4-trimethylpentane) as a means of rating motor fuels. He found that by using mixtures between the limits of 60 per cent normal heptane and 40 per cent isoöctane, and 40 per cent normal heptane and 60 per cent isoöctane the knock rating of any fuel could be expressed in terms of these mixtures. Figure 3 shows the auto-ignition temperature of mixtures of these two substances. Although similar in composition, structure, and vapor pressure, one of them, n-heptane, knocks readily in the engine while the other, isoöctane, is quite free from any such tendency. In this case the curve is quite regular. This relationship is of some significance in correlating knock and auto-ignition temperature, as the auto-ignition temperatures are nearly additive as in the case of knock rating.

Relation of Auto-Ignition Temperatures to Detonation

It has already been pointed out that many observers have suspected or noted a general qualitative relationship between auto-ignition temperatures and the detonating characteristics of fuels. For example, benzene is a fuel with a high auto-ignition temperature (A. I. T.) (656° C. on platinum) and shows but little tendency to knock.[20] Diethyl ether, on the other hand, has a low A. I. T. (491° C. on platinum) and knocks badly in a motor.[20] On

Figure 3

the basis of this and similar observations, it was assumed that fuels of high A. I. T. would show little tendency to knock while fuels of low A. I. T. would knock readily. Unfortunately, however, this simple relationship is not strictly correct, as many substances do not occupy their proper place on a curve relating A. I. T. and
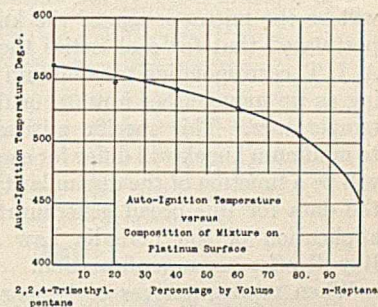
knock rating. In an attempt to arrive at any definite relationship between A. I. T. and knock, the authors have been somewhat handicapped by two facts. First, the knock rating of a number of pure substances is unknown to the authors, no comprehensive list having been published i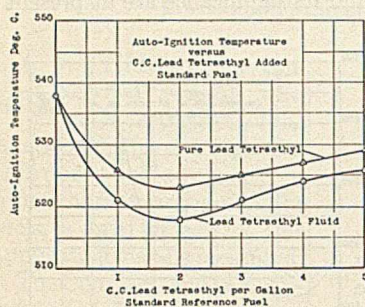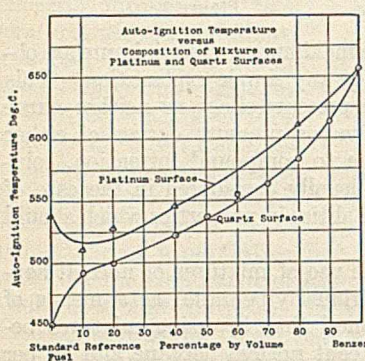n the literature. Second, such knock ratings as have been published are dependent on the test condition.[16,17,18] However, the data of Ricardo[4] have shown that ethyl alcohol is the best fuel in the list of pure substances given. The A. I. T. of ethyl alcohol is 557° C. It appears from a comparison of the list of A. I. T. already published[11] with the results of Ricardo that pure substances have a maximum antidetonating value when the A. I. T. is in the vicinity of 557° C. Accordingly, in the series benzene-toluene-xylene we might expect xylene (618° C.) to detonate less than toluene (633° C.), which in turn might be expected to detonate less than benzene (656° C.). Such an order seems to hold for any given series of homologous compounds, but it cannot be used accurately to compare substances that are not closely related in structure and properties. In the n-hydrocarbon series the order would be reversed—i. e., pentane would show the least tendency to knock, followed by hexane, heptane, etc. However, the absence of published data on the detonating characteristics of pure substances makes it impossible to confirm the above deduction or arrive at generalizations evaluating knock and A. I. T. of pure substances. It is postulated, however, that in any homologous series the A. I. T. and the knock rating will pass through or move toward or away from a maximum or minimum as one moves up or down the series. It is also postulated that the curve of A. I. T. versus number of carbons will parallel the curve of knock rating versus number of carbon atoms, or the A. I. T. curve will be the mirror image of the knock curve. It is further postulated that for each series there will then be a critical A. I. T. corresponding to minimum knock, the knock increasing as we move either upward or downward away from this temperature. This specific critical A. I. T. corresponding to minimum knock will differ for each series and the difference will be a function of the dissimilarity of the series. Although the data for this broad generalization are scanty, the wide application of the Periodic Law and the observations of Boyd[19] offer some confirmation.

When representatives of two or more homologous series are present in a mixture, it seems practically impossible at present to predict the A. I. T. or knock of the mixture. Gasolines are complex hydrocarbon mixtures, the composition being unknown in most cases. They may also differ widely as to the structure of the individual components. Whereas the knock ratings of pure substances are not available, gasolines whose knock rating has been determined according to certain relative standards for a given engine and conditions

Figure 4

Figure 5

are available. If there is any relation between knock rating and A. I. T. it should manifest itself in the form of a simple curve. If the gasoline is composed of members of widely different series, then the A. I. T. would not necessarily be related to the knock by any simple curve.

Determination of Knock Rating

A number of gasolines of varied composition were obtained and their knock ratings determined as follows: A modified one-cylinder Lockwood-Ash engine, compression ratio 7:1, equipped with a Prony brake, tachometer, and special carburetor to give a constant fuel-air mixture over a wide range of throttle opening, was used. The engine was run at constant speed (1200 r. p. m.) with the intake air preheated to 60° C. and the cylinder jacket outlet water temperature maintained at 68° C. First a reference fuel (a straight-run midcontinent gasoline) was run in the engine. The throttle was slowly opened until an audible knock was heard. A mercury manometer, with an arbitrary scale and attached to the intake air line, was used to measure the throttle opening. Immediately after the reference fuel had been run, the carburetor was drained and filled with the fuel to be tested. The throttle was again opened slowly until the unknown fuel knocked with the same intensity as the standard reference fuel. The observed manometer scale reading of the unknown fuel was subtracted from that of the standard and the difference was then translated to percentage of benzene or cubic centimeters of lead tetraethyl per gallon which must be added to the reference fuel to cause it to knock at the same throttle opening as the unknown fuel. This translation was effected by means of a throttle calibration curve which had been previously determined by actually adding benzene or lead tetraethyl to the standard fuel and evaluating the blended fuels as described for the unknown fuel.

Effect of Benzene and Lead Tetraethyl on Reference Fuel

As blends of the standard reference fuel with benzene or lead tetraethyl are used to express the knock rating of unknown fuels, it is of distinct interest to ascertain how the A. I. T. of the reference fuel varied with the addition of
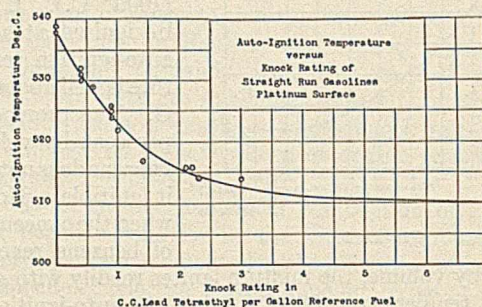
Figure 6

benzene and lead tetraethyl in increasing amounts. Figure 4 shows the effect on the A. I. T. of adding various amounts of pure lead tetraethyl and lead tetraethyl fluid (lead tetraethyl in ethylene dibromide). In the case of the lead tetraethyl fluid the amount taken is expressed in terms of pure lead tetraethyl. The surface used was platinum-lead alloy. It will be observed that lead tetraethyl dissolved in the ethylene dibromide has a greater effect on the A. I. T. of the standard fuel than the same amount of pure lead tetraethyl. Egerton and Gates[12] have shown that the decomposition products of the lead tetraethyl are more effective than pure lead tetraethyl itself. Both curves show a distinct minimum at about 2 cc. of lead tetraethyl and are practically

parallel over the essential portions. It is important to note that, contrary to Egerton and Gates, the effect of lead tetra-ethyl is to lower and then raise the A. I. T. of the fuel, but within the range plotted it did not raise the A. I. T. to the original value for the pure fuel. However, a concentration of 250 cc. lead tetraethyl per gallon gave an A. I. T. above that of the original fuel. It should be noted also that there is a tendency for the curves to flatten out in a relatively narrow range of A. I. T. This effect of lead tetraethyl to bring the fuel to within a certain range of A. I. T. will be developed in subsequent curves.
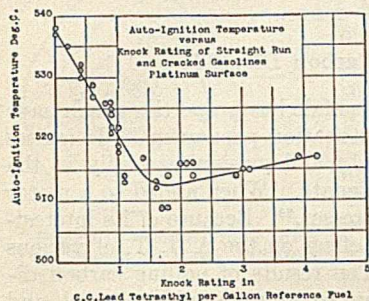
Figure 7

Figure 5 shows the effect of adding benzene in increasing amounts to the standard fuel. Two types of surfaces were used—one, platinum, of high catalytic activity, and the other, quartz, of low catalytic activity. It has been pointed out in a previous paper[11] that the nature of the surface used is very important in measuring A. I. T., and that, all other factors being equal, the A. I. T. would be higher on surfaces of greater catalytic activity. This is illustrated in Figure 5. It has also been shown previously[16] that the catalytic effect is not the same for all substances. The same substance may give widely different A. I. T.'s on surfaces; for example, in the case of nitrobenzene the A. I. T. is 556° C. on platinum and 513° C. on silver. On the other hand, the results on two different surfaces may be identical, the A. I. T. of aniline on platinum and silver being identical at 620° C. The curves in Figure 5 illustrate this phenomenon. The standard reference fuel gives different A. I. T.'s on platinum and quartz, whereas benzene gives identical results on these surfaces. This accounts for the convergence of the two curves, but would not account for the minimum in the case of the platinum surface. It has frequently been observed that those substances which show the least tendency to detonate in the motor are least affected by change in the character of the igniting surface.

Auto-Ignition Temperatures of Straight-Run Gasolines

The A. I. T.'s of a number of straight-run gasolines were determined and compared with their knock ratings determined as described above. The gasolines were chosen at random, their only common characteristic being that they were all straight-run and conformed to the Navy specifications for motor gasolines. The resulting curve is given in Figure 6. The relationship is quite regular, the various points lying on a smooth curve. For gasolines of low knock rating, below approximately the equivalent of 2 cc. of lead tetraethyl per gallon, the curve is very nearly straight. It seems to be almost horizontal for high knock ratings, showing that the A. I. T. is less affected with increase in knock rating. The curve also approaches a minimum A. I. T. in the vicinity of approximately 510° C. As has been previously outlined, there exists for each homologous series a critical or optimum A. I. T. corresponding to a maximum of antiknock characteristics for that particular series. Apparently the optimum does not correspond to the same number of carbons for any particular series. The critical A. I. T. for the straight-chain normal saturated hydrocarbons is estimated to be approximately 500° C. (on platinum), which is below the critical A. I. T. for most gasolines.

Cracked Gasolines

A number of gasolines of widely different knock rating were procured from various sources and the A. I. T. on platinum of high catalytic activity of each was determined. The resulting curve is shown in Figure 7. In analyzing this curve a number of factors must be taken into consideration. The wide variation in composition of the gasolines and the many different series of saturated and unsaturated compounds present would be expected to result in a mixture or combination of many optima A. I. T.'s. However, since the influence of one series on another is as yet unknown, no predictions can be made as to specific effects. Furthermore, the inherent error in allowing for the catalytic effect of the surface must be considered because the effect is not constant for all series. Finally, there is a chance for error in measuring knock rating, especially as the fuel-air ratio does not remain constant over all ranges of throttle opening.[18] For these reasons it was not expected that the points would fall so as to make possible a smooth curve joining all of them. Because of the wide scattering of the points, some difficulty was experienced in attempting to draw a curve which would be representative. When, however, a curve was drawn which had the points well distributed, it was found to bear resemblances to other curves such as are shown in Figures 4 and 5—i. e., the type of curve having a minimum. Samples of gasoline obtained from other laboratories, where different methods of measuring detonation are used, gave the same general type of curve.

Catalytic Effect of Surface on A. I. T. of Gasolines

In view of the marked effect of composition of the igniting surface on the A. I. T., it seemed desirable to determine the A. I. T.'s of a given set of gasolines using several different surfaces. The results of such a study are shown in Figure 8.
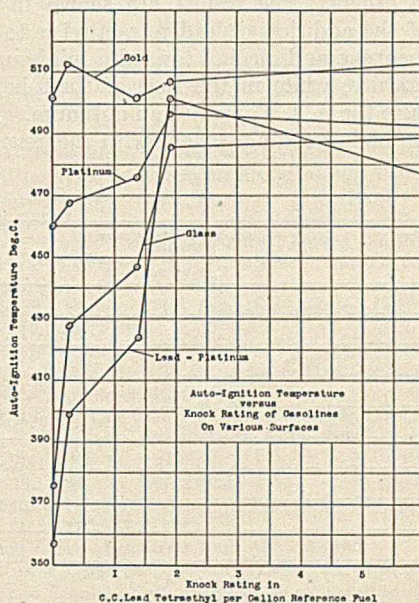
Figure 8

The surfaces were selected on the basis of difference in catalytic activity as shown by previous experience. The gasolines were selected on the basis of wide differences in composition and were those prepared by the Texas Company and sent to various laboratories to be rated on the basis of knock. Their knock ratings were determined by the method previously described. The importance of the catalytic effect of various surfaces when studying gasolines is well illustrated by these curves. Gasolines that detonate readily are very sensitive

to the catalytic effect of the igniting surface, whereas gasolines that do not detonate readily (that is, have a high knock rating) are but slightly affected by the nature of the surface. As the knock rating improves the A. I. T. moves upward
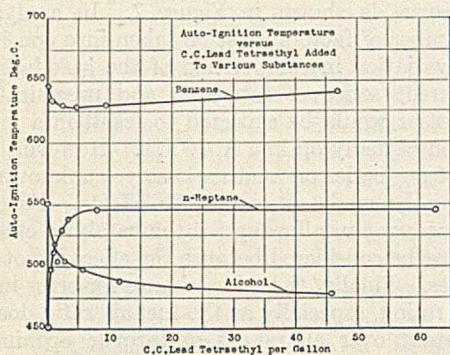
Figure 9

toward an optimum. The net effect is a series of curves which are concave downward and become horizontal in the region of the optimum temperature.

Effect of Lead Tetraethyl on Pure Compounds

Various investigators have shown that the effect of lead tetraethyl is to raise the A. I. T. of a given fuel. The effect of lead tetraethyl has already been shown in the case of gasolines. However, in view of the complex nature of gasolines and the fact that the A. I. T. obtained is only an average of the components present, it was decided to study the effect of lead tetraethyl on several pure liquids. The three liquids selected—benzene, n-heptane, and ethyl alcohol—were chosen because of their different A. I. T.'s, benzene has a high A. I. T., n-heptane a low A. I. T., while that of ethyl alcohol lies between the others. The results are shown in Figure 9. The effect of the addition of lead tetraethyl is to lower the A. I. T. of benzene and alcohol toward a minimum or optimum temperature, while in the case of the n-heptane, the effect is to raise the A. I. T. toward an optimum. The effect here seems to be in good agreement with the general theory postulated.
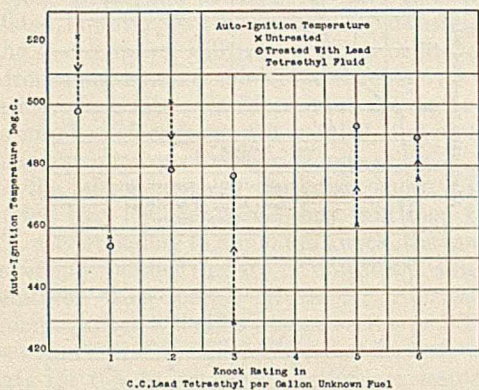
Figure 10

Effect of Lead Tetraethyl on Gasolines

According to the experimental data thus far obtained, the effect of lead tetraethyl on a substance of high A. I. T. is to lower the A. I. T., while in the case of a substance of low A. I. T. the effect is to raise the A. I. T. It was decided, therefore, to study the effect of lead tetraethyl on gasolines of known knock rating. Six gasolines of widely different knock rating were obtained from the Ethyl Gasoline Corporation.

The A. I. T. of each was determined. To each gasoline was then added sufficient lead tetraethyl to give it the same knock rating as the reference fuel—that is, to give equal antidetonation characteristics to all six. The results are shown in Figure 10. The effect of the lead tetraethyl on the first three gasolines (rated as fair) is to lower the A. I. T. while on the remaining three (rated as poor) the effect is to raise the A. I. T. This is in accordance with the action postulated, that the A. I. T. is raised or lowered toward the optimum, as the case may be, on addition of lead tetraethyl. As the gasolines are brought within the range of equal antidetonating characteristics, the A. I. T.'s are brought within an equally narrow temperature range.

Effect of Carbon Disulfide

As a motor fuel carbon disulfide has properties which have long puzzled students of detonation phenomena. It ignites very readily in air (149° C.) and pre-ignites badly in the motor,[20] but it does not detonate. When added to a motor fuel it acts as a knock suppressor.[20] Because of its interesting behavior, therefore, its effect on the A. I. T. of various substances was studied. The results of adding carbon disulfide in increasing amounts to benzene, ethyl alcohol, and ether are shown in Figure 11. The general shape of the curves for these three substances is as should be expected from the general theory; that is, the effect of the carbon disulfide is to change the A. I. T. toward an optimum temperature.

Discussion of Results

In determining the A. I. T. of a pure liquid the composition of the drop striking the igniting surface will have the same composition as the drop leaving the needle. The only change taking place will be in the size of the drop. As the time interval between leaving the needle and striking the surface is very small (less than 1 second), this change is probably extremely small. Again in passing through the heated zone, before striking the igniting surface, a slight thermal decomposition may take place. However, this factor is probably also negligible in view of the small time interval.
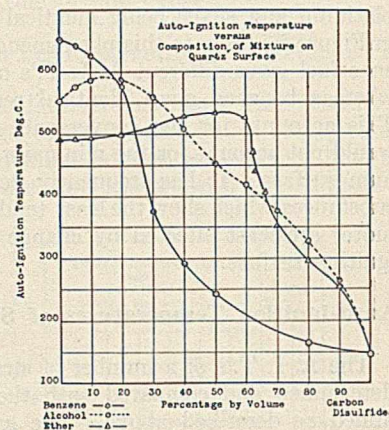
Figure 11

In dealing with mixtures of liquids of widely different vapor pressures there exists the possibility that, owing to fractional distillation, the composition of the drop striking the surface will not be the same as that leaving the needle. As the change in A. I. T. with composition is being measured, this factor may become important, the extent to which this must be taken into consideration will depend on the combination of liquids. In the case of such mixtures as 2,2,4-trimethylpentane and n-heptane (Figure 3) it is negligible as both substances have practically the same vapor pressure; so it may be assumed that the drop suffered no essential change in composition in approaching the surface, and that the curve obtained is a true one for the conditions. With some gasolines this factor is probably more pronounced and does alter the curves. However, this effect is probably small

and not sufficient to affect the fundamental character of the curves. With other mixtures, especially those containing diethyl ether, the effect is probably greater, but nevertheless not enough to change the basic character of the curve.

It is fully realized in all this work that a very important factor—i. e., the fuel-air ratio—is apparently unknown. This is, however, not strictly so. The instant the liquid leaves the needle a film of vapor begins to form around the spheroidal drop. In approaching the igniting surface, through the heated zone, two processes are taking place—(1) increase in the thickness of the fuel vapor film surrounding the drop, and (2) diffusion of air (O_2) into the fuel film and diffusion of the fuel vapor into the surrounding air (O_2).
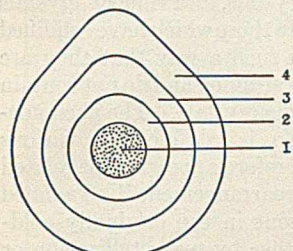
Figure 12—Condition of Drop Just before Striking Igniting Surface

The condition of the system immediately prior to striking the igniting surface may be represented by Figure 12. In the figure, (1) represents the core of unvaporized liquid, (2) represents a series of layers of vapor too rich to ignite, (3) consists of a series of layers whose composition is within the explosive limits for the system, and (4) is composed of a series of layers of films too lean to ignite. Upon striking the igniting surface layer (4) is displaced by impact with the surface, thereby exposing the series of films (3), which ignite. The heat of the reaction and that of the plate vaporize the core (1) and the high turbulence increases the diffusion causing the combustion of the remainder. During this period cracking unquestionably takes place, especially in the rich films. The time interval during which these series of reactions take place is so small that for all practical purposes, based upon numerous observations, the reaction may be considered instantaneous. Whereas the explosive limits vary with different substances, there is a fuel-air ratio of minimum ignition temperature.[13,21] Somewhere in the series of concentric films in region 3 such a fuel-air ratio exists. Assuming that the temperature of the films is nearly uniform, this film will accordingly be the first to ignite. Since the results reported are the lowest temperatures at which a drop may be caused to ignite, it may be assumed that, within the limits of the apparatus, the A. I. T. reported will be approximately the ignition temperature of the fuel-air ratio of lowest ignition temperature. Whereas for many systems this ratio is unknown, the apparatus gives the temperature required to ignite such a ratio. As might be suspected, the ignition temperature of the fuel-air ratio of minimum ignition temperature will depend upon the composition of the igniting surface. This has been demonstrated in previous papers.[11] A comprehensive discussion of this phase of the subject, however, goes far into the field of catalysis, which is apart from the general purposes of this paper, and as it has already been discussed in a general manner,[11] nothing further need be added at this time.

Conclusions

1—The effect of lead tetraethyl is to raise or lower the auto-ignition temperature of pure substances and gasoline as toward an optimum auto-ignition temperature corresponding to decreased detonation characteristics.

2—Straight-run gasolines show a regular relationship between auto-ignition temperature and knock rating. The curve is a straight line in the range of greatest usefulness and interest.

3—Cracked gasolines do not show so regular a relationship, but give a characteristic curve similar to certain mixtures of pure substances.

4—For each homologous series there will be an optimum composition corresponding to a minimum knock rating. Similarly for each homologous series it is predicted there will be an optimum composition corresponding to minimum or maximum auto-ignition temperature, which in turn corresponds to minimum detonation characteristics. Some homologous series pass through a maximum and others through a minimum auto-ignition temperature. Depending on the nature of the series, this maximum or minimum auto-ignition temperature will correspond to minimum detonation characteristics. This accounts for the close relationship between knock and auto-ignition temperature in the case of straight-run gasolines. In the case of cracked gasolines, consisting of representatives of many homologous series, a number of optima will be represented giving rise to a concealed or complex critical auto-ignition temperature. This makes difficult the demonstration of a definite relationship between knock rating and auto-ignition temperature in the case of cracked gasolines.

5—In accordance with the above, the auto-ignition temperature will move upward or downward with improvement in knock rating through the addition of lead tetraethyl or other knock suppressors.

6—Lead tetraethyl fluid showed greater activity than pure lead tetraethyl.

7—Whereas the fuel-air ratio undergoing initial ignition is not known definitely, no attempt having been made to determine the same directly, nevertheless its ignition temperature is probably measured. The temperatures reported are thought to be the ignition temperatures of the fuel-air ratio having the minimum ignition temperature. Accordingly the term "auto-ignition" may be revised and "relative ignition temperature" substituted, the term "relative" being appropriate because the ignition temperature is dependent upon a number of factors which must be fully stated for each reported value.

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German Production of Nitric Acid—The I. G. Farbenindustrie A. G. and the cyanamide works at Piesteritz and Trostberg in Bavaria dominate German development in producing nitric acid by oxidation of ammonia. Both activated iron oxide and platinum are used as catalysts. The chief interest of the German dye trust in producing nitric acid by ammonia oxidization lies in its subsequent manufacture of calcium nitrate. This is manufactured at Oppau and Merseburg. Germany's annual production of nitric acid, exclusive of that made by the dye trust for calcium nitrate manufacture, is approximately 85,000 metric tons.

Crystalline Changes in Copper Due to Annealing[1]

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Crystalline changes upon annealing a rod of cold-worked copper have been investigated using a strong etching reagent. The laminated structure of etched crystals of copper which because of its regularity is probably due to some physical property has been photographed at relatively high magnification. Two recommendations are made for further work.

IN ORDER to make copper suitable for certain purposes, it is sometimes necessary to increase its tensile strength by cold-working. Cold-working of a metal produces deformations and sets up strains by the very nature of the process. Strains are relieved by giving the metal a suitable heat treatment or annealing. By annealing is understood all heating of the specimen in the equilibrium area of its existing phase. Annealing causes the grains to grow in size; consequently there is a diminution in the total number of grains, the small grains disappearing at the expense of the larger grains. Annealing causes the recrystallization of the mass.[3] This recrystallization increases with increase of temperature and time. Thus, it may readily be seen that a study of the changes in the structure of annealed copper would be of great importance.

The purpose of this work was to see if any more facts could be brought out, by means of a strong or drastic etching reagent, concerning the crystalline changes occurring during the annealing of a rod of cold-worked copper.

Historical

So-called etching figures have been noted for a long time when polished metal surfaces are etched with certain chemical reagents. Sauveur[4] gives drawings of typical figures which usually take the form of squares, triangles, and angles. In the case of copper when etched with nitric acid, odd, regular, and systematic etching figures are observed. Pulsifer[5] gives the name "cells" to grain and "granules" to the laminations seen with a nitric acid etch. He further states that the constants determining the size of the laminations or the distance between strata or the sizes of cubic figures are at present unknown. The granules are possibly determined by some physical constant and have more significance than merely the progressive outline of the solution force. Some support for the conception that the ultimate granules are physical subdivisions comes from the observation that the offsets in worked or slipped stock are of the same order of magnitude as the granules. There is no hint of any more minute texture or smaller order of crystalline units. This, of course, means that the chemicals used for etching have too gross an effect to disclose any demarcation even if it should exist.

Carpenter and Tamura[6] grew large crystals (4 inches long) of commercially pure copper by producing critical strain and then giving an appropriate heat treatment. They found all their crystals to contain numerous twins which were oriented in as many as three directions. Later these same men[7] studied the formation of twinned metallic crystals. They state that metal crystals may be formed by a rearrangement of the atoms in primary crystals giving rise to "secondary crystals." Primary crystals are those which have solidified in such a way that they are unstrained and do not contain twin crystals. The phenomenon is confined to various types of secondary crystals, and therefore appears to be related to what may be called "atomic rearrangement." Twinned crystals in copper which are present in the originally cold-worked metal are not removed either by recrystallization or by subsequent growth, although during the former process all the old crystals are replaced by new ones and during the latter a large number of crystals are absorbed into a few large ones. Twin crystals develop by boundary migration and growth occurs until crystals meet with sufficient resistance. Twin crystals of copper cannot be removed on heating at 1050° C. for several hours, though outlines change slowly and tend to become smoother and more perfect. The capacity for forming annealing twins appears to be closely related to the atomic arrangement in the crystal lattice of the metal. Lucas[8] says: "As the strained specimen is heated there proceeds a removal of the strained condition and distorted structure. You get a perfect keying of the crystalline elements of one grain into the crystalline elements of an adjoining grain. Twinned areas gradually develop by a reorientation process." Rowdon[9] states that the origin of these twinned forms is the rotation of the crystalline units as a consequence of the side of "growth." However, this work was concerned with the formation of twins in very thin layers of copper electrolytically deposited.

Material and Method

Only one rod of cold-worked copper was used. It was drawn cold and annealed at 749° C. to successively lesser diameters by the manufacturer. However, in the final operation it was cold-drawn to $1/2$ inch round in one operation and left hard.

The copper rod was held at 700° C. in a small electric furnace for a definite time. This temperature was used as higher temperatures lessen the mechanical properties.[10] The specimen would then be allowed to cool in the air. The end of the rod, transverse section to the direction of rolling, was polished for examination and etched. After examination the specimen was replaced in the furnace and held there for a further definite period. Thus, for a period of 4 hours at 700° C. the specimen was heated three times as detailed by the captions under the accompanying microphotographs.

Discussion of Results

Figures 1 and 2 show quite clearly the contrast in the appearance of the specimens etched with different reagents. With concentrated nitric acid, the grain boundaries, twinning, etching pits, and fine grain structure are observed. With ammonia and hydrogen peroxide, twinning and etching pits,

[1] Received January 28, 1929.

[2] Present address, U. S. Tariff Commission, Washington, D. C.

[3] Guillet and Portevin, "Metallography and Macrography," p. 71, G. Bell and Sons, Ltd., London, 1922.

[4] Sauveur, "Metallography and Heat Treatment of Iron and Steel," p. 90, University Press, Cambridge, 1916.

[5] Pulsifer, Trans. Am. Inst. Mining Met. Eng., 1926, No. 1524E.

[6] Carpenter and Tamura, Proc. Roy. Soc. (London), 113A, 28 (1926).

[7] Carpenter and Tamura, Ibid., 113A, 161 (1926).

[8] Lucas, J. Franklin Inst., 201, 177 (1926).

[9] Rowdon, Met. Chem. Eng., 15, 406 (1916).

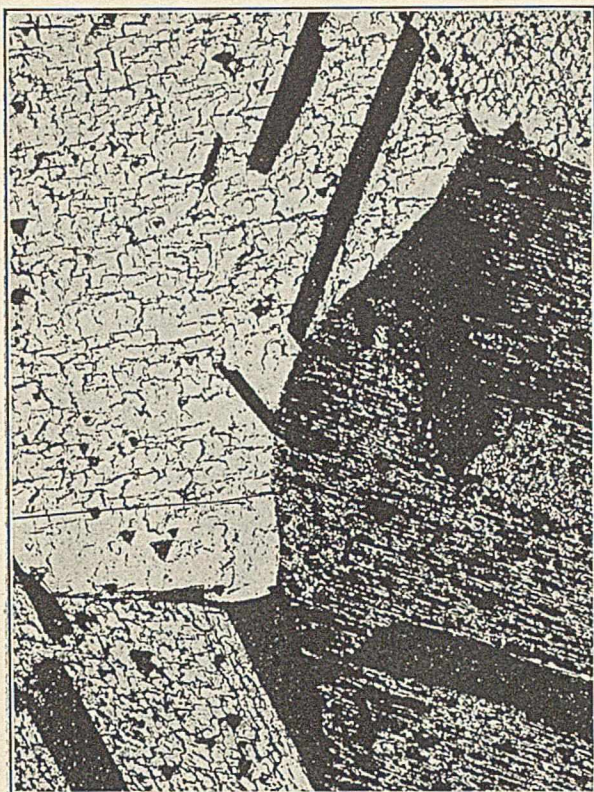[10] Hoyt, "Metallography," Part II, p. 14, McGraw-Hill Book Co., 1920.

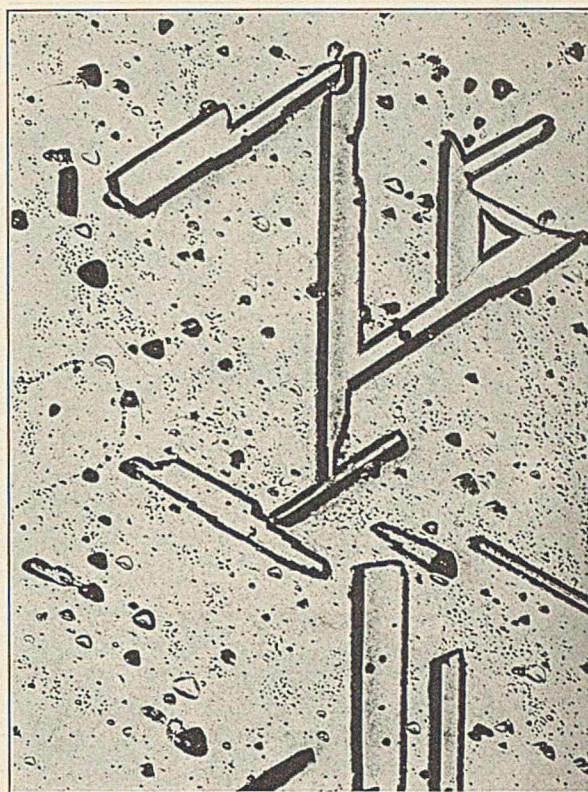Figure 1—Concentrated Nitric Acid Etch.　150 ×

Figure 2—Same Specimen as in Figure 1 Repolished and Etched with Ammonia and Hydrogen Peroxide.　150 ×
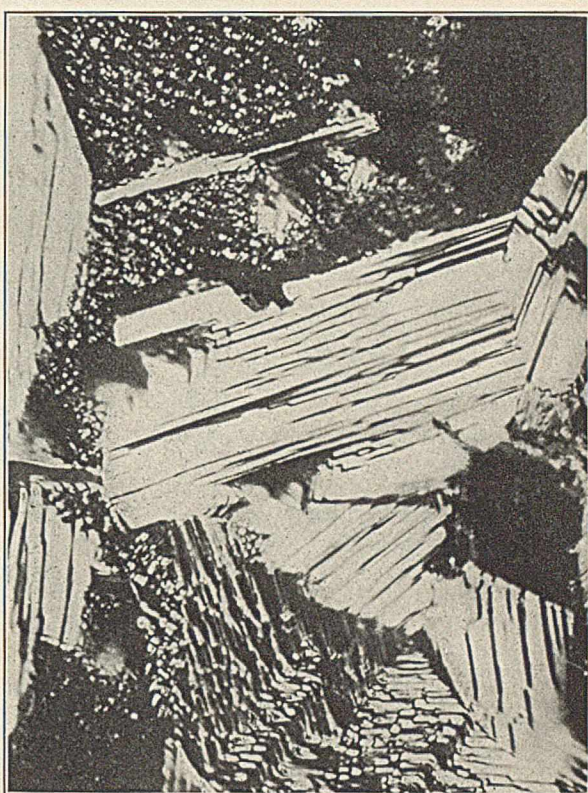

Figure 3—Original Specimen.　1300 ×

Figure 4—After 3 Hours at 700° C.　1300 ×

and in some cases grain boundaries, are observed, but in no case is there the same type of fine structure as when nitric acid was used. The succeeding specimens were etched with concentrated nitric acid.

The microphotographs show clearly how grain growth con-tinues with repeated heating. The structure of the original specimen is shown in Figure 3. A study of the picture gives further insight into the effect of heat treatment on the distance between laminations, size of etching pits, grain growth, and orientation.
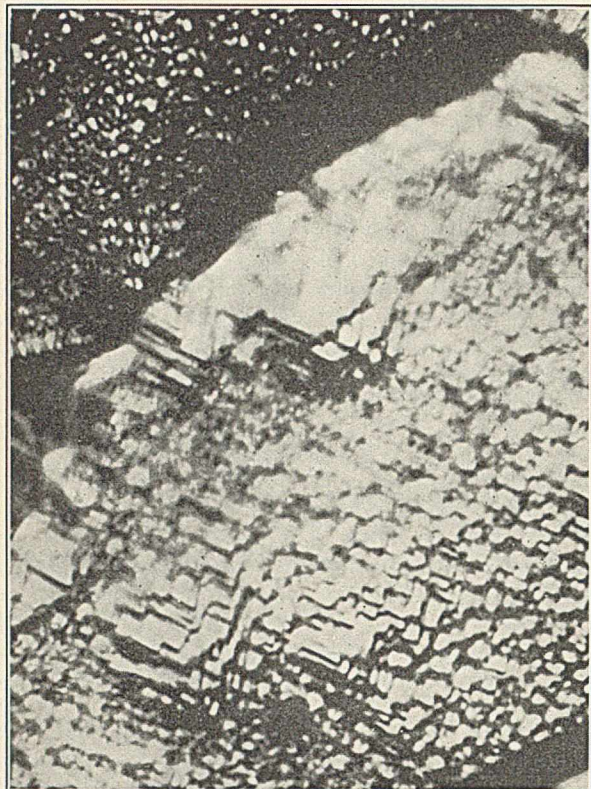
Figure 5—After 4 Hours at 700° C.   2500 ×

Figure 6—After 24 Hours at 700° C.   1300 ×
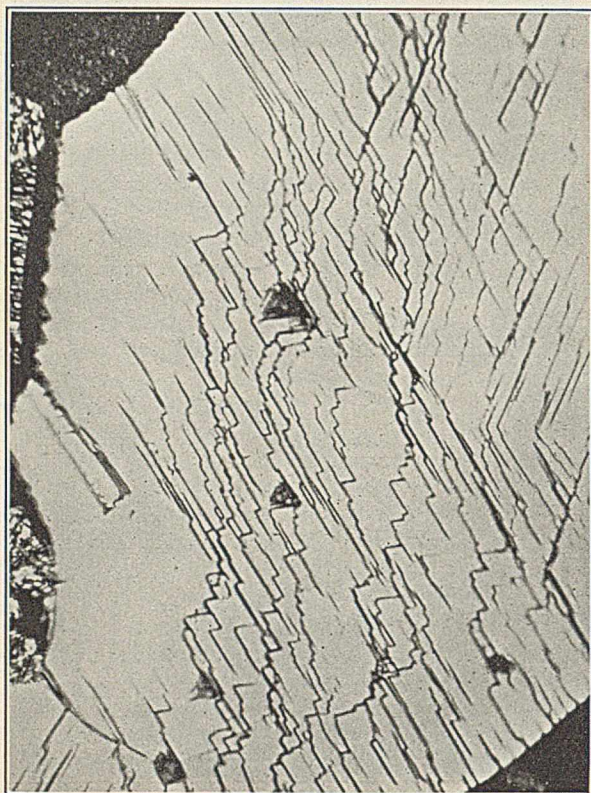
Figure 7—After 40 Hours at 700° C.   1300 ×
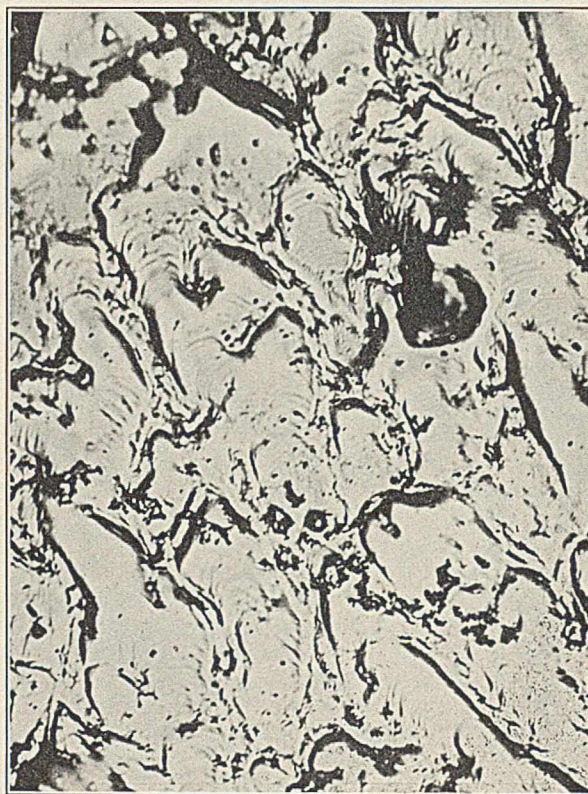
Figure 8—After 80 Hours at 700° C. and Also a Further
Treatment for 6 Hours at 1000° C.   1300 ×

The so-called "triangular etching pits" are shown clearly in Figures 4, 6, and 7, and it will be noted that one or two sides are practically parallel with laminations in the grains themselves, and in most cases at extreme magnifications they themselves show laminations.[11]   Figure 5 shows a fine, regular, saw tooth structure observed in some of the grains.

[11] Dunn, "Heat Treatment of Cold Rolled Copper," Thesis, University of Illinois, 1928.

The striking regularity and uniformity of the laminations must be of some real significance, and are probably due to some inherent physical characteristic of the grain. Figure 6 shows a number of evidences of twinning, and in one case the twinning has included one of the triangular etching pits.

Figure 7 is of particular interest to users or workers of metal in that it shows that often under such drastic heat treatment grains of copper are still susceptible to chemical attack and have not returned to the original cast condition. Some of the lines are much darker than others, which leads one to speculate whether or not these may not be the former grain boundaries that have disappeared to form the new grains.

After 80 hours of heat treatment at 700° C., laminations were still visible and the result of further heat treatment of 6 hours of 1000° C. is shown in Figure 8. This photograph indicates that probably there was a slight flow of metal and that the original laminations have disappeared, but there is still an indication of a laminated structure shown by circular dark lines of a marked degree of regularity and uniformity, which might be due to the distortion of these laminations with some "healing," or else to new strains being set up by the flow of material.

Conclusions

1—An etching reagent has been used that brings out crystal details.

2—Twinning is observed in three directions.

3—Details of laminated structure in etched crystals are brought out only at high magnifications.

4—The constantly recurring regularity and uniformity of the laminations in etched crystals may be due to some physical property of the substance.

5—If the angle at which a crystal was oriented with respect to the microscope could be measured and the distance between the laminations determined, the crystal space lattice or some multiple might be found.

6—The complete removal of strains and distortions as shown by x-ray diagrams should be correlated with some corresponding microphotographs. Thus, by looking for some distinctive standard, as grain count, size of crystals, or regularity of outline of secondary crystals, the more piercing tests of the x-ray would be indirectly applied through microphotographs and visual microscopical examination.

Some Observations on Rubbers with Low Nitrogen Content[1]

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SINCE it was first discovered that rubber contained protein, many researches have been carried out to determine just what part this material played in the structure and properties of the rubber. The present work shows that the protein is of less importance than has often been supposed.

Note—Some confusion exists regarding the terms "protein-free" and "nitrogen-free." Most of the published articles fail to mention what method was used for proving the absence of nitrogen. Consequently it is often difficult to tell whether the terms may be synonymous. In this paper "nitrogen-free" will be used only with reference to rubber containing an amount of nitrogen which cannot be detected by sensitive colorimetric methods. Rubber containing a known amount or an unstated percentage above 0.001 per cent will be called "nitrogen-poor" or "protein-free."

Many attempts have been made in this laboratory to prepare pure rubber hydrocarbon free from nitrogen or protein and to test its physical properties when vulcanized. This seemed more important than ever in view of the work reported by Dinsmore[2] in which it was found that rubber coagulated from latex under varying pH values showed widely different rates of cure and physical properties. The effects noted were

Rubber has been prepared protein-free, although not entirely nitrogen-free, by digesting latex with caustic soda, as recommended by Pummerer and Pahl. Rubbers with a nitrogen content of from 0.004–0.0096 per cent have been prepared by a slight modification of the original procedure. This rubber can be compounded and cured to give good quality vulcanizates, which compare very favorably with the controls. Protein-free rubber, when acetone-extracted, becomes nitrogen-free. This can still be vulcanized, although it cures slowly. The rate of cure of rubber from protein-free latex is affected very little by the pH of the coagulating medium whereas with full-nitrogen rubber rate of cure varies considerably with change in pH value at the time of coagulation. It was also found that protein-free rubber could be racked. Data on the preparation, coagulation and nitrogen content as well as the vulcanization results of protein-free rubber are presented. The observations lead to the conclusion that protein is not the key to the explanation of the physical properties of rubber.

attributed to different conditions of the rubber protein as determined by the pH value of the latex at the time of coagulation. However, more definite proof seemed desirable and it was decided to repeat in part the work mentioned above using protein-free latex prepared according to the method of Pummerer and Pahl.[3] Previous investigators have stated, as noted below, that they have prepared nitrogen-free rubber, but there are few, if any, data available in the literature as to the exact procedure used in determining the absence of nitrogen or of protein, or as to the physical properties of the vulcanizates formed from such rubbers. For these reasons it was decided to carry out the present research.

Historical

Beadle and Stevens[4] have investigated the influence of the insoluble constituent on the physical properties of vulcanized rubber. They prepared from smoked sheet a sample of rubber poor in nitrogen and another rich in nitrogen. The nitrogen-poor rubber combined with sulfur very slowly and gave a poor vulcanizate, while the nitrogen-rich sample vulcanized more rapidly than the control and gave better physical properties.

[1] Presented before the Division of Rubber Chemistry at the 76th Meeting of the American Chemical Society, Swampscott, Mass., September 10 to 14, 1928.

[2] Dinsmore, Ind. Eng. Chem., **18**, 1140 (1926).

[3] Pummerer and Pahl, *Ber.*, **60**, 2152 (1927).

[4] Beadle and Stevens, *India Rubber J.*, **44**, 554, 603 (1912).

Spence and Young[5] have also shown that the lower the quantity of nitrogen in the rubber the more slowly sulfur entered into combination.

Stevens[6] has investigated the influence of additions of various substances on the vulcanization of smoked sheet from which most of the insoluble matter had been removed. The results confirm previous conclusions regarding the importance of the insoluble matter. Peptone, casein, and litharge all speeded up the cure. The effect of the absence of the

Figure 1—Preliminary Test

insoluble matter is essentially to reduce the rate of vulcanization. A sample cured for a very long time showed results approximating those given by the original, untreated rubber.

Eaton and Grantham[7] found that the addition of casein or peptone had little effect on the rate of cure in rubber already containing the insoluble matter.

Freundlich and Hauser[8] digested latex with trypsin and found that on coagulation by the usual methods the rubber came down in a lump, apparently without first forming a flocculent precipitate.

Feuchter[9] compared the tensile properties of KD rubber (ether-soluble diffusion rubber, protein-free) with those of smoked sheet cured equal periods of time in a mix containing rubber, zinc oxide, accelerator, and sulfur. There was practically no difference in the two rubbers as shown by tensile at break and at 500 per cent elongation.

More recently Pummerer and Pahl[3] purified rubber by treating latex with caustic soda until free from protein and state that its capacity for vulcanization was normal.

Hauser has reported that the soluble and insoluble fractions from protein-free rubber when combined vulcanize approximately equal to the original. Later, however, Pummerer, Andriessen, and Gündel[10] state that the "total rubber" made by the caustic process from ammonia-preserved latex, although fairly protein-free, was not nitrogen-free, and conclude from an analysis that the residual nitrogen is present as amine nitrogen and not as protein nitrogen.

Protein in rubber has often been connected with the mechanism of coagulation of latex and the physical structure of the resulting coagulum. The changing opinion of rubber technologists in regard to the importance of the protein as an aid in explaining rubber behavior is reflected in a statement by De Vries[11] that "it seems probable that the protein will have to

be more or less dethroned and driven back to the second plane as our knowledge advances." An investigation by the same author[12] on rubber containing 0.03 per cent or less of nitrogen indicated that the "absence of proteins had not caused striking changes in the coagulation phenomena."

Experimental

In this investigation 30 per cent ammonia-preserved latex from the Goodyear plantations was used. It was treated with 2 per cent sodium hydroxide solution according to the method of Pummerer and Pahl.[3] The resulting cream was washed, dialyzed, coagulated with acid, and a sample dried *in vacuo.*

A Kjeldahl determination was made using Nessler's method for estimation of the ammonia produced. The result showed about 0.015 per cent nitrogen. The major portion of the coagulum was air-dried after addition of a synthetic antioxidant. On vulcanization this showed tensile properties substantially equal to rubber from latex which had received just heat treatment for the same length of time as the alkalipurified latex. (Figure 1)

As an attempt to produce a more nearly nitrogen-free product than this first lot, a run was made doubling the changes of caustic. After the sixth change of alkali the caustic layer separated water-white, and on test with permanganate in very dilute solution the green manganate stage was still present at the end of 24 hours. Analysis of the cream after washing showed 0.004 per cent nitrogen calculated on the dry rubber.

[12] De Vries, *Caoutchouc & gutta-percha,* **23,** 13082 (1926).
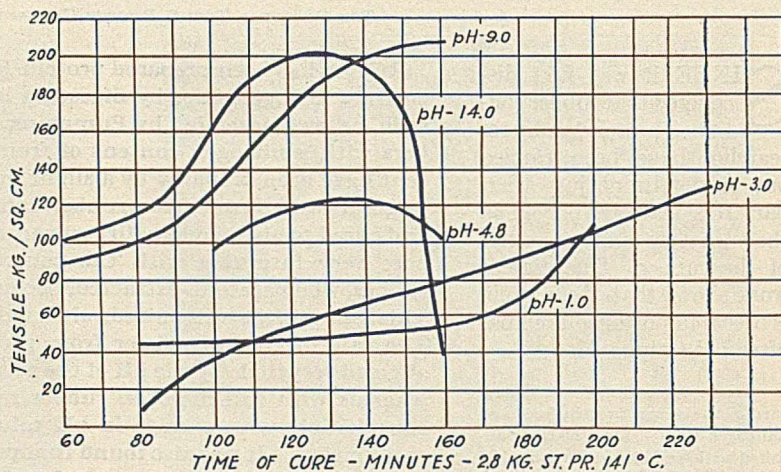

Figure 2—Maximum Tensile, Rubber-Sulfur Mix. Full Nitrogen Content. Data from Dinsmore[2]
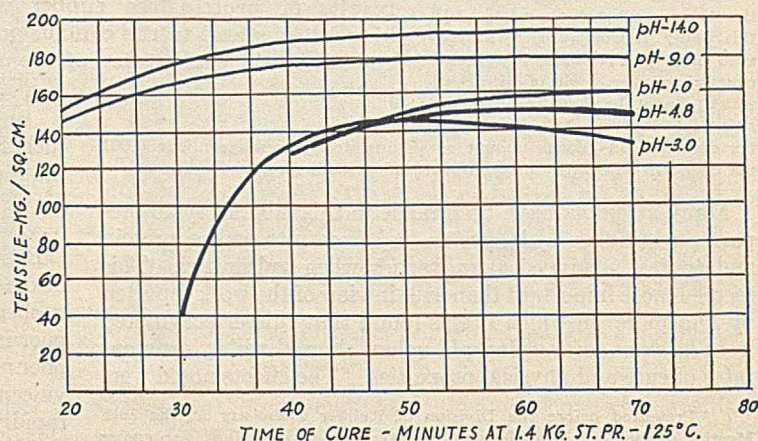

Figure 3—Maximum Tensile, Mercapto Stocks. Full Nitrogen Content. Data from Dinsmore[2]

[5] Spence and Young, *Kolloid-Z.,* **13,** 265 (1913).
[6] Stevens, *Ibid.,* **14,** 91 (1914).
[7] Eaton and Grantham, *J. Soc. Chem. Ind.,* **35,** 715 (1916).
[8] Freundlich and Hauser, *Kolloid-Z.,* Spec. No., April 1, 1925, p. 15; *India Rubber J.,* **69,** 663, 693 (1925).
[9] Feuchter, *Gummi-Ztg.,* **40,** 1691 (1926).
[10] Pummerer, Andriessen, and Gündel, *Ber.,* **61,** 1583 (1928).
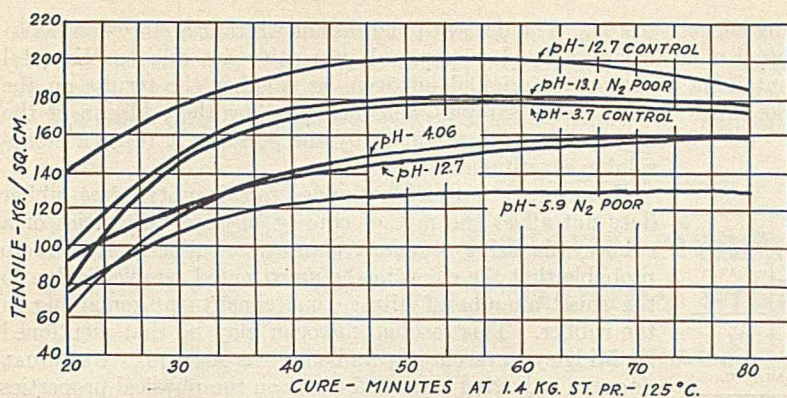[11] De Vries, *Trans. Inst. Rubber Ind.,* **3,** 284 (1927).

Figure 4—Maximum Tensile, Accelerated Stocks. Nitrogen-Poor Rubbers
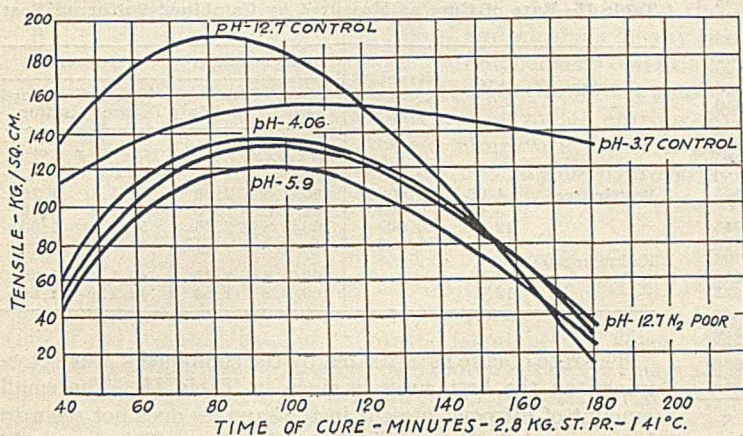

Figure 5—Maximum Tensile, Rubber + Sulfur. Nitrogen-Poor Rubbers

As it seemed to be of considerable interest to find out the effect of pH of the coagulating medium on the properties of this protein-free rubber, rather large quantities of the purified latex were prepared, the caustic being changed six times in every case. The nitrogen content ran from 0.006 to 0.009 per cent.

Coagulation was carried out by addition of the treated latex to excess of alcohol to which had been added suitable amounts of acid or alkali. The pH of the serum was determined by means of the hydrogen electrode. The coagulum was then washed and, as it oxidized very rapidly, was treated with 5 per cent of a commercial antioxidant before drying.

As suggested in the most recent article by Pummerer,[10] a specimen of the protein-free rubber analyzing 0.009 per cent nitrogen was extracted with acetone. This reduced the nitrogen content to so low a value that it could not be accurately measured by the method used. This rubber was vulcanized in the same type formulas as the other rubbers, but without antioxidant.

It is also worthy of note that the rubber with low nitrogen content could not be plated out readily by electrolysis. The absence of the protein renders the rubber too good an insulator, so that even a thin film had great resistance. The addition of a solution of sodium chloride gave increased conductivity and permitted the building up of a film of nitrogen-poor rubber by electrolysis. The nitrogen-poor rubber could also be racked.

Controls were prepared as follows:

(1) Latex was heated for the same length of time and at the same temperature as the lots from which the protein was removed. This was coagulated at pH 12.7. It was, of course, impossible to duplicate the effect, if any, of the caustic on the rubber hydrocarbon.

(2) Latex which had received no special treatment at all was coagulated at pH 3.7.

The rubbers prepared as described above were compounded in two formulas as follows:

	RUBBER-SULFUR MIX	ACCELERATED MIX
Rubber	100.00	100.00
Zinc oxide	5.00	5.00
Sulfur	10.00	3.00
Stearic acid	1.50	1.50
Antioxidant	5.00	5.00
Captax	....	0.50

Both mixes were cured in a steam platen press, the accelerated mix at 125.6° C. (258° F.) and the rubber-sulfur mix at 141.7° C. (287° F.). The physical tests were made on an autographic stress-strain machine. The best cures were determined by hand tests.

Discussion of Results

The complete curing data are shown in Table I. The results are plotted graphically on Figures 2 to 5. Figures 2 and 3, showing the results described by Dinsmore,[2] are given as a matter of reference. On Figure 6 the times of best cure are plotted and compared with the results obtained in previous work. It should be noted that the rate of cure of the nitrogen-poor rubbers is quite constant in both formulas, while in the full-nitrogen rubbers it varies according to the pH value existing at the time of coagulation. This difference is more noticeable in the pure-gum mix than in the accelerated stock.

The physical properties of the nitrogen-poor rubber (Figure 5) are also more uniform in the pure-gum mix than is the case with rubbers having full protein content (Figure 2). Results at different pH values are in close agreement. Good vulcanizates are obtained. The difference from the controls
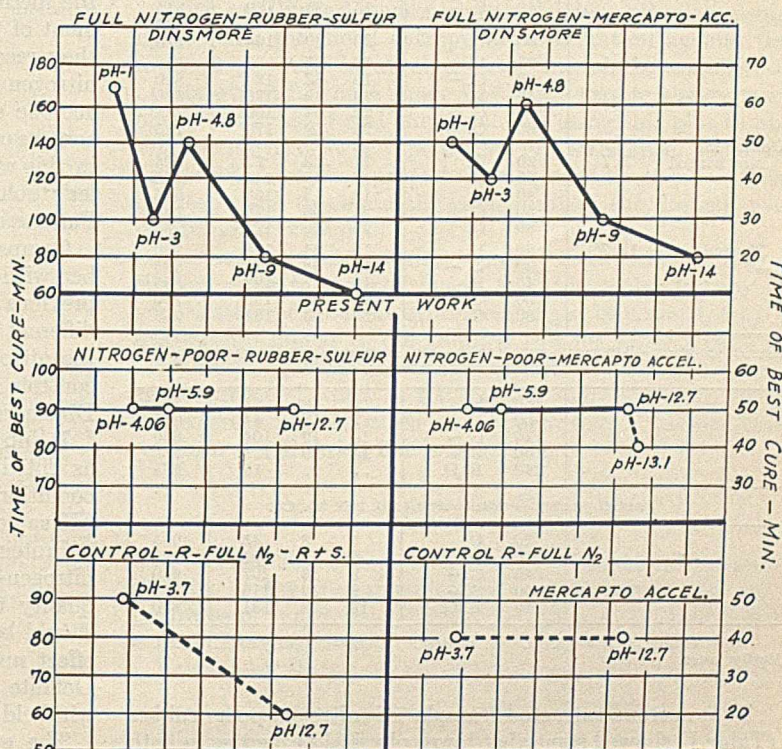

Figure 6—pH Coagulating Medium *vs.* Time of Best Cure

is relatively small and is probably due to the activating effect of hydrogen ions on the protein in the controls. There is not so much difference between the accelerated stocks containing little nitrogen (Figure 4) and the same type of stocks as reported by Dinsmore (Figure 3).

Table I—Curing Data

RUBBER	pH	CURE			TENSILE			ELONGATION AT BREAK
		Time	State hand test		400%	600%	Break	
		Min.			Kg. per sq. cm.			%

UNACCELERATED STOCKS—CURED AT 2.8 KG. PER SQ. CM. AND 141.7° C.

RUBBER	pH	Time	State hand test	400%	600%	Break	Elong.
Protein-free	4.06	40	U.	13	25	60	795
		60	U. G.—	14	28	116	860
		90	B.	17	36	129	795
		120	G.+S.O.	21	50	133	745
		180	B. O.	26	..	30	440
	5.9	40	U.	11	20	44	825
		60	U.	12	23	76	850
		90	B. G.+	17	39	120	780
		120	O.	22	53	113	710
		180	B. O.	..	..	24	350
	12.7	40	U.	10	19	50	850
		60	U. G.—	13	26	89	850
		90	B. G.+	18	37	134	800
		120	O.	19	43	125	750
		180	B. O.	27	..	36	465
Controls: Not heated	3.7	40	U.	14	33	114	845
		60	G.—	17	40	133	810
		90	G.+	19	47	152	795
		120	O.	23	62	138	720
		180	B. O.	29	83	133	675
Heated	12.7	40	U.	14	31	134	855
		60	G.— B.	18	44	177	820
		90	G.+	25	68	190	750
		120	B. O.	31	108	126	590
		180	B. O.	..	..	18	225

ACCELERATED STOCKS—CURED AT 1.4 KG. PER SQ. CM. AND 125.6° C.

RUBBER	pH	Time	State hand test	400%	600%	Break	Elong.
Protein-free	4.06	20	U.	10	19	64	850
		30	U.	14	29	116	830
		40	G.—	15	33	124	800
		50	B.	17	37	138	790
		80	O.	20	51	160	755
	5.9	20	U.	11	20	74	850
		30	U.	13	26	109	865
		40	G.—	13	28	104	825
		50	B.	16	36	126	800
		80	O.	18	44	130	755
	12.7	20	U.	11	20	93	890
		30	U.	13	23	100	850
		40	G.—	15	31	120	815
		50	B.	17	34	145	830
		80	O.	20	49	160	775
	13.1	20	U.	12	25	96	850
		30	G.—	15	33	124	820
		40	B.	19	49	176	800
		50	G.+	22	64	160	735
		80	O.	26	89	179	715
Controls: Not heated	3.7	20	U.	11	23	77	825
		30	G.—	17	40	145	815
		40	B.	19	48	168	805
		50	G.+	21	58	178	780
		80	O.	23	68	176	755
Heated	12.7	20	U.	15	34	140	830
		30	G.—	17	38	172	835
		40	B.	19	47	193	805
		50	G.+	21	55	190	780
		80	O.	22	63	184	755

NITROGEN-POOR—ACETONE-EXTRACTED—NO ANTIOXIDANT—UNACCELERATED—CURED AT 2.8 KG. PER SQ. CM.

		60	U.	5	8	25	895
		80	U.	7	11	44	895
		120	G.—	10	19	104	880
		160	B.	15	29	127	805
		240	B. O.	..	..	15	265

ACCELERATED—CURED AT 1.4 KG. PER SQ. CM.

		20	U.	5	8	45	955
		30	U.	7	13	91	920
		40	G.—	9	16	107	910
		50	G.—	9	19	116	885
		80	B. G.+	13	28	131	820

U = Under. G. = Good. B. = Best. S. O. = Slightly over. B. O. = Badly over.

The acetone-extracted sample of nitrogen-poor rubber (Table I) showed somewhat lower physical properties in both types of test formulas. No acetone-extracted control was tested. The data at hand do not warrant a statement as to whether the low physical properties are due to the total absence of original nitrogen, or whether the results on the unextracted samples were benefited by the addition of the nitrogenous antioxidant or by the presence of other acetone-soluble constituents.

However, the antioxidant added to this protein-free rubber does not affect the rate of cure or physical properties of a rubber mix using standard plantation rubber. It is more probable that the effect in the unextracted samples is due to the small amount of nitrogenous constituent remaining in the rubber. This residual nitrogen may be that mentioned by Midgley in recent papers before the AMERICAN CHEMICAL SOCIETY as having a marked effect on the physical properties of rubber. Further tests are to be made on this subject.

Table II—Rate of Cure as Measured by Combined Sulfur on Best Cures

RUBBER	pH	NITROGEN CONTENT	UNACCELERATED		MERCAPTO	
			Best cure	Combined sulfur	Best cure	Combined sulfur
		%	Min./kg./ sq. cm.	%	Min./kg./ sq. cm.	%
Protein-free	4.06	0.0085	90/2.8	2.26	50/1.4	1.76
	5.9	0.0096	90/2.8	2.06	50/1.4	1.76
	12.7	0.009+	90/2.8	2.26	50/1.4	1.68
	13.1	0.006	....	..	40/1.4	1.80
Full nitrogen	3.7		90/2.8	2.15	40/1.4	1.38
	12.7		60/2.8	1.85	40/1.4	1.64

The rate of cure as measured by the combined sulfur determined on the best cures is given in Table II. The small amount of nitrogen present in the samples does not seem to have retarded the combination of sulfur. This is not in agreement with the findings of earlier investigators, but here again it is possible, although not probable, that the nitrogenous antioxidant may have influenced the results.

Conclusions

Rubber cannot be prepared absolutely nitrogen-free by the method of Pummerer and Pahl, even though the treatment of the latex with caustic is continued twice as long as they recommend. The residual 0.004 to 0.009 per cent of nitrogen is not protein nitrogen, since it is removable by acetone extraction and the amount of nitrogen falls so low as to be unmeasurable with accuracy by the exact method used in this research—i. e., colorimetric determination with Nessler's solution. The authors note with satisfaction that Pummerer has come to exactly the same conclusion.

Comparison of the results of vulcanizing protein-free rubber with those of the controls and with the results of the previous research shows that the rate of cure is constant under different conditions of coagulation and that the quality of the nitrogen-poor vulcanizates compares very well with the controls and with the earlier mentioned work described by Dinsmore.

It appears, therefore, that the variation in cure and quality as noted by Dinsmore was due entirely to some particular condition of the rubber protein brought about by the varying pH values existing at the time of coagulation.

Protein-free rubber, after acetone extraction, is practically nitrogen-free and cures slowly to give vulcanizates of lower quality than is obtained with the protein-free rubber. It should be remembered, however, that, as stated above, this effect may not be due entirely to the absence of nitrogen. Definite conclusions on this phase of the question must be withheld until more experiments are made.

The evidence presented shows that protein-free rubber can be compounded and cured to give good quality products.

Hence the protein is not an essential factor in producing the physical properties of vulcanized rubber. The condition of the protein does affect the rate of cure and so exerts an indirect effect upon the quality of the rubber.

Calculation of Latent Heats of Vaporization of Hydrocarbons and Alcohols[1]

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THE latent heat of vaporization for substances is needed frequently for use in the design of commercial apparatus involving evaporation, distillation, and drying. A search of the literature reveals several methods that may be used to calculate latent heats, but most of these are restricted to a definite temperature or else involve the use of several constants and unknowns, which makes them difficult to apply. One of the methods used to obtain the latent heat of substances at atmospheric pressure is Trouton's rule.[2] This rule, which states that the molal entropy of vaporization at 760 mm. pressure is approximately constant for most substances, may be written

$$\frac{Mr}{T} = 20.7$$

where M is the molecular weight, r the latent heat, and T the absolute boiling point at 760 mm. pressure. Several workers have shown that this ratio is by no means constant and have modified the rule to take into account the variation of the constant with boiling temperature. For instance, Nernst[3] proposes

$$\frac{Mr}{T} = 9.5 \log T - 0.007T$$

where T is the absolute boiling point. A similar formula has been suggested by de Forcrand.[4] Another which was derived by Cederberg[5] includes the critical pressure π_0 in atmospheres and the absolute critical temperature δ_0. This equation is expressed as

$$\frac{Mr}{T} = \frac{4.571 \log \pi_0}{1 - \frac{T}{\delta_0}}\left(1 - \frac{1}{\pi_0}\right)$$

Hildebrand[6] has shown that a more constant value of Mr/T can be obtained by comparing the molal entropies of substances where the vaporization takes place at the same concentration of vapor, instead of comparing molal entropies of substances at 760 mm. pressure, as Trouton did. He also mentions that the comparison does not necessarily need to be limited to any definite vapor concentration or pressure. The rule, which was demonstrated graphically by Hildebrand, can be explained more clearly by writing the Clausius-Clapeyron equation as:

A method of calculating the latent heats of hydrocarbons and alcohols at any temperature is discussed. The method consists essentially in establishing a Dühring line from the boiling points at at least two temperatures and a molal entropy line from two or three known temperatures. The method has been applied successfully to four hydrocarbons and two alcohols for temperatures nearly up to the critical.

$$\frac{d \log p}{d \log T} = \frac{Mr}{RT}$$

Then, if log p is plotted against log T for any substance and a tangent is drawn to the resulting curve at any point, the slope of the tangent will represent the entropy of vaporization divided by the gas constant, R. If tangents all having the same slope are drawn to the curves obtained for different substances by plotting log p against log T, it will be possible to draw a straight line through the points of tangency, whose equation will be

$$\log p = \log T + K$$

where K is a constant. This constant is numerically equal to log Rc obtained from the familiar expression

$$p = cRT$$

$$\text{or } \log p = \log T + \log Rc$$

where c is the concentration. It follows that along such a line c is constant.

Lewis and Weber[7] made use of the Hildebrand relationship by plotting the molal entropy of vaporization against the ratio of pressure to absolute temperature. A number of hydrocarbons fall on a single line, but separate curves were obtained for water and ammonia. In using this plot to obtain the latent heat of vaporization of a substance, one must decide which of the curves to use or whether to interpolate between them to obtain the latent heat at the desired temperature and pressure.

The author, while working with the method of Lewis and Weber, came to the conclusion that the molal entropy of vaporization of different substances might be correlated by a relationship similar to the Dühring rule for vapor pressures.

Dühring[8] plotted the boiling points of pure substances against those of water at the same pressure and found that the experimental values fell on a straight line. The algebraic equation of a Dühring line is as follows:

$$\frac{T_1 - T_2}{\theta_1 - \theta_2} = K$$

where T_1 and T_2 are the boiling points of the pure substance or solution at the corresponding vapor pressures of the temperatures θ_1 and θ_2, respectively, and K is a constant which is the slope of the line.

Baker and Waite[9] tested the Dühring rule for aqueous

[1] Received December 10, 1928.
[2] *Phil. Mag.,* [5] **18,** 54 (1884).
[3] Nernst, *Nachr. Ges. Wiss. Göttingen,* **1906.**
[4] de Forcrand, *Compt. rend.,* **156,** 1439, 1648, 1809 (1913).
[5] Cederberg, *Z. physik. Chem.,* **77,** 498 (1911).
[6] Hildebrand, *J. Am. Chem. Soc.,* **37,** 970 (1915).

[7] Lewis and Weber, *J. Ind. Eng. Chem.,* **14,** 485 (1922).
[8] Dühring, "Neue Grundgesetze zur rationelle Physik und Chemie," Leipzig, 1878.
[9] Baker and Waite, *Chem. Met. Eng.,* **25,** 1137 (1921).

solutions and found that at pressures of one atmosphere or less the rule worked perfectly. They concluded that this rule was applicable to aqueous solution where the dissolved substance exerts no appreciable vapor pressure.
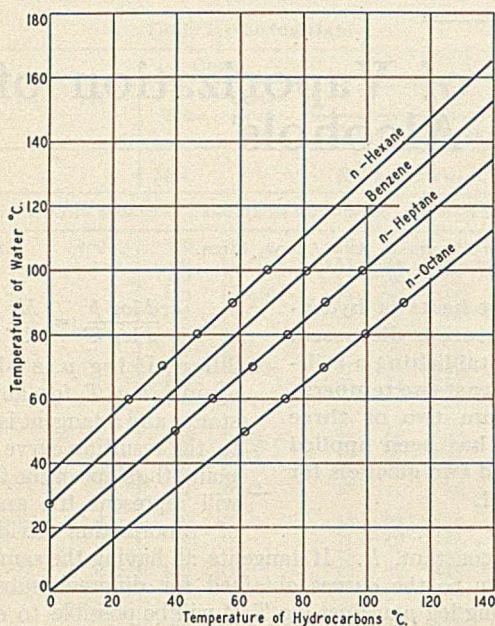

Figure 1—Dühring Lines for the Hydrocarbons

Leslie and Carr[10] investigated Dühring's rule in relation to solutions of organic liquids. Keeping in mind the conclusions of Baker and Waite, they found that Dühring's rule was applicable to solutions of hydrocarbons or, in general, to all binary and ternary solutions whose components exert an appreciable vapor pressure, and that the rule holds remarkably well over limited ranges of pressure.

It was decided to plot for a number of substances the molal entropy of the substance in question against the molal entropy of water at the same pressure. A number of points for different pressures were found to define a straight line.

This method has been applied so far only to pure substances, but it is planned in the future to study mixtures. Stated algebraically the equation of these lines is

$$\frac{\left(\frac{Mr}{T}\right)C - \left(\frac{Mr}{T}\right)D}{\left(\frac{Mr}{T}\right)B - \left(\frac{Mr}{T}\right)A} = m$$

where $(Mr/T)C$ and $(Mr/T)D$ are the molal entropies of the hydrocarbons at the corresponding vapor pressure of the molal entropies (Mr/T) B and $(Mr/T)A$ of water, respectively, and m is equal to the slope of the line.

Method of Calculation

Latent heats of hydrocarbons at all customary operating temperatures can be obtained by use of a Dühring line and a molal entropy line whose derivation is shown in Figure 2. The method in question will be described, referring to n-octane. The Dühring lines giving the vapor pressures of n-octane as well as the other hydrocarbons studied are shown in Figure 1. The lines were constructed from the experimental values of Leslie and Carr, which cover only a small temperature range, but in this work the lines were extended to the higher temperatures assuming that they would still be straight lines. The latent heat of n-octane at the

[10] Leslie and Carr, IND. ENG. CHEM., 17, 810 (1925).

temperatures 120°, 150°, and 180° C., given by Young,[11] were used to construct the curve shown in Figure 2. From the Dühring line the temperatures 120°, 150°, and 180° C. were taken at which water exerts the same vapor pressures as n-octane. The corresponding temperatures for water are 96.5°, 120°, and 140° C., respectively. The value of the latent heat of n-octane at 120° C. is 71.43 calories per gram. This multiplied by its molecular weight, 114.2, and divided by the absolute boiling point $(120 + 273)$ gives 20.7. Water at 96.5° C. has a molal latent heat of 9736 calories per gram-molecule, and this divided by its absolute boiling point $(96.5 + 273)$ gives 26.35. This locates point (a) of the curve. A similar procedure was followed to obtain the points (b) and (c) of Figure 2. By the use of such a line together with the Dühring line the latent heat can be calculated at any temperature desired. For instance, if the latent heat of n-octane is desired at a particular temperature, the corresponding temperature of water is found from the Dühring line by reference to Figure 1. The latent heat of water at this temperature can be found in a steam table and the ratio of Mr/T determined. Referring now to Figure 2, the value of Mr/T for n-octane corresponding to Mr/T for water can be read from the curve and the latent heat in calories per gram for n-octane calculated.
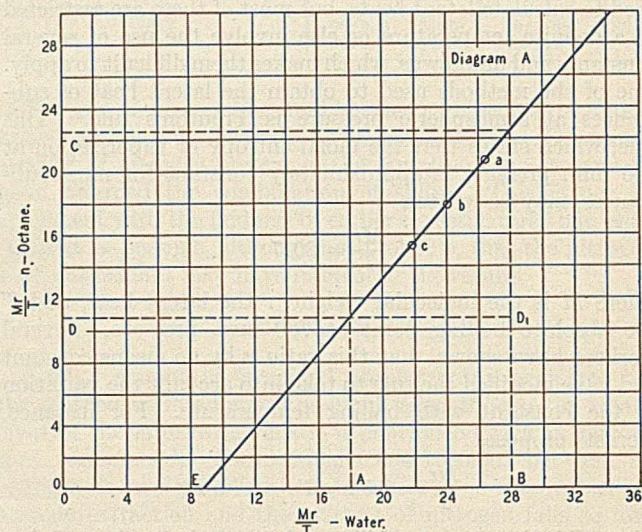
Figure 2—Molal Entropy Curve for Octane-Water

Mathematical Discussion

It has been shown that the equation of the line relating the molal entropy of vaporization of water to the hydrocarbons can be expressed algebraically as:

$$\frac{\left(\frac{Mr}{T}\right)C - \left(\frac{Mr}{T}\right)D}{\left(\frac{Mr}{T}\right)B - \left(\frac{Mr}{T}\right)A} = m \qquad (1)$$

This is the point-slope equation of a straight line and upon expanding becomes

$$\left(\frac{Mr}{T}\right)C - \left(\frac{Mr}{T}\right)D = m\left[\left(\frac{Mr}{T}\right)B - \left(\frac{Mr}{T}\right)A\right] \qquad (2)$$

When $(Mr/T)D = 0$, and $(Mr/T)A = a$, at point E of Figure 2, Equation 2 reduces to the form

$$\left(\frac{Mr}{T}\right)C = m\left[\left(\frac{Mr}{T}\right)B - a\right] \qquad (3)$$

[11] Young, *Proc. Roy. Dublin Soc.*, 12, 374 (1910).

Table I—Comparison of Calculated Latent Heats of Hydrocarbons at Various Temperatures with Values Obtained by Other Observers

| HEPTANE | | | | HEXANE | | | | OCTANE | | | | BENZENE | | | |
Temp.	Calcd.	Expt.	Observer	Temp.	Calcd.	Expt.	Observer	Temp.	Calcd.	Expt.	Observer	Temp.	Calcd.	Expt.	Observer
°C.				°C.				°C.				°C.			
0	93.82	...	....	0	89.51	89.20	Jahn	0	85.55	...	....	0	106.20	109.0	Regnault
40	87.39	...	....	40	83.68	...	....	40	81.57	...	....	40	101.00	100.71	Marshall
70	81.88	80.44	Young	60	80.32	80.82	Young	80	76.74	...	....	70	96.40	96.70	Young
80	79.89	...	....	80	76.92	...	....	120	71.33	71.43	Young	80	94.18	92.90	Wirtz
100	75.70	75.80	Young	90	74.87	75.51	Young	150	66.80	66.45	Young	100	90.85	91.41	Young
120	71.32	...	....	120	68.54	69.29	Young	160	65.11	...	....	130	87.07	84.74	Young
130	68.72	69.37	Young	150	61.57	61.03	Young	180	61.61	60.91	Young	140	82.33	...	....
160	61.79	62.65	Young	160	59.25	...	....	200	57.92	...	....	160	80.05	78.94	Young
190	51.10	56.05	Young	180	52.00^a	50.93	Young	240	46.00^a	45.97	Young	180	73.19	...	....
200	50.84	...	....	200	42.00^a	...	....	270	34.00^a	34.38	Young	190	69.61	71.76	Young
220	45.12	46.46	Young	210	35.00^a	37.29	Young	280	29.00^a	28.26	Young	220	63.33	62.24	Young
240	35.00^a	...	....	220	29.00^a	30.37	Young	290	21.00^a	19.10	Young	240	52.00^a	49.47	Young
250	30.00^a	31.25	Young	230	20.00^a	19.73	Young	296	00.00^a	...	....	250	46.50^a	...	....
260	22.00^a	21.90	Young	235	00.00^a	...	....	...	...	...	....	280	22.00^a	27.43	Young
267	00.00^a	...	....	...	...	...	....	...	...	...	....	288	00.00^a	...	....

^{a} From data graphically interpolated.

This equation has been reduced to the slope-intercept form of a straight line of the type

$$y = m (x - a)$$

where y is the ordinate, x the abscissa, m the slope, and a the x intercept. The slope of the curve for n-octane was found to be 1.1811, the x intercept, 8.8. Substituting these values in Equation 3 and calculating the latent heat of n-octane at 0° C., the result is obtained as follows:

$$\left(\frac{Mr}{T}\right)C = 1.1811 \left[\left(\frac{Mr}{T}\right)B - 8.8\right]$$

$$r = 1.1811 \left(\frac{10703}{274.5} - 8.8\right)\frac{273}{114.2}$$

$$r = 85.5 \text{ calories per gram}$$

Equation 3 shows there are two unknowns, m and a. If two experimental determinations of $(Mr/T)C$ for a hydrocarbon at different temperatures are known, two equations can be written substituting the values of $(Mr/T)C$ for the hydrocarbon and $(Mr/T)B$ for water and the values m and a determined. Thus, the latent heat can be calculated at any temperature after the values of m and a are known.

Table II—Comparison of Calculated Latent Heats of Alcohols at Various Temperatures with Values Obtained by Young

| TEMP. | ETHYL ALCOHOL | | PROPYL ALCOHOL | |
	Calcd.	Expt.	Calcd.	Expt.
°C.				
20	219.8	220.6	192.5	
40	218.0	218.7	187.1	
60	208.5	213.4	180.6	
80	201.4	206.4	172.1	173.0
100	194.5	197.1	163.1	164.0
120	184.0	184.2	152.3	153.0
160	159.5	156.9	128.4	129.0
200	129.6	116.6	100.1	102.2
240	81.5	40.3	61.6	63.4
243	00.0^a	00.0	00.0^a	00.0
			(263.7° C.)	

^{a} From data graphically interpolated.

Table III—Values of Slope m and Intercept a of the Molal Entropy Curves

	m	a
n-Heptane	1.3215	10.50
n-Hexane	1.1190	8.20
n-Octane	1.1811	8.80
Benzene	1.0950	7.00
Ethyl alcohol	1.0428	0.00
Propyl alcohol	1.2403	3.80

Latent Heats of Benzene, Heptane, Hexane, Octane, Ethyl Alcohol, and Propyl Alcohol

The latent heats of the four hydrocarbons, benzene, n-heptane, n-hexane, and n-octane, have been calculated from 0° C. to their respective critical temperatures, and the values are shown in Table I, together with the experimental values

of other observers. On comparing the values determined by others with those calculated by this method, it is evident that the agreement is good except in the vicinity of the critical temperature. This inaccuracy is not serious because in engineering practice use of values near the critical temperature is seldom necessary. However, even this error near the critical temperature can be corrected materially by a graphical method. Since the latent heat must be zero at the critical temperature, the latent heat–temperature curve must intersect the abscissa at the critical temperature. The dotted portion of the curve of Figure 3 shows the method of graphic interpolation.
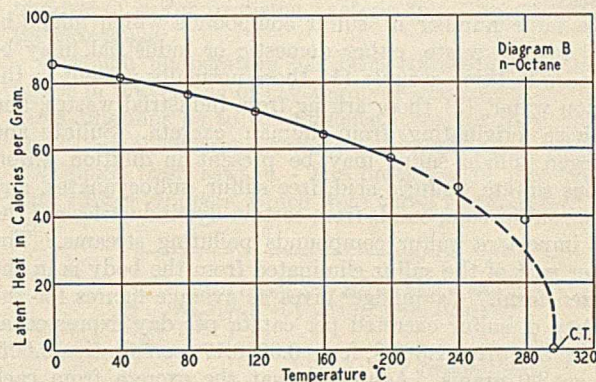

Figure 3—Latent Heat–Temperature Curve for Octane

The same procedure was attempted for the alcohols but the points of the molal entropy of vaporization fell on a straight line only up to pressures of one atmosphere when plotted against water. Therefore, it was decided to construct Dühring lines and entropy lines using methanol as a reference substance instead of water. By doing this, the points fell on a straight line within a much wider range of temperatures. The latent heats of ethyl and propyl alcohol were calculated in the same manner as octane, except that methanol was used as the reference substance. Table II shows the agreement between calculated and experimental values.

Table III shows the values of the slope, m, and x-intercept, a, obtained from the entropy lines of four hydrocarbons and two alcohols. The hydrocarbons were plotted against water and the alcohols against methanol.

Changes of Sulfur Compounds during Sewage Treatment[1,2]

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STABILIZATION of organic matter, by which is meant converting it by either oxidation or reduction into a form such that it will not take up dissolved oxygen, is normally a very complicated process. The stabilization of sulfur compounds, particularly in sewage, has not been studied in detail. From the standpoint of odor control, stabilization of sulfur compounds is particularly important. An odor nuisance will bring a complaint to a sewage-plant operator very quickly. The failure to study the fate of sulfur compounds in the degradation of organic matter is probably due to the extreme difficulties in making the analytical determinations.

The large number of sulfur compounds which might be found in any waste, either domestic or industrial, may be divided into three groups: (1) those normally present in the dilution water, (2) those arising from industrial wastes, and (3) those originating from human excreta. Sulfate and hydrogen sulfide sulfur may be present in dilution water. Ferrous sulfate, sulfuric acid, free sulfur, sulfocyanates, and organic sulfur compounds from certain dye industries are the most important sulfur compounds polluting streams. The greater part of the sulfur eliminated from the body is in the oxidized form. Cammidge[3] gives as average figures for the quantity of sulfur excreted per capita per day expressed as SO_3: in the urine 1.8–2.8, feces 0.06–0.17, perspiration 0.005, average 3.0 grams. Assuming that the excreta from each individual is diluted with 100 gallons of water, the sulfur addition amounts to only 3 to 4 p. p. m. in the sewage.

Methods for Determining Sulfur Compounds in Organic Matter

It has been shown that sulfur in sewage may exist in various forms, the quantity of which is usually very small. Of all the sulfur compounds present in sewage, determinations have thus far been made for inorganic, ethereal, organic, elementary, cystine, and cysteine sulfur, and hydrogen sulfide. For the determination of inorganic and ethereal sulfur the procedures given in standard texts of physiological chemistry were used. The precipitates of barium sulfate obtained by these procedures were ignited and weighed. The figures reported for inorganic sulfur represent both inorganic and ethereal sulfur. The quantity of ethereal sulfur was always quite low and the significance of the figures obtained from its determination does not appear to warrant considering it separately. If the quantity of organic sulfur was small, as

Human excreta account for but a small percentage of the sulfur found in sewage. Reduction of the sulfur content of sewage during sewage purification is small. Absence of obnoxious odors during treatment of sewage in nidus tanks was noted.

Anaerobic sludge digestion produces disagreeable odors unless the pH of the digesting sludge is kept above 7.0. The reduction of sulfates in raw sewage is very rapid at 37° C., fairly rapid at 22° C., and slow at 10° C.

The biochemical oxygen demand of several sulfur compounds has been determined.

Methods for determining various forms of sulfur have been adapted for use in sewage investigations.

is the case in raw sewage or effluents from units of treatment processes, the method of Bach[4] was used. For total sulfur in sewage sludge the method of Schreiber[5] was used.

Hydrogen sulfide was determined by the colorimetric method described by Almy.[6] The method depends upon the formation of methylene blue by adding solutions of *p*-amino dimethylaniline hydrochloride and ferric chloride to hydrogen sulfide solutions. The reagents used are: standard hydrogen sulfide solution for preparing standards; 0.04 gram *p*-aminodimethylaniline hydrochloride per 100 cc. 1:1 hydrochloric acid; 0.02 *M* ferric chloride; 0.6 per cent zinc acetate. Standards were prepared in 50-cc. Nessler tubes by adding 5 cc. of *p*-aminodimethylaniline hydrochloride and 1 cc. of ferric chloride to 44 cc. of distilled water containing a known quantity of hydrogen sulfide per 50-cc. tube. The standards ranged from 0.001 to 0.050 mg. of hydrogen sulfide per 50-cc. tube.

To 1-liter samples which were used for determining hydrogen sulfide in sewage, 50 cc. of concentrated hydrochloric acid were added and the flask containing the sample was aspirated with carbon dioxide for 30 minutes. The hydrogen sulfide was collected in 0.6 per cent zinc acetate and determined by adding the reagents in proportions as given for preparing standards. For quick approximate estimation of hydrogen sulfide, 10 cc. of sewage may be treated directly with 5 drops of *p*-aminodimethylaniline hydrochloride and 1 drop of ferric chloride solutions. A little experience will enable one to estimate the amount of hydrogen sulfide from the depth of color produced. Further work is being done on the development of this test for field use.

Such a small quantity of elementary sulfur is present in sewage that it is exceedingly difficult to determine it accurately. Extraction of the sulfur with carbon disulfide and oxidation of the sulfur in the extracted material have been used. The presence of elementary sulfur in laboratory experiments with sewage and sludge under complete anaerobic conditions has not been detected. The procedure used for determining cystine and cysteine was the iodate method of Okuda[7] as modified by Mr. Neave of this laboratory. (A titration temperature of 20–25° C. was maintained to give a more rapid titration, and a starch-iodide end point used, not only to increase the sensitivity of the determination, but also to adapt it for use in colored or turbid culture media and sewages.) The following are the average results obtained for cysteine: raw sewage = 0, in nidus tank effluent = trace, in liquor from digesting sludge = 0–2 p. p. m. The cystine content of raw sewage and nidus tank effluents varied from 0 to 2 p. p. m., and liquor from digesting sludge varied from 2.1 to 4.0 p. p. m.

[1] Presented before the Division of Water, Sewage, and Sanitation Chemistry at the 76th Meeting of the American Chemical Society, Swampscott, Mass., September 10 to 14, 1928.

[2] Abstract of thesis submitted by A. L. Elder in partial fulfilment of the requirements for the degree of doctor of philosophy in chemistry in the Graduate School of the University of Illinois.

[3] Cammidge, "Feces of Children and Adults," p. 22 (1914).

[4] Bach, *Gesundh. Ing.*, **46**, 370 (1923).

[5] Schreiber, U. S. Dept. Agr., Bur. Chem., *Circ.* **56** (1910).

[6] Almy, *J. Am. Chem. Soc.*, **47**, 1381 (1925).

[7] Okuda, *C. A.*, **21**, 3212 (1927).

Sulfur Removed during Sewage Treatment

The quantity of sulfur removed during sewage purification is so small that it is necessary to collect composite samples over long periods in order that sampling error may be minimized. From the data in Table I it appears that human excreta account for but a small percentage of the sulfur found in sewage. The Champaign-Urbana water supply contains only about 0.4 p. p. m. of sulfur, while the sulfur content of the sewage is about 40 p. p. m. This sewage contains practically no industrial wastes, so the increase in sulfur other than that accounted for by human excreta must come largely from other wastes and infiltration water which carries as much as 150 p. p. m. of sulfur.

Determinations have been made of the quantity of sulfur removed during the purification of sewage. (Table I)

Figure 1

From these data it appears that very little sulfur is removed during sewage purification processes. (The determinations made on activated-sludge plant samples were collected at Decatur, Ill. Industrial wastes account for the high sulfur content.)

Odor Control

During the anaerobic decomposition of sewage sludge hydrogen sulfide may be produced in sufficient quantity to create an odor nuisance. The addition of lime to sludge to keep the pH of the digesting sludge above 7 is of value in reducing odors. Introduction of

$$(H_2S \rightleftharpoons H_2S \rightleftharpoons H^+ + (HS)^-)$$
Gas   Dissolved
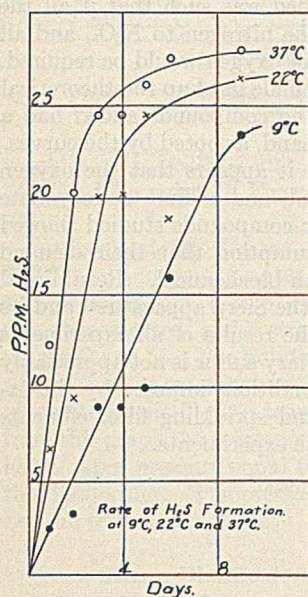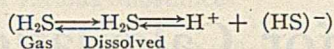
equilibria into the

$$H_2O + CO_2 \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + (HCO_3)^-$$
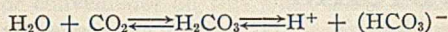
equilibria suggested by Johnston[8] indicates the value of adding lime to keep the pH above 7.

Table I—Average Sulfur Content of Samples of Raw Sewage, Imhoff Tank Effluent, Nidus Tank Effluent, and Activated Sludge Plant Effluent

SOURCE OF SAMPLE	NO. OF ANALYSES	PERIOD OF COLLECTION Days	INORGANIC SULFUR P. p. m.	ORGANIC SULFUR P. p. m.
Raw sewage	3	139	36.4	0.2
Nidus tank effluent	3	139	34.4	0.8
Raw sewage	3	107	35.9	2.2
Imhoff tank effluent	3	107	34.5	1.3
Raw sewage	1	5	92.8	Trace
Activated-sludge plant effluent	1	5	90.6	Trace

The decomposition of sludge yields little hydrogen sulfide during the first few weeks of digestion; after this period it gradually increases. In the experiments conducted maximum hydrogen sulfide production preceded maximum methane production, and the quantity of hydrogen sulfide in the gas was less than the theoretical quantity which might be present.

Different methods of sewage treatment result in varying quantities of hydrogen sulfide being produced. Enslow[9] has

pointed out the value of chlorine as a deodorant in sewage treatment. The value of the nidus tank as an intermediate device between the activated sludge process and the settling tank–trickling filter process is described by Buswell, Shive, and Neave.[10] Hydrogen sulfide determinations have been made over a long period on samples of raw sewage and effluent from nidus and Imhoff tanks dosed with this sewage. The results of several of these determinations are recorded in Table II.

Table II—Hydrogen Sulfide in Raw Sewage, Nidus Tank Effluent, and Imhoff Tank Effluent

SAMPLE	RAW SEWAGE P. p. m.	NIDUS TANK EFFLUENT P. p. m.	IMHOFF TANK EFFLUENT P. p. m.
1	0.2	0.25	0.64
2	0.25	0.2	0.6
3	0.25	0.2	0.5
4	0.2	0.2	0.4
5	0.2	0.2	0.3
6	0.1	Trace	0.3
7	0.2	0.1	0.5

The data in Table II represent determinations made at different times of the year. The effluent from the nidus tank never was found to contain more than 0.3 p. p. m. of hydrogen sulfide, while the Imhoff tank effluent has contained over 1.0 p. p. m. of hydrogen sulfide.

Bacteriological determinations have also shown the value of nidus tanks in lowering the hydrogen sulfide content of the sewage. Sulfate-reducing organisms increased in sewage during its treatment in the Imhoff tank and decreased in the nidus tank. No appreciable difference was noted in the number of sulfur oxidizing bacteria found in the effluent of the two tanks.

Although temperature has been considered an important factor in preventing or causing hydrogen sulfide odors, exact determinations as to its influence have not heretofore been made. In an experiment thirty 1-liter bottles were filled with well-mixed fresh sewage. The bottles were then stoppered with rubber stoppers, which were wired very tightly in place.
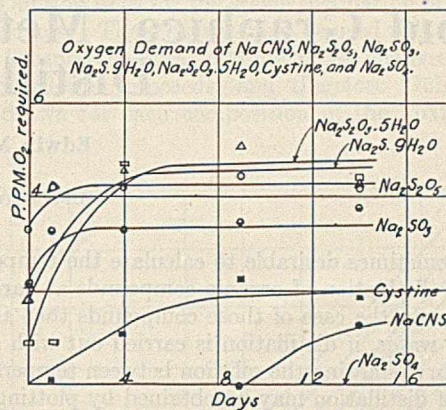

Figure 2

The bottles were placed in series of ten at three different temperatures—9°, 20°, and 37° C. The sewage[11] at the start of the experiment contained 28.1 p. p. m. inorganic sulfur, had an initial pH of 7.8, contained 0.09 p. p. m. hydrogen sulfide and a trace of dissolved oxygen. At the close of the experiment the pH of the sewage kept at 9° C. was 7.2, that at 22° C. was 7.0, and that at 37° C. was 6.6. Figure 1 shows the increases in hydrogen sulfide which were noted at various dates. The sulfate reduction was practically complete at the two higher temperatures.

[8] Johnston, J. Am. Chem. Soc., 38, 947 (1916).

[9] Enslow, U. S. Pub. Health Service, Pub. Health Rept. 42, 1623 (1927).

[10] Buswell, Shive, and Neave, Illinois State Water Survey, Bull. 25 (1928).

[11] The chemical character of this sewage has been described in detail in Illinois State Water Survey, Bull. 18, Appendix II.

Sulfur Balance Using a Synthetic Mixture

In some experiments on synthetic mixtures Rudolfs and Zeller[12] found that only a small percentage of the sulfate sulfur at the start of the experiment was found as hydrogen sulfide in gas from the digesting material. Experiments have been conducted by the authors to show that practically all the sulfur could be accounted for, provided an analysis of the digesting material was made at the close of the experiment. One of these experiments consisted in placing a known quantity of sludge, sodium sulfate, magnesium sulfate, and distilled water in a bottle. A gas collector was connected, and the gas collected and analyzed. Table III gives the sulfur balance for one of these experiments which was continued for 109 days. Mention should be made of the fact that in this experiment, as well as in all others in which the flasks were kept well sealed, no elementary sulfur was found at the close of the experiment. From the data in Table III one notes that sulfate reduction was practically complete and that 95 per cent of sulfur at the start was accounted for at the close of the experiment.

Biochemical Oxygen Demand of Sulfur Compounds

The biochemical oxygen demand of a substance is defined in Standard Methods of Water Analysis (1923) as the oxygen in parts per million required during the stabilization of the substance by aerobic bacterial action. Theriault[13] has pointed out the value of studying the rate of oxidation of pure substances, as by so doing one may estimate the effect of a known quantity of the substance on a stream. Using the procedure recommended in Standard Methods of Water Analysis and the dilution water used by Greenfield, Elder, and McMurray[14]

[12] Rudolfs and Zeller, IND. ENG. CHEM., **20**, 48 (1928).
[13] Theriault, U. S. Pub. Health Service, *Pub. Health Rept.* **173** (1927).
[14] Greenfield, Elder, and McMurray, IND. ENG. CHEM., **18**, 1276 (1926).

the oxygen demand of several compounds containing sulfur has been determined.

Table III—Sulfur Balance Obtained from Digestion Experiment with Synthetic Mixture

(Time, 109 days; temperature, 20° C.; 48,100 cc. of solution)

START OF EXPERIMENT	SULFUR	END OF EXPERIMENT	SULFUR
	Grams		*Grams*
Sludge	0.0398	Hydrogen sulfide evolved	0.2200
Sodium sulfate	4.9700	Sulfate sulfur	0.1240
Magnesium sulfate	0.9860	Hydrogen sulfide in soln.	5.1560
Peptone	0.7500	Organic sulfur	0.9150
Total	6.7458	Total	6.4150

95 per cent of sulfur recovered.
98 per cent of sulfate sulfur reduced.

In Figure 2 are given the results of one set of biochemical oxygen demand determinations. The percentage of the theoretical oxygen demand may be obtained from this figure, as the quantity of each salt added was such that if all the sulfur was oxidized to SO_3, all the nitrogen to N_2O_5, and all the carbon to CO_2, 5 p. p. m. of oxygen would be required. Sodium thiosulfate and sodium sulfide used up the theoretical quantity of oxygen. Some of the compounds added had a very high immediate oxygen demand, as noted by the curves. From the shape of these curves it appears that the oxygen demand of cystine is biochemical, and sodium sulfocyanate may be biochemical. The other compounds studied showed so rapid a rate of oxygen consumption that their demand appears to be more chemical than biochemical. Resublimed elementary sulfur was placed in the Sierp apparatus[15] and its oxygen demand determined. The results of all experiments thus far have shown that elementary sulfur is not appreciably oxidized in 30 days under the conditions imposed by the experiments. Both raw sewage and sprinkling filter effluents have been used as inocula in these experiments.

[15] Sierp, IND. ENG. CHEM., **20**, 247 (1928).

Rapid Graphical Method for Calculation of Steam Distillation Problems[1]

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IT IS sometimes desirable to calculate the temperature of steam distillation of organic compounds at various pressures. In the case of those compounds that are immiscible with water, if distillation is carried out with saturated steam, a curve showing the relation between temperature and pressure of distillation may be obtained by plotting the sum of the vapor pressures of water and the substance as ordinates against corresponding temperatures as abscissas. The making of this plot, however, requires considerable time; and it is the purpose of this paper to present a more rapid graphical method based on the use of Dühring lines.[2]

Dühring lines are lines obtained by plotting the temperatures at which a substance exerts certain vapor pressures, as ordinates, against the temperatures at which some suitable reference liquid, such as water, exerts the same pressures, as abscissas. The points so obtained fall very nearly upon a straight line.[3,4] This relationship depends on the fact that

[1] Received November 9, 1928.
[2] "Neue Grundgesetze zur nationelle Physik und Chemie," Erste Folge, Leipzig, 1878.
[3] Baker and Waite, *Chem. Met. Eng.*, **25**, 1137 (1921).
[4] Leslie and Carr, IND. ENG. CHEM., **17**, 810 (1925).

the vapor pressure–temperature curves of practically all substances are similar in shape.

In the steam distillation of liquids immiscible with water, the pressure at any given temperature is the sum of the partial pressures of the steam and the substance being distilled. Most substances follow Dühring's rule closely when plotted against water; and water plotted against itself necessarily gives a straight line. It is therefore to be expected that if the temperatures required for steam distillation were plotted against the temperatures at which water exerted vapor pressures equal to the sum of the partial pressures of steam and the substance being distilled, the result would be a straight line.

Steam Distillation of Chloroform

In Figure 1, curve *A* is the Dühring line for steam, curve *B* for chloroform, and curve *C* for the steam distillation of chloroform. Curve *C* was obtained as follows: At 30° C. the vapor pressure of chloroform is 246 mm. while that of water is 31.7 mm., giving a total pressure of 277.7 mm. If the steam distillation is to be carried out at 30° C., the pressure therefore
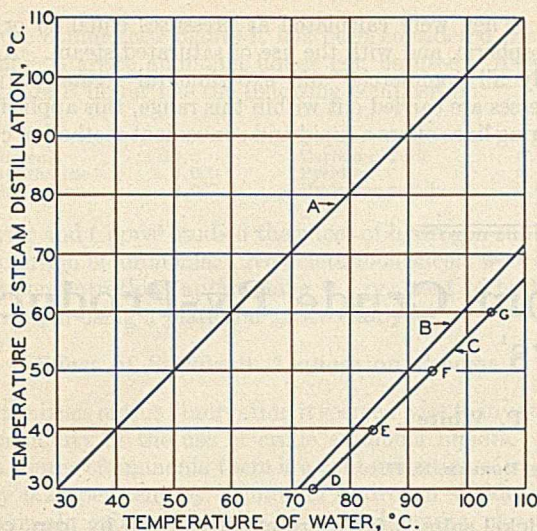
Figure 1—Dühring Lines: A—for Steam; B—for Chloroform; C—for Steam Distillation of Chloroform

would have to be 277.7 mm., which is the pressure of water at 74° C. The point D, Figure 1, is plotted with these coördinates.

Similarly at 60° C. the vapor pressure of chloroform is 739.6 mm. and that of water 149.2 mm. Water exerts a pressure of 888.8 mm. (739.6 + 149.2) at 104.4° C. The point G is then plotted, and a straight line drawn through the two points D and G. The points E and F are similarly calculated points, and show the correctness of this method. At any given steam distillation temperature there can be easily read from this graph the corresponding temperature at which water has a vapor pressure equal to that necessary for carrying out the distillation. The pressure of steam distillation may then be read from steam tables.

Steam Distillation of Various Substances

Figure 2 presents Dühring lines for the steam distillation of a number of substances, plotted against water as a reference liquid. For convenience on this chart there is also plotted the vapor pressure curve of water (OJ). To find the pressure
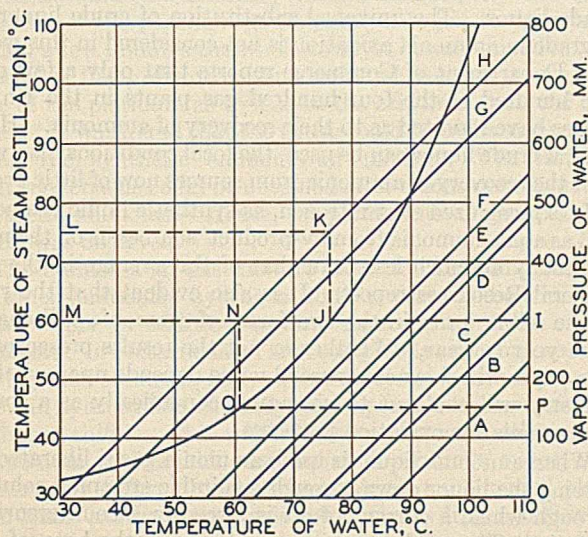
at which any of the substances may be steam-distilled at a particular temperature, it is merely necessary to go horizontally across the chart to the Dühring line, then down to the vapor pressure curve of water, and across to read the pressure. Line MNOP illustrates the use of this calculation to determine the pressure at which aniline would steam-distil at 60° C. Point M is the temperature of distillation (60° C.), point N is the corresponding temperature at which water exerts the same vapor pressure, and point O or P is this pressure, which is 152 mm.

Table I—Data for the Steam Distillation, with Saturated Steam, of Various Substances

		SLOPE AND INTERCEPTS OF DÜHRING LINES	
		Intercept on 100° C. H₂O	Intercept on 50° C. H₂O
SUBSTANCE BEING DISTILLED	Slope	line	line
Carbon bisulfide	0.994	43.2	−6.5
Acetone	0.972	52.3	3.7
Chloroform	0.984	55.6	6.4
Carbon tetrachloride	1.000	67.0	17.0
Benzene	0.992	69.5	19.9
Isopropyl iodide	0.986	74.7	25.4
Chlorobenzene	0.968	91.0	42.6
Aniline	0.980	98.6	49.6
12.39% octane–87.61% hexane	0.978	65.0	16.1
51.3% octane–48.7% hexane	1.032	78.8	27.2
12.4% hexane–87.6% heptane	0.992	76.9	27.3
48.04% hexane–51.96% heptane	1.014	69.7	19.0
87.0% hexane–13.0% heptane	1.008	63.3	12.9
9.74% heptane–90.26% octane	0.972	88.8	40.2
50.6% heptane–49.4% octane	0.984	83.8	34.6
86.6% heptane–13.4% octane	0.978	79.9	31.0

To find the temperature of steam distillation at a fixed pressure it is necessary to start from the pressure ordinate, go to the vapor pressure curve for water, then to the Dühring line, and then to the temperature of steam distillation. Thus the line IJKL shows that at 300 mm. total pressure aniline would steam-distil at 75.0° C.

Steam Distillation of Complex Solutions

The method is equally applicable to the steam distillation of complex solutions which obey Dühring's rule. Figure 3 presents Dühring lines for the steam distillation of a number of such systems. These curves must be used with discretion, however, because the organic liquid phase changes composition as distillation proceeds, and therefore Dühring lines must be drawn for each composition of the mixture being distilled.

Figure 2—Dühring Lines for Steam Distillation of Various Pure Substances (Left-Hand Ordinates) and Vapor Pressure of Water (Right-Hand Ordinates)

A—Carbon bisulfide
B—Acetone
C—Chloroform
D—Carbon tetrachloride
E—Benzene
F—Isopropyl iodide
G—Chlorobenzene
H—Aniline
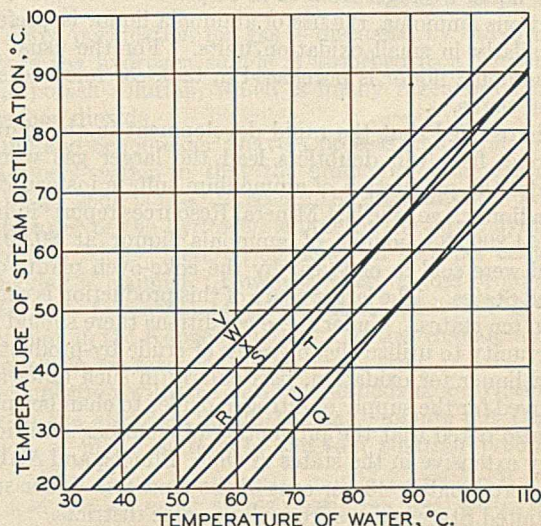
Figure 3—Dühring Lines for Steam Distillation of Various Organic Solutions

Q—12.39% octane–87.61% hexane
R—51.3% octane–48.7% hexane
S—12.4% hexane–87.6% heptane
T—48.04% hexane–51.96% heptane
U—87.0% hexane–13.0% heptane
V—9.74% heptane–90.26% octane
W—50.6% heptane–49.4% octane
X—86.6% heptane–13.4% octane

Data for Steam Distillation Lines

A straight line is very readily determined if the slope and an intercept are known. Table I gives data for the steam distillation lines of the substances and solutions plotted in Figures 2 and 3. For convenience these data are given as the slope and intercept on both the 50° and the 100° C. water line. They were calculated at pressures equal to or below atmospheric, and with the use of saturated steam. As practically all commercial and experimental steam distillation processes are carried out within this range, this application of Dühring lines offers a rapid and convenient method of calculation.

Oxidation of Ammonia from Crude By-Product Liquors[1]

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Crude coke-oven ammonia liquor in the air-stripping column cannot be used as the source of ammonia owing to the action of the volatile sulfur compounds upon the platinum catalyst. The air oxidizes some of the hydrosulfide of the ammonia liquor in the presence of the ammonium hydrogen carbonate to sulfur. This finely divided sulfur is eliminated in the exit liquor and does not cause stoppage of a properly designed column.

The iron oxide shavings mixture cannot be used as an adsorber of the sulfur compounds owing to the rise in temperature caused by the high adsorption of ammonia and a resultant pre-oxidation of the ammonia of the gas mixture. A liquid purification process using aqueous sodium carbonate solutions results in imperfect elimination of the sulfide compounds of the gas mixture due to the reversibility of the reactions in the presence of the large excess of carbon dioxide in the gas mixture. The cost of this process is also a serious factor.

The catalysis of the oxidation reaction

$$NH_4HCO_3 + NH_4HS + {}^1\!/{}_2O_2 \rightleftharpoons S + (NH_4)_2CO_3 + H_2O$$
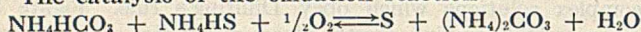
by nickel salts is far more effective than by iron, copper, or manganese salts. An explanation of the influence of the nickel salt is suggested.

The addition of an auxiliary gas washer to the exit line of the usual aqua ammonia stripping column makes possible the use of crude coke-oven gas liquors for the oxidation of ammonia by a platinum catalyst. The fluid of the scrubber consists of a soluble 0.2 formal nickel salt, which is converted in part to nickel sulfide, which is suspended in the washer. A small amount of the nickel compound causes the elimination of large amounts of sulfur in the gas. However, it is necessary to remove the accumulation of sulfur in the gas washer from time to time. The sulfur can be easily separated from the suspended nickel sulfide by using a flotation column, and most of the nickel thereby recovered.

Oxidation efficiencies at the platinum gauze, using synthetic ammonia as compared with the gas from purified crude ammonia liquor, check within 1 per cent.

. . . .

THE small ammonia oxidation unit is becoming a very important factor in chamber sulfuric acid plants.[2] Since the cost per pound of ammonia content of ammonia liquor averages from 12 to 15 per cent less than that of anhydrous ammonia, the use of ammonia liquor is preferred, particularly in small oxidation units. For the usual plant the ammonia liquor is purchased in tank-car lots and stored in iron tanks.

It is realized that the rapid development in the synthetic ammonia field will doubtless lead the larger gas works to consider the production of ammonium sulfate instead of ammonia liquor; yet the last Mineral Resources report[3] indicates that 54,809,335 pounds of ammonia liquor at $0.091 per pound were sold in one year by the coke-oven plants of the United States. The larger share of this production is confined within ten states. Under these conditions there should be an opportunity to utilize cheap grades of crude by-product ammonia liquor for oxidation, particularly in such units as are employed for the supply of nitrogen oxides to chamber plants. It is also noted that the production of chamber sulfuric acid is very extensive in the states of Ohio, Illinois, and Alabama, and approximately 40 per cent of the ammonia liquor sold in the United States comes from these same districts.

While no definite relative costs of ammonia in the form of grade B as compared with the crude by-product material could be obtained from the producers, it is realized that the shipping charges per pound of pure ammonia on the crude 14 per cent liquor will be greater than on the 29 per cent B grade liquor. The universal substitution of crude liquor for B grade in ammonia oxidation is not considered in this work. The Department of Commerce reports that only a few over one hundred of the four hundred gas plants in the United States have reported as to their recovery of ammonia. However, if crude liquor can be used, the local conditions may warrant the recovery of ammonia from sources now of little profit.

It is recognized that nitrogen, as synthetic liquid ammonia and as aqua ammonia from by-product sources, is on the market today at much less than that of the average in the last Mineral Resources report. It is also evident that the ratio of the selling price in the two forms of ammonia will change from year to year. Whether or not the results presented in this paper will show commercial value depends upon whether industry will continue to use aqua economically as a source of ammonia for oxidation purposes.

When ammonia liquor is used, ammonia gas is liberated by passing the liquor down through a suitable stripping column[4] through which a current of air is forced in a countercurrent direction. The weak liquor accumulating at the base of the column is heated to drive off the residual gas. This heat is now secured by the heat exchange from the hot exit gases of the converter.[2]

[1] Received December 18, 1928.

[2] Spangler, *Chem. Met. Eng.*, **35**, 343 (1928).

[3] Bur. Mines, *Mineral Resources* (January 9, 1928).

[4] Zeisberg, *Chem. Met. Eng.*, **28**, 9 (1923).

In the commercial plants it has been considered that not less than B grade ammonia liquor can be used. A typical high-grade B liquor has the following composition:

	Per cent		Gram per liter
Ammonia	29.5	Carbon dioxide	0.06
Naphthalene	0.009	Pyridine	0.11
Soluble tar	0.037	Hydrogen sulfide	0.00

Taylor and Capps[5] studied the effect of hydrogen sulfide on the oxidation of ammonia. No deleterious effects were noted in gas concentrations approaching 0.1 per cent of hydrogen sulfide when using a platinum gauze catalyst.

Effect of Sulfide in Liquors on Process

On the basis of this observation it seemed wise to investigate the possibility of the use of crude ammonia liquors. With such a source of ammonia there is a contamination of approximately 0.26 per cent by volume of hydrogen sulfide in the ammonia-air mixture. This corresponds quite closely to the concentration of some commercial coke-oven gases which contain about 0.5 per cent. At the present time there is considerable variation in the composition of the crude ammonia liquors on the market. A crude liquor was obtained from the Merrimac Chemical Company, of Woburn, Mass., which had the following composition:

	Per cent
Ammonia	13.83
Carbon dioxide	15.70
Sulfur	0.68
Combined ammonia	92.80

It was believed that the high content of ammonia combined as bicarbonate and carbonate with the small amounts of combined sulfur was representative of as nearly bad conditions as ever could be encountered.

A laboratory stripping column of glass, packed with glass rings, was installed in connection with an ammonia oxidation apparatus using two layers of horizontal platinum gauze of 0.076 mm. (0.003 inch) diameter and 80 mesh. Provision was made for preheating the ammonia-air mixture in an electrically heated quartz tube just before entrance to the platinum gauze. A test using synthetic ammonia was always made as a basis of comparison. The ammonia-air mixture from the stripping column was turned into the system in place of the synthetic ammonia mixture; almost immediately the temperature of the platinum gauze catalyst began to drop until within a few minutes the whole catalyst became inactive. A deposit of finely divided sulfur collected over the whole surface of the platinum as well as in the exit lines from the oxidizer. It was found that the gauze could be easily revived by using the synthetic ammonia–air mixture. The initially high conversions could be obtained after a considerable use of synthetic ammonia. Hence, no permanent effect upon the gauze was observed.

The ammonia-air-gas mixture from the stripping column contains ammonia, hydrogen sulfide, carbon dioxide, and water vapor in addition to air. Aqueous solutions of the carbonate or bicarbonate are completely decomposed on boiling into ammonia and carbon dioxide. Ammonium sulfide and hydrosulfide are easily decomposed into ammonia and hydrogen sulfide. It is well known that aqueous solutions of ammonium hydrosulfide decompose in air into water, ammonia, and sulfur. It seems probable that the heated platinum gauze catalyzes the oxidation of the hydrogen sulfide by air with the resultant precipitation of sulfur over the whole gauze surface. Many efforts using a wide range of preheat temperatures were attempted. It was obvious that in order to use crude by-product liquor in the stripping column some secondary method of purification must be employed.
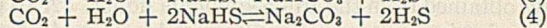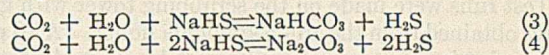
Search for Purification Method

The use of iron oxide for removing hydrogen sulfide from city gas gave the first general method for investigation. Dunkley and Leitch[6] have made a careful study of iron oxides, and some of their results upon activity, capacity, and revivability were found helpful. One commercial oxide was obtained and several other mixtures were made up in the laboratory. A suitably designed adsorber was placed between the crude-ammonia stripping column and the ammonia oxidation apparatus. All the tests gave the same ultimate results. All the solid mixtures had very high adsorptive capacities for the ammonia gas in the air mixture. This adsorptive action was so intense that enough heat was evolved within the iron oxide shavings to promote the partial oxidation of the ammonia. In most instances the shavings of the iron oxide mixture were changed to a carbonized mass. This preoxidation of the ammonia by a solid adsorber for the hydrogen sulfide made continued investigation of this method almost useless.

The next possibility seemed to be a liquid purification method. There are many patents and a goodly number of published papers upon the various liquid purification processes as applied to coal and water gas. The Seaboard liquid purification process has been described by Sperr,[7] Broker,[8] Bird,[9] and others. The process involves two reversible reactions:

$$H_2S + Na_2CO_3 \rightleftharpoons NaHS + NaHCO_3 \qquad (1)$$
$$CO_2 + H_2O + Na_2CO_3 \rightleftharpoons 2NaHCO_3 \qquad (2)$$

and possibly

$$CO_2 + H_2O + NaHS \rightleftharpoons NaHCO_3 + H_2S \qquad (3)$$
$$CO_2 + H_2O + 2NaHS \rightleftharpoons Na_2CO_3 + 2H_2S \qquad (4)$$
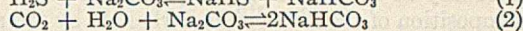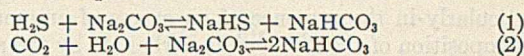
A 1 to 3 per cent sodium carbonate solution is used. The usual consumption of carbonate in the purification of coal gas is about 1 pound for every 8 pounds of hydrogen sulfide removed. Towers packed with coke, wooden hurdles, spiral tile, or steel turnings have all been used. However, this process removes only about 85 per cent of the hydrogen sulfide in the gas.

The Koppers or modified process[10,11] secures higher efficiencies at a cost of only $0.0077 per thousand cubic feet of coal gas. The fundamental absorption reaction is in accord with Equation 1 and is then followed by Reaction 5.

$$3NaHS + 3NaHCO_3 + 2Fe(OH)_3 = Fe_2S_3 + 3Na_2CO_3 + 6H_2O \quad (5)$$
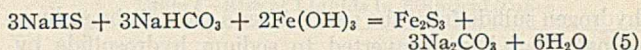
Petit's wet purification for gas is discussed by Stavorinus,[12] and here the hydrogen sulfide is absorbed in a 25 per cent caustic potash solution, which is finally regenerated by air and carbon dioxide.

Glund and Schonfelder[13] have a process which differs from the Koppers system in that the ammonia of the gas rather than added soda is used to secure the alkalinity for accelerated transfer of the hydrogen sulfide to the ferric hydroxide or hydrous oxide. Here an efficiency of 99.9 per cent with no clogging is claimed. However, there is loss of ammonia due to high formation of thiosulfates. This loss is much higher than in the Koppers method, but the fixed ammonia in the liquor can be recovered in ammonia stills.

In connection with the various methods of recovering the sulfur in the absorber liquid, Cundall[11] points out that the addition of nickel sulfate to the foul solution produces a

[5] Taylor and Capps, J. IND. ENG. CHEM., **11**, 27 (1919).

[6] Dunkley and Leitch, Bur. Mines, *Tech. Paper* **332** (1924).

[7] Sperr, *Gas Age-Record*, **51**, 639 (1923); IND. ENG. CHEM., **16**, 1237 (1924).

[8] Broker, *Gas Age-Record*, **51**, 499 (1923).

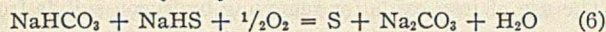[9] Bird, *Chem. Met. Eng.*, **29**, 16 (1923).

[10] Sperr, *Gas Age-Record*, **52**, 553 (1923).

[11] Cundall, *Chem. Met. Eng.*, **34**, 143 (1927).

[12] Stavorinus, *Gas*, **42**, 183 (1923).

[13] Glund and Schonfelder, *Chem. Met. Eng.*, **34**, 742 (1927).

nickel sulfide catalyst for Reaction 6 which is very effective and in which only very small amounts of nickel are needed.

$$NaHCO_3 + NaHS + \frac{1}{2}O_2 = S + Na_2CO_3 + H_2O \quad (6)$$

Time and thoroughness of contact are essential. In the Koppers recovery system the $Fe_2S_3.3H_2O$ serves a similar purpose.

An experimental system consisting of an iron pipe as an ammonia-air generating column filled with glass rings,[4] 60 inches high by 2 inches diameter, was erected. This column was operated with the usual control as employed in any system which generates an ammonia-air mixture by a counter-current flow of air. The crude ammonia liquor was metered into the top of the column, while the intake air and steam were metered into the base of the column. The gas left the top of the column at an average of 35° C., while the temperature at the base remained at 70° C. In series with this column a second iron column, 36 inches high by 2 inches diameter, served as the means of removal of sulfur compounds. This last tower was packed with glass rings in some tests and with iron filings in other tests.

In all these tests it was noted that the liquid from the base of the gas-generating column was very high in finely suspended sulfur. It seemed rather conclusive that this was caused by Reaction 7,

$$NH_4HCO_3 + NH_4HS + \frac{1}{2}O_2 \rightleftharpoons S + (NH_4)_2CO_3 + H_2O \quad (7)$$
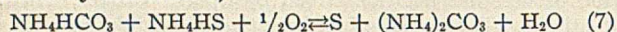
particularly in the presence of an excess of ammonia. The decomposition of the ammonium carbonate by the air stream forces this reaction in a favorable direction.

Test runs were made on the scrubbing tower with gas mixtures obtained from the crude ammonia liquor. A 10 per cent ammonia-air mixture was generated by control of the exit temperature of the column. A 15 per cent sodium carbonate solution was circulated at different rates over the glass-filled, as well as the iron-filings-filled, scrubbing tower; yet in each instance considerable hydrogen sulfide remained in the gas.

In view of the fact that there was much suspended sulfur in the generating column and yet imperfect elimination of sulfur in the gas from the absorption column, it seemed that possibly poor contact was being obtained between the liquid and gas. To verify this a set of liquid washers was substituted for the absorption column. It was found that during the first few minutes of use there was quite complete removal of hydrogen sulfide from the gas. After a part of the sodium carbonate had been converted to sodium hydrosulfide by Reaction 1, the hydrogen sulfide began to pass. This was possibly due to Reaction 3 or 4.

Since Reactions 1, 2, 3, and 4 indicate equilibrium types of reactions, it seemed logical to expect incomplete elimination of hydrogen sulfide in the presence of carbon dioxide except when a very large mass effect of sodium carbonate prevailed. then, too, hasty calculations indicated that the theoretical daily consumption of sodium carbonate by a cubic foot of gas per minute ammonia oxidizer would approximate 110 pounds. It is obvious that this method is unsatisfactory economically as well as from the imperfect elimination of sulfur from the gas.

Reaction 7 is the analog of Reaction 6 and should be susceptible to catalysis. The use of such catalysts as the sulfides of nickel, iron, manganese, and copper seemed to present a more economical solution to the problem. A water suspension of any one of these sulfides should scrub out the hydrogen sulfide and carbon dioxide. In the presence of the ammonia there should be formed ammonium hydrogen carbonate and ammonium hydrosulfide, and this should undergo oxidation in accord with Equation 7. By proper catalysis this reaction can be made to continue until the surplus of sulfur begins to contaminate the sulfide catalytic surface. The large excess of ammonia provides the necessary alkalinity for the contact

action. The only source of trouble might be the slight formation of thiosulfates, causing an abnormal loss of ammonia.

An ammonia-air mixture was generated from the crude ammonia liquor and a series of tests upon equivalent amounts of water suspensions of the four sulfides was made to determine their relative catalytic powers. Each test was conducted under the same conditions of contact time, gas temperatures, etc. An intake temperature of 82° C. and an exit temperature of 20° C. were maintained. The contact time of the gas with the aqueous suspension of sulfide was purposely maintained at only a fraction of a second. The observations of Table I were noted.

Table I—Relative Catalytic Powers of Various Sulfide Suspensions

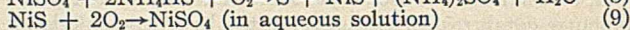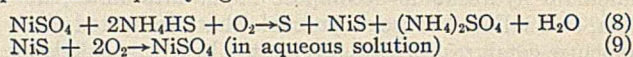| TYPE OF SUSPENSION	TIME BEFORE H₂S BROKE THROUGH WASHER	NH₃ REMAINING IN 82° C. WASHER
	Minutes	Per cent
Pure water	3.5	0.49
NiS	More than 5 hours	1.12
CuS	18	1.00
MnS	9	0.79
Fe₂S₃	9	0.75

These data clearly show that nickel sulfide is far superior to the other sulfides in the catalysis of Reaction 7.

Efficiency Tests with Nickel Sulfide as Catalyst

The efficiency of this method, as applied to the laboratory ammonia-oxidation equipment, was next studied. The passage of air through the ammonia-liquor stripping column eliminates a part of the sulfur in accord with the uncatalyzed Reaction 7. The air carrying ammonia, carbon dioxide, hydrogen sulfide, and sulfur compounds in accord with the temperature conditions at the gas exit of the scrubber was then passed to a gas washer in which was placed a definite amount of 0.2 formal $NiSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$. After passage through the purifying washer, the ammonia-air mixture was introduced into the oxidation apparatus using a platinum gauze catalyst.

Each test was started upon ammonia air obtained by mixing metered quantities of synthetic ammonia and air. Efficiency tests were carried out upon the gauze catalyst for a given set of conditions and then the gas was quickly changed to the crude-liquor purification equipment. No difference could be detected in the physical appearance of the platinum catalyst when the change was made. Efficiency determinations under the two different gas supplies did not show a variation of more than 1 per cent. The purified gas mixture was tested for 1-minute continuous periods with lead acetate paper and no trace of sulfide was indicated. The purifying washer consisted of three sections and the gas-exit section remained blue during the whole 3-hour period. The quantity of nickel salt present theoretically would be converted to sulfide by the hydrogen sulfide in the mixture within the first 37 minutes of operation; hence the catalytic efficiency was established.

During the tests it was observed that, although the first washing section always remained very black, the second section fluctuated at times between a dark and a bright color. At the end of a 3-hour test air was circulated through the washer and the color of the second washer was immediately changed to white and a continued deposition of sulfur occurred. It seemed as if Reactions 8 and 9 might be taking place in the purifying washer:

$$NiSO_4 + 2NH_4HS + O_2 \rightarrow S + NiS + (NH_4)_2SO_4 + H_2O \quad (8)$$
$$NiS + 2O_2 \rightarrow NiSO_4 \text{ (in aqueous solution)} \quad (9)$$

The cycle of these reactions over and over again will account for the very large amount of gaseous sulfide which a given amount of a nickel salt will decompose. Those sulfides which appear to be the most effective in this reaction are those which are readily oxidized in moist air. Of course, in the presence of the excess of ammonia the complex salt with

nickel sulfate is the material involved rather than the simple salt. The gas-intake section of the purifying washer always consisted of a mixture of sulfur and nickel sulfide, while the gas-exit section consisted of the ammoniacal nickel sulfate and remained a clear blue solution.

The tests were not made to determine the exact life of the nickel salt. However, the action is distinctly catalytic, yet owing to the sulfur precipitation it is necessary to draw off the purifier washer liquors from time to time in order to separate the sulfur, which accumulates as a heavy sludge. The sulfur is so finely divided that it is easily separated from the nickel sulfide and accompanying liquor by a simple flotation process

in an auxiliary column, and hence there is very little loss of nickel sulfide. The actual loss of ammonia in these liquors is also very small. If Reaction 8 is taking place it is noted that the ammonia lost as fixed nitrogen is related to the sulfur removed in the gas washer and hence must be relatively very small. A small amount of thiosulfate may also be formed.

In all the large-scale tests there was a tendency for the purifying washers to develop frothing, and accordingly the design of this unit must take the frothing factor into account.

All the tests were very convincing as to the efficiency of this method for the utilization of crude coke-oven liquors for any form of platinum-catalyst oxidation units.

Capillary Phenomena in Non-Circular Cylindrical Tubes[1]

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IN SPITE of the volume of literature dealing with capillarity, little attention has been given to the consideration of phenomena occurring in non-circular cylindrical tubes, a problem of some practical importance.

From the fundamental principles of capillarity the force exerted on any element in the meniscus-wall contour is directed perpendicular to the contour in a plane tangent to the meniscus at that point. Let φ be the angle between the vertical z axis and the direction of this force on an element ds of the contour. The total force in the z direction is therefore

$$\sigma \int_S \cos \varphi \, ds$$

taken around the contour, where σ is the surface tension. For a cylindrical capillary this is equal to $\sigma P \cos \vartheta$, where P is the perimeter of the cross section of the tube and ϑ is the angle of contact—that is, the angle between the tangent to the liquid surface and the wall.

This total force sustains a weight of liquid $\int_S \rho \, gz \cos \alpha \, dS$ where ρ is the density, g the acceleration of gravity, and dS is an element of meniscus surface at a height z above the free liquid and inclined at an angle α to the horizontal, the integral being taken over the entire meniscus S. Hence

$$\sigma \int_S \cos \varphi \, ds = \sigma P \cos \vartheta = \int_S \rho \, gz \cos \alpha \, dS \quad (1)$$

We may put $z = z_0 + \Delta z$, where z_0 is the height of the lowest point of the meniscus above the free liquid and Δz that of any element of the surface S above the plane $z = z_0$. Then

$$\sigma P \cos \vartheta = \rho \, g z_0 \int_S \cos \alpha \, dS + \rho g \int_S \Delta z \cos \alpha \, dS \quad (2)$$

The integral $\int_S \cos \alpha \, dS$ is simply the cross-sectional area A of the tube. The first term on the right of Equation 2 represents the supported weight of liquid below the plane $z = z_0$, while the second term is the weight of liquid above this plane. The latter quantity may be neglected for capillaries of small sectional dimensions so that as an approximation we obtain

$$z_0 = \sigma P \cos \vartheta / \rho \, gA \quad (3)$$

For a tube of rectangular cross section with the sides a and b we have

$$z_0 = 2 \, \sigma(a + b)/\rho \, gab \quad (4)$$

For an elliptical tube having the semi-axes a and b

$$z_0 = 4 \, \sigma \, E(k)/\pi \, b\rho g \quad (5)$$

where $E(k)$ is the complete elliptic integral of the second kind and $k = (1 - b^2/a^2)^{1/2}$. Equation 3 is obviously applicable to much more complicated forms of cylindrical capillaries— for example, the space enclosed by a bundle of circular rods, etc.

Frequently non-circular capillaries have been treated as circular capillaries of equivalent cross section. This in general, however, leads to erroneous results. As an illustration, data are given in Table I for the rise of carbon tetrachloride and pure water, respectively, in ordinary thermometer tubing of elliptical cross section.

Table I—Rise of Liquids in Elliptical Tubes

2a	2b	CAPILLARY RISE z_0			
		Obs.	Eq. (5)	$r = \sqrt{ab}$	$r = (a + b)/2$
Mm.	Mm.	Cm.	Cm.	Cm.	Cm.
CARBON TETRACHLORIDE AT 19° C.					
0.133	0.101	6.00	5.98	5.90	5.84
0.305	0.192	2.94	2.94	2.82	2.75
0.128	0.062	8.50	8.45	7.66	7.21
0.223	0.142	4.00	3.98	3.84	3.74
	$\sigma = 26.5$	$\rho = 1.58$	$g = 981$	$\vartheta = 0$	
PURE WATER AT 24° C.					
0.142	0.223	17.2	17.2	16.6	16.1
0.192	0.305	12.6	12.6	12.2	11.8
	$\sigma = 72.2$				

This agreement between the observed data and those computed by Equation 5 is within the error of the measurements. The fifth column shows the values computed on the assumption of a circular tube of equivalent cross section, and the sixth column values computed for a circular tube having a radius equal to the arithmetical mean of the semi-axes of the ellipse. Both of the last two methods are in current use but do not seem to be so satisfactory.

There are references[2] in the literature to the fact that the vapor pressure over a meniscus surface is different for circular and non-circular capillaries of the same cross-sectional area. This readily follows from a consideration of the above dis-

[2] For example, Schultze, Kolloid-Z., 36, 65 (1925).

cussion. In a closed system let p_0 be the vapor pressure over the free liquid, p_1 that over the meniscus, and d the mean vapor density. Then $p_0 - p_1 = dgz_0$ and from Equation 3

$$p_0 - p_1 = d \sigma P \cos \vartheta / \rho A \qquad (6)$$

This equation is usually sufficient for practical purposes, but

may be easily extended by replacing ρ with $(\rho - d)$ and by considering the variation in density of the vapor column. The formula so obtained is as follows:

$$\log p_ /p_1 = d_0 \sigma P \cos \vartheta / p_(\rho - d)A \qquad (7)$$

where d_0 is the vapor density over the free liquid.

Free Energy Charts for Predicting Equilibrium Pressures and Concentrations[1]

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A DESIRE has often been felt for thermodynamic charts from which physical and chemical equilibria could be predicted directly, with little or no calculation. In this paper a form of chart is suggested which allows practically direct reading of equilibrium pressures or concentrations, if a chart be prepared for each pure substance in question. It is intended to prepare these charts for such substances as are met in the work of this organization. Meanwhile the idea is presented here in the hope that charts of this kind may find favor elsewhere and, through criticism and coöperation, be developed in the most convenient form.

A form of chart is suggested which allows practically direct reading of physical and chemical equilibrium concentrations, if a single chart be prepared for each pure substance in question. The chart involves lines of constant pressure or concentration, with temperature as abscissa and a function of the free energy as ordinate. Various suggestions are given as to methods of preparation of the charts, and their extension to ions and solutions of electrolytes. Sample charts are given for oxygen.

It is believed that the construction of these charts, with suitable modifications, from available thermodynamic data or free energy equations will result in a considerable saving of time to those making frequent calculations of chemical equilibrium concentrations. If free energy charts for a number of common compounds could be standardized and published, they would probably come into general use, even by those unfamiliar with thermodynamics, and serve a purpose in chemistry similar to that served by the heat-entropy charts in engineering.

dition can be reached because a given weight of a substance contains less free energy at a low concentration than at a high concentration. As far as thermodynamics is concerned, every reaction involving the formation of a dissolved substance will occur to at least a very slight extent when only the reactants are mixed, unless $\Delta F°$ is infinite.

While we cannot easily overestimate the value of these "free energy equations," there are a number of practical difficulties attending their use. In the first place, it is not the numerical value of the standard change in free energy in which we are primarily interested. The driving force or the direction of a reaction could just as well be considered in other terms related to the free energy. In the majority of cases the quantity desired is the equilibrium pressure or concentration of a substance under certain conditions. This requires the calculation of the equilibrium constant from the free energy equation, which is a time-consuming operation, and finally, the calculation of the desired quantity from the equilibrium constant, which often necessitates the conversion of activities to concentrations. Again, the free energy equation for the formation of a compound from its elements must hold for any temperature at which we desire to use it for some other reaction involving this compound, if the equations are to be of general use. This requires an adequate equation for the specific heat, not only of the compound in which we are interested, but of its elements, in which we may not be interested. The difficulties attending the derivation of a simple but accurate specific heat equation for a large temperature range are well known. These difficulties may be overcome to a certain extent by the use of charts, as will be shown subsequently. The use either of charts or of free energy equations is subject to the assumption that the thermodynamic properties of any substance are not affected by the presence of the other substances involved in the given reaction. This assumption, however, can sometimes be removed by the use of special charts or equations for a given reaction.

Use of Free Energy Equations

The most common method of applying thermodynamics to the prediction of equilibria consists in expressing the change in free energy involved when a given reaction occurs with all components of the reaction (both resultants and reactants) present at unit "'effective" concentration (activity).[2] This "standard change in free energy," $\Delta F°$, is usually given for a standard temperature or as a function of the absolute temperature, and is determined by making use of heats of reaction, specific heats, measured equilibrium concentrations, the third law, and electromotive force measurements, in various combinations. For the sake of condensation, the standard free-energy changes involved in the formation of a number of compounds from their elements may be tabulated, and the standard free-energy change for any reaction involving several of these compounds found by addition.

Since all spontaneous reactions must occur with a decrease of free energy, the sign of $\Delta F°$ tells in what direction the given reaction will proceed when both reactants and resultants are mixed at unit activity. If the concentrations change during the course of the reaction, the magnitude of $\Delta F°$ determines the concentrations finally reached at equilibrium —that is, the point at which a further proceeding of the reaction would involve an increase in free energy. In other words, at equilibrium ΔF (not $\Delta F°$) is zero. Such a con-

Description and Use of Free Energy Charts

The charts presented here are based upon the principles given above, employing the idea of constant pressure lines

or constant composition lines, as in the Mollier charts used in power and refrigeration. Suppose the function F/T for a pure substance be plotted against the Centigrade temperature where F is the molal free energy with reference to some standard and T is the absolute temperature at the given Centigrade temperature on the chart. This function gives curves of more convenient shape and spacing than the free energy itself. For a perfect gas, for instance, the 1-atmosphere curve would be $2.303 R$ below the 10-atmosphere curve. In the analytical method of Lewis and Randall the reference point varies with the temperature. For instance, the free energy of the most common state of an element at unit activity is zero at any temperature.

It will be seen that, in general, there will be a single curve for each allotropic solid form of the substance, a curve for the pure liquid, and a curve for any one pressure of the gas. (Figures 1 to 3) These curves will intersect at the temperature where two forms or states are in equilibrium. This is in conformity with the principle that at equilibrium $\Delta F = 0$. The vertical distance between any two lines at a certain temperature, multiplied by the absolute temperature, gives the free energy change involved in passing from the one state to the other. The lower lines, therefore, represent the more stable condition. The constant pressure lines for the gas intersect the liquid curve at the saturation temperatures corresponding to the given pressures.

In addition to the curve for the pure liquid, lines of constant composition of the liquid phase may be plotted. In the case of hydrochloric acid, for instance, these lines may refer to the aqueous solution. In other cases they may be plotted on the assumption that Raoult's law is obeyed. The ordinates in such a case represent partial molal quantities. The intersections of the vapor curves with these liquid
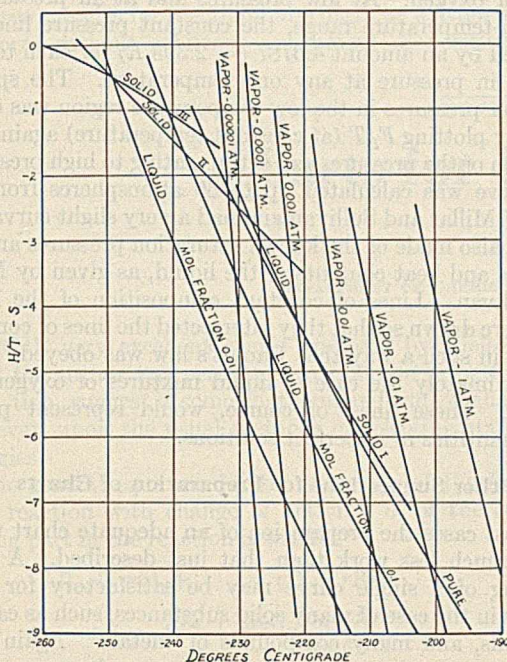
Figure 1—Free Energy of Solid, Liquid, and Gaseous Oxygen

curves represent the vapor pressure of the solution or the solubility of the gas, as the case may be. The intersection of the solid curve with the liquid curves shows the freezing point of the solution or the solubility of the solid.

In order that the charts may be used in the prediction of chemical equilibria, it is necessary that the free energy of any compound be referred to the elements from which it is formed. For example, the free energy of carbon monoxide at any tem-

perature may be referred to carbon and oxygen at 25° C. and 1 atmosphere pressure. The free energy of all substances charted, including the elements, would then have to be taken as relative to the elements at 25° C., in order that the charts may be combined for the prediction of chemical equilibria. In the method of Lewis and Randall the reference point varies with the temperature, as mentioned before. The application of the charts to chemical equilibria may best be shown by an example:

Suppose, in the reaction

$$C(s) + H_2O(g) = H_2(g) + CO(g)$$
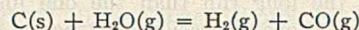
it is required to find the partial pressure of CO in the presence of H_2 at 0.2 atmosphere and H_2O at 0.7 atmosphere at 1000° C. Find the ordinate on the carbon chart at 1000, add the ordinate on the H_2O chart corresponding to 1000 and to 0.7 atmosphere pressure, and subtract the ordinate on the H_2 chart corresponding to 1000 and 0.2 atmosphere. The difference is the ordinate on the CO chart corresponding to 1000 and to the required pressure of CO.
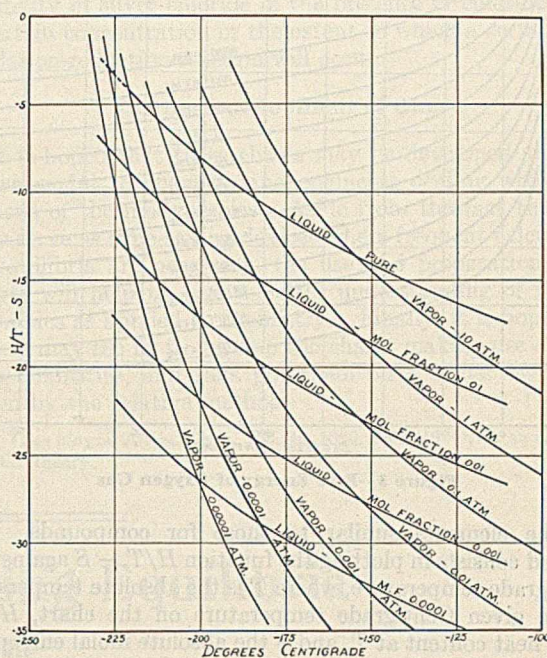

Figure 2—Free Energy of Liquid and Gaseous Oxygen

Methods of Preparation

There is some question as to what function is the best to plot in these charts. For convenience in the shape and spacing of the curves, it seems that the free energy relative to some standard, divided by the absolute temperature, is the best. We can, for instance, plot directly the equations developed by Lewis and Randall for the free energies of various compounds, after dividing out one power of T. In the case of elements which are liquid or solid at room temperature, we shall have a horizontal straight line corresponding to $F/T = 0$ for the state most stable at room temperature. Lines for the other states will then cross this line at the proper places, and be so spaced as to give the free energy of change of state at any one temperature, divided by the absolute temperature. The charts do not show the change of free energy of a given state with temperature, a quantity which, admittedly, is seldom desired. The constant composition and constant pressure lines are spaced in accordance with the free energy of dilution and expansion. For perfect solutions or perfect gases the vertical distance between two curves, one of which corresponds to ten times the concentration of the other in mol fractions, is $2.303 R$. In the case of a substance which is normally a gas at room temperature, the 1-at-

mosphere curve will usually deviate a little from the equation, corresponding to the difference between the free energy of the gas at unit pressure and that at unit fugacity. These charts can probably be built up most easily by the algebraic method, and afterwards adjusted further by the use of more equilibrium data. Since the equations are not to be used after the charts are constructed, more adequate specific heat equations can be used than is normally done, or different equations used for different ranges.

There is another method which, it is believed, will be more satisfactory in the long run than the one just described. In the first place, it enables easier construction of the charts without the use of equations. In the second place, it eliminates the necessity of knowing the specific heat, over a large range, of both a compound and its elements, when only the chart for the compound is desired. It also makes the charts
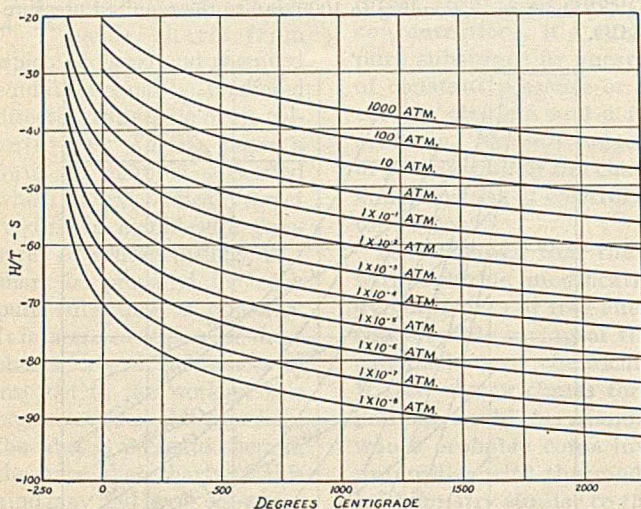

Figure 3—Free Energy of Oxygen Gas

for the elements similar to those for compounds. This method consists in plotting the function $H/T - S$ against the Centigrade temperature, where T is the absolute temperature at the given Centigrade temperature on the chart, H the molal heat content at T, and S the absolute molal entropy at T. The heat content of any substance is relative to the pure solid elements composing the substance at absolute zero. As long as the chart is used for an equilibrium at uniform temperature, this function works by virtue of the fact that $\Delta H - T\Delta S$ is zero at equilibrium. The specific heats of the elements need be known only between absolute zero and the temperature at which the heat of formation of the compound is known, unless it is desired to use the equilibrium data for the reaction involving the formation of the compound, in which case charts would probably be prepared for the elements. The charts would, of course, be adjusted by the use of equilibrium constants, where these are known, after a rough preparation from thermal data.

The charts prepared by this method can therefore be made as accurate as those prepared by the previous method, even though the absolute heats and entropies themselves are not accurately known. The preparation of the charts may, however, lead to fairly accurate values of these fundamental quantities, and thus make the chart for each substance more or less permanent. For instance, charts for oxygen, hydrogen, water, and carbon and its oxides may be prepared as a start, and adjusted to correlate all the best available data on these substances. There are, in fact, quite accurate thermal data now available on all these substances. Other charts can then be added and correlated with these. The charts could conveniently be published as

tables showing the relation of $H/T - S$ to composition at a number of temperatures. Each individual could then prepare his own charts from the tables by the method of double plotting described in the next paragraph.

The accuracy with which the charts can be read depends, of course, upon the size of the charts. Charts drawn on millimeter paper about 18 by 24 inches (46×61 cm.) are easily readable to within 1 per cent, without an unreasonable number of curves. This is probably within the limits of accuracy of the method itself.

The Charts for Oxygen

Some suggestions as to methods of preparing these charts may be had from an explanation of the charts for oxygen shown here. For convenience, the free energy chart for oxygen was made in three sections. These are, of course, very much reduced, the original being on large sheets of millimeter paper and containing more lines. Figure 1 is for a very small low-temperature range, showing equilibria in the solid, liquid, and gaseous phases. Figure 2 shows the solution-vapor portion of the chart and Figure 3 the gaseous curves for a large temperature range. The heat contents were calculated by graphical integration of the specific heats, using a calculating machine, and adding the heats of the various transformations at the proper temperatures. The entropies were calculated in the same way, except that the plot used was one of 2.303 times the specific heat, against $\log_{10} T$. The data used were those of Eucken[3] for solid and liquid oxygen, the tables of Millar and Sullivan[4] for liquid and gaseous oxygen at low temperatures and high pressures, and a specific heat curve drawn from data given by Goodenough and Felbeck[5] and by Partington and Shilling[6] at high temperatures. It is, however, not the purpose of this article to submit a reliable chart for oxygen. At low pressures and at all pressures in the high-temperature range, the constant pressure lines are separated by an amount 4.5787 ($= 2.303 R$) for each tenfold increase in pressure at any one temperature. The spacing for higher pressures in the low-temperature region was determined by plotting F/T (at constant temperature) against the logarithm of the pressure, and extrapolating to high pressures. This curve was calculated up to 60 atmospheres from the tables of Millar and Sullivan and had a very slight curvature. Use was also made of the known saturation pressures and the entropies and heat contents of the liquid, as given by Millar and Sullivan. Lines of constant composition of the liquid phase were drawn so that they intersected the lines of constant pressure in such a way that Raoult's law was obeyed. This is approximately the case in liquid mixtures of oxygen and nitrogen. These lines, of course, would represent partial molal quantities in imperfect solutions.

Other Suggestions for Preparation of Charts

In most cases the preparation of an adequate chart would involve much less work than that just described. A chart consisting of a single curve may be satisfactory for most purposes in the case of many solid substances, such as carbon, the metals, and many compounds of metals. Again only charts for a certain range of temperature or from one phase may be required. Charts may often be prepared directly from known equilibria, with the aid of other charts. If an accurate chart is available for carbon and carbon monoxide, for instance, a fairly reliable chart for carbon dioxide may be prepared from known equilibria in the reaction $C + CO_2 =$

[3] Eucken, *Ber. physik. Ges.*, **18**, 4 (1916).
[4] Millar and Sullivan, Bur. Mines, *Tech. Paper* **424** (1928).
[5] Goodenough and Felbeck, University of Illinois, *Bull.* **139** (1924).
[6] Partington and Shilling, "Specific Heat of Gases," D. Van Nostrand Co., New York, 1924.

2CO, for the range over which these equilibria are known. Known saturation pressures of liquids and solutions, solubilities, freezing points, etc., help to locate points on the charts. As pointed out previously, the spacing of the constant composition curves may be determined by plotting F/T at constant temperature against the logarithm of the composition. A straight line is obtained for any one temperature if the gas or solution is perfect. In the case of gases at low temperatures and high pressures, the compressibilities or Joule-Thomsen coefficients may have to be used if a very accurate chart is desired, but this double plotting helps to prepare a very complete free energy chart from only a few accurately known points at different temperatures. In the case of hydrochloric acid lines of constant composition in aqueous solution may be accurately located with the aid of saturation pressures and of activity coefficients. In many cases, of course, charts covering only a limited range may be sufficient, or even charts showing only physical equilibria for one substance without employing the same free energy function as the other charts. The latter form obviously cannot be used in connection with other charts.

Ions and Electrolytes

These charts may be extended to solutions of electrolytes or to ions, if desired. Hydrochloric acid has already been mentioned. In the case of potassium chloride, the curve for solid potassium chloride intersects the lines of constant molality in aqueous solution at the temperatures and molalities corresponding to saturation. Thermal data for solid potassium chloride, and the activity coefficients of aqueous potassium chloride help to complete the chart. In conjunction with the charts for potassium and chlorine, this chart should predict the electromotive force of the cell K, KCl (x molal), Cl_2 (y atm.) at various temperatures. Equilibria and free energies for reactions which can be written in molecular form without arbitrary assignment of positive ions to

negative ions may be predicted by these charts for electrolytes. This includes such reactions as

$$Cu + CuCl_2(aq.) = 2CuCl(s)$$
$$Zn + 2AgCl(s) = ZnCl_2(aq.) + 2Ag$$
$$H_2 + Cl_2 = 2HCl(aq.)$$
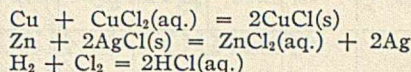
This is, in fact, the only kind of reaction for which the use of the "mean activity of the ions" or the "activity coefficient" of the electrolyte is mathematically exact.

The free energy charts for individual ions would probably be made on the assumption that the standard free energy of the reaction $H_2 = 2H^+$ is zero at 25° C. Since most of the data are at 25° C., these charts had probably best consist in a plot of $F/298$ against composition (or the logarithm of the composition). A curve could then be drawn for each of several ionic strengths, in accordance with the "principle of the ionic strength" of Lewis and Randall and the Debye-Hückel theory.[7] These ionic charts could be used in conjunction with the other charts to predict electromotive forces and ionic equilibrium concentrations—as, for instance, the solubility of silver chloride in the presence of chloride ion at a certain concentration or the extent to which a certain ionic oxidation-reduction reaction will occur.

Further Development of Charts

It is hoped that these charts may be developed and may prove useful to chemists and engineers dealing with applications of thermodynamics. Aside from the fact that they may serve as time-saving devices where frequent calculations of equilibria are necessary, the use and preparation of the charts will help to give a better understanding of thermodynamics as applied to chemistry. Finally, it is hoped that others may see fit to develop the charts making use of absolute quantities, and thus put them on a firmer basis than given by the relative method.

[7] See Noyes, *J. Am. Chem. Soc.*, **46**, 1080, 1098 (1924), for an exposition of this theory.

Charts for Predicting Equilibria[1]

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THE very excellent charts proposed by Nielsen,[2] which the author was permitted to examine prior to publication, suggest a somewhat similar form of chart based, however, upon the usual methods of selecting standard free energies.

The general equation for the variation of the free energy of a reaction with change of activity, a, of the substances taking part in the reaction is written[3]

$$lL + mM + \cdots = qQ + rR + \cdots \qquad (1)$$

$$\Delta F = \Delta F° + RT \ln \frac{a_Q{}^q\, a_R{}^r \cdots}{a_L{}^l\, a_M{}^m \cdots} \qquad (2)$$

where ΔF is the free energy of the reaction when the substances are at the indicated activities, $\Delta F°$ is the standard free energy or the free energy when all the substances are at unit activity, R the gas constant, T the absolute temperature, and the final quotient is known as the activity quotient.

[1] Received March 18, 1929.
[2] Nielsen, IND. ENG. CHEM., **21**, 568 (1929).
[3] For derivation of equations and definition of the various quantities see Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923.
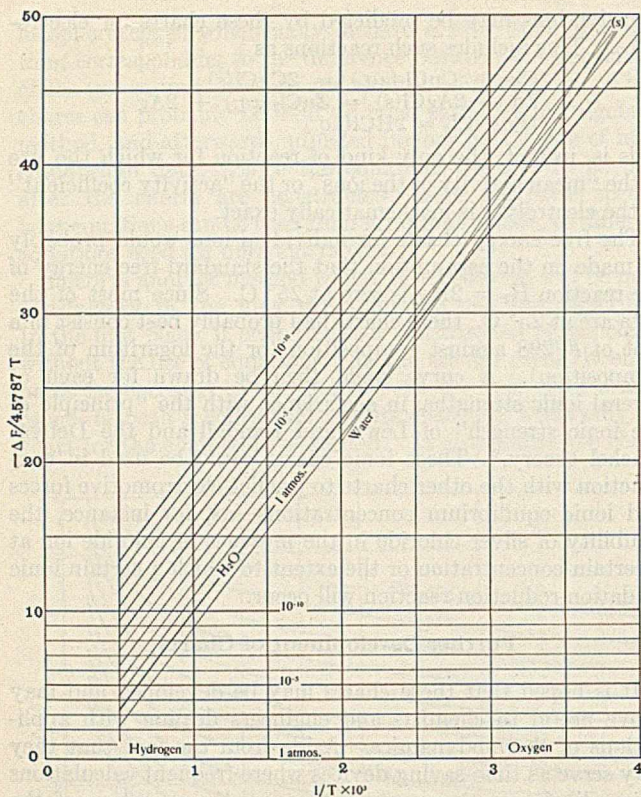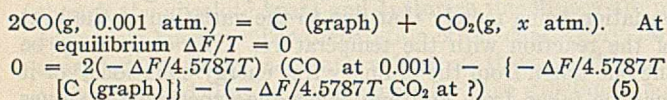
The special value of the activity quotient when the reaction is at equilibrium is known as the equilibrium constant.

Let us divide Equation 2 by $-4.5787\, T$, whence we obtain

$$-\frac{\Delta F}{4.5787\, T} = -\frac{\Delta F°}{4.5787\, T} - \log \frac{a_Q{}^q\, a_R{}^r \cdots}{a_L{}^l\, a_M{}^m \cdots} \qquad (3)$$

If we have equilibrium conditions $\Delta F/4.5787\, T$ is zero and $-\Delta F°/4.5787\, T$ is equal to $\log K$, where K is the equilibrium constant. If the substances are all at unit activities, we have $\Delta F = \Delta F°$. We now plot $-\Delta F°/4.5787\, T$ or $\log K$ against $1/T$, and obtain in the case of water vapor, the plot shown in Figure 1. This plot is nearly a straight line, the variation being merely that due to the variation of the heat of the reaction with the temperature. The curve may be the one taken from the ordinary free energy equations,[3] or it may be taken from and may show the experimental values of the equilibrium constants.

In the case of water vapor at low pressures, the activity of the vapor is equal to its pressure in atmospheres. From an inspection of Equation 3 it is evident that if the activity of the water vapor is 0.1, the activities of the oxygen and hydrogen being unity, the curve of $-\Delta F/4.5787\, T$, or the curve

Figure 1—Function of Free Energy of Hydrogen, Oxygen, and Water

Figure 2—Function of Free Energy of Carbon Oxides

for the free energy of formation of water vapor at 0.1 atmosphere, will be parallel to the standard curve but one unit higher; and so with the other curves shown. For water vapor above atmospheric pressure, parallel curves would represent tenfold increases in the activity, but the actual curve is drawn diagrammatically to represent actual water vapor at 10 atmospheres.

We also show in Figure 1 the curves for the free energy of formation of liquid water at unit activity and at activity = 0.1. We also show the curve for ice. As in the case of the curves of Nielsen,[2] the intersection of two curves represents equilibrium between the phases at the particular temperature of the intersection. Thus the intersection of the 1-atmosphere water vapor curve with the 1-atmosphere liquid curve is at $1/T = 0.0002680$ or 373.1° K.

Since the free energy of the elements in their standard condition is taken as zero at all temperatures, the curves of $-\Delta F/4.5787T$ for gaseous elements (when gas is chosen for the standard condition) are a series of lines parallel to horizontal axis and spaced one unit apart with values equal to $-\log P$ or $-\log a$. Thus we have straight lines instead of the curved lines of Figure 3 of Nielsen, which are different for each gas. We also give in Figure 2 the chart for carbon, carbon dioxide, and carbon monoxide.

For illustration, let us find the pressure of carbon dioxide in equilibrium with carbon and carbon monoxide at 1000° K. and 0.001 atmosphere pressure. From the equations

$2CO$(g, 0.001 atm.) = C (graph) + CO_2(g, x atm.). At equilibrium $\Delta F/T = 0$
$0 = 2(-\Delta F/4.5787T)$ (CO at 0.001) $-$ {$-\Delta F/4.5787T$ [C (graph)]} $- (-\Delta F/4.5787T$ CO_2 at ?)   (5)

Reading 2 times the ordinate of the 0.001 CO(g) curve (= 24.8), less the ordinate of the C (graph) curve at $1/T = 0.001$ (= 0), we have $-\Delta F/4.5787 T$ for the CO_2 (g) = 24.8. Whence interpolating, we find that this is the value which falls at $1/T = 0.001$ on a curve for CO_2 (g) at 2×10^{-5} atm. This will be the equilibrium pressure of the carbon dioxide.
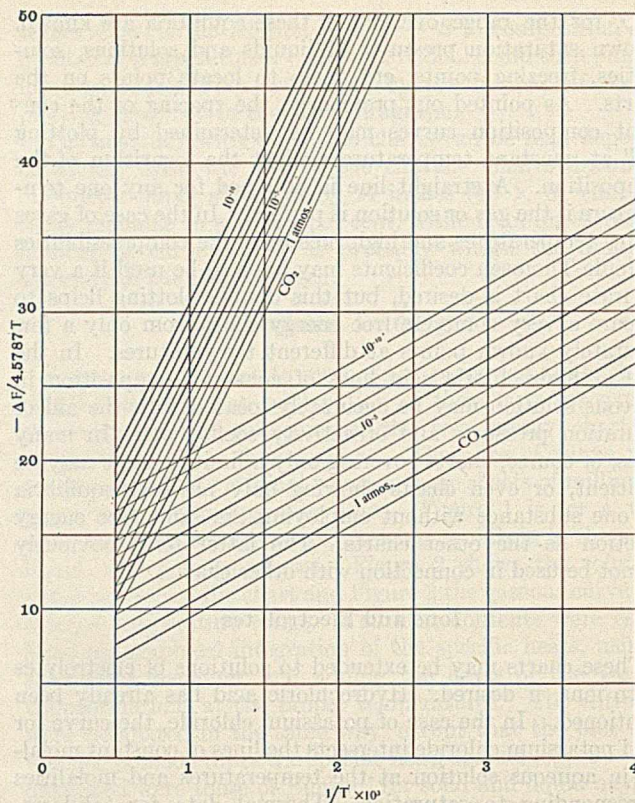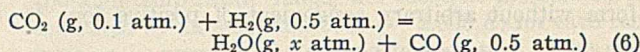
Again, considering the water gas reaction at the same temperature, what is the pressure of water vapor at 1000° K. when carbon dioxide is at 0.1, hydrogen at 0.5, carbon monoxide at 0.5 atmosphere?

CO_2 (g, 0.1 atm.) + H_2(g, 0.5 atm.) =
        H_2O(g, x atm.) + CO (g, 0.5 atm.)   (6)

As before, we subtract from the sum of the ordinate for H_2 at 0.5 and CO_2 at 0.1 atmosphere the ordinate for CO (g) at 0.5 atm., whence $-\Delta F/4.5787 T$ for the H_2O (g) is 11.1 which at 1000° K. corresponds to the H_2O curve at about 0.09 atmosphere. In this case, since the hydrogen and carbon monoxide were assumed at the same pressure, we could equally well have taken the values at 1 atmosphere for these two substances, thus reducing the uncertainty of the interpolation.

It is hardly necessary to give examples of charts of dissolved substances, or of ions. In these cases, the plots are made at tenfold multiples of the mol fraction or molalities, or mean molalities of the substances as the case may be. The activity coefficient must be taken into consideration in plotting the charts, and in general the curves for electrolytes will not be spaced exactly one unit apart, except in very dilute solution.
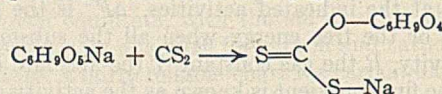
Corrections

Some Scientific Aspects of Packaging and Quick-Freezing Perishable Flesh Products

II—Packaging Flesh Products for Quick-Freezing[1]

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BECAUSE many flesh products are decidedly seasonable, and because it will be desirable to package such products largely during times of oversupply, the finished product should be capable of prolonged cold storage at or near the point of manufacture. Therefore, let us consider some of the principal sources of trouble during storage.
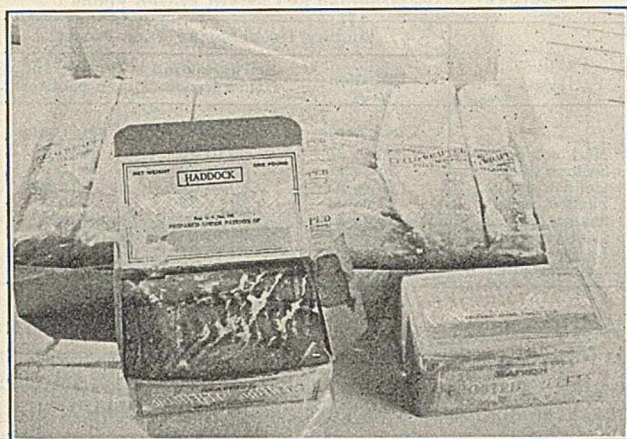
Figure 1—One-Pound Carton Containing Three Portion-Size Haddock Fillets, and Separately Wrapped Haddock Fillets Assembled into a 10-Pound Carton

Causes of Deterioration

Desiccation is one important cause of deterioration and is due largely to the lack of constancy and uniformity of temperatures throughout the storage room. Heat penetrates into the room through the walls and open doors and is given off by lights and by the bodies of workmen; and this heat is absorbed by the refrigeration pipes. The stored product is of course warmer than the pipes and the saturation point of the air is lower at the pipes than at the product. Thus moisture is continuously absorbed from the product, carried by convection currents to the refrigeration pipes, and deposited there in the form of frost. Obviously this moisture evaporation from the fish is more or less in direct proportion to the surface area exposed. The extent of this evaporation may be seen from Table I.

The experiments reported in Table I were carried out with unglazed fish under European storage conditions, at a temperature of −7° C. and 85 to 90 per cent humidity. Peterson[2] says that in Europe fish are usually frozen suspended individually in air at from −15° to −7° C., more often at the higher temperature. In the United States, however, only approximately 25 to 40 per cent are frozen individually, the remainder being frozen in blocks; and sharp-freezer temperatures are very low—from −23° to −34° C. For these and other reasons, the desiccation shown in Table I is very much greater than is usual under the United States practice of sharp-freezing and cold-storing whole fish.

As will be noted from the table, the factors of size, shape, and leanness or fatness control the rate of evaporation to a certain extent. A small fish dries faster than a large one of the same species. Lean fish dry faster than those protected by a subcutaneous layer of fat. Yet the eel, which is fattier than the mackerel, dries faster during the first stage, because of the larger ratio of surface to bulk. Since these figures are according to European technic, they are slightly higher than will be the case in our domestic freezers, but they illustrate the great necessity for protection against evaporation during storage.

Table I—Loss in Weight during Freezing and Cold Storage of Whole Fish[a]

KIND OF FISH	INITIAL WEIGHT	NUMBER OF DAYS STORED							
		10	20	40	60	80	100	120	140
	Grams	*Grams*	*Grams*	*Grams*	*Grams*	*Grams*	*Grams*	*Grams*	*Grams*
Coalfish	3827	5.9	8.9	15.0	21.0	..	..	..	..
Cod	2674	7.4	11.0	18.2	25.5	..	..	..	..
Haddock	858	11.4	18.2	28.6	37.3	43.0	..	..	..
Haddock	318	17.0	27.6	42.7	52.0	57.5	60.0	61.6	62.3
Plaice	570	9.6	16.6	28.1	37.2	44.8	..	..	..
Plaice	179	15.1	26.2	43.3	54.2	62.0	65.0	65.5	66.5
Mackerel	421	3.3	7.8	14.9	19.9	24.2	27.2	29.4	31.1
Eel	349	8.3	12.3	17.7	20.9	22.6	..	..	..

[a] Zentral-Einkaufsgesellschaft m. b. H. Berlin, 1916.

Oxidation is another prolific source of trouble, for the fats of most flesh products are readily oxidized by contact with the air during cold storage. The rate of oxidation decreases with the temperature of the storage room, and increases as the fat-containing tissues are broken down by autolysis. It is most rapid on exposed cut surfaces, and may best be held in check by a practically air-tight protective coating and low storage-room temperatures.

The natural bright color ("bloom") of flesh is often changed during prolonged cold storage to a brownish tinge. This is caused by conversion of the hemoglobin of the product to
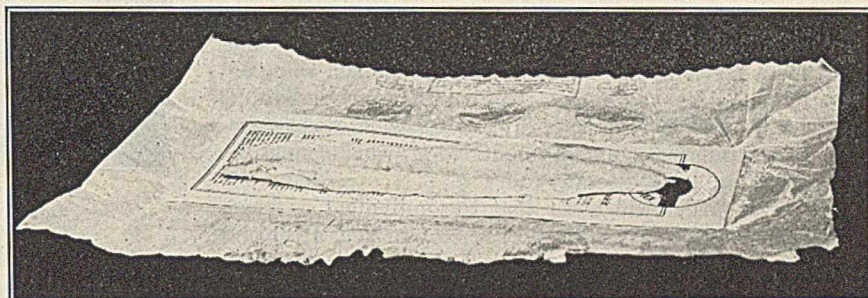

Figure 2—Individually Frozen and Wrapped Haddock Fillet

methemoglobin through contact with the gases of the air.[3] Discoloration, like oxidation, is most pronounced in exposed surface areas.

Flavor is another quality which may suffer during prolonged storage and subsequent distribution. This is due, among other causes, to desiccation, evaporation of volatile

[1] Received April 15, 1929.
[2] Peterson, *Refrigerating World*, September, 1924.
[3] Taylor, "Refrigeration of Fish," Appendix VIII to report of U. S. Commissioner of Fisheries for 1926, p. 523.

substances, oxidation of fats, and absorption of odors from contaminated storage rooms, refrigerated freight cars, and dealers' ice boxes. All these factors are minimized by reducing the exposed surface area and utilizing an air-tight protective coating.

Heat leakage into a cold-storage room, refrigerated car, or insulated shipping container is in direct proportion to the surface exposed; and the amount of heat which the product can absorb without thawing is dependent upon the quantity of the product. The greatest care must be taken to prevent thawing of carloads of quick-frozen products during transfer
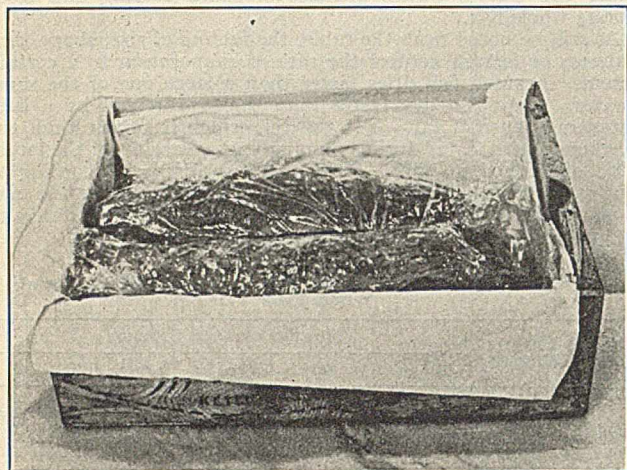
Figure 3—Individually Frozen Salmon Fillets

from one storage point to another, for if the product is allowed to soften it will be slow-frozen when it again enters storage. Therefore, it is essential that the product be packed as compactly as possible.

Bacterial contamination of flesh products is difficult to control, and it is obviously desirable that the products be protectively packaged as soon as possible after having been dressed.

Manufacturing and Marketing Requirements

The requirements of the manufacturer, distributor, and consumer must be met satisfactorily if quick-frozen, packaged, perishable flesh products are to become a commercial success. From the manufacturer's viewpoint the product must be packed so as to facilitate quick-freezing and in such a manner as to require the minimum of wrapping and cartoning material for a given weight of product. Economical shipment from manufacturer to dealer requires that the individual packages be packed in strong, dry, inexpensive, non-returnable, heat-insulated shipping containers, which must be rectangular and packed solidly full.

The retail dealer will insist that the individual packages themselves be clean, dry, and odorless; retain their attractive appearance after being thawed; and require the minimum weighing and wrapping before delivery.

Most important of all, perhaps, are the demands of the ultimate consumer. First among these must be uniform high quality—the goods must be packaged at or near the point of production and must have the flavor, juiciness, color, and appearance characteristic of the best unfrozen materials. They must be absolutely clean to start with, sanitarily handled throughout the production process, and effectively protected from contamination until they reach the consumer's kitchen. They must keep fresh the maximum time after thawing, and be free from inedible portions, ready to cook the moment they are taken from the package,

of convenient size, and trade-marked in such a manner that the brand carries through to the consumer's kitchen.

Packaging before and after Freezing

It will have become apparent from the foregoing that a successful package of quick-frozen flesh products must be completely full, with the minimum amount of air within the package. This can be accomplished only by packing the product first and freezing it afterward. Unfrozen flesh products—even those containing a considerable proportion of large bones—are comparatively soft and yielding, and the individual cuts can be made to fit together so as to fill compactly the carton in which they are packed. After such products are frozen, however, they are unyielding and usually of irregular shape, and therefore cannot be compactly assembled into a package. These facts are well illustrated in Table II.

Table II—Space Occupied by Certain Frozen Foods

| PRODUCT | VOLUME OCCUPIED BY ONE POUND | | |
	Unfrozen	Packaged and then frozen	Frozen and then packaged
	Cubic inches	*Cubic inches*	*Cubic inches*
Haddock fillets	26 to 27	29 to 30	54 to 90
Salmon fillets	26 to 27	29 to 30	64 to 70
Codfish steaks	26 to 27	30 to 31	51 to 55
Shelled oysters	27 to 28	29 to 30	56 to 59
Sea scallops	26 to 27	29 to 30	57 to 59
Lamb kidneys	26 to 27	28 to 29	38 to 43
Lamb chops	26 to 28	30 to 31	44 to 48
Sirloin steaks	26 to 28	29 to 30	45 to 47

It is significant that a carton of product packed before it is frozen usually exposes very much less surface area than the same weight of that product frozen before it is packaged. Thus, in a one-pound package of haddock fillets, $1^7/_8 \times 3 \times 5$ inches (Figure 1), composed of three portion-size pieces
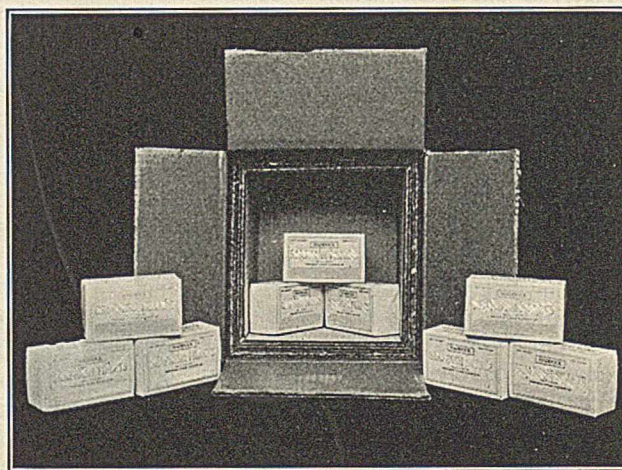

Figure 4—Insulated Container for Shipping

of fillet fitting snugly against each other and completely filling the package, the surface exposed to desiccation and oxidation amounts to only 60 square inches—i. e., to the area of the ends, sides, top, and bottom of the package. Two half-pound haddock fillets laid out flat and frozen individually present approximately 177 square inches of surface area. These same two half-pound haddock fillets separately wrapped and then assembled into a ten-pound container before being frozen will have a total surface area of 106 square inches—and in actual practice only about an average of 25 per cent of this area would be exposed at the surface of the block of product within the carton.

A moisture-vapor-proof and air-tight covering has been

shown to be another essential feature of packaged quick-frozen flesh products. This is an additional reason why the products should be packaged before being frozen, because both the necessity for and the cost of wrapping increases with the amount of surface which must be protected. The 14-ounce individually frozen haddock fillet shown in Figure 2, placed on a sheet of cardboard and then wrapped in parchment paper, required 280 square inches of wrapping material; while a fillet of the same weight individually wrapped and then packed with others in a carton required only 127 square inches of wrapping to cover it completely. The individually frozen salmon fillets shown in Figure 3 occupied 66 cubic inches per pound of fillets, and required 188 square inches of wrapping material.
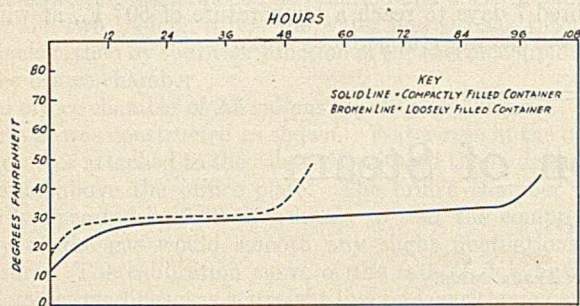
Figure 5—Temperature Rise in Centers of Two Identical Corrugated Shipping Containers, One Compactly Filled with Two Ten-Pound Cartons of Haddock Fillets Packaged before Being Frozen and the Other Loosely Filled with Single Fillets Frozen Separately before Being Packed. Average Room Temperature, 60° F.

Kinds of Packaging Materials

Now let us consider the relative merits of various wrapping and cartoning materials available for use in packaging quick-frozen flesh products. The first material to be used extensively for this purpose was pure vegetable parchment paper, paraffin-coated on both sides. This is a thoroughly excellent wrapping material, one of its most valuable characteristics being that it will not disintegrate in the presence of water—it can, in fact, be boiled for a prolonged period without becoming weakened. Ordinary transparent cellulose sheets—e. g., Cellophane and Crystal Klear—have been used for wrapping flesh products and have the benefit of displaying the products to excellent advantage. This class of material has, however, proved unsatisfactory, chiefly because it is not moisture-vapor-proof, and the sheets adhere tightly to each other both while the product is frozen and after it has thawed.

Compact cardboards, containing a minimum of air spaces and cold-waxed on both sides, have been extensively used for cartoning quick-frozen flesh products and have proved very satisfactory. It is probable that the inclusion of a thin asphalt layer in the center of the board considerably increases its vapor-proof value.

Glassine paper, paraffin-coated on both sides, is being successfully used as a heat-sealed wrapping for the outside of small cartons. This material has a relatively high resistance to the passage of moisture vapor and is fairly transparent. However, it loses strength when kept wet for a prolonged period and is therefore not suitable for use in direct contact with a product.

Probably the most nearly moisture-vapor-proof and air-tight wrapping available is an improved cellulose material known as Moistureproof Cellophane. This material is al-

most completely transparent and has a very high resistance to the passage of moisture vapor and other gases. The individual sheets do not stick together and the material is in itself water-tight and greaseproof. It is, however, more expensive than other wrapping materials, and its field of usefulness is limited by that fact. The relative moisture-vapor-proofness of some of the above materials was determined as follows:

The paper to be tested is sealed tightly over the top of a glass crystallizing dish. One edge is then broken just enough to allow the insertion of a pipet. About 10 or 15 cc. of water are placed in the dish, after which the broken edge is tightly sealed again. These dishes are placed in the constant temperature oven, which is regulated to within 0.5° C. and in which calcium chloride or concentrated sulfuric acid is distributed so that the atmosphere in which the dishes are exposed represents a practically zero relative humidity. The atmosphere inside of the dish, of course, represents 100 per cent relative humidity. The air in the oven or the desiccator is constantly agitated by a small fan connected to a small motor. The covered dishes are weighed to an accuracy of 1 mg. before the test and then placed in the constant-temperature oven for 24 hours. They are then removed, brought to room temperature and again weighed. The loss in weight is calculated back to the grams of water vapor lost per square meter of surface exposed per 24 hours, at 38.33° C.

Table III—Relative Moisture-Vapor-Proofness of Several Wrapping Materials[a]

Sample	Wrapping Material	Moisture-Vapor-Proofness
1	Regular Cellophane	1920
2	Parchment, lightly waxed one side	1350
3	Glassine, unwaxed	1250
4	Parchment, unwaxed	1130
5	White glassine, waxed both sides	384
6	White waxed paper, waxed both sides	220
7	Brown waxed paper, waxed both sides	100
8	Glassine, waxed both sides	70
9	Kraft, waxed both sides	42
10	Glassine, waxed both sides	36
11	Kraft, waxed both sides	35
12	Glassine, waxed both sides	17
13	White waxed paper, waxed both sides	17
14	Kraft, waxed both sides	12
15	Moistureproof Cellophane	5

[a] These papers were taken from a variety of packages most of which contained bread or other bakers' products. The list includes some of the poorer grades of paper, some of the average grades, and three of the very best of the hundreds which were tested.

The results are shown in Table III. Although no tests have been conducted at temperatures of less than 10° C., there is excellent reason to believe that the moisture-vapor-proof qualities of Moistureproof Cellophane improve as the temperature is lowered to that at which frozen flesh products
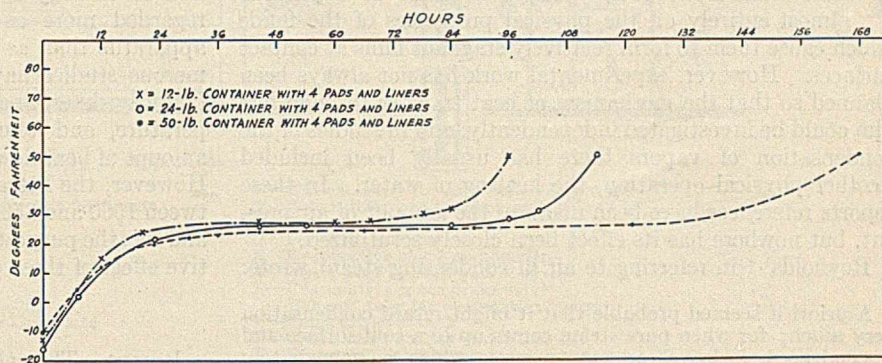

Figure 6—Temperature Rise in Center of Corrugated Shipping Containers, Filled with One-Pound Cartons of Frozen Haddock Packed before Being Frozen. Average Outside Temperature, 65° F. Container Similar to That Shown in Figure 4

should be cold-stored; while the general tendency of waxed papers seems to be toward becoming relatively less vaporproof at very low temperatures—probably because at low temperatures the paraffin tends to contract or crystallize, thereby less completely covering the paper.

Insulated Shipping Cases

For commercial reasons it is desirable that inexpensive non-returnable insulated shipping cases be used in distributing

quick-frozen packaged products. This precludes containers from such materials as cork board, balsa wood, and the various proprietary insulating materials.

Corrugated fiber board has been found to be a very satisfactory material from which to manufacture insulated shipping containers, and considerable quantities are now being used for that purpose. It has approximately the same heat-insulating value as cork board or balsa wood, is light, strong, and inexpensive. Fiber board may be made with either straw or chip corrugations, and with kraft, jute, chip, or straw liners. It has approximately the same heat-insulating value no matter from which materials it is made.

Although the construction and thickness of the corrugated containers used by different producers of quick-frozen products vary greatly, an excellent container may be made by

placing four pads or liners within an ordinary slotted carton of the proper dimensions (Figure 4). The container should be as nearly cubical as possible, so as to expose the minimum surface to heat penetration; and, when possible, the corrugations in the liners should run horizontally so as to lessen convection currents. Obviously, the shipping container should be packed solidly full, because the heat leakage into the container is approximately in proportion to its surface area, whereas the amount of heat which can be absorbed by the product with a given temperature rise is in proportion to the volume of product (Figure 5).

Figure 6 indicates the effectiveness of corrugated fiberboard cases in protecting their contents from outside heat. It will be noted that the contents of the 50-pound container required 7 days to reach a temperature of 50° F., at which time the fish was still perfectly fresh.

The Condensation of Steam[1]

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An apparatus has been built for studying the effect of temperature, concentration of small amounts of air, and temperature drop on the rate of condensation of steam on an isothermal condensing surface.

Within the experimental range and errors, the following empirical equations define the coefficient as determined by these individual independent variables:

$$f = a(\Delta T)^b$$
$$\frac{1}{f} = dC + e$$
$$f = Fg^T$$

where f is coefficient, ΔT is temperature drop, C is composition expressed as per cent air by volume, T is temperature in degrees Fahrenheit, and the other letters represent empirical constants. These individual equations have been combined with certain simplifying assumptions into a single equation:

$$\log f = \log \Delta T\ [1.213 - 0.00242T] + \left[\frac{\log \Delta T}{3.439} - 1\right] \times [\log(C + 0.505) - 1.551 - 0.009T]$$

Several theoretical reasons for the variations indicated by the equations have been pointed out in the light of the resistance concept.

The process of condensation of impure steam and that of gas absorption have been compared.

. . . .

I T HAS been realized for almost a century that the rate of heat transfer between fluids and solids is dependent almost entirely on the physical properties of the fluids which cause them to form relatively stagnant films at contact surfaces. However, experimental work has not always been planned so that the mechanism of heat transfer through one film could be investigated independently, and in studies of the condensation of vapors there has usually been included another physical operation, the heating of water. In these reports references have been made to the amount of air present, but nowhere has its effect been closely scrutinized.

Reynolds[1],* in referring to air in condensing steam, wrote:

A priori it seemed probable that it might retard condensation very much; for when pure steam comes up to a cold surface and is condensed, it leaves an empty space which is immediately filled with fresh steam; so that the passage of steam up to the cold surface is unobstructed.* * * If, however, the steam is mixed with air, then the steam will be condensed and the air be left between the fresh steam and the cold surface; so that after condensation has commenced that surface will be protected by a stratum of air, and fresh steam will have either to displace this or pass through it before it in turn can be condensed.

Later work[2] to [18] has not changed the conclusions of Reynolds and other early experimenters, and many reports are to be regarded more as efficiency tests on specific commercial apparatus than as sources of data of general interest. Numerous studies have been made, but they have not satisfactorily determined the effect of non-condensable gas, temperature, and temperature drop from steam to tube (or amount of heat flowing) on the rate of condensation of steam. However, the literature shows that the coefficient varies between 1500 and 3500 (B. t. u. per square foot per hour per ° F.), and it is the purpose of the present work to show the quantitative effect of these conditions on this variation.

Apparatus

BOILER—The ends of a 38-inch section of standard 12-inch iron pipe were closed by welding on steel disks fitted with valves, packing boxes, etc., as shown in Figure 1. The inner surface was nickel-plated after the ends were machined for the fittings.

VAPORIZATION SPACE AND CONDENSER—If water is passed through a tube surrounded by condensing steam, the water is heated and hence the temperature of the tube is not constant. In order to avoid lengthwise variation in tube temperature, water was boiled inside the tube at a lower pressure than that of the steam outside, and the vapor formed was suitably condensed and the condensate returned. (To prevent ambiguity the outer 12-inch shell will be hereinafter

identified as the "boiler," and the tube system as the "vaporization space.")

The construction of this evaporator tube, its auxiliary condenser, and fittings is indicated in Figure 1. The tubular members were brazed together and the 3-inch o. d. by 47-inch evaporator tube was soldered to thin copper collars which absorbed expansion strains. These collars were soldered to the boiler ends. The tube was fitted with thermocouples previously attached by a nickel-plating process already described.[19]

Cooling-Water System—A constant-level tank (V, Figure 1) was installed three floors above. After passing the valve (M) and before entering the two $7/8$-inch tubes, the water flowed by a thermocouple junction and a thermometer. After the two $7/8$-inch tubes, the water flowed back through the jacket, then by the other junction of the thermocouple and to the orifice chamber.

An orifice chamber of 2.5 gallons capacity (Y, Figure 1, and Figure 2) was constructed as shown. Water rose in the open manometer attached to the can and indicated the hydrostatic pressure above the orifice plate. The orifice chamber was usually operated half filled with air, so that the compressibility of the gas would smooth any slight fluctuations of pressure. The calibration curve of the rate of flow against manometer readings was a straight line on logarithmic paper.

The three systems of water used in the apparatus may be

zation tube would boil toward one end, the boiler rested in its steel and asbestos setting at an angle of about 5 degrees with the horizontal (not shown in Figure 1). Two gas heaters were made by drilling small holes in two sections of pipe supplied with city gas and compressed air (D in Figure 1). The hot gases passed through a hood to the stack.

The two 2000-watt General Electric heaters (B, Figure 1) were installed as auxiliary and more readily adjustable sources of heat. Their small heat capacity and high rate of heat conduction to the water allowed an almost instantaneous change in the steam temperature to be produced by a small change in the current. The boiler temperature could be kept constant within 0.01° C. for days at a time by means of a thermostatic regulator described in another article.[20]

Air Manometer—A device for the analysis of the gas phase *in situ* was necessary. The partial pressure of air might be found by subtracting the vapor pressure of water from the total pressure, but the multiplicity of corrections and calibrations necessary to obtain this small difference accurately were undesirable. Other possible methods[21,22] were also discarded and an apparatus was devised to indicate the partial pressure of the air directly on a manometer.[23]

Thermocouple System—The accuracy of the results depended largely on three measurements: (1) the temperature of the steam, (2) the temperature of the tube, and (3) the rise in temperature of the cooling water.
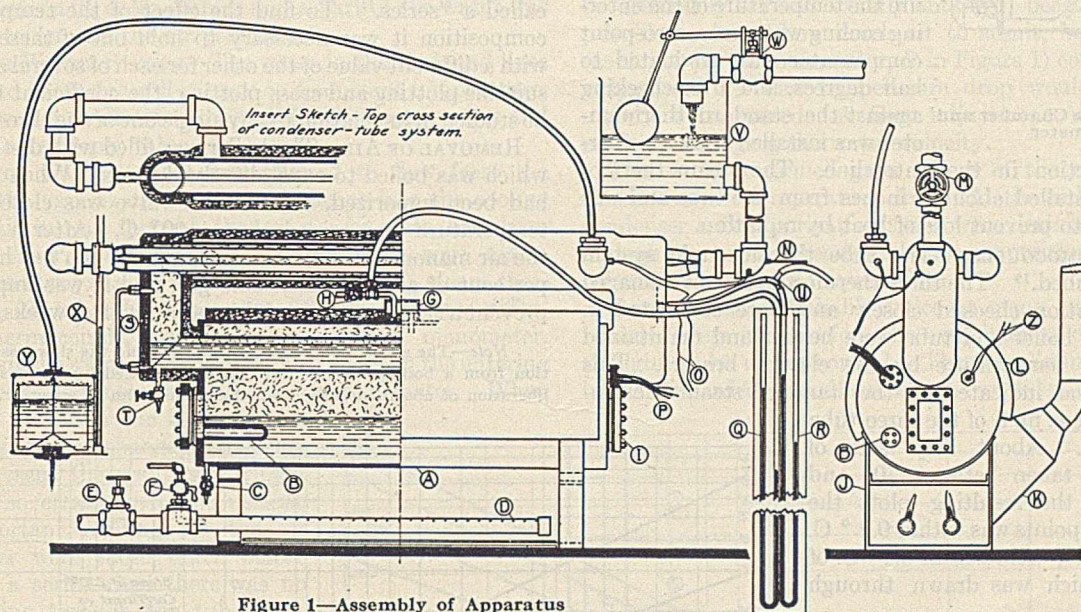

Figure 1—Assembly of Apparatus

A—Boiler body of 12-inch iron pipe
B—Electric heaters, 2 General Electric 2000-watt
C—Boiler drain valve
D—Gas heaters
E—Gas valve
F—Air valve
G—Water trap on manometer
H—Blow-off valve
I—Peep glass and hand hole packing plate
J—Iron stand for boiler
K—Hood and flue for hot gases
L—Asbestos insulation
M—Valve regulating cooling water

N—Thermometer for entering cooling water
O—Water-difference thermocouple wires
P—Tube thermocouple wires
Q—Boiler manometer
R—Evaporative space manometer
S—Water gage in evaporative space
T—Evaporative space drain valve
U—Exhaust tube for evaporative space
V—Constant-level tank
W—Float valve on city water line
X—Water orifice manometer tube
Y—Orifice chamber
Z—Standard steam thermocouple wires

summarized: (1) the water boiling in the boiler, the steam from which condensed on the lower tube of the vaporization space in which (2) water was boiling at a lower temperature and pressure, the steam from which was condensed both on the inner wall of the upper 3-inch tube and the outer walls of the two $7/8$-inch tubes through which (3) cooling water was circulated. The lower 3-inch tube was the one on which the heat transfer experiments were made, the upper tubes serving merely to discharge this latent heat to the cooling water, where it could be measured as sensible heat.

Heating System—In order that the water in the vapori-

The steam temperature and the rise in temperature of the cooling water were measured with thermocouples of copper-constantan. The steam thermocouple was an ordinary two-junction type, and the "water-difference" thermocouple was composed of two of these in series. These thermocouples were calibrated with an A. H. Thomas thermometer graduated to 0.1° C., accurate to 0.02° C. and standardized by the Bureau of Standards. Their hot junctions were tied to the thermometer bulb and immersed in a liquid, the temperature of which could be varied. The cold junctions were immersed in melting ice in a Dewar flask. (The melting point of the
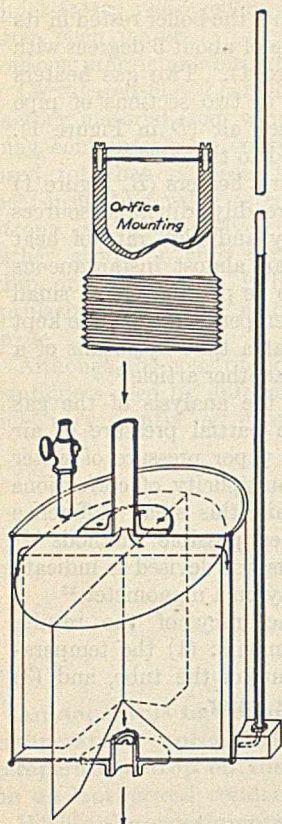
Figure 2—Orifice Chamber and Manometer

ice used in this and later work and that of ice frozen from conductivity water was compared with an accurate resistance thermometer and found to differ by less than 0.01° C.) The free ends were connected by a selective switch to a special Type K potentiometer. The sensitivity of the galvanometer was such as to allow accurate readings to a microvolt. The standard cell was checked at intervals against an Eppley standard cell recently checked at the Bureau of Standards.

About fifty readings were taken in the desired range. The method adopted for using these and similar data was to plot them on sheets of millimeter graduated cross-section paper 50 cm. in width, as a series of nearly parallel lines, each of which represented 10° or 20° C. The thermometer used to measure the temperature of the entering cooling water as a zero-point compensator was graduated to half degrees, and after checking against the standard thermometer was installed next the thermocouple junction in the water line. The steam thermocouple was installed about 3 inches from the tube and was so shielded as to prevent loss of heat by radiation.

TUBE THERMOCOUPLES—The tube thermocouple system has been described.[19] The three thermocouples not damaged in the installation checked closely and were connected in parallel. The boiler and tube were heated and maintained at a constant temperature by the electric heaters. This temperature was indicated by the standard steam thermocouple, and the e. m. f. of the three-tube thermocouples. About fifty sets of readings were taken between 70° and 120° C. On the resulting plots the farthest of the points was within 0.2 ° C. and the majority were within 0.1° C. of the curve which was drawn through them.

The temperature measurement desired in this work was that of the tube surface. In practice, the temperature as indicated by this calibration was the temperature of the nickel-copper interface and not that at the surface. The thickness of this nickel plate was known and the temperature gradient through it was found by Newton's law

$$q = kA \frac{\Delta T}{\Delta L}$$

where q is the rate of heat flow, k is thermal conductivity of nickel, A is the surface area, ΔT is temperature difference, and ΔL is thickness.

Note—This formula may be used instead of the logarithmic equation for the cylindrical flow of heat because the thickness of the plate is very small compared with the radius.

This correction was always evaluated and used in finding the temperature of the surface of the tube.

PROTECTION AGAINST HEAT LOSSES—The boiler above the setting was covered with a layer of magnesia insulation $1\frac{1}{4}$ inches thick. The vaporization space and its water jacket were similarly insulated, and both surfaces were given several coats of a varnish suspension of aluminum powder. Heat losses from the vaporization space were small, not only because the temperature difference between it and the room was small, but also because over half of the copper tubular rectangle outside of the boiler was water-jacketed, and the heat which otherwise would have been lost through the insulation was absorbed by the cooling water. In most cases the average temperature of the water was lower than room temperature, and the small amount of heat flowing into the cooling water from the outside would tend to balance the small amount flowing out from the rest of the surface.

Operation

CLASSIFICATION OF EXPERIMENTS—In a systematic study two of the three variables defining the coefficient must be kept constant while the effect of the third is studied. The temperature drop was altered more easily than either the temperature or composition of the steam, and it was changed during progressive experiments. When it also was fixed and a steady state was reached, the several readings were taken. Several of these runs taken at constant steam temperature and composition, but with different temperature drops, were called a "series." To find the effect of the temperature or composition it was necessary to hold one of these constant, with a different value of the other for each of several series. By suitable plotting and cross plotting, the coefficient could then be studied in its relation to any single one of the three variables.

REMOVAL OF AIR—The boiler was filled with distilled water which was boiled to expel dissolved gases. When about half had been vaporized, the exhaust valve was closed and the temperature maintained above 100° C. After a few hours the air manometer indicated the presence of a few hundredths per cent of a non-condensable gas, and it was impossible to prevent a slow evolution of this gas even after weeks of boiling.

Note—The absorption of air by water[24,25] and the slowness of its evolution from a boiling liquid[26] have been mentioned by various writers. A liberation of absorbed gases from the surface film of water or, more prob-
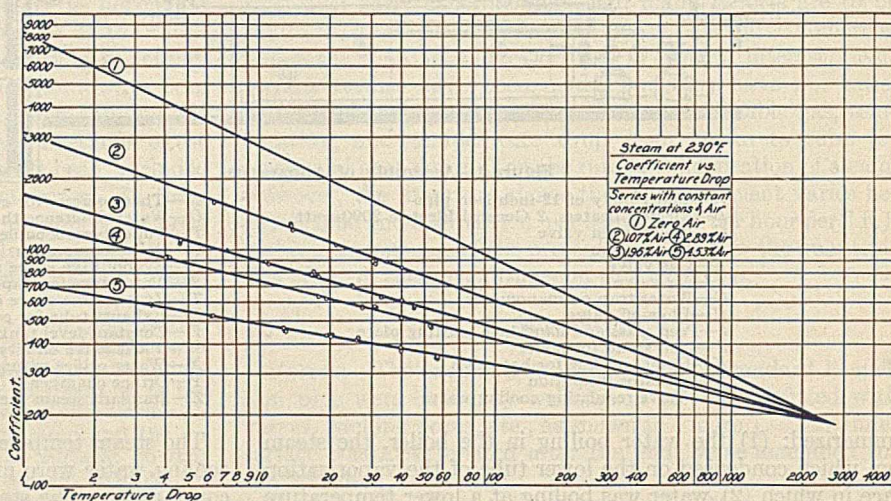

Figure 3

ably, the action of steam on iron incompletely covered by nickel to form hydrogen would account for that found in these experiments.

When gas-free steam was desired, a valve on the end (not shown in Figure 1) allowed a slight exhaust. This prevented the "air" from increasing to a measurable concentration during the time necessary to make a series. Air was ad-

mitted when desired by connecting this valve to a source of compressed air. The slight evolution of non-condensable gas was not consequential when a relatively large amount of air had been purposely introduced.

VAPORIZATION SPACE—The boiler conditions being fixed, the vaporization space was evacuated and the lower tube filled with water. Heat was supplied to this tube by the condensa-
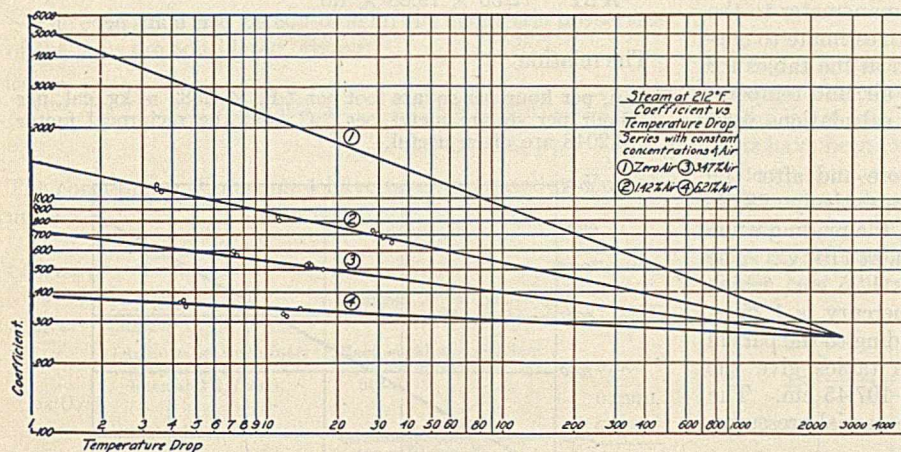

Figure 4

tion of steam on its outer surface and a part of the water was boiled off to remove the air present.

COOLING WATER SYSTEM—The water in the tank and lines was drained to waste until it came to a constant temperature. The flow was then diverted through the condenser tubes and adjusted to its proper value.

READINGS TAKEN—Heat was allowed to flow from the boiler to the vaporization space and thence into the cooling water until it was thought that a steady state had been reached. After a reasonable period, readings were made. These were always taken in the same order: (1) steam thermocouple, (2) tube thermocouples, (3) cooling-water differential thermocouple, and (4) water-orifice manometer. Throughout the series readings were also made on the entering cooling water thermometer and the air manometer. When there was no air in the boiler the air manometer was unchanged, but when air was present the readings during a run were so erratic as to be useless. The important readings of the air manometer were those taken before and after a series when there was no heat flowing through the tube wall. These were perfectly definite and their average was taken as indicative of the air present during the runs.

Note—Smith[5] reported a similar variation of the amount of air and attributed the difference between that calculated at equilibrium and that calculated at a steady state of heat flow to large deviations from Dalton's law of partial pressures. Instead, there is probably a gradient of composition throughout the steam space of the boiler. Thus the total amount of air present could be found during a time when heat was flowing only by the integration of the composition at a large number of points. It must be noted in subsequent discussion that the average amount of air before the run is not the same as the average amount in the free space during a run since some will be held in a gas film around the tube. This work makes no distinction and its results are based on the total amount of air present.

After the first readings the apparatus was allowed to run 10 or 15 minutes before a second set. If these checked, a steady state had been reached and the coincidence of a third set 5

minutes later established the value of the coefficient under the given conditions. The tables in this report include only such data which by duplication indicate the attainment of a steady state.

CHANGING THE TEMPERATURE DROP—Every series was made with the temperature drop as the single independent variable. The largest temperature drop of the series was that of the first run after which it was necessary to lessen it. Two methods were available—the first to reduce the flow of cooling water, and the second to diminish the coefficient of heat transfer from the low-pressure steam to the cooling water by introducing air into the vaporization space. This air would reduce the rate of heat transfer from the vaporization space to the condenser almost instantly, the temperature of the tube would immediately rise, and the heat supplied to the boiler would have to be diminished. A new temperature drop would be established and the second point on the curve of coefficient *versus* temperature drop could be obtained. This new temperature drop could not, however, be arbitrarily set and exactly obtained, because it was not possible to know how much air to admit, but the amount (as shown by the manometer, R in Figure 1) could be roughly judged and the new temperature drop would be approximately that desired. A finer adjustment was sometimes made by changing the water velocity.

This work continued gave values of the coefficient as a function of the temperature drop. At the end of a series the condenser and vaporization space were drained of water, the air manometer was read, and the composition of the vapor calculated at thermal equilibrium.

DATA TAKEN—Probably twice as many runs as are here reported were made before the experimental difficulties were thought to be under control. These preliminary data have been disregarded, but all subsequent work is tabulated except
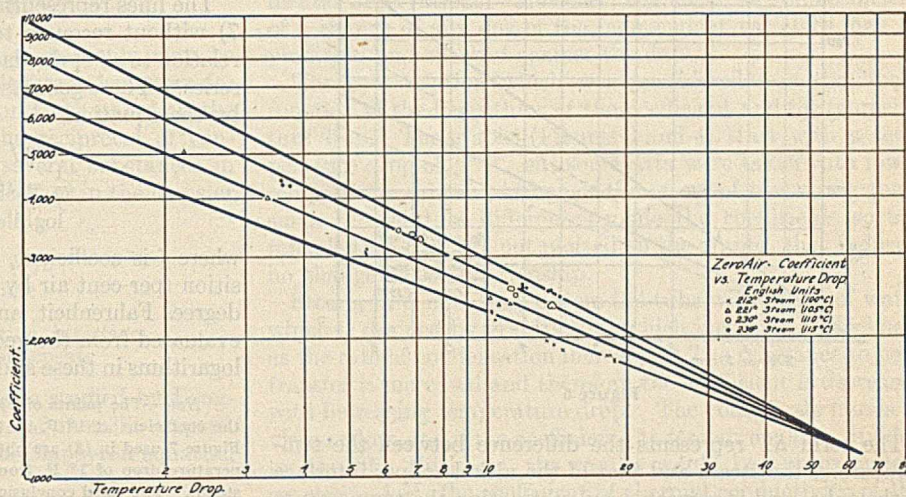

Figure 5

those individual readings taken before the attainment of a steady state. The three sets of series reported include (1) coefficient *versus* temperature drop at a very low or "zero" concentration of air and constant temperatures of 100°, 105°, 110°, and 115° C.; (2) coefficient *versus* temperature drop at a constant temperature of 100° C. and various constant percentages of air; and (3) the same for 110° C.

Sample Calculations

The results presented were calculated from the values read on the calibration curves with a 20-inch slide rule. The data taken were not all in one set of units, as is unfortunately the case rather often in engineering practice. The thermocouples were calibrated in Centigrade degrees and the water manometer in pounds of water per second. The potentiometer was read to the closest microvolt, and the manometer to the closest millimeter, although it was possible to estimate to one-tenth these values. The set of data shown in the tables for approximately 110° C. steam, 1.07 per cent air, and temperature drop of about 20° C. will have the calculations indicated.

The readings of the air manometer before and after the series and their arithmetic averages were respectively: 28.05, 27.65, and 27.85 cm. The zero point—i. e., the reading when there was no air in the boiler—was 29.10 cm. at 110° C. The difference between this and the average is 1.25 cm., which when corrected for the water above the mercury is 1.25 − 1.25/13.6 = 1.157 cm. of mercury corresponding to the partial pressure of air in the boiler. Peabody's tables give the pressure of saturated steam at 110° C. as 107.45 cm. The total pressure in the boiler is the sum of the partial pressures, and the air present is thus

$$\frac{1.157 \times 100}{1.157 + 107.45} = 1.066 \text{ per cent}$$

Since the temperature of the steam was held within 0.1° C. by the thermostat, the average of the e. m. f.'s for a series was converted to degrees instead of using the temperature for each run individually. The values from the respective charts follow:

	° C.
Steam temperature	110.04
Interface temperature	89.93
ΔT	20.11
Rise in water temperature	22.50

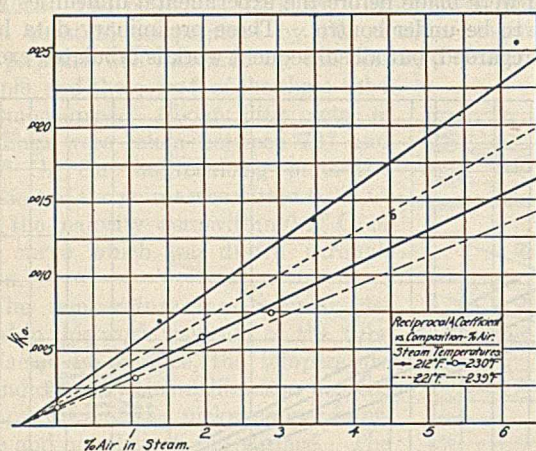Weight of cooling water, 0.507 lb. per second

Figure 6

The term ΔT represents the difference between the temperature of the steam and that of the nickel-copper interface of the tube, and is corrected by subtracting the temperature drop through the nickel plate which is found, as mentioned above, from the relation $q = kA \, \Delta T/\Delta L$. The heating surface is 2.36 square feet (cylinder 35.75 × 3.025 inches) and the thermal conductivity of nickel is 0.1133 B. t. u. per square foot per second per ° F. per inch. q is the product of the weight of water per second flowing through the condenser by the increase in its temperature, or in English units

$$0.507 \times 22.50 \times 1.8 = 20.53 \text{ B. t. u. per second}$$

If the equation for heat flow is rearranged and the appropriate values substituted, the correction for the drop through the nickel is 0.43° C. and the corrected value of ΔT is 20.11 − 0.43 = 19.68° C.

The steam film coefficient may not be calculated. It is equal to

$$f = \frac{q}{A \, \Delta T} = \frac{20.53 \times 3600}{2.36 \times 19.68 \times 1.8} = 883 \text{ B. t. u. per square foot}$$
$$\text{per hour per ° F.}$$

The relation

B. t. u. per hour per square foot per ° F. × 4.882 = kg. cal. per hour per square meter per ° C. and the reciprocal factor 0.2048 are often useful.
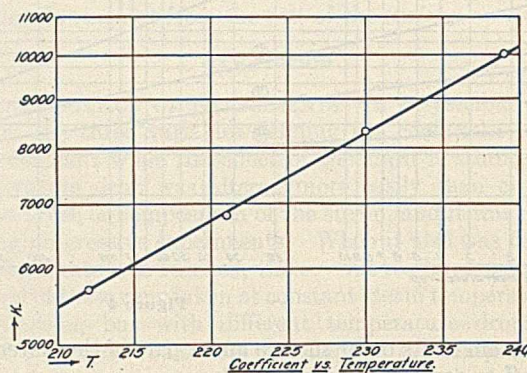

Figure 7

An Empirical Equation

Several empirical relationships between the coefficients obtained and the values of the independent variables were noticed: (1) With constant temperature and concentration the logarithm of the coefficient is a linear function of the logarithm of the temperature drop; (2) with constant temperature drop the reciprocal of the coefficient is a linear function of the composition expressed as per cent air by volume; (3) with constant temperature drop and concentration the logarithm of the coefficient is a linear function of the temperature.

The lines representing these data were drawn (Figures 3 to 7) without recourse to the method of least squares, but in relation to all of the data and not merely that of the individual series. These generalizations may, respectively, be expressed by the equations:

$$\text{Log } f = \log a + b \log \Delta T \qquad (1)$$
$$\frac{1}{f} = sC + p \qquad (2)$$
$$\log f = \log h + (\log F)T \qquad (3)$$

where f is coefficient, ΔT is temperature drop, C is composition (per cent air by volume), T is temperature of steam in degrees Fahrenheit, and the other letters are constants to be evaluated from the geometric properties of the graphs. The logarithms in these and later equations are to the base 10.

Note—The points of Figure 6, used in (2) are obtained from values of the coefficient at 1° F. on the lines of Figures 3, 4, and 5. The points of Figure 7 used in (3) are obtained by reading values of coefficient at a temperature drop of 1° F. from Figure 5 where there is no air present in the steam. The third conclusion and Equation 3 is thus based only on experimental data for zero air. Values of the coefficient, when a measurable amount of air was present, were taken at only two temperatures of the steam and the third generalization may be definitely made only for the case where there is no air present in the steam. However, the final equation is applicable at these two temperatures to the data taken with air present.

Equation 2 and Figure 6 state that if the reciprocals of values read from the lines of Figure 3 or 4 are plotted against the per cent air, the resulting lines will be straight. If that is accepted, it may be shown that the lines of Figure 3 or 4 cannot converge to a common point although the intersections of any pair of lines may be infinitesimally close. Within the admittedly large experimental errors, this is of no consequence and since

the data indicate the possibility of such convergence and the mathematical handling is greatly simplified by its assumption, these lines are drawn as sheafs. This common intersection is, however, too far to the right to have any physical significance. The intersections have the same abscissas for both steam temperatures studied, but the ordinate of the higher steam temperature is the smaller. If the lines of Figure 5 representing different temperatures are extended through their pole, the intersections with the common ordinate of the poles of Figures 3 and 4 may be considered as poles of other sheaves. A plot of the ordinates of such intersections, constant A in Figure 8, is a straight line.

The equations may be combined if the geometric properties of the lines are considered, giving:

$$\log f = \frac{\log \Delta T \left[\log w + (\log u) T\right] + \left[\log (C + r) + \log(1/r) - \log h - T \log F\right]}{\log B}$$
$$\times \left[\log \Delta T - \log B\right] \quad (4)$$

The constants in Equation 4 have been tabulated in English units.

CONSTANT	GEOMETRICAL SIGNIFICANCE	GRAPH	VALUE
log w	Intercept	Constant A vs. temperature (Figure 8)	4.1737
log u	Slope		−0.00832
r	Distance between intersection of $1/f$ vs. C lines and $1/f$ axis	Reciprocal of coefficient vs. composition (Figure 6)	0.505
log (1/r)			0.2970
log h	Intercept	Coefficient vs. temperature (Figure 7)	0.1848
log F	Slope		0.00900
log B	Logarithm of abscissa of intersection of lines of different compositions	Coefficient vs. temperature drop at constant T (Figures 3 and 4)	3.439

If these values are substituted in Equation 4 there follows:

$$\log f = \log \Delta T [1.213 - 0.00242\, T] + \left[\frac{\log \Delta T}{3.439} - 1\right] \times$$
$$[\log (C + 0.505) - 1.551 - 0.009\, T] \quad (5)$$

This relation expresses in B. t. u. per square foot per hour per ° F. the logarithm of the coefficient as a function of temperature, temperature drop, and composition of the steam. The constants are individually evaluated in the metric system and in kg. cal. per square meter per hour per ° C.

$$\log f = \log \Delta T [1.442 - 0.0047T] + \left[\frac{\log \Delta T}{3.184} - 1\right] \times$$
$$[\log (C + 0.505) - 2.6568 - 0.0139T] \quad (6)$$

Physical Discussion

Most problems dealing with potential gradients may be attacked by a method understood by workers in heat transfer and the analogous field of gas absorption to be based on the "resistance concept." Resistance is the reciprocal of conductivity, and the total resistance of several substances in series is the sum of the separate resistances, or in the transfer of heat from a condensing vapor to a solid:

$$1/f = 1/f_G + 1/f_C + 1/f_L$$

where f = coefficient from steam to tube
f_G = coefficient across gas film
f_C = coefficient at the condensation interface
f_L = coefficient across film of condensate

The mechanism of condensation may be studied by Langmuir's equation[27] for the condensation of metallic vapors. This may be combined with the Clausius-Clapeyron equation and the gas laws to give:

$$q = \sqrt{\frac{R}{2\pi M}} \times \frac{dP}{dT} \times (T_V{}^{3/2} - T_L{}^{3/2})$$

where q is the rate of heat transfer, T_V and T_L are absolute temperatures of the vapor and liquid sides of the interface, M is molecular weight, R is the gas constant, and dP/dT is the slope of the vapor-pressure curve which is assumed to be a straight line in this very narrow range. When the experimental values of q are substituted with the other quantities,

the temperature difference across the interface is found to be very small and the corresponding resistance negligible, which agrees with what Reynolds[1] said: "In fact there is no limit to the rate at which pure steam will condense but the power of the surface to carry off the heat." The total resistance may therefore be considered as due to the gas and condensate films, and the formula corresponding to Ohm's law might be written

$$\frac{q}{A} = \frac{\Delta T}{R}$$

where q/A is the rate of heat flow per unit of surface, ΔT is the temperature drop from steam to tube, and R is the sum of resistances of gas and liquid films. Few published experiments have been expressed in units of resistance.

The mathematical analysis of the mechanism of heat transfer through the liquid and vapor films is hindered by the large number of physical properties to be evaluated. Such things as the rate of mutual diffusion of steam and air; the viscosity, specific heat, thermal conductivity, and density of the air,
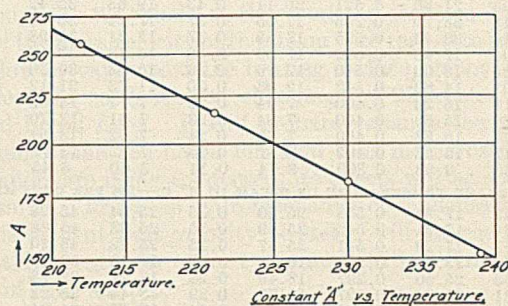

Figure 8

condensate, and steam; and the latent heat of the latter determine the amount of heat passed. These values all change with varying temperatures through the films, and the mean values can only be approximated. A knowledge of the thickness of the condensate film and of the air concentration and temperature at its surface would also be valuable. Because most of these data are not accurately known, a basic theory was not formulated for comparison with the experimental observations. However, the effect on the coefficient of a change of any one of the independent variables may be predicted and checked against the data.

The first relation which was considered was the linear function of the logarithms of the coefficient and the temperature drop. The graphs (Figures 3 and 4) start with a temperature drop of 1° F., but some data were taken with lower temperature drops. Although the errors of measuring these small temperature differences made the coefficients so unreliable that they are not plotted on the graphs, they indicate no change of the relationship.

Steam, in condensing, covers the tube with a film of water which is drained by gravity, but which increases in thickness as the rate of condensation increases. The resistance to heat transfer is increased and therefore the coefficient is decreased with increasing temperature drop. The condensate film is in viscous flow, and if the coefficients at zero air could be divided by the film thickness, the results would be approximately constant—i. e., the coefficient of thermal conductivity of the condensate. Since the coefficient is more easily determined than the film thickness, the latter may be calculated from the thermal conductivity of water which according to Jakob[28] varies as $k = 0.001325 (1 + 0.002984t)$, where k is the conductivity in calories per sq. cm. per second per ° C. per cm., and t is Centigrade degrees up to 80° C. Preliminary work in this laboratory has verified this equation up to 120° C.

The plot of the coefficients obtained with practically pure

steam (Figure 5) show comparatively large irregularities. The large amount of heat passed in these runs caused an uneven boiling in the vaporization space and a larger variation in tube temperature. Another reason was that a very slight amount of air makes a large difference in the coefficient when the steam is practically pure. The series at 212°, 221°, and 230° F. were made with a small amount of steam exhausting, to prevent a building up in the boiler of an appreciable concentration of non-condensable gas. The series for steam at 239° F. was obtained just after the steam had been freed from air by "boiling out," but with the exhaust valve closed during the series itself. The first points obtained on this last series are those with the highest temperature drops, and they are seen to be consistent with the lines of lower temperatures, but those which were taken several hours later at lower temperature drops are considerably lower than expected. This shows that a slow evolution of non-condensable gas during a few hours had reduced the coefficient, and the line as drawn is based only on the points which were taken first, when the steam was substantially pure.

Some experimenters have indicated that a change of temperature of pure steam did not appreciably affect the coefficient. In the present work the coefficient is shown to increase with increasing temperature by the line in Figure 7 derived from the lines in Figure 5. This might be expected since the properties of water vary with temperature. At a given temperature drop the condensate drains faster and forms a thinner film when the viscosity is lowered by an increase of

Data

AVERAGE TEMPERATURE OF STEAM 110.04° C.—1.066 PER CENT AIR

Tube Temp. °C.	Water Diff. Temp. °C.	Water Lb./sec.	ΔT °C.	Δθ Nickel °C.	ΔT (cor.) °C.	ΔT (cor.) °F.	f
89.93	22.50	0.507	20.11	0.43	19.68	35.42	883
89.93	21.86	0.521	20.11	0.43	19.68	35.42	882
92.46	33.70	0.295	17.58	0.37	17.21	30.98	881
92.46	33.43	0.295	17.58	0.37	17.21	30.98	873
92.95	17.98	0.542	17.09	0.36	16.73	30.12	888
92.85	18.00	0.540	17.19	0.36	16.83	30.30	881
98.01	14.82	0.542	12.03	0.30	11.73	21.12	1045
102.10	15.23	0.400	7.94	0.23	7.71	13.88	1205
102.20	15.69	0.400	7.84	0.23	7.61	13.70	1258
102.28	15.83	0.400	7.76	0.24	7.52	13.54	1284
102.17	16.58	0.402	7.87	0.25	7.62	13.72	1334
106.30	9.38	0.399	3.74	0.14	3.60	6.45	1585

AVERAGE TEMPERATURE OF STEAM 110.03° C.—1.96 PER CENT AIR

Tube Temp. °C.	Water Diff. Temp. °C.	Water Lb./sec.	ΔT °C.	Δθ Nickel °C.	ΔT (cor.) °C.	ΔT (cor.) °F.	f
84.35	17.34	0.538	25.69	0.35	25.34	45.28	561
84.35	17.61	0.540	25.69	0.36	25.33	45.28	572
84.57	17.29	0.541	25.47	0.35	25.12	45.20	568
91.32	25.68	0.297	18.72	0.29	18.43	33.17	631
91.55	25.56	0.297	18.49	0.28	18.21	32.78	636
91.31	25.73	0.297	18.73	0.29	18.44	33.22	632
96.00	21.34	0.296	14.04	0.24	13.80	24.85	698
96.15	21.22	0.296	13.89	0.24	13.65	24.59	702
96.05	21.19	0.297	13.99	0.24	13.75	24.75	697
100.65	16.07	0.295	9.39	0.18	9.21	16.58	784
100.45	16.84	0.295	9.59	0.19	9.40	16.91	806
100.13	16.97	0.293	9.91	0.19	9.72	17.51	780
99.98	16.97	0.295	10.06	0.19	9.87	17.78	774
103.85	11.68	0.294	6.19	0.13	6.06	10.91	864
104.00	11.75	0.294	6.04	0.13	5.91	10.64	892
107.40	6.29	0.293	2.64	0.07	2.57	4.62	1094
107.40	6.18	0.293	2.64	0.07	2.57	4.62	1075

AVERAGE TEMPERATURE OF STEAM 110.04° C.—2.89 PER CENT AIR

Tube Temp. °C.	Water Diff. Temp. °C.	Water Lb./sec.	ΔT °C.	Δθ Nickel °C.	ΔT (cor.) °C.	ΔT (cor.) °F.	f
80.10	19.31	0.470	29.94	0.34	29.60	53.30	468
80.10	19.28	0.470	29.94	0.34	29.60	53.30	467
80.45	19.24	0.470	29.59	0.34	29.25	52.65	472
92.48	13.67	0.470	17.56	0.24	17.32	31.18	566
92.62	13.72	0.470	17.42	0.24	17.18	30.94	572
94.82	11.92	0.471	15.22	0.21	15.01	27.06	571
94.72	11.92	0.471	15.32	0.21	15.11	27.20	567
94.72	11.99	0.471	15.32	0.21	15.11	27.20	570
99.98	13.73	0.298	10.06	0.15	9.91	17.83	630
99.28	14.55	0.295	10.76	0.16	10.60	19.08	617
107.92	4.63	0.294	2.12	0.05	2.07	3.73	1004
107.72	4.67	0.294	2.32	0.05	2.27	4.09	922
107.76	4.63	0.294	2.28	0.05	2.23	4.02	932

AVERAGE TEMPERATURE OF STEAM 110.04° C.—4.53 PER CENT AIR

Tube Temp. °C.	Water Diff. Temp. °C.	Water Lb./sec.	ΔT °C.	Δθ Nickel °C.	ΔT (cor.) °C.	ΔT (cor.) °F.	f
78.55	20.77	0.345	31.49	0.27	31.22	56.20	350
78.55	20.65	0.345	31.49	0.26	31.23	56.20	348
78.63	20.65	0.345	31.41	0.27	31.14	56.00	349
87.94	16.00	0.344	22.10	0.21	21.90	39.40	383
87.94	15.98	0.343	22.10	0.21	21.89	39.40	382
87.94	16.05	0.344	22.10	0.21	21.89	39.40	384
95.53	11.39	0.342	14.51	0.14	14.37	25.85	413
95.53	11.35	0.342	14.51	0.14	14.37	25.85	412
99.28	9.98	0.301	10.76	0.11	10.65	19.17	430
99.05	10.18	0.302	10.99	0.11	10.88	19.58	431
98.95	10.31	0.302	11.09	0.12	10.91	19.75	432
98.80	10.31	0.302	11.24	0.12	11.12	20.00	427
102.95	7.03	0.302	7.09	0.08	7.01	12.62	462
102.82	6.96	0.302	7.22	0.08	7.14	12.85	449
102.87	7.03	0.301	7.17	0.08	7.09	12.76	455
106.50	3.92	0.304	3.54	0.04	3.50	6.30	519
106.50	3.93	0.304	3.54	0.04	3.50	6.30	520

AVERAGE TEMPERATURE OF STEAM 110.04° C.—6.59 PER CENT AIR

Tube Temp. °C.	Water Diff. Temp. °C.	Water Lb./sec.	ΔT °C.	Δθ Nickel °C.	ΔT (cor.) °C.	ΔT (cor.) °F.	f
71.42	12.90	0.410	38.62	0.19	38.43	69.20	210
71.68	13.02	0.410	38.36	0.19	38.16	68.64	213
71.85	12.95	0.410	38.19	0.19	38.00	68.40	213
87.03	9.35	0.407	23.01	0.14	22.87	41.18	254
87.08	9.32	0.407	22.96	0.14	22.82	41.10	253
86.95	9.51	0.409	23.09	0.14	22.95	41.32	259
96.00	6.06	0.412	14.04	0.09	13.95	25.12	273
95.77	6.01	0.413	14.27	0.09	14.18	25.53	267
95.77	6.00	0.413	14.27	0.09	14.18	25.52	267
101.68	7.11	0.300	8.36	0.08	8.28	14.90	393
101.17	7.11	0.302	8.87	0.08	8.79	15.82	372
101.63	7.11	0.302	8.41	0.08	8.33	14.99	393
102.05	7.20	0.301	7.99	0.08	7.91	14.24	418
101.78	5.92	0.303	8.39	0.07	8.32	14.98	329
106.58	3.39	0.303	3.56	0.04	3.52	6.34	445
106.54	3.52	0.303	3.58	0.04	3.54	6.61	459
106.54	3.53	0.303	3.70	0.04	3.66	6.59	446

AVERAGE TEMPERATURE OF STEAM 99.97° C.—1.42 PER CENT AIR

Tube Temp. °C.	Water Diff. Temp. °C.	Water Lb./sec.	ΔT °C.	Δθ Nickel °C.	ΔT (cor.) °C.	ΔT (cor.) °F.	f
80.78	19.02	0.421	19.19	0.30	18.89	34.00	647
82.12	18.70	0.422	17.85	0.30	17.55	31.57	686
82.34	18.51	0.421	17.63	0.29	17.34	31.20	686
83.22	18.12	0.421	16.75	0.29	16.46	29.61	707
83.89	17.93	0.421	16.08	0.28	15.80	28.44	729
93.69	7.90	0.420	6.28	0.12	6.16	11.09	822
93.69	7.99	0.420	6.28	0.13	6.15	11.07	832
93.55	7.87	0.420	6.42	0.12	6.30	11.34	800
98.02	3.26	0.419	1.95	0.05	1.90	3.42	1097
98.02	3.39	0.419	1.95	0.05	1.90	3.42	1142
97.92	3.33	0.419	2.05	0.05	2.00	3.60	1065

AVERAGE TEMPERATURE OF STEAM 99.97° C.—3.47 PER CENT AIR

Tube Temp. °C.	Water Diff. Temp. °C.	Water Lb./sec.	ΔT °C.	Δθ Nickel °C.	ΔT (cor.) °C.	ΔT (cor.) °F.	f
90.14	10.04	0.317	9.83	0.12	9.71	17.48	500
91.31	9.24	0.317	8.66	0.11	8.55	15.39	523
91.48	9.16	0.317	8.49	0.11	8.38	15.08	529
91.58	8.98	0.317	8.39	0.11	8.28	14.90	525
95.77	4.92	0.317	4.20	0.06	4.14	7.44	575
95.90	4.95	0.317	4.07	0.06	4.01	7.21	598

AVERAGE TEMPERATURE OF STEAM 99.99° C.—6.21 PER CENT AIR

Tube Temp. °C.	Water Diff. Temp. °C.	Water Lb./sec.	ΔT °C.	Δθ Nickel °C.	ΔT (cor.) °C.	ΔT (cor.) °F.	f
92.18	5.71	0.302	7.81	0.06	7.75	13.95	340
93.18	4.64	0.302	6.81	0.05	6.75	12.15	317
93.41	4.58	0.302	6.58	0.05	6.53	11.75	323
97.50	1.98	0.301	2.49	0.02	2.47	4.44	368
97.55	1.93	0.301	2.44	0.02	2.42	4.35	366
97.45	1.90	0.301	2.52	0.02	2.52	4.53	346

AVERAGE TEMPERATURE OF STEAM 100.06° C.—11.44 PER CENT AIR

Tube Temp. °C.	Water Diff. Temp. °C.	Water Lb./sec.	ΔT °C.	Δθ Nickel °C.	ΔT (cor.) °C.	ΔT (cor.) °F.	f
74.32	10.85	0.303	25.74	0.12	25.62	46.09	196
74.32	10.85	0.303	25.74	0.12	25.62	46.09	196
74.08	11.04	0.304	25.98	0.13	25.85	46.49	198
84.57	8.23	0.303	15.49	0.09	15.40	27.70	247
84.12	8.57	0.303	15.94	0.10	15.84	28.50	250
84.12	8.50	0.301	15.94	0.10	15.84	28.50	247
84.29	8.33	0.303	15.77	0.09	15.68	28.20	246

AVERAGE TEMPERATURE OF STEAM 99.96° C.—ZERO AIR

Tube Temp. °C.	Water Diff. Temp. °C.	Water Lb./sec.	ΔT °C.	Δθ Nickel °C.	ΔT (cor.) °C.	ΔT (cor.) °F.	f
89.50	23.38	0.508	10.46	0.45	10.01	18.01	1810
89.10	24.11	0.508	10.86	0.46	10.40	18.72	1797
89.10	23.97	0.508	10.86	0.46	10.40	18.72	1787
89.32	23.80	0.508	10.64	0.45	10.19	18.34	1810
92.15	18.80	0.508	7.81	0.36	7.45	13.41	1957
91.63	19.24	0.507	8.33	0.37	7.96	14.33	1871
91.86	19.05	0.507	8.10	0.36	7.74	13.93	1904
93.88	16.36	0.507	6.08	0.31	5.77	10.39	2196
93.98	16.58	0.507	5.98	0.32	5.66	10.20	2266
93.98	16.71	0.506	5.98	0.32	5.66	10.19	2280
96.70	12.32	0.506	3.26	0.23	3.03	5.45	3138
96.70	12.06	0.506	3.26	0.23	3.03	5.45	3071
96.70	12.68	0.505	3.26	0.24	3.02	5.43	3236

AVERAGE TEMPERATURE OF STEAM 105.02° C.—ZERO AIR

Tube Temp. °C.	Water Diff. Temp. °C.	Water Lb./sec.	ΔT °C.	Δθ Nickel °C.	ΔT (cor.) °C.	ΔT (cor.) °F.	f
98.44	19.11	0.502	6.58	0.36	6.22	11.20	2363
98.81	18.38	0.493	6.21	0.34	5.87	10.57	2355
99.04	18.25	0.493	5.98	0.34	5.64	10.15	2435
102.96	10.04	0.491	2.06	0.18	1.88	3.38	4000
103.64	8.25	0.489	1.38	0.15	1.23	2.21	5005

AVERAGE TEMPERATURE OF STEAM 109.97° C.—ZERO AIR

Tube Temp. °C.	Water Diff. Temp. °C.	Water Lb./sec.	ΔT °C.	Δθ Nickel °C.	ΔT (cor.) °C.	ΔT (cor.) °F.	f
101.91	23.21	0.506	8.06	0.44	7.62	13.71	2352
101.96	22.89	0.507	8.01	0.44	7.57	13.62	2339
101.82	23.28	0.506	8.15	0.44	7.71	13.88	2332
103.36	20.51	0.506	6.61	0.39	6.22	11.20	2546
103.27	20.27	0.506	6.70	0.38	6.32	11.38	2477
103.32	20.70	0.506	6.65	0.39	6.26	11.27	2553
103.36	20.60	0.506	6.61	0.39	6.22	11.20	2557
106.08	16.07	0.506	3.89	0.31	3.58	6.44	3463
105.88	16.58	0.505	4.09	0.31	3.78	6.80	3380
105.67	16.84	0.505	4.30	0.32	3.98	7.16	3260

AVERAGE TEMPERATURE OF STEAM 115.04° C.—ZERO AIR

Tube Temp. °C.	Water Diff. Temp. °C.	Water Lb./sec.	ΔT °C.	Δθ Nickel °C.	ΔT (cor.) °C.	ΔT (cor.) °F.	f
108.00	37.35	0.302	7.04	0.42	6.62	11.91	2600
108.00	36.61	0.303	7.04	0.42	6.62	11.91	2559
107.93	36.52	0.306	7.11	0.42	6.69	12.05	2550
106.62	23.86	0.535	8.42	0.48	7.94	14.29	2454
106.91	23.68	0.535	8.13	0.47	7.66	13.79	2523
107.03	23.21	0.535	8.01	0.47	7.54	13.57	2513
112.82	11.98	0.473	2.22	0.21	2.01	3.62	4300
112.82	12.32	0.473	2.22	0.22	2.00	3.60	4443
112.73	12.32	0.474	2.31	0.22	2.09	3.76	4260

temperature, and from Jakob's equation the thermal conductivity increases. Both tend to increase the coefficient at higher temperatures.

The enormous decrease of the rate at which nearly pure steam condenses when a slight amount of air is added shows that the non-condensable gas must be localized around the tube. The decrease of the coefficient by 50 per cent caused by adding 0.5 per cent air cannot be explained if the air is evenly distributed, since there would then be almost no change in the partial pressure of steam at the interface and condensation would take place unimpeded. There is, however, a backward diffusion of the air against the flow of steam and a steady state is reached when the rate of diffusion of the air away from the tube is balanced by the rate at which it is carried up to it. Obviously, the steady state is reached when the rate of diffusion of the steam through this air film is just equal to the rate at which condensation may take place as determined by the resistance of the condensate film. This rate of heat transfer through the condensate film probably depends only on the partial pressure of the steam at the interface and is independent of the presence or absence of air if the partial pressure of steam is unchanged.

The process of heat transfer from a vapor containing a non-condensable gas is seen from these considerations to be exactly analogous to the problem of gas absorption developed by Lewis and Whitman[29] and others. The air film is comparable to the stagnant gas film in the absorption of a gas from a mixture with one which is inert, and both are caused by molecular diffusion. In the case of a pure vapor passing over a liquid absorbent, Lewis and Whitman show that the resistance of the vapor film is negligible compared with the resistance of the liquid film. The absence of a film between pure vapor and condensate has been shown in another experiment in this laboratory, which will not be described here.

The heat flowing from steam to tube passes first through the gas film if air is present, then through the condensation interface, and finally through the film of water. The reciprocal of the coefficient represents the resistance and when plotted (Figure 6) it is seen to increase as a linear function of the per cent of air present. These lines do not intersect at the origin, and the resistance is not zero at zero air because of the resistance of the condensate film. The intersection of the lines on the graph does occur, however, at a point where the resistance to the flow of heat would be zero or the coefficient is infinity (since $1/\infty = 0$) and at this point the thickness of the water film approaches an infinitesimal.

From the fact that at zero air the only resistance is that of the condensate film, it is apparent that as the amount of air is increased the proportional effect of the condensate resistance to the total resistance becomes less and a given change of the thickness of the condensate film affects the coefficient to a smaller degree. At a given temperature of steam the thickness of the water film is largely dependent on the amount of heat flowing, which is in turn dependent on the temperature drop. The generalization which may be drawn from this is: Under constant temperature conditions, the rate of change of coefficient with respect to temperature drop varies inversely with concentration of air. Mathematically this may be formulated

$$\left[\frac{\delta f}{\delta(\Delta T)}\right]_T \propto \frac{1}{C}$$

The graphs in Figures 3 and 4 show the rate of change of the logarithm of the coefficient with the logarithm of the temperature drop (the slopes of the indicated lines) to decrease with increasing concentrations of air.

The curves of the reciprocal of the coefficient against composition (Figure 6) show that adding 0.5 per cent air decreases the coefficient to one-half its value at zero air, a second increase of 0.5 per cent air decreases it to a third, a third increase of 0.5 per cent decreases it to a fourth, etc. In practice, air in a concentration of only a few per cent in the steam seriously reduces the capacity of steam-condensing equipment.

The points with the largest amounts of air in both the 212° and 230° F. series are seen to be off the line as determined by the other points in the graph in Figure 6. This is not believed to indicate the failure of the relation between the coefficient and the composition for steam with 6 or more per cent air, but was due instead to experimental difficulties. Until the runs with large concentrations of air were made, the reading made with the greatest ease and controlled with the greatest facility was that of the steam temperature. When, however, the air exceeded 4 per cent, this temperature varied considerably during readings, even though the pressure was kept constant by the relay circuit. Since it could not be accurately determined, the temperature drop and coefficient varied over an even greater range. The plotted values at these higher concentrations of air were therefore given less weight in drawing the representative lines.

Throughout the whole of this work no mention has been made of the mass velocity of the steam with regard to the tube. With flow of vapor past the heating surface, vapor velocity will affect the coefficient by changing the thicknesses of the gas and liquid films. It will probably change the gas film much more than the liquid film and thus in the case where pure vapors are being condensed, its effects will be comparatively small. From the hydromechanics of condensate drainage it is evident that velocity of steam will change the coefficient differently for every type, angle with horizontal, and length of tube surface.

Acknowledgment

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Influence of Hydrogen-Ion Concentration on the Color of Vegetable Tanned Leather[1]

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THE influence of the pH value of a tan liquor on its color has been studied by Wilson and Kern,[2] who showed that the color of solutions of gambier and quebracho extracts was a function of their hydrogen-ion concentration, the color darkening steadily with increasing pH. This change was reversible in the absence, but irreversible in the presence, of air.

As practical experience, however, has shown that the color of a tan liquor is not necessarily an index of the color it will give to a hide or skin tanned in it, and as no detailed information of the relation of pH value to leather color could be found in the literature, the following study of this relationship was made.

Change in Color with Variation in pH

Hide pieces from the butt of an ox hide after soaking in water for 48 hours were placed for 6 days in saturated lime-water, in presence of excess lime made 0.01 normal in sodium sulfide. After being unhaired, the pieces were bated in the usual manner with pancreatin in the presence of ammonium chloride, and were then well washed. This procedure gives a standard that is easily reproducible. The hide pieces were then placed in 0.1 M phosphoric acid solutions to which hydrochloric acid or sodium hydroxide had been added in quantities sufficient to give a series of solutions ranging in pH value from 1.0 to 9.0 as determined by the hydrogen electrode. The pieces were left in these solutions for 48 hours, the pH value being adjusted where necessary after the first 24 hours.

Two tan liquors were prepared, one from wattle bark and the other from chestnut wood extract, materials selected as representing two types of tanning agents widely different in nature and behavior. From the stock solutions series of liquors were prepared containing in each case 25 grams of solid matter per liter, and by the addition of hydrochloric acid or sodium hydroxide made to range in pH value from 1.0 to 9.0. Both wattle and chestnut liquors when at pH 5 were free from insoluble matter, but in the case of chestnut a precipitate was formed at lower pH values.

The hide pieces on removal from the buffer solutions were placed in tan liquors of corresponding pH, thus insuring that there would be no significant change in hydrogen-ion concentration during the tanning process. After 24 hours in the tan liquors the pieces were removed and their colors compared. With both tanning materials it was found that, whereas the liquors showed a progressive darkening of color with increasing pH value, the variation in color of the leathers themselves did not show a corresponding straight-line progression but followed closely the curve of swelling. Thus in both cases the color of the leather was a minimum at pH 5, rising to a maximum at pH 2 with a marked fall toward pH 1. With both wattle and chestnut this fall was accompanied by a change to a somewhat redder shade. In the case of the chestnut, as there is considerable precipitation at low pH values, it is conceivable that the lightening in color may be due to the

decrease in amount of tannin in solution, but with the wattle, as there is no precipitation even at pH 1, such an explanation is not possible.

At pH values above 5 the color of the leather darkens, gradually up to pH 7, but very appreciably at pH 8, especially in the case of chestnut, and still more noticeably at pH 9. With wattle the darkening is not so marked at pH 8, but becomes prominent at pH 9. These color differences persist without much alteration when the leather pieces are dried, except that pieces tanned at pH 8 and above have a greater tendency than the others to darken by oxidation.

Cause of Color Changes

As it appeared probable that the observed color changes were due to actual changes in hide structure brought about by variation of hydrogen-ion concentration, a second series of experiments was run to test this view.

Hide pieces treated as before were brought into equilibrium with a buffer solution of pH 5 and tanned at the same pH in wattle bark liquors containing, as before, 25 grams solid per liter. They were then transferred to a series of wattle bark liquors of the same concentration but with pH values of from 1 to 9, corrected after 24 hours. After 48 hours in these solutions the leather pieces showed a regular gradation in color. That from the solution of pH 1 was the lightest, with a progressive deepening of shade up to pH 9, although the color of the leather from the liquor of pH 9 was not so dark as that of the hide piece immersed in a liquor of this pH value directly on removal from the buffer solution.

In a further set of experiments standard hide pieces were placed for 48 hours in buffer solutions of high and low pH value, respectively, then brought to equilibrium with a buffer solution of pH 5, and finally tanned as before in wattle bark solutions of pH 5, together with pieces brought to a pH value of 5 without pretreatment. In each case the color of the pretreated pieces was darker than that of the standard, the increase in color being approximately equal for pieces pretreated at pH values of 2 and 13, respectively.

These experiments indicate that pretreatment of hide with solutions of varying pH value produces in the collagen itself changes which affect the color of the resultant leather. When the pretreated hide is tanned at pH 5, these changes correspond to the changes in swelling produced by such pretreatment.

This result is in striking agreement with the work of Gustavson,[3] on the effect of pretreatment of hide powder on the fixation of vegetable tannins. This investigator states that the amount of fixed tannin plotted against the pH values of the solutions employed in the pretreatment gives a curve with a first maximum at a pH between 2 and 3, a minimum in the isoelectric range, and a very pronounced maximum at a pH of about 12, exhibiting a close resemblance to the swelling curve of hide powder. Also in his work on the behavior of formaldehyde-tanned hide powder towards chromium compounds,[3] Gustavson shows that it is the pH value of the formaldehyde solution which determines the amount of chromium oxide that combines with the hide powder. The

[1] Presented before the Division of Leather and Gelatin Chemistry at the 76th Meeting of the American Chemical Society, Swampscott, Mass., September 10 to 14, 1928.

[2] Wilson and Kern, J. IND. ENG. CHEM., 13, 1025 (1921).

[3] Gustavson, J. Am. Leather Chem. Assocn., 22, 125 (1927).

same author[4] also shows that acid or alkali pretreatment shifts the isoelectric point of hide powder.

The color of the leather formed in solutions of vegetable tanning materials is apparently yet another property that is determined by the acid or alkali pretreatment of the hide, and a property that varies in the same manner as the power of tannin fixation.

4 Gustavson, *J. Intern. Soc. Leather Trades Chem.*, **10**, 203 (1926).

Summary

The color of leather tanned in chestnut wood or wattle bark liquors is a function of the pH value, rising to a first maximum at about pH 2, falling to a minimum at a pH value in the neighborhood of 5, and rising sharply again at a pH value between 8 and 9.

This color change is due to the action of solutions of varying pH on the hide itself rather than to their direct influence on the actual combination of hide substance and tannin.

Sulfur Compounds in Pressure-Cracked Naphtha and Cracked Naphtha Sludge[1]

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SOME time ago it was decided to attempt the isolation and identification of the sulfur compounds in pressure-cracked naphtha in order to establish a logical foundation for further work on their technical removal. The first step was to devise a method of obtaining a concentrated mixture of these substances. In the small amount of work that has been done in the past on the removal of sulfur compounds from petroleum,[2] the light oil obtained by diluting, neutralizing, and distilling a sulfuric acid sludge has been the source of raw material. In removing substances of unknown structure with a drastic reagent such as sulfuric acid, there is no certainty that the compounds obtained are the same as those originally present in the oil, though in a few instances the same compounds have been obtained from the oil by less doubtful means, as were found in the acid sludge. Under these circumstances it was decided to develop, if possible, a method of fractional extraction using inert solvents. It was found, as will be shown later, that the compounds obtained by this means were very different from those obtained by the use of sulfuric acid.

A method is described for obtaining a concentrated mixture of the sulfur compounds in cracked naphtha by the use of inert solvents. It has been found that the sulfur compounds in cracked naphtha are members of the thiophene series, a number of which have been isolated and identified. It has been further found that the sulfur compounds in the light oil obtained by diluting and distilling cracked naphtha acid sludge are of a very different character, being sulfides of unknown structure, probably cyclic.

GENERAL PROCEDURE

Solvents

Choice of a suitable solvent was governed by four considerations: (1) selectivity of the solvent for sulfur compounds, (2) solubility of naphtha in the solvent, (3) ease of separation of solvent and extracted oil, and (4) cost. After trial of a great many solvents, both organic and inorganic, three were finally chosen as best satisfying the conditions— liquid sulfur dioxide, aniline, and ethylene glycol diacetate. (Other solvents showing good selectivity for the sulfur compounds were furfural, triacetin, and acetic anhydride.)

These solvents were used in the order named. The solubility of the original naphtha in these solvents decreases in this order and the cost increases. As the successive extractions

1 Received October 13, 1928.
2 Mabery and Smith, *Am. Chem. J.*, **13**, 232 (1891); Mabery and Quayle, *Proc. Am. Acad. Sci.*, **41**, 89 (1906). Since the commencement of our work several further papers on the sulfur compounds in petroleum have appeared: Thierry, *J. Chem. Soc.*, **127**, 2756 (1925); Birch and Norris, *Ibid.*, **127**, 898 (1925); Tomekichi Kan, *J. Soc. Chem. Ind. (Japan)*, **30**, 129 (1927); *C. A.*, **21**, 1344 (1927).

proceed the extracted naphtha becomes more and more soluble in the solvent until the two finally become miscible. When this stage has been reached a new solvent is used in which the naphtha is only partially soluble, but which if used in earlier extractions would have had insufficient solvent powers. The more costly solvents were used when the volume of naphtha to be treated has been reduced by the previous use of a cheaper material. Decreasing the temperature of treatment decreases the solubility without changing the sulfur content of the extracted oil.

Fractional Extraction

The naphtha used in this work was a product from the cracking of a fuel oil (specific gravity 0.953 at 15° C.) from California Midway crude. It had an initial boiling point of about 30° C., and an end point of 250° C. The specific gravity was 0.786 at 15° C. and the sulfur content 1.0 per cent.

Two hundred and twelve liters of this material were extracted with liquid sulfur dioxide at temperatures between −20° and −30° C. Six successive washes of 25 per cent by volume were made. The sulfur dioxide was boiled off the extract by heating to 40° C. in a still with a 10-foot (3-meter) packed column using a reflux condenser cooled with liquid ammonia to prevent loss of naphtha. The recovered oil was neutralized with sodium hydroxide and water-washed. This treatment gave:

	SULFUR PER CENT	SPECIFIC GRAVITY AT 15° C.
Extract oil (37.8 liters)	3.5	0.850
Residual oil	0.3	0.767

The extract oil was submitted to a series of fractional extractions, first with aniline and then with ethylene glycol diacetate, at temperatures from −10° to −20° C. Each wash was 12.5 per cent by volume of the naphtha treated. The oil from each wash was separated and analyzed for sulfur. These oils were then combined into groups depending on their sulfur content and submitted to further extraction. The extracted oils were freed from aniline by washing with 3 N hydrochloric acid, and from ethylene glycol diacetate by washing with a 25 per cent alcohol and water mixture. A diagrammatic summary of this work is given in Figure 1.

The final yield was 13.6 liters of oil containing 5.5 per cent sulfur and having a specific gravity of 0.900 at 15° C. This extract contains 40 per cent of all the sulfur present in the original naphtha. Of the rest, 25 per cent remained in the residual oil from the sulfur dioxide treatment and the remaining 35 per cent in the various low-sulfur oils discarded from the extractions with aniline and ethylene glycol diacetate.

Fractional Distillation

The sulfur compounds in the extract oil were further concentrated by systematic fractional distillation. The stills used in this work had columns insulated with silvered and evacuated jackets.[3] They were electrically heated and the rate of heating was controlled by an electrically operated thermoregulator. An air- or water-cooled reflux condenser in the head controlled the run-back. In using these stills a constant distillation rate of about one drop a second was maintained. With this rate the heater and planer were so adjusted as to maintain at all times the maximum reflux the column would permit.

The extract oil was distilled up to 160° C. at atmospheric pressure and the distillation completed at 120 mm. pressure taking 2.5° C. cuts throughout. Only the oil distilling at atmospheric pressure will be discussed at this time. This oil was refractionated once taking 2.5° C. cuts and the lower boiling fractions up to 90° C., which were found to be too small to be handled successfully in the size still required for the main body of the distillate, were twice fractionated separately in smaller apparatus also taking 2.5° C. cuts. The still used had a 75 × 1.0 cm. column packed with glass pearls. The main portion of the oil from 90° to 160° C. was redistilled four times taking 2.5° C. cuts. The still had a 150 × 1.4 cm. column packed with very short pieces of 5-mm. glass tubing. The results of the two final fractionations are shown in Table I and Figure 2. It will be seen that the fractions of large volume are also those of high sulfur content and that they occur at the boiling points of the aromatic hydrocarbons. This immediately suggests the presence of the thiophene homologs, which show remarkable similarity to the aromatics in their boiling points and other properties.

Table I—Volume and Sulfur Content of Fractions Distilled at Atmospheric Pressure

Boiling Range	Volume	Sulfur	Boiling Range	Volume	Sulfur
° C.	Cc.	Per cent	° C.	Cc.	Per cent
Start 50.0[a]	18	0.09	100.0–102.5	19	0.93
50.0–55.0	23	0.09	102.5–105.0	36	2.76
55.0–57.5	18	0.08	105.0–107.5	17	4.45
57.5–60.0	23	..	107.5–110.0	140	6.86
60.0–62.5	7	..	110.0–112.5	303	10.11
62.5–65.0	4	..	112.5–115.0	20	10.33
65.0–67.5	35	..	115.0–117.5	16	4.89
67.5–70.0	9	0.24	117.5–120.0	33	0.88
70.0–72.5	16	0.77	120.0–122.5	97	0.23
72.5–75.0	31	1.35	122.5–125.0	81	0.49
75.0–77.5	7	3.22	125.0–127.5	53	0.50
77.5–80.0	7	4.30	127.5–130.0	44	1.50
80.0–82.5	9	3.99	130.0–132.5	28	3.11
82.5–85.0	12	2.66	132.5–135.0	102	4.75
85.0–87.5	19	1.12	135.0–137.5	187	4.93
87.5–90.0	37	..	137.5–140.0	516	6.30
90.0–92.5	27	0.30	140.0–142.5	266	9.56
92.5–95.0	4	..	142.5–145.0	250	7.34
			145.0–147.5	82	6.06
			147.5–150.0	30	..
90.0–92.5[b]	11	..	150.0–152.5	32	4.14
92.5–95.0	20	0.42	152.5–155.0	29	3.78
95.0–97.5	..	..	155.0–157.5	31	..
97.5–100.0	34	0.92	157.5–160.0	...	..

[a] Fractionated twice.
[b] Fractionated four times.

The group of fractions in the neighborhood of toluene and thiotolene (107.5° to 117.5° C.) were refractioned once in 1.2° and 1.3° C. cuts. Nearly all of the large fraction 110.0–111.3° C. came over between 110.3° and 110.6° C. The fractions in the xylene-thioxene range, from 130.0° to 147.5°

[3] Loveless, IND. ENG. CHEM., 18, 826 (1926).

C., were refractionated three times taking 1.2° to 1.3° C. cuts. The results of these fractionations are shown in Table II and Figure 2. The sulfur analyses of these oils were made by the oxygen bomb method.[4]

Table II—Volumes, Specific Gravities, and Sulfur Content of Thiotolene and Thioxene Groups

| Boiling Range	Volume	Specific Gravity	Sulfur
° C.	Cc.	15°/4° C.	Per cent
107.5–108.8[a]	30	...	5.22
108.8–110.0	50	0.861	6.38
110.0–111.3	297	0.865	9.04
111.3–112.5	32	0.882	13.68
112.5–113.8	12	0.877	14.20
113.8–115.0	...	...	...
128.8–130.0[b]	9	...	1.27
130.0–131.3	24	...	3.11
131.3–132.5	11	...	4.48
132.5–133.8	33	...	4.85
133.8–135.0	45	0.834	5.20
135.0–136.3	71	0.843	5.26
136.3–137.5	132	0.846	4.65
137.5–138.8	275	0.855	5.18
138.8–140.0	183	0.875	6.92
140.0–141.3	148	0.893	8.72
141.3–142.5	90	0.903	13.15
142.5–143.8	127	0.857	9.73
143.8–145.0	97	0.879	4.97
145.0–146.3	31	...	4.17

[a] Refractionated once.
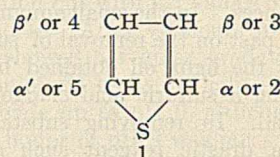[b] Refractionated three times.

EXPERIMENTAL

Thiophenes and Mercuric Chloride[5]

The homologs of the benzene and thiophene series show great similarity both in their physical properties and in their behavior toward reagents, as might be expected from their similar structure.
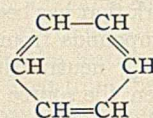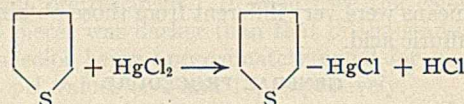

Benzene

Thiophene
(Showing conventional mode of numbering atoms)

The chief differences are in degree, thiophene usually entering more readily into reaction than benzene. For example, the reaction with mercuric chloride, which is difficult in the benzene series, proceeds readily with thiophene.

This reaction is of great value in separating and identifying thiophene isomers. It usually requires the presence of a compound such as sodium acetate to bind the liberated hydrochloric acid. The compounds formed are true primary valence compounds containing a carbon-to-mercury bond and are quite stable. They differ from the addition compounds formed by organic sulfides and mercuric chloride, which involve only residual valences.

$$R_2S + yHgCl_2 \longrightarrow R_2S(HgCl_2)y$$

These compounds contain varying numbers of mercuric chloride molecules and are not very stable, usually smelling of sulfide during crystallization.

The reaction of thiophenes and mercuric chloride is governed by the following rules:

[4] Griffin, "Technical Methods of Analysis," p. 191, McGraw-Hill Book Co.

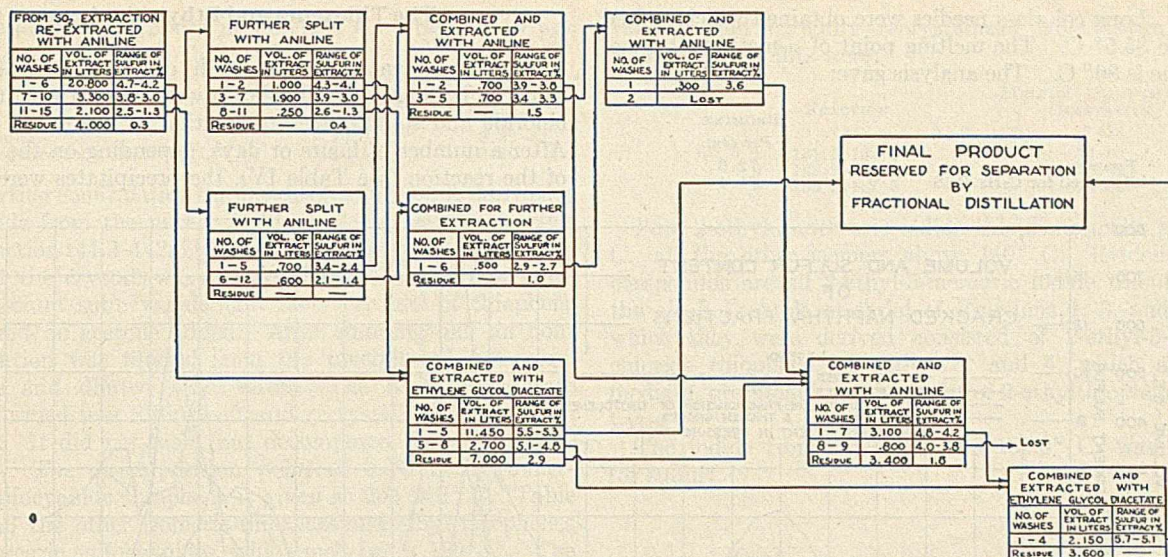[5] Steinkopf and Bauermeister, Ann., 403, 50 (1914); Steinkopf, Ibid., 413, 310 (1916); 424, 23 (1921).

Figure 1—Concentration of Sulfur Compounds in Pressure Naphtha by Fractional Solution in Aniline and Ethylene Glycol Diacetate

(1) If one of the alpha positions is unoccupied, alpha-substituted monomercuric chloride derivatives are formed. These compounds are soluble in alcohol and other common solvents.

(2) If both of the alpha positions are alkylated, a beta-monomercuric chloride is formed. This reaction is much slower than the first. These compounds are also soluble in alcohol and other solvents.

(3) If both of the alpha positions are unoccupied, a mixture of α-mono- and α,α'-dimercuric chloride compounds is usually formed. Sometimes the di compound is formed to the exclusion of the mono. The dimercuric chloride compounds are extremely insoluble in all the common solvents.

METHOD OF IDENTIFICATION—The thiophene isomers were partially separated in the fractional distillation. The separation was completed and the compounds were purified by use of the mercuric chloride reaction. The compounds were identified by the analysis and melting points of the mercuric chloride derivatives. A second derivative was formed and its melting point and composition determined as confirmation. Table III shows the melting points of the compounds mentioned in the text.

Table III—Boiling Points of Thiophene Homologs and Melting Points of Derivatives

THIOPHENE HOMOLOG	BOILING POINT	MELTING POINTS OF DERIVATIVES			
		$-HgCl$[a]	$-HgI$[a]	$-HgSCN$[a]	Tribromide[b]
	° C.	° C.	° C.	° C.	° C.
Thiophene	84	183	116–117	196–197	..
2-Methylthiophene	112–113	204	111–112	202–204	86
3-Methylthiophene	114	128–129	.....	169	34
2-Ethylthiophene	132–134	147–148	96– 97	167.5–169	..
3-Ethylthiophene	135–136	64	.....	......	..
2,3-Dimethylthiophene	136–137	213–214	.....	Darkens at 200–202	..
2,4-Dimethylthiophene	137–138	138–139	137–138	173–175	..
2,5-Dimethylthiophene	135.5–137.5	156–157	175	177–177.5	..
3,4-Dimethylthiophene	144–146	137–138	142	178–179	..

[a] Data from Steinkopf, *Ann.*, **424**, 23 (1921).
[b] Meyer, "Die Thiophene Gruppe," 1888.

Thiotolenes

A preliminary examination having shown the presence of a thoiphene homolog in fraction 110.0–111.3° C., 10 cc. were dissolved in alcohol and treated with mercuric chloride and sodium acetate solutions.

All the precipitations with mercuric chloride were made as follows: The oil, dissolved in sufficient alcohol to make the concentration of the resulting mixture about 20 per cent in alcohol, was added to twice the quantity of 0.25 M aqueous mercuric chloride solution required to form the monomercuric

chloride derivative. To this was added six times the quantity of 4 M sodium acetate required to combine with the liberated hydrochloric acid. The calculations were made on the assumption that all the sulfur present was in the form of thiophene homologs. Alcoholic mercuric chloride solution was also tried, but showed no advantages except that the reaction was somewhat more rapid.

The mixture was allowed to stand 40 hours with occasional shaking. A white putty-like mass of precipitate containing occluded oil was obtained. This was pressed out on a porous plate and obtained as a dry powder. After washing with ethyl and petroleum ethers and drying, the weight was 10.5 grams. In the next 48 hours the reaction mixture gave only 0.4 gram of a white powdery precipitate. The mixed precipitates were submitted to exhaustive extraction with hot absolute alcohol, the soluble material which precipitated at the bottom of the extraction apparatus being withdrawn from time to time. By this means there were obtained 5.7 grams of alcohol-soluble and 3.0 grams of alcohol-insoluble material.

α-Methylthiophene

A part of the alcohol-soluble material was twice recrystallized from alcohol. It formed small prisms, melting at 205–205.5° C. The melting point of 2-methyl-5-mercuric chloride thiophene is 204° C. (Table III)

Most of the thiophene derivatives sinter before melting, and if heated for too long a time decompose. The procedure used was to place the melting point tube in the bath at 10° to 15° C. below the melting point.

Analyses of this material gave:

	CHLORINE Per cent	SULFUR Per cent
Found	11.33	9.98
Required for $C_5H_5S.HgCl$	10.65	9.61

All analyses of derivatives for sulfur and halogen were made by the Carius method.

The remainder of the alcohol-soluble mercuric chloride compound was decomposed by distilling with 6 N hydrochloric acid. It yielded a colorless oil of a clean, toluene-like odor, denser than water; 0.5 cc. of this oil was treated with bromine water in excess and the resulting pasty mass dried on a porous plate and recrystallized from hot absolute

alcohol. Long colorless needles were obtained which melted at 85° to 85.5° C. The melting point of α-methyltribromo-thiophene is 86° C. The analysis gave:

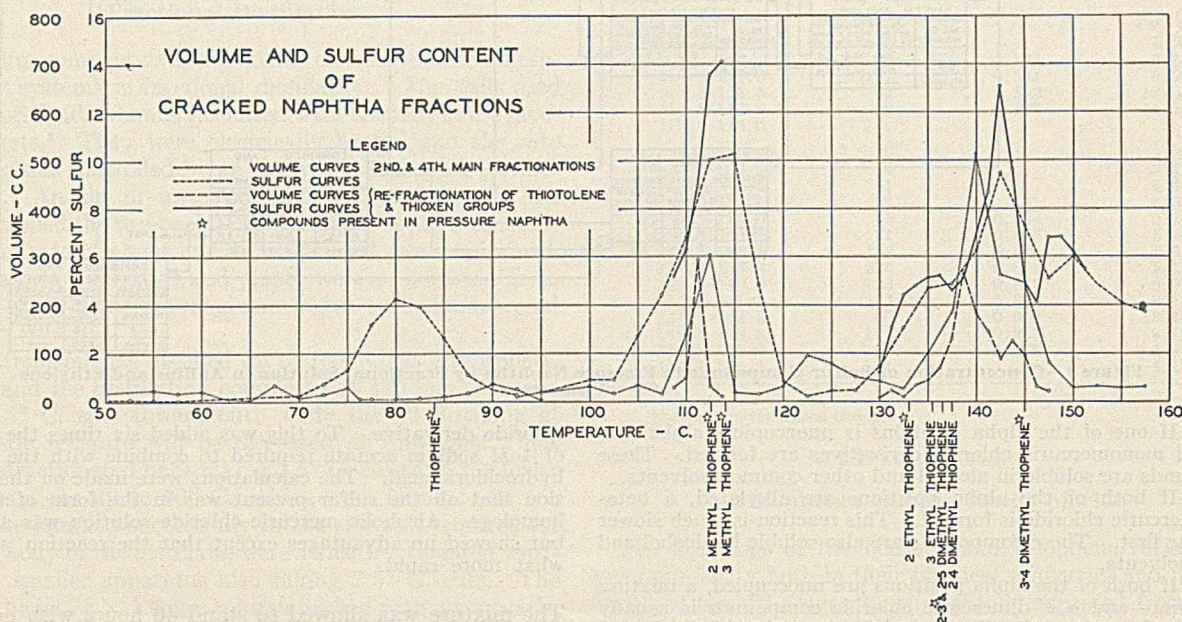|	BROMINE Per cent
Found	72.0
Required for $C_5H_3.Br_3S$	71.4

Figure 2

β-Methylthiophene

The alcohol-insoluble portion of the precipitate was analyzed for sulfur and chlorine with the results:

	CHLORINE Per cent	SULFUR Per cent
Found	12.35	5.62
Required for $C_5H_4S.2HgCl$	12.47	5.51

Evidently the material is practically pure 2,5-dimercuric chloride 3-methylthiophene. It was decomposed by distilling with 6 N hydrochloric acid. An oil denser than water was obtained. A small quantity (0.4 cc.) was treated with excess bromine water and the resulting oil dissolved in warm alcohol and crystallized by cooling to 0° C. Fine, white, silky needles were obtained. After recrystallizing once from alcohol they melted sharply at 33.5° C. The melting point of tribromomethyl thiophene is 34° C. The analysis gave:

	BROMINE Per cent
Found	73.7
Required for $C_5H_3.Br_3S$	71.4

Four-tenths cubic centimeter of the methylthiophene was treated with mercuric chloride and sodium acetate solutions and 0.75 gram of precipitate was obtained. This was extracted with hot absolute alcohol; 0.32 gram remained insoluble. By diluting the alcohol 0.39 gram of precipitate was obtained, which melted without recrystallizing at 123–124° C. After recrystallizing from alcohol the melting point was raised to 127–128° C. The melting point of 2-mercuric chloride 3-methylthiophene is 128–129° C. The analyses gave:

	CHLORINE Per cent	SULFUR Per cent
Found	11.08	9.30
Required for $C_5H_5S.HgCl$	10.65	9.61

The Thioxenes and Ethylthiophene

Ten cubic centimeters of each of the fractions in the thioxene boiling range (Table II) were treated with mercuric chloride and sodium acetate solution in the usual manner. After a number of hours or days, depending on the velocity of the reaction (see Table IV), the precipitates were filtered off and washed with water, a small amount of alcohol, and much petroleum ether. The lower fractions gave precipitates of the color and consistency of butter due to occluded oil; reaction was slow and incomplete. After washing, the precipitates were obtained as dry yellow powders. The higher fractions reacted much more rapidly and completely (precipitation was nearly complete in 24 hours) and gave dry flaky precipitates, nearly free from occluded oil. The color ranged from cream to white.

The crude precipitate from each fraction was submitted to exhaustive extraction with hot absolute alcohol. It will be observed that the sum of the alcohol-soluble and alcohol-insoluble material obtained after extraction is in some cases considerably less than the weight of crude precipitate. This does not represent decomposition caused by the hot alcohol during extraction, but is chiefly occluded oil in the crude precipitate which was not removed by the petroleum-ether washing. The per cent completion of reaction shown in Table IV is calculated from the weight of alcohol-soluble precipitate and the weight and sulfur content of the alcohol-insoluble precipitate; on the assumption that the alcohol-soluble precipitates are monomercuric chloride thiophenes and the alcohol-insoluble precipitates dimercuric chloride derivatives plus impurities such as mercurous chloride. The proportion of thiophene derivatives in the latter is indicated by the sulfur content.

2,3-Dimethylthiophene

Columns 9 and 10 of Table IV give data on the recrystallizations and melting points of the alcohol-soluble portion of the precipitates. Comparison of the melting points of the alcohol-soluble material from Fractions 6, 9, 10, and 11 with the data for the pure monomercuric chloride compounds in Table III shows that these precipitates consist of 2, 3-dimethyl-5-mercuric chloride thiophene, pure in Fractions

9, 10, and 11 and impure in Fraction 6. Fraction 10 was analyzed for sulfur and chlorine:

	CHLORINE	SULFUR
	Per cent	Per cent
Found	10.05	9.22
Required for $C_6H_7S.HgCl$	10.19	9.20

As further confirmation the mercuric sulfocyanide derivative was made from the unrecrystallized alcohol-soluble crystals from fraction 141.3–142.5° C. (No. 9). Ninety-six hundredths gram of the crystals was dissolved in acetone and 0.62 gram of potassium sulfocyanide (2.3 mols per mol of thiophene compound) in acetone added. After standing half an hour the solution was filtered from the precipitated potassium chloride and diluted with water. The white precipitate which formed was filtered off and recrystallized from ethyl acetate. It did not melt, but decomposed sharply at 200–203° C. The decomposition point of 2,3-dimethyl-5-mercuric sulfocyanide thiophene is given as 200–202° C. (Table III) All the other isomeric thioxenes and ethyl thiophenes give mercuric sulfocyanides, which melt below 180° C. The yield in this reaction was 100 per cent. The analysis of the material gave:

	SULFUR
	Per cent
Found	17.34
Required for $C_6H_7S.HgSCN$	17.30

The alcohol-soluble portion of the precipitates from Fractions 7, 8, and 12, which are intermediate to Fractions 6, 9, 10, and 11, presumably also consists of 2,3-dimethyl-5-mercuric chloride thiophene.

2-Ethylthiophene

Considering now the alcohol-soluble precipitates from the lower boiling fractions: Fraction 1 from its melting point may be 2,4 or 3,4-dimethyl- or perhaps impure 2-ethyl- or 2,5-dimethyl-monomercuric chloride thiophene. The same applies to Fraction 3, though recrystallization would probably have raised this melting point, eliminating from consideration 2,4- and 3,4-dimethylthiophene. Fractions 2 and 4 appear to be pure 2-ethylthiophene derivatives, though there is the possibility of impure 2,5-dimethyl. The same applies to Fraction 5.

vacuum and carefully recrystallized from warm alcohol. The melting points were:

FRACTION		MELTING POINT OF HgI DERIVATIVE
	° C.	° C.
1	131.3–132.5	91–92
3	133.8–135.0	94–95
5	136.3–137.5	91–92

Pure 2-ethyl-5-mercuric iodide thiophene melts at 96–97° C., all the other isomers above 140° C. Evidently these compounds are all 2-ethyl-5-mercuric iodide thiophene and the alcohol-soluble material of Fractions 1, 3, and 5, from which they were derived consisted of 2-ethyl-5-mercuric chloride thiophene. Fractions 2 and 4, which are intermediate, presumably, also consist of 2-ethylthiophene derivatives.

The iodide from fraction 133.8–135.0° C. was analyzed for sulfur:

	SULFUR
	Per cent
Found	7.03
Required for $C_6H_7S.HgI$	7.29

3,4-Dimethylthiophene

This compound, having two free alpha positions, is capable of forming an alcohol-insoluble dimercuric chloride compound. It boils at 144–146° C. and should be present in the alcohol-insoluble precipitate from the higher boiling fractions of the thioxene group. The alcohol-insoluble material from Fractions 11 and 12 was analyzed for sulfur and chlorine:

FRACTION	CHLORINE	SULFUR
° C.	Per cent	Per cent
143.8–145.0 (No. 11)	11.92	5.30
145.0–146.3 (No. 12)	11.22	5.11
Required for $C_6H_6S.2HgCl$	12.17	5.49

Evidently the precipitate from Fraction 11 is practically pure 3,4-dimethyl-2,5-dimercuric chloride thiophene. The material from Fraction 12 is slightly less pure.

The alcohol-insoluble material from Fraction 12 was decomposed by distilling with 6 N hydrochloric acid; 0.6 cc. of a pale yellow oil slightly denser than water was obtained. The mercuric chloride compound was again formed using only 50 per cent in excess of the requirements for the formation

Table IV—Properties of Precipitates from Fractions in Thioxene Group

No.	BOILING RANGE	WEIGHT OF PRECIPITATES			SULFUR IN ALCOHOL-INSOLUBLE	TIME OF RE-ACTION	COMPLETION OF RE-ACTION	ALCOHOL-SOLUBLE PRECIPITATE RECRYSTALLIZED FROM ALCOHOL	
		Crude	Alcohol-soluble	Alcohol-insoluble				Number of recrystallizations	Melting point
	° C.	Grams	Grams	Grams	Per cent	Hours	Per cent		° C.
1	131.3–132.5	3.58	1.22	1.12	1.17	144	33	2	138–140
2	132.5–133.8	3.91	1.72	0.96	1.41	144	42	3	143.5–144
3	133.8–135.0	4.92	1.81	1.67	1.31	408	43	Not recrystallized	138–139
4	135.0–136.3	5.17	1.33	1.95	1.13	408	33	3	147–148
5	136.3–137.5	3.43	1.60	0.59	..	144	..	5	150–151
6	137.5–138.8	4.6	2.42	0.26	..	96	..	2	170–180 (indefinite)
7	138.8–140.0	...	...	..	..	..	..	.	.....
8	140.0–141.3	...	...	..	..	...	..	.	.....
9	141.3–142.5	17.03	9.65	0.63	..	44	83	Not recrystallized	200–210
10	142.5–143.8	10.4	9.8	0.3	..	96	95	5	213–213.5
11	143.8–145.0	5.40	2.91	1.51	5.30	24	84	Not recrystallized	210–213
12	145.0–146.3	5.98	0.91	3.60	5.11	144	80	.	.....

It will be seen from Table III that the iodide derivatives melt over a much wider range than the corresponding chlorides and are therefore better suited for establishing identity.

The mercuric iodides of Fractions 1, 3, and 5 were formed as follows: 0.3 gram of the unrecrystallized alcohol-soluble crystals, dissolved in acetone, was mixed with 0.15 gram of HgI₂ (over 1 mol per mol of thiophene compound), dissolved in acetone, and allowed to stand a few hours. The precipitated sodium chloride was filtered off and the acetone diluted with water. The precipitated iodides were filtered off under

of the mono compound in the hope of obtaining a mixture of the mono and di compounds. A snow-white precipitate was formed which proved to be entirely the insoluble dimercuric chloride compound. The analysis gave:

	CHLORINE	SULFUR
	Per cent	Per cent
Found	12.17	5.34
Required for $C_6H_6S.2HgCl$	12.17	5.49

This result is contrary to the experience of Steinkopf,[6]

[6] Steinkopf, Ann., **403**, 50 (1914).

who, using a larger excess of mercuric chloride solution, obtained a mixture of mono and dimercuric chloride compound.

3-Ethylthiophene

This also has two free alpha positions and can form an alcohol-insoluble dimercuric chloride derivative. This homolog boils at 135–136° C., and if present should be contained in the alcohol-insoluble precipitates from the lower boiling fractions in the thioxene range. The first four fractions, which contained the largest percentage of alcohol-insoluble material, were analyzed for sulfur. They contained, as shown in Table IV, 1.1 to 1.4 per cent sulfur. The pure dimercuric chloride compound contains 5.5 per cent, so that these precipitates can contain at most only about 20 per cent of the thiophene derivatives. The remainder is probably mercurous chloride.

The four fractions whose analyses are given were mixed and distilled with 6 N hydrochloric acid, about 0.1 cc. of an oil of the same or slightly greater density than water was obtained. This was dissolved in alcohol and mixed with mercuric chloride and sodium acetate solutions, then shaken for 8 hours; after 24 hours 0.16 gram of precipitate was obtained. This was boiled two or three times with small quantities of absolute alcohol, the solution partly evaporated and cooled to 0° C.; 0.06 gram of colorless crystals was obtained which melted sharply at 147–148° C. without recrystallizing. This agrees with the melting point of 2-ethyl-5-mercuric chloride thiophene.

As further confirmation, this compound was dissolved in acetone and treated with 0.03 gram of sodium sulfocyanide. The mixture was allowed to stand 2 or 3 hours and the clear solution poured into water. The white precipitate which formed was filtered and dried. It melted at 168–169° C. The melting point of 2-ethyl-5-mercuric sulfocyanide thiophene is 167.5–169° C.

Evidently the sulfur in these alcohol-insoluble precipitates was due chiefly to small residues of 2-ethylthiophene-monomercuric chloride, not entirely removed by extraction with alcohol. The very small residue which remained after dissolving out the 2-ethyl compound with hot alcohol above may have contained a derivative of 3-ethylthiophene, but the amount of material was too small to work with. This compound if present in pressure naphtha is there only in inappreciable traces.

Thiophene

From Table II it will be seen that fractions 77.5–80.0° and 80.0–82.5° C. contain the largest percentages of sulfur in this group. This suggests the presence of thiophene, which boils at 84° C. In order to prove its presence, 10 cc. of a mixture of the fractions from 75° to 85° C. were treated with mercuric chloride and sodium acetate in the usual way. The reaction mixture was allowed to stand 2 weeks; 2.51 grams of a yellow precipitate were obtained. This was submitted to exhaustive extraction with hot absolute alcohol. By diluting the alcohol 0.29 gram of precipitate was obtained. After recrystallizing from acetone containing a small amount of water, crystals were obtained. These were slightly brownish and melted at 182–184° C. A second crop melted at 179–180° C. The melting point of pure 2-mercuric chloride thiophene is 186–187° C. The quantity of material was insufficient to permit of further purification. The two crops were mixed and analyzed for sulfur and chlorine:

	CHLORINE *Per cent*	SULFUR *Per cent*
Found	9.05	9.65
Required for C₄H₃S.HgCl	11.12	10.03

The alcohol-insoluble portion of the precipitate from the above extraction was decomposed by distilling with 6 N

hydrochloric acid, about 0.05 cc. of an oil denser than water was obtained. The mercuric chloride compound was again formed; after standing 48 hours 0.18 gram of precipitate was obtained. This was boiled two or three times with acetone, a little water added, and the acetone cooled to 0° C. About 0.05 gram of crystals was obtained which melted in the neighborhood of 180° C. These were dissolved in 1.5 cc. of acetone and 0.5 cc. of sodium sulfocyanide solution (slightly over 1 mol) was added. After standing an hour, the liquid was poured off the small amount of precipitate which had formed and diluted with water. Fine silky needles were obtained. Placed in the melting point bath at 175° C. without recrystallizing, they melted at 179.5–180° C. The melting point of 2-mercuric sulfocyanide thiophene is 179–180° C. The quantity of material was too small for analysis.

Distribution of Thiophene Homologs in Naphtha

From the volume, gravity, and sulfur content of each fraction, the weight of sulfur present in each group of thiophene isomers may be calculated. From these values and the total weight of sulfur in the extract oil before fractionation, the portion of the total sulfur due to each group may be calculated, correction being made for the losses during distillation. Assuming that the compounds extracted from the original naphtha are removed in equal proportion, which since they are members of an homologous series is not unreasonable, these are also the percentages present in the original naphtha. This calculation results in:

	Per cent
Sulfur in pressure naphtha present as:	
Thiophene	1
Thiotolene	7
Thioxene	15
	—
Total	23
Remainder in naphtha boiling above 160° C.	77

Sulfur Compounds from Pressure Naphtha Sludge Oil

In order to determine the character of the compounds present in the oil from cracked naphtha sludge, an acid sludge which had been formed in low-temperature refining of naphtha[7] was drawn, settled, separated from the supernatant naphtha, and diluted with ice and water. Two hundred liters of the light tar which separated were neutralized with lye and steam-distilled until no more oil came over. By this means 38 liters (18.8 per cent of the charge) were obtained which contained 8 per cent sulfur. Twenty-eight liters of this oil were treated with an equal volume of 95 per cent sulfuric acid at about −10° C. The oil obtained by diluting the sludge thus formed was about 13 liters (45 per cent); 11 liters were insoluble in the acid. The treating loss, 4 liters (15 per cent), probably represented sulfonated oil. The insoluble oil contained only 0.2 per cent sulfur. The oil from the sludge was steam-distilled from an alkaline solution; 11 liters (85 per cent) were recovered which contained 12.8 per cent sulfur. This was roughly fractionated several times taking 2.5° C. cuts.

As a preliminary experiment to compare the properties of these sulfur compounds with those originally present, cracked naphtha was agitated with aqueous mercuric chloride solution (no sodium acetate was present), the sulfur was not appreciably lowered. Upon treating a sample of the sludge oil, largely diluted with sulfur-free oil with aqueous mercuric chloride solution, the sulfur was practically all removed. This would indicate that in the case of cracked naphtha at least the compounds obtained by diluting the sludge and distilling are very different from those originally present in the naphtha.

On treatment with alcoholic mercuric chloride solution

[7] Halloran, Am. Petroleum Inst., *Bull.* **9**, 153 (1928).

these sludge compounds give thick, oily precipitates which congeal to brown solids. If the precipitates are decomposed by triturating with sodium sulfide and the regenerated oil is recovered by steam distillation and reprecipitated, the material comes down as a colorless solid. If the process is repeated a third time, immediate white crystalline precipitates are obtained. The secondary or tertiary precipitates after three or four crystallizations from benzene melt sharply. The analyses correspond to addition compounds of sulfides and 2 to 4 molecules of mercuric chloride. The molecular weights of the compounds are too large for analyses to show whether they are aliphatic sulfides or cyclic or unsaturated sulfides.

The sludge oils react with methyl iodide to give water-soluble crystalline sulfonium compounds which sublime without melting. They give double addition compounds with methyl iodide and mercuric iodide and methyl iodide and iodoform, which are yellow, crystalline compounds that melt readily. Oxidation with potassium permanganate yields sulfones, which are yellow liquids slightly soluble in water. These oils react with bromine to give addition compounds which are sometimes liquids and sometimes crystalline solids. Hydrobromic acid is evolved at the same time. These reactions identify these compounds as sulfides; their properties are, however, quite different from those of the normal alkyl sulfides. With methyl iodide the reaction goes much more readily than it does with the alkyl sulfides, and the tendency to exchange radicals, forming methyl sulfide and methyl sulfonium iodide, is very much less.

In reacting with bromine neither the normal alkyl sulfides nor allyl sulfide evolve hydrobromic acid, though this behavior might well be expected of a highly branched alkyl radical or a cyclic sulfide containing more reactive hydrogen. On account of the evolution of hydrobromic acid, this reaction cannot be used to determine unsaturation. It appears, however, that the oxygen number method of Nametkin[8] can be applied to these compounds.

The reaction of these sulfides with bromine is similar to that of the sulfides which Mabery and Quayle[2] isolated from a sludge formed in refining Canadian kerosene. The boiling points, densities, and refractive indices also show a rather close agreement:

	CARBON ATOMS	BOILING POINT °C.	DENSITY	REFRACTIVE INDEX
Normal alkyl sulfide[a]	8	182	0.839	1.454
Sulfide from Canadian sludge[c]	8	167–169	0.892	1.468
Sulfide from California pressure Naphtha sludge	8	162–168	0.900	1.468
Normal alkyl sulfide[a]	11	215–220[b]	0.840[b]	1.458[b]
Sulfide from Canadian sludge[c]	11	224–228	0.915	1.480
Sulfide from California pressure Naphtha sludge	11	229–230	...	1.486

[a] Data from International Critical Tables.
[b] These values obtained by interpolation.
[c] Mabery and Quayle's, reference 2.

Grishrevich-Trorimosky[9] has shown that the gravities and refractive indices of the cyclic sulfides are higher than those of the corresponding aliphatic compounds.

The data in the literature are insufficient to make possible the identification of these compounds by comparison of the melting points and analyses of their derivatives with those of known compounds. For example, from a fraction boiling at 102.5–105.0° C. at 120 mm. pressure the mercuric chloride addition compound was made, decomposed, the oil recovered and again precipitated with alcoholic mercuric chloride. After separating the precipitate and diluting the alcohol, additional precipitate was obtained. Both of these precipitates were recrystallized twice from benzene-toluene by cooling to 0° C. The melting points and analyses were:

8 Nametkin, *Neftyanoe Khozyaistvo*, **10**, No. 7, 58 (1926); or more briefly, *J. prakt. Chem.*, **115**, 56 (1927).
9 Grishrevich-Trorimosky, *Russ. Phys. Chem. Soc.*, **48**, 880 (1916).

	PER CENT CHLORINE		PER CENT SULFUR	
	I	II	I	II
Crystals by precipitation (m. p., 147.5–148° C.):				
Found	22.7	22.8	3.03	2.98
Required for $(C_8H_{18}S)_2.7HgCl_2$	22.6		2.96	
Crystals by dilution (m. p., 130–130.5° C.):				
Found	21.9	21.9	3.48	3.16
Required for $C_8H_{18}S.3HgCl_2$	22.1		3.33	

A sample of the material from the second precipitation with mercuric chloride was decomposed and the oil recovered and analyzed for sulfur:

	PER CENT SULFUR	
	I	II
Found	21.20	21.28
Required for $C_8H_{18}S$		21.92

The results show these compounds to be derivatives of a sulfide containing 8 carbon atoms; although the formulas assigned are those of aliphatic sulfides, the compounds might very well be cyclic or unsaturated; the variation in the chlorine and sulfur contents caused by the loss of two hydrogen atoms is within the limit of experimental error.

The corresponding compounds made under the same conditions from n-butyl and isobutyl sulfide are as follows:

	PER CENT CHLORINE		PER CENT SULFUR	
From di-n-butyl sulfide: (m. p., 110–110.5° C.):				
Found	20.48		4.45	
Required for $(C_4H_9)_2S.2HgCl_2$	20.55		4.64	
		II	I	II
From diisobutyl sulfide: (m. p., 131.5–132° C.):				
Found	21.21	21.42	3.70	3.65
Required for $[(C_4H_9)_2S]_2.5HgCl_2$	21.45		3.87	

Both these compounds were recrystallized four times from benzene-toluene. Analyses from earlier crystallizations showed contamination with a lower addition compound.

Note—In the course of this work the following derivatives of pure sulfides were made and their melting points and composition determined:

COMPOUND	FORMULA	MELTING POINT °C.
Ethyl sulfide mercuric chloride	$(C_2H_5)_2S.3HgCl_2$	131.5–132
n-Propyl sulfide mercuric chloride	$(C_3H_7)_2S.2HgCl_2$	126.5–127.5
Allyl sulfide tetrabromide	$(C_3H_5Br_2)_2S$	94–95.5

All that these data show is that the sludge sulfide contains 8 carbon atoms and is neither n-butyl nor isobutyl.

The only methods for identifying these compounds are those involving decomposition and study of the decomposition products or replacement of the sulfur by some other atom where compounds and derivatives are better known than those of the sulfides. Some tentative experiments have been made along these lines.

Reaction of Sulfides with Methyl Iodide

Butyl sulfide heated 13 hours at 150° C. with methyl iodide under pressure yielded almost quantitatively butyl iodide, which was identified as the butyl ester of 3,5-dinitrobenzoic acid. Allyl sulfide required more gentle treatment. Heating 24 hours in a sealed tube at 95–100° C. yielded 80–90 per cent of allyl iodide, which was identified as the trimethyl-allyl ammonium iodide.

The sulfide mentioned above as containing 8 carbon atoms was heated under pressure with methyl iodide. It was found to be much more stable than either allyl or butyl sulfide, heating for 24 hours at 100° C. yielding mostly unchanged sulfide. Finally, a sample was heated 48 hours at 150° C. This yielded an oil which required distillation under vacuum to prevent decomposition; it contained only carbon, hydrogen, and iodine, and was free from sulfur. The iodine content was lower than expected, indicating 13 or 14 carbon atoms; the compound was probably impure. An attempt was made to purify it by forming the trimethyl ammonium salts, but it reacted with the trimethyl amine
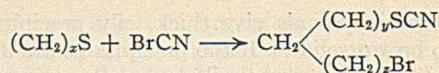
forming tetramethyl ammonium iodide and an oil of particular but not unpleasant odor which was possibly an amine and may have contained the original radical. The quantity was insufficient for further investigation.

The reaction of a sulfide with bromocyanogen[10] is also a possible means of determining the radicals attached to sulfur:

$$R_1R_2S + BrCn \longrightarrow R_1Br + R_2SCN$$
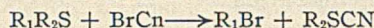
or

[10] Von Braun, *Ber.*, **43**, 545 (1910); **56**, 1573 (1923).

$$(CH_2)_xS + BrCN \longrightarrow CH_2\begin{cases}(CH_2)_ySCN \\ (CH_2)_zBr\end{cases}$$

The sludge sulfides have been found to react with bromocyanogen, but the products of reaction have not been investigated.

The high densities and refractive indices of these sulfides together with their reactions with bromine and methyl iodide make it probable that they have a cyclic structure.

Place of Synthetic Amyl Products among Lacquer Solvents[1]

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ALL who have worked with lacquer are familiar with the acetate made from fusel oil which has been sold for years under the name "amyl acetate." Within the last two years a synthetic amyl acetate has been developed and used in lacquer work under the name "Pent-acetate." The corresponding alcohol is also used under the name "Pentasol." This paper attempts to show the place Pentasol and Pent-acetate occupy in relation to the other commonly used solvents for lacquer.

The specifications for Pentasol and Pent-acetate are given in Table I.

Recent additions to the present group of lacquer solvents are synthetic amyl alcohol and synthetic amyl acetate. This alcohol is made from pentane as a raw material. The synthetic amyl alcohol is practically a duplicate of the so-called high-test fusel oil offered in the past. The synthetic amyl acetate is prepared from the alcohol and acetic acid. In lacquer formulation this acetate ranks in the general class of high boilers, including butyl propionate, fusel oil acetate, Cellosolve acetate, etc.

Laboratory data are given showing various relations between these and other solvents. These comparisons are based on the usual methods of testing the suitability of solvents, and consist of data on distillation, tolerance of nitrocellulose solutions for hydrocarbons, viscosities of nitrocellulose solutions, evaporation rates, and solubility of resins.

Distillation and Evaporation Data

Comparative distillation curves of certain nitrocellulose solvents are given in Chart No. 1. All distillations were made according to standard A. S. T. M. methods. Comparative evaporation rates are shown in Chart No. 2. These two charts should always be shown together, because most solvents used today are not single chemical compounds and consequently vary to some extent with the source of supply. Even ethyl and butyl acetate vary quite a few degrees in boiling range from the boiling points of the pure materials. The method of determining rate of evaporation will be described later. It is seen from Chart No. 2 that butyl acetate and fusel oil acetate evaporate more rapidly than does Pent-acetate; Pent-acetate and butyl propionate evaporate at about the same average rate, while the other materials shown all evaporate more slowly than does Pent-acetate.

Table I—Specifications for Pentasol and Pent-acetate

	PENTASOL	PENT-ACETATE
Color	Water white	Water white
Specific gravity at 20° C.	0.812–0.820	0.860–0.870
Acidity	None	Less than 0.03 per cent
Water content	None	None
Non-volatile at 100° C.	Less than 0.02 per cent	Less than 0.02 per cent
Halogen content	None	None
Petroleum or coal-tar hydrocarbons	0.0000 per cent	0.0000 per cent
Weight per gallon	6.8 lbs.	7.2 lbs.

Distillation

PENTASOL	PENT-ACETATE
100 per cent above 112° C.	100 per cent above 126° C.
95 per cent above 118° C.	95 per cent above 130° C.
50 per cent above 125° C.	75 per cent above 135° C.
15 per cent above 130° C.	25 per cent above 140° C.
End point not above 140° C.	End point not above 155° C.

These specifications are based on the usual A. S. T. M. methods.

The Pentasol is a mixture of five of the amyl alcohols. The mixture contains about 75 per cent of primary alcohols and 25 per cent of secondary alcohols. About one-third of the primary alcohol content is normal primary amyl alcohol.

The Pent-acetate is the acetate made from Pentasol and acetic acid.

The source of Pentasol is the pentane fraction of natural gasoline. This pentane fraction is chlorinated to form amyl chloride and the amyl chloride is converted to amyl alcohol by treatment with caustic soda.

Dilution Ratios

The tolerance of various nitrocellulose solutions for toluene and petroleum naphtha is shown in Table II.

Table II—Dilution Ratios—Hydrocarbon to Solvent

SOLVENT	TOLUENE	LACTOL NO. 1
Butyl acetate	2.50	1.37
Pent-acetate	1.90	1.27
Butyl propionate	1.96	1.14
Ethyl lactate	4.43	0.61
Ethyl oxybutyrate	4.00	1.14
Butyl cellosolve	2.78	1.86
Cellosolve	4.43	0.88
Cellosolve acetate	2.42	0.76
Fusel oil acetate	2.25	1.27
Pent-acetate, 60 parts } Butyl acetate, 40 parts }	2.20	1.27

The toluene used was the usual commercial grade and the petroleum naphtha was the material sold as Lactol Spirits No. 1 having a boiling range from 80° to 130° C. The method used in obtaining these dilution ratios was to dissolve 5 grams of dry half-second nitrocellulose in such an amount of the solvent under test that the final volume at the precipitation or gel point was 40 cc. This gives constant final concentration of nitrocellulose for each solvent.

An attempt was made to find the most economical ratio of ester-alcohol-hydrocarbon to use in lacquer. In Chart No. 3 is shown graphically the dilution ratios of various ester-alcohol-hydrocarbon blends. These dilution ratios were determined by adding the indicated blends of alcohol and hydrocarbon to solutions of nitrocellulose in either butyl acetate or Pent-acetate. The usual precipitation of nitrocellulose was taken as the end point. As in the previous dilution tests, these tests were all adjusted so that the concentration of nitrocellulose at the end point was the same in each case. The ratio as shown was determined by dividing the volume of alcohol-hydrocarbon blend used by the amount of ester used. It is noted that in the blends high in hydrocarbon and low in alcohol the effect of the alcohol is more marked in the case of the petroleum compounds. In the blends high in alcohol the effect of the alcohol is more marked in the case of the coal-tar compounds. V. M. P. naphtha shows about the same ratio as Lactol Spirits No. 1.

Viscosities of Nitrocellulose Solutions

Viscosities of solutions of half-second nitrocellulose determined by the usual falling-ball method are given in Table III.

Table III—Viscosities of Nitrocellulose Solutions

	Minutes
Butyl acetate	0.09
Pent-acetate	0.18
Butyl propionate	0.19
Fusel oil acetate	0.10
Pent-acetate, 60 parts } Butyl acetate, 40 parts }	0.11
Ethyl lactate	0.05
Cellosolve	0.05
Cellosolve acetate	0.09

The solutions were made of 72 grams of dry half-second nitrocellulose in 300 cc. of solvent which consisted of equal parts by volume of toluene and the respective solvent. These tests were made at 25° C.

Solubility of Resins

The solubility of various resins in Pent-acetate and Pentasol is shown in Table IV.

Table IV—Solubility of Gums

	PENTASOL	PENT-ACETATE
Ester gum	S	S
Shellac	S	IS
Kauri	S	S
Pontianac	S	S
Sanderac	S	S
Congo	Gels	Gels
East India	PS	PS
Manila	S	S
Dammar	PS	PS
Cumar	PS	S
Amberol	IS	S

S—soluble; IS—insoluble; PS—partly soluble.

These solutions all consisted of 4 pounds (1.8 kg.) of gum to a gallon (3.78 liters) of solvent. None of these resins received any previous treatment to render them soluble. Any treatment of such resins as congo, kauri, or pontianac to increase their solubility aids as much in increasing their solubility in Pentasol and Pent-acetate as in other solvents.
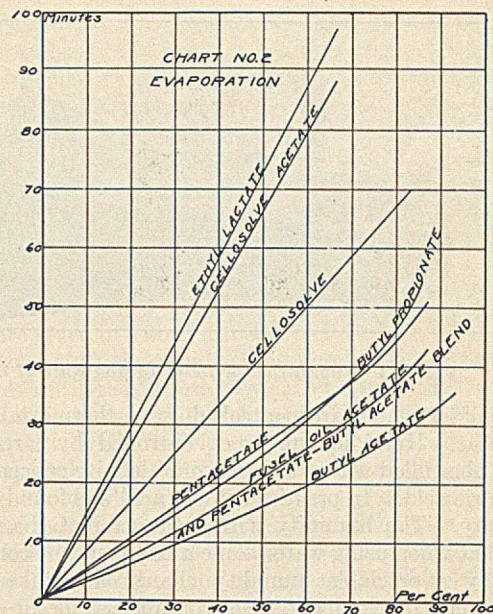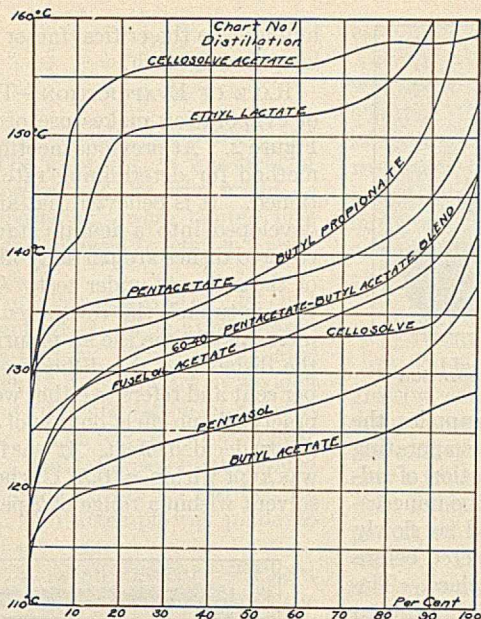
Comparison of Blends Containing High-Boiling Solvents

The majority of lacquers contain, in their solvent portion, a blend of hydrocarbon, ethyl acetate, and some higher boiling acetate or other nitrocellulose solvent. It was thought that the best way of getting a more exact comparison of some of the higher boiling solvents was to incorporate them in such blends and compare the blends. It was believed that the closest comparison would be between blends having about the same final time of complete evaporation. Such blends were prepared and tested for rate of evaporation and blush resistance. Since the methods used were not accepted as standard methods, the result of the blush tests cannot be shown.

BLUSH RESISTANCE—The method used in determining blush resistance is one that was developed in the laboratory of
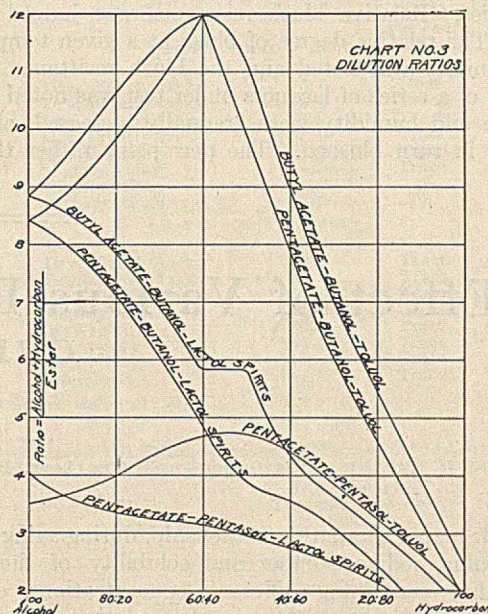
the Sherwin-Williams Company at Chicago. The apparatus used is illustrated in Figure 1. The cubical chamber is divided equally into an upper and a lower compartment by two horizontal aluminum baffle plates about 1 inch (2.5 cm.) apart. These plates are perforated with 0.5-inch (1.3-cm.) holes. The lower compartment is the one in which the humidity and temperature are controlled. A battery of electric light bulbs,
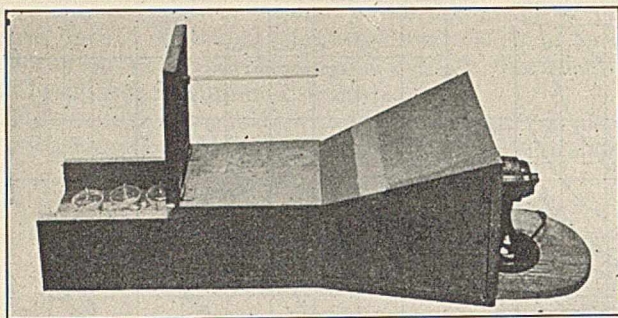
Figure 1—Apparatus for Determining Rate of Evaporation

half of which are controlled by a thermostat, supplies the heat. Humidity may be controlled by large evaporating dishes filled with a solution of a definite concentration of sulfuric acid. In practice sulfuric acid was found to be unnecessary. The humidity within the cabinet changed so slowly that when using water alone a test could be completed before any appreciable humidity change had taken place. The lower compartment also contains a motor-driven fan to promote air circulation. The upper compartment contains a rotating drum, motor-driven from the outside. A circular shelf is built around the bottom of this drum to hold the test panels. Sufficient panels for a given test are placed on this shelf around the drum, the entire cabinet is brought to the conditions desired, and the panels are then flow-coated with the respective test lacquers through a small hole in the top of the cabinet. The drum is then rotated until the panels are dry and the relative degree of blush is noted. Humidity is calculated from readings of wet and dry bulb thermometers placed in the upper compartment of the cabinet. This apparatus can be built in any shop at a very small cost.

In this apparatus consistent checks can be obtained on a series of lacquers over a range of temperature and humidity. Relative blush resistance of a series of lacquers as determined by this apparatus is the same at varying temperatures and humidities. Relative blush resistance was judged in two ways. The relative degree of blush at a given temperature and humidity was noted and the blush resistance of each member of a series of lacquers under test was noted as temperature and humidity were gradually increased, and each member in turn blushed. The dew point rather than the

humidity is the critical factor in determining whether a given lacquer will blush.

RATE OF EVAPORATION—The method of determining rate of evaporation makes use of a small air tunnel as shown in Figure 2. At previous meetings the desirability of a standard method for determining rate of evaporation has been mentioned. It is believed that an air tunnel such as this could be developed into a definite standard. Weighed, ground-glass-covered dishes are partially filled with equal weighed volumes of the solvents under test. These dishes are then placed in the air tunnel, the covers removed, and the fan started. At intervals of time the air is turned off, the covers are placed on the dishes and the dishes weighed. The loss is recorded in per cent and refers to either weight or volume. Humidity has practically no effect on rate of evaporation. Temperature has a very decided effect. It was found that when the temperature was kept within ± 0.5° C. checks could be obtained on a given solvent within a range of 2 per cent.
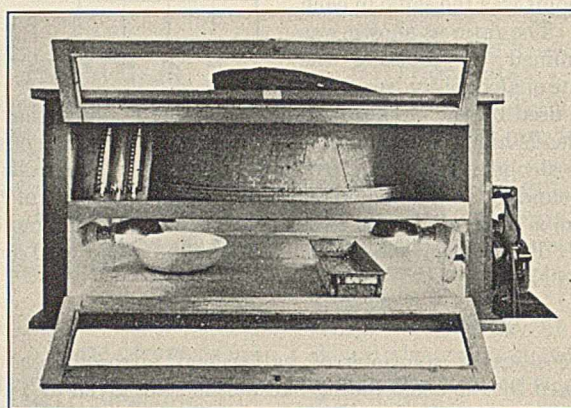
Figure 2—Apparatus for Determining Blush Resistance

In standardizing this test it would be necessary to use a standard test liquid as a basis of comparison rather than to attempt to build standard air tunnels. A standard test liquid could be such a thing as a carefully purified fraction of butyl acetate. In running this test a constant voltage should be used on the fan motor or a rheostat and voltmeter should be in the line to control voltage.

Effect of Various Driers on Linseed Oil Films during Aging[1]

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THIS paper shows the relationship, during aging, of acid value, iodine number and solubility of linseed oil films containing different concentrations of lead, manganese, and cobalt. It presents a continuation of previously reported experiments,[2] in which it was concluded that the acid value of linseed oil films containing cobalt acetate

as a drier is an increasing function of the drying time; and of other experiments[3] which attempted to show that the iodine number of linseed oil films during drying bear a general inverse relationship to the acid value and the concentration of the cobalt bears a definite relationship to the decreasing iodine number.

Experimental Procedure

The refined linseed oil that was used in these experiments had the following constants:

[1] Presented under the title "The Effect of Age on the Acid Value and Iodine Number of Linseed Oil Films Containing Various Concentrations of Lead, Manganese, and Cobalt Driers" before the Division of Paint and Varnish Chemistry at the 76th Meeting of the American Chemical Society, Swampscott, Mass., September 10 to 14, 1928.

[2] Evans, Marling, and Lower, IND. ENG. CHEM., **18**, 1229 (1926).

[3] Evans, Marling, and Lower, IND. ENG. CHEM., **19**, 640 (1927).

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Acid value............................    2.8
Iodine number (Wijs)..................   176.0
Molecular weight.....................    730.0
Refractive index at 20° C.............   1.4815
Specific gravity at 15.5° C...........    0.933
```

The linseed oil was heated in Pyrex beakers to 270° C. and the drier was added slowly. The temperature was held at 265–270° C. for 30 minutes, in order that the drier might be completely dissolved. The prepared oils were poured into glass bottles, tightly stoppered, and allowed to age for 1 week before the films were prepared.

The treated oils were brushed on glass plates (37 × 50 cm.) and one coat was applied to each glass. The approximate weight of oil for each surface was 4 grams. The coated plates were placed approximately 1 inch (2.5 cm.) apart in wooden racks in a glass-covered box and free circulation of air was supplied from an air-pressure line. The box was located near a west window in the laboratory. Only diffused light reached the films and the temperature ranged from 20° to 30° C. during the 3 months of aging. No attempt was made to regulate the humidity of the test cabinet.

Similar films were exposed to a 15-cm. mercury arc light at a distance of 75 cm. from the arc, the temperature of the cabinet being 40° to 50° C. The oil films were removed from the glass plates with a safety-razor blade and digested in a solution of 2 parts toluene and 1 part alcohol by volume. The digestion was continued for from 1 to 5 hours, according to the solubility of the film. The digestion was made in Pyrex flasks and heated over a hot-water bath. The insoluble material remaining at the end of 5 hours was measured by filtering through fine cotton cloth and washing with toluene-alcohol solution. The residue was dried to constant weight in an electric oven and weighed. The acid value was calculated on the soluble portion of the film. The free acid was titrated from the toluene-alcohol oil film solution with 0.1 N

alcoholic potash, using phenolphthalein as the indicator. The end point was very indefinite, and the alcoholic potash was added at a regular rate until a pink color showed in the solution. This reading was recorded. Then 0.2 cc. was added and if the color was a deep red the previous reading was taken as the end point. The iodine number was determined by the Wijs method for shellac. The solubility was fairly satisfactory, although the films did not completely dissolve in a few instances.

Discussion

The results are given in Tables I to IV.

In Table I the acid values and iodine numbers have progressive changes until the fiftieth day, after which they remain constant. The lower lead concentration attains a 30 per cent insolubility, while the higher lead concentration has only a trace of insoluble at the ninety-fourth day of aging.

In Table II the acid values increased to the end of the aging period, while the iodine numbers reached the minimum value earlier. The insoluble portion was greater in the lower manganese concentration than the higher, at the end of the aging period. The films of both concentrations at the end of the aging period gave a semi-paste condition and had enough flowing properties to determine the refractive indices. These values are 1.4885 for the lower concentration and 1.4875 for the higher. These values are lower than the refractive index of heavy heat bodied linseed oils.[4]

Table III shows the higher cobalt concentration to have a higher acid value, lower iodine number, less insoluble, and greater flowing properties than the lower concentration at the end of the aging period. The refractive index of the higher cobalt concentration was 1.4900, while the low cobalt

[4] Frishkorn, Larsen, Marling, and Shepherd, Paint Mfrs.' Assocn. U. S., *Tech. Circ.* 341 (November, 1928).

Table I—Linseed Oil Films Containing Lead Acetate as Drier

AGE Days	PHYSICAL APPEARANCE OF FILM	ACID VALUE	INSOLUBLE IN TOLUENE-ALCOHOL SOLN. Per cent	IODINE NUMBER
	0.2 PER CENT LEAD			
1	Wet	20.0	None	82.0
2	Set, slightly tacky	41.0	None	46.0
3	Dry, slightly tacky	48.0	None	40.0
23	Dry, slightly tacky	57.0	None	30.0
36	Slightly soft	60.0	None	28.0
50	Slightly sticky	63.0	None	27.0
59	Slightly sticky	64.0	Trace	27.0
73	Slightly sticky	64.0	19	27.0
94	Considerably sticky	66.0	30	27.0
	2.0 PER CENT LEAD			
1	Set	36.0	None	60.0
2	Dry, slightly tacky	45.0	None	48.0
3	Dry, slightly tacky	48.0	None	44.0
23	Dry, slightly tacky	60.0	None	34.0
42	Slightly soft	65.0	Trace	27.0
50	Slightly sticky	66.0	Trace	26.0
59	Slightly sticky	66.0	Trace	26.0
73	Slightly sticky	66.0	Trace	26.0
94	Slightly sticky	66.0	Trace	26.0

Table II—Linseed Oil Films Containing Manganese Acetate as Drier

AGE Days	PHYSICAL APPEARANCE OF FILM	ACID VALUE	INSOLUBLE IN TOLUENE-ALCOHOL SOLN. Per cent	IODINE NUMBER
	0.02 PER CENT MANGANESE			
1	Set	34.0	None	70.0
2	Dry, slightly tacky	40.0	None	60.0
7	Dry, slightly tacky	56.0	Trace	28.0
20	Slightly soft	90.0	Trace	23.0
38	Slightly soft	98.0	Trace	20.0
58	Very soft	106.0	4	16.0
79[a]	Semi-paste	110.0	6	16.0
	0.20 PER CENT MANGANESE			
1	Set	38.0	None	60.0
2	Dry, slightly tacky	42.0	None	54.0
7	Dry, slightly tacky	65.0	Trace	30.0
20	Slightly soft	100.0	Trace	12.0
28	Considerably soft	110.0	Trace	12.0
38	Considerably soft	118.0	Trace	12.0
58	Very soft	134.0	Trace	12.0
79[b]	Semi-paste	140.0	1	12.0

[a] Refractive index at 20° C., 1.4885.
[b] Refractive index at 20° C., 1.4875.

Table III—Linseed Oil Films Containing Cobalt Acetate as Drier

AGE Days	PHYSICAL APPEARANCE OF FILM	ACID VALUE	INSOLUBLE IN TOLUENE-ALCOHOL SOLN. Per cent	IODINE NUMBER
	0.015 PER CENT COBALT			
1	Set	61.0	None	36.0
2	Dry, slightly tacky	75.0	None	28.0
3	Dry, slightly tacky	77.0	Trace	27.0
14	Dry, slightly tacky	82.0	Trace	25.0
27	Dry, slightly tacky	82.0	Trace	20.0
33	Slightly soft	83.0	Trace	18.0
50	Slightly tacky	84.0	Trace	18.0
64	Slightly sticky	84.0	8	18.0
84	Slightly sticky	88.0	20	18.0
	0.30 PER CENT COBALT			
1	Set	75.0	None	31.0
2	Dry, slightly tacky	92.0	Trace	26.0
3	Dry, slightly tacky	98.0	Trace	23.0
14	Dry, slightly tacky	112.0	Trace	17.0
33	Slightly soft	123.0	Trace	13.5
40	Very soft	130.0	Trace	13.0
50	Very sticky	136.0	Trace	13.0
64	Very sticky	142.0	Trace	13.0
84[a]	Semi-paste	144.0	Trace	13.0

[a] Refractive index at 20° C., 1.4900.

Table IV—Linseed Oil Films Exposed to Mercury Arc Light, without Drier and with Two Concentrations of Cobalt Acetate

AGE Hours	ACID VALUE	INSOLUBLE IN TOLUENE-ALCOHOL SOLN. Per cent	IODINE NUMBER
	WITHOUT DRIER		
2	27.0	None	61.0
4	40.0	Trace	45.0
8	48.0	4	34.0
16	60.0	24	24.0
	0.015 PER CENT COBALT		
2	38.0	None	49.0
4	54.0	2	35.0
8	68.0	19	30.0
16	86.0	33	22.0
	0.30 PER CENT COBALT		
2	46.0	None	46.0
4	73.0	10	26.5
8	110.0	33	20.0
16	123.0	34	18.0

concentration was not soft enough to make a refractive index determination.

Table IV gives the comparison of linseed oils films without drier and with two concentrations of cobalt in the mercury arc light. All these films show an increasing acid value and decreasing iodine number during the 16-hour exposure period. The acid value of the lower cobalt concentration reached 86 in 16 hours, while the same cobalt concentration required 84 days in the indoor aging test to reach an acid value of 88. Also the insoluble portion was greater in the mercury light exposure. The insoluble portion was greater in the higher cobalt concentration. This condition was reversed in the indoor aging tests. The iodine numbers reach a lower limit and the acid values reach a higher limit in the higher cobalt concentration than the linseed film without drier or the lower cobalt concentration during the same time period.

Summary

1—Linseed oil films containing two concentrations of lead, manganese, or cobalt drier increased in acid value and decreased in iodine number during indoor aging.

2—Linseed oil films containing the higher concentration of cobalt or manganese gave the highest acid values and the lowest iodine numbers; these films also showed the greatest flowing at the end of the aging period. The two lead concentrations reached a similar acid value and iodine number; these films showed no evidence of flowing properties.

3—The lower drier concentration of linseed oil films with lead, manganese, or cobalt had the greater insoluble percentage in a toluene-alcohol solution at the end of the aging period than the higher concentration of the same drier.

4—Linseed oil films containing manganese as a drier gave a more plastic film at a low concentration than either lead or cobalt at the end of the aging period. The higher cobalt concentration gave a more plastic film than the higher lead concentration.

5—Linseed oil films without drier or with cobalt drier in mercury-arc light exposure showed an increase in acid value and decrease in iodine number during the 16-hour period. This agrees with the results of the linseed oil films of similar cobalt concentration in indoor aging.

Reflection Factors of White Paints[1]

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TWO of the most important optical properties of a paint are its brightness and its opacity or hiding power. Both properties are dependent upon the color and the particle size of the pigment, upon the ratio of the refractive index of the pigment to that of the vehicle, and, to a lesser extent, upon the oil absorption and the structure of the pigment particles. There is, however, no necessary and universal relationship between opacity and brightness. Colored paints are usually more opaque than white ones although the white paints reflect a larger fraction of the incident light. In the true white paints high reflecting power is usually associated with high hiding power.

When a beam of light falls upon the surface of a paint film, a portion of the light is reflected from the surface of the film itself. For any given paint the fraction of the light thus reflected at the film surface is constant and independent of the thickness of the film. The amount of this "surface reflection" depends upon the roughness and the texture of the surface; paints which dry to a glossy film show less surface reflection than do "flat" or "eggshell" paints.

A portion of the light which actually enters the film is reflected at the interfaces between the pigment and the vehicle while the remainder penetrates to the underlying base surface. The amount of light reflected from within the film increases with the film thickness up to the point at which the film becomes so thick that it is opaque; further increase in thickness of film produces no further increase in the amount of light

The effects of the addition of known amounts of carbon black, Prussian blue, and aluminum powder upon the brightness and the hiding power of white paints are measured. Small amounts of carbon black or of Prussian blue decrease the brightness only slightly and increase the hiding power markedly. With larger amounts of the colored pigments the decrease in the brightness becomes relatively more pronounced. With very small amounts of Prussian blue the ratio of the increase in hiding power to the decrease in brightness is greater than with carbon black. The addition of aluminum powder greatly increases the hiding power, but lowers the brightness and causes the dry film to have a flecked appearance. The use of aluminum powder in undercoats for white finishing coats is of advantage.

reflected. The total amount of light reflected from an opaque film may be termed the "ultimate brightness" of the paint.

The ultimate brightness is a function of the opacity of the paint and of the transparency of the pigment and the vehicle of which the paint is composed. Of truly white paints made from transparent pigment and transparent vehicle, those which are the most opaque will show the highest brightnesses. The addition of a dark or colored pigment decreases the brightness but increases the opacity. When only small amounts of the dark pigment are added, there is usually a very marked increase in hiding power accompanied by relatively small decrease in brightness. In certain cases where extremely high brightness is not required— as, for example, in undercoats for white finishing coats—the addition of a small amount of dark pigment should make it possible to increase the opacity and thus to decrease the amount of paint required to hide the underlying surface. The investigation described in this article was undertaken for the purpose of determining quantitatively the effects of small amounts of dark pigments upon the brightness and the hiding power of a few typical white paints.

Experimental Work

MATERIALS USED—Pure refined linseed oil from North American seed was used. The pigments were lithopone, zinc oxide, white lead (basic carbonate, by Dutch process), white lead (basic carbonate, by Carter process), sublimed white lead (basic sulfate), barytes (ground native barium sulfate),

"Timonox" (antimony oxide), carbon black (from natural gas), Prussian blue, and aluminum powder. The drier was a mixture of lead linoleate and manganese linoleate. The drier solution was prepared by heating a mixture of 54 grams of lead linoleate paste and 33 grams of manganese linoleate paste with 280 cc. of pure gum turpentine. This solution was then mixed with linseed oil in the ratio of 4.5 parts of weight of solution to 100 parts of oil, giving a final drier solution containing 0.09 per cent of lead and 0.0155 per cent of manganese, as metal.

PREPARATION OF PAINTS—The required amount of drier solution and a small amount of oil were added to a weighed quantity of the pigment and the mixture was ground until a smooth, thick paste was obtained. More oil was then added, gradually and with continued grinding, until the desired amount had been introduced, and finally the required amount of thinner (turpentine) was added. In the preparation of paints containing carbon black or Prussian blue the dark pigment was screened through a 200-mesh sieve. A weighed quantity of the screened pigment was added to a known amount of linseed oil and the mixture was shaken until a uniform and fairly permanent suspension was obtained. The suspension of carbon black contained 2 mg. of pigment per gram of oil; that of Prussian blue was made up with 10 mg. of pigment per gram of oil. In mixing the final tinted paint sufficient of the suspension of the dark pigment was substituted for pure linseed oil to provide the desired amount of colored pigment in the paint. In preparing paints containing aluminum powder, the required amount of aluminum powder was added directly to the white pigment before mixing.

The formulas of the various paints studied are given in Table I.

Table I—Formulas for Paints

PAINT	PIGMENT	PIGMENT Grams	LINSEED OIL Grams	DRIER SOLN. Grams	TURPEN- TINE Grams
1	Lithopone	60	40	1.8	30
2	Zinc oxide	60	40	1.8	40
3	White lead, Dutch	60	40	1.8	5
4	White lead, sublimed	60	40	1.8	5
5	White lead, Carter	60	40	1.8	0
6	Barytes	80	20	1.2	0
7	Timonox	60	40	1.8	10
8	Lithopone	60	40	2.4	30
9	Zinc oxide	60	40	2.4	35
10	White lead, Dutch	70	30	1.8	0
11	Lithopone	60	40	2.4	25
12	Zinc oxide	60	40	2.4	35
13	White lead, Dutch	60	40	2.4	0

To each paint various amounts of the dark pigments were added, as indicated in the tables giving the experimental results.

METHOD OF TESTING—Test films of the various paints were applied on panels of yellow pine which were 10 by 76 cm. The panels were sanded, painted with a flat black paint to insure a uniform background, and then covered with two coats of orange shellac to prevent the black from bleeding through the subsequent coats of white paint. The shellac was rubbed to a dull finish with fine steel wool to give surface to which the paint would adhere well. Six contiguous areas, 10 by 10 cm., were marked off and numbered consecutively from one end.

A beaker containing a small amount of the well-mixed paint, together with the brush, was weighed accurately. The paint was then applied over the desired area and the beaker, brush, and unused paint were again weighed. The difference between the original and the final weight was, of course, the weight of the paint applied. The first coat of paint was applied to area 6. After this was thoroughly dry, a second coat was applied to cover areas 6 and 5. Successive coats were thus put on, each coat covering one more area than the preceding one, until six coats had been applied. In this way a series of areas covered with 6, 5, 4, 3, 2, and 1 coat of paint

was obtained. The brightness of each of these areas was then measured. With a few paints ultimate brightness was not attained, even with six coats. In such cases measurements were made as usual and then one or two final coats were applied over the entire panel, measurements being made on each of the final coats.

The measurements of the brightness of the painted surfaces were made with a reflectometer similar to that described by Taylor.[2] This instrument measures the brightness directly,
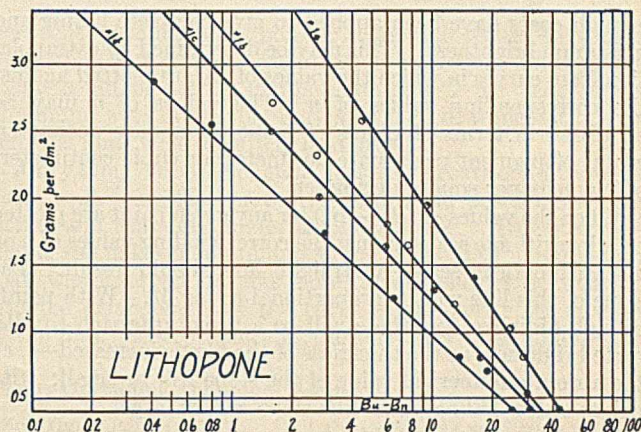
Figure 1

in terms of the ratio of the intensity of the reflected light to the intensity of the incident light.

CALCULATIONS—Since the area covered by each coat of paint and the exact weight of paint applied in each coat were known, the weight of paint per unit of area may be calculated. From these data and the percentage by weight of pigment in the paint, the weight of paint applied to each unit area can be determined. From the known densities of the individual pigments[3] the volume of pigment applied to each unit area can be calculated.

The general relationship between the brightness and the thickness of a film of white paint may be expressed by the equation:[4]

$$B_u - B_n = (B_u - B_1)M^{(n-1)} \qquad (1)$$

in which B_u = ultimate brightness of the paint
B_n = brightness of a film of n unit thicknesses of paint
B_1 = "surface brightness" of paint—i. e., brightness due to reflection from surface of film
M = constant characteristic of paint
n = number of unit thicknesses of paint in film

They furthermore defined M as being equal to T^2S^2, in which

T = that portion of light incident to any unit layer of paint which is transmitted to next lower layer, and
S = $(1 + R_1 + R_2 + R_3 \cdots + R_n)$
in which R = that portion of light incident to any unit layer which is reflected upward to next upper layer

From Equation 1 we derive:

$$\log (B_u - B_n) = K + (n - 1)\log M \qquad (2)$$
$$= K + (n - 1)\log T^2S^2$$

The brightness of any given paint film (B_n) may be determined directly by the reflectometer. For any given paint the ultimate brightness (B_u) is the brightness attained when

[2] Taylor, Bur. Standards, *Sci. Paper* **405**.
[3] U. S. Geol. Survey, *Bull.* **579** (1921).
[4] Rhodes and Fonda, IND. ENG. CHEM., **18**, 130 (1926).

Table II—Brightness and Hiding Power

	LITHOPONE PAINTS				ZINC OXIDE PAINTS				DUTCH WHITE LEAD PAINTS			
Per cent carbon black $\times 10^3$	0.00	3.33	8.33	16.66	0.00	3.33	8.33	16.66	0.00	1.66	5.00	8.33
B_u	93.5	90.0	86.0	78.0	92.0	88.0	79.5	71.0	92.0	85.5	78.0	74.5
B_1	28.5	31.0	29.0	30.0	36.0	38.0	31.5	26.0	34.0	27.5	20.0	19.5
Hiding power:												
Grams paint per sq. dm.	3.40	2.63	2.35	1.91	3.60	3.15	2.25	1.80	4.0	3.15	2.35	1.95
Grams pigment per sq. dm.	1.55	1.20	1.07	0.87	1.52	1.33	0.95	0.76	2.25	1.77	1.32	1.09
Cc. pigment per sq. dm.	0.356	0.276	0.266	0.20	0.291	0.254	0.254	0.182	0.338	0.266	0.199	0.164
Per cent decrease in B_u	....	3.7	8.02	16.6	....	4.35	13.6	22.8	....	7.08	15.2	19.0
Per cent increase in hiding power	....	22.4	30.9	43.8	....	12.7	37.4	50.2	....	18.5	35.8	45.0

enough coats have been applied to give complete hiding and maximum brightness. This may be determined by extrapolation from curves in which the values of B_n are plotted against the corresponding values of n. The values of n may be expressed in terms of grams of paint per square decimeter, grams of pigment per square decimeter, or cubic centimeters of pigment per square decimeter.

When the values of $(B_u - B_n)$ for any given paint are plotted on a logarithmic scale against the corresponding values of n on an arithmetical scale, a straight line should result. The slope of this line will be proportional to log M. With paints of high hiding power there will be a rapid approach to ultimate brightness as the thickness of the film is increased—i. e., the absolute numerical value of the slope will be small; with paints of low hiding power the slope will be larger.
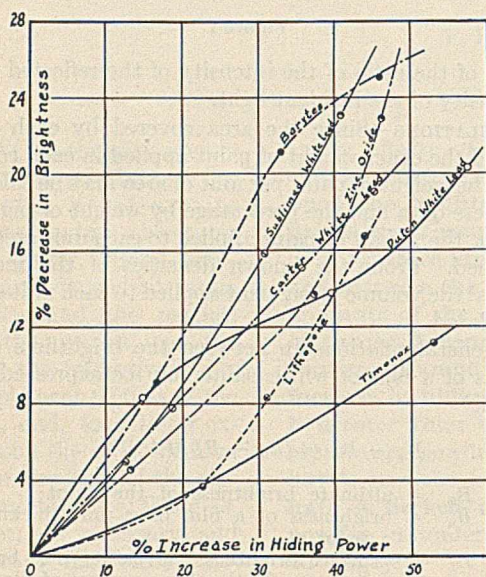
Figure 2

Since the eye cannot distinguish differences in brightness of less than about 2 per cent, a film that has a brightness of within 2 per cent of the ultimate brightness for that paint will afford complete hiding. As a criterion of the hiding power of a paint we may therefore take the amount of paint required per unit area to bring the brightness to within 2 per cent of the ultimate brightness for the paint.

The intercept when the graph of n plotted against $(B_u - B_n)$ is extrapolated to zero film thickness indicates the difference between the ultimate brightness and the surface brightness. From the ultimate brightness of a paint and the form of the graph obtained by plotting the values of $(B_u - B_n)$ against n, the fraction of the incident light which is reflected at the film surface may be calculated.

Experimental Results

EFFECT OF CARBON BLACK—The data for a typical series of paints, the lithopone paints containing carbon black, are shown in Figure 1. The results obtained with all of the various paints containing carbon black are summarized in Table II. In this table the hiding power is expressed in terms of grams of paint, grams of pigment, and cubic centimeters of pigment per square decimeter required to bring the brightness of the film to within 2 per cent of the ultimate brightness for the paint.

In every case the addition of carbon black to a white paint decreases the ultimate brightness and increases the hiding power. When only very small amounts of the dark pigment are added, the effect upon the hiding power is large in comparison with the effect upon the brightness; with increasing amounts of carbon black the effect upon the brightness increases more rapidly than does the effect on the hiding power. The theoretical basis for this observed effect of small amounts of dark pigments in increasing the opacity has been discussed by Rhodes and Fonda.[4]

The ratio of the percentage increase in hiding power to the percentage decrease in brightness varies with the different pigments (Figure 2). In general, this ratio appears to increase with increase in the fineness of the pigment. The relationship is not quantitative or universal, however. It is probable that the ratio also depends to some extent upon the refractive index of the pigment, the manner and extent to which the pigment is flocculated in the paint, and other factors.

EFFECT OF PRUSSIAN BLUE—Theoretically, any dark pigment should show an effect analogous to that of carbon black in increasing the hiding power of a white paint. The use of colored pigments for this purpose is, however, often inadvisable, because if sufficient colored pigment is added to produce any marked effect upon the hiding power the paint may be given a faint but definite tint. While this is generally true, there is an exception in the case of the blue pigments.

Table III—Brightness and Hiding Power of Paints Containing Prussian Blue

	LITHOPONE PAINT (No. 8)				ZINC OXIDE PAINT (No. 9)				DUTCH WHITE LEAD PAINT (No. 10)			
Per cent Prussian blue $\times 10^3$	0.0	16.6	50.0[a]	83.3[b]	0.0	16.6	33.3[a]	83.3[b]	0.0	28.6[a]	71.4[b]	142.8[b]
B_u	93.5	90.6	86.0	80.0	92.0	90.5	88.5	83.0	92.0	91.0	80.0	74.0
B_1	31.5	28.6	20.0	19.0	35.0	36.5	35.5	28.0	33.0	32.0	18.0	12.0
Hiding power:												
Grams paint per sq. dm.	3.45	2.6	1.72	1.35	3.60	2.90	1.90	1.55	4.0	3.3	2.34	1.35
Grams pigment per sq. dm.	1.55	1.18	0.78	0.61	1.52	1.27	0.83	0.68	2.36	2.27	1.61	0.93
Cc. pigment per sq. dm.	0.356	0.27	0.18	0.14	0.291	0.243	0.159	0.130	0.338	0.322	0.242	0.14
Per cent decrease in B_u	....	3.1	8.0	14.4	....	1.14	3.81	9.8	....	1.09	13.0	19.6
Per cent increase in hiding power	....	24.2	49.5	60.8	....	16.5	45.4	55.4	....	4.7	28.4	58.0

[a] Paint had a very faint blue tint, noticeable only on close inspection.
[b] Paint was distinctly blue in tint.

of Paints Containing Carbon Black

Sublimed White Lead				Carter White Lead Paints				Barytes Paints				Timonox Paints		
0.0	1.66	5.0	8.33	0.0	3.0	5.0	7.5	0.0	1.25	2.5	5.0	0.0	3.33	8.33
92.0	87.5	77.5	71.0	90.0	82.5	78.0	71.5	56.5	51.5	44.5	42.5	94.0	90.5	83.5
8	14.5	11.5	11.5	28.0	27.5	24	28.5	12.6	12.5	17.5	19.5	50.0	49.5	47.5
3.4	2.96	2.35	2.0	4.0	3.4	2.42	1.70	8.7	7.3	5.8	4.7	2.65	2.05	1.25
1.91	1.67	1.32	1.12	2.36	2.02	1.43	1.0	6.88	5.77	4.59	3.72	1.42	1.10	0.67
0.298	0.261	0.206	0.177	0.356	0.305	0.216	0.151	1.53	1.28	1.02	0.83	0.273	0.212	0.129
....	4.9	15.8	22.9	....	8.3	13.3	20.3	...	9.0	21.4	24.9	....	3.72	11.2
....	12.4	30.8	40.6	....	14.3	39.0	57.3	...	16.3	32.4	45.7	....	22.4	52.3

Most so-called white paints tend to become slightly yellow when dry, owing to the darkening of the vehicle. The addition of a trace of blue pigment neutralizes this yellow tint and may give a faintly gray paint which appears whiter than the paint to which no blue has been added. Of course, if the amount of blue pigment added is in excess of that required to neutralize the yellow color, the resulting paint will have a noticeable blue or green tint. Prussian blue is commonly added to commercial white paints to neutralize the natural yellow tint. The effects of the addition of small amounts of Prussian blue to various white paints are summarized in Table III.

per cent of aluminum powder appeared white on casual inspection, but on close examination occasional flecks of the metal could be seen. Paints containing 2 per cent of the aluminum were noticeably gray and flecked, while with 5 per cent the films were definitely lead gray.

A dry film composed of eight successive coats of a lithopone paint containing 2.5 per cent of aluminum powder was sectioned and examined under the microscope. No concentration of the flakes of aluminum at the surface of the individual coats was observed, nor was there any evidence of "leafing" or oriented arrangement of the particles parallel to the surface of the film. The presence of the relatively large amount of

Table IV—Brightness and Hiding Power of Paints Containing Aluminum Powder

	Lithopone Paints (No. 11)				Zinc Oxide Paints (No. 12)				Dutch White Lead Paints (No. 13)			
Per cent aluminum powder	0.0	1.0	2.0	5.0	0.0	1.0	2.0	5.0	0.0	1.0	2.0	5.0
B_u	93.5	79.0	69.5	52.0	92.0	74.0	66.5	59.0	92.0	74.5	74.0	58.0
B_l	38.5	28.0	33.5	30.0	30.0	38.0	36.5	31.0	27.0	24.5	25.0	14.0
Hiding power:												
Grams paint per sq. dm.	3.45	1.42	1.10	0.65	3.6	1.66	0.95	0.52	4.0	1.96	1.47	0.90
Grams pigment per sq. dm.	1.57	0.67	0.52	0.31	1.52	0.72	0.41	0.23	2.25	1.15	0.86	0.53
Cc. pigment per sq. dm.	0.362	0.154	0.12	0.07	0.291	0.137	0.08	0.045	0.338	0.173	0.13	0.08
Per cent decrease in B_u	....	18.5	25.6	38.0	....	19.6	27.8	35.9	....	19.0	19.6	37.0
Per cent increase in hiding power	....	57.5	71.0	98.0	....	53.0	72.5	84,5	....	48.8	61.5	76.4

In all the paints studied the amount of colored pigment required to effect a given increase in hiding power is greater with Prussian blue than with carbon black. With the lithopone and zinc oxide paints the ratio of the increase in hiding power to the decrease in ultimate brightness is considerably greater with Prussian blue than with carbon black. On the other hand, the extent to which the hiding power can be increased without affecting the tint is less with the blue pigment than with the black. With these pigments Prussian blue is to be preferred to carbon black in those cases in which it is desired to increase the hiding power with minimum sacrifice of brightness, but when large increase in hiding power is desired and ultimate brightness is not so important, carbon black is the better. With the white lead paints carbon black appears to be more satisfactory than Prussian blue in all cases.

Effect of Aluminum Powder—Some measurements of the effect of the addition of aluminum powder upon the opacity of white paint have been made by Edwards and Wray.[5] These investigators worked with only one type of paint, containing a mixture of white lead, zinc oxide, and silicate filler, and made no measurements of the effect of the added aluminum powder upon the ultimate brightness. Gardner,[6] who studied the durability of white paint containing aluminum powder, found that 1.5 per cent of aluminum gives no appreciable color to the paint. He made no quantitative measurements of brightness or hiding power.

The effects of the addition of aluminum powder upon the optical properties of certain white paints are shown in Table IV.

In every case the addition of even relatively small amounts of aluminum powder had a marked effect upon both the brightness and the hiding power. The paints containing 1

lithopone apparently inhibited the orientation of the flakes which has been observed in films from paints containing large amounts of aluminum powder.

Because of the low brightness, paints containing aluminum powder would not ordinarily be suitable for use as finishing coats. By the use of one or more priming coats of such paint followed by a finishing coat of a paint of high brightness, it should be possible to combine high brightness and high hiding power. The addition of aluminum powder to the priming coats should be of particular value when the surface to be painted is very dark. To demonstrate the value of aluminum powder in priming coats, black panels were covered with various combinations of coats of straight lithopone paint and of lithopone paint containing 1 per cent of aluminum and the final brightness was measured. The amount of paint applied in each coat was approximately the same, and was about the amount which would be applied in ordinary practice. The results are given in Table V.

Table V—Effect of Aluminum Powder in Priming Coats

Treatment	Brightness
	Per cent
1 coat primer alone	59.6
1 coat finish alone	51.2
2 coats primer alone	70.0
2 coats finish alone	69.4
1 coat primer plus 1 coat finish	76.4
3 coats primer alone	75.6
3 coats finish alone	77.5
1 coat primer plus 2 coats finish	82.2
2 coats primer plus 1 coat finish	82.9

Name of Certified Dye Changed

"Buttercup Yellow," the name of a new food dye recently placed on the list of dyes permitted for certification by the Department of Agriculture, has been changed to "Sunset Yellow F. C. F.," according to officials of the Food, Drug, and Insecticide Administration of the United States Department of Agriculture.

[5] Edwards and Wray, Ind. Eng. Chem., **17**, 639 (1925).
[6] Gardner, Paint Mfrs.' Assocn. U. S., *Circ.* **199**.

The Spontaneous Decomposition of Sugar-Cane Molasses[1]

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Periodical analyses of two samples of sugar-cane molasses which had undergone spontaneous deterioration during a period of fourteen years showed: (1) a progressive lowering in polarization; (2) a constantly increasing loss of sucrose; (3) a slow, irregular increase in the percentage of invert sugar; (4) a constantly increasing loss in the total sugars after inversion; (5) a constant increase in the percentage of organic non-sugars. These changes were the result of chemical activities going on within the molasses and not of fermentation by microörganisms.

An examination of the organic non-sugars of the two molasses showed them to have a carbon content of approximately 52 per cent, which is higher than the carbon content of the organic non-sugars of fresh cane molasses. Formic acid, acetic acid, and organic colloidal substances of a mixed nitrogenous and non-nitrogenous character were present in both molasses. The spontaneous decomposition of the two molasses is believed to be a retarded type of the so-called "froth" or "hot-room" fermentation for which two explanations have been proposed: (1) the formation of unstable compounds (glucic acid) by the action of the lime used in clarification upon the reducing sugars of the cane juice; and (2) the formation of unstable compounds by the action of the amino acids of the molasses upon the reducing sugars. The probable part played by each of these factors in the deterioration of the molasses is considered with special reference to the process of dehydroxylation by which organic non-sugars of high carbon content are produced. The results of the investigation indicate that explanation (1) plays the chief part in the spontaneous deterioration of sugar-cane molasses.

. . . .

P REVIOUS studies upon the deterioration of food products conducted by the author have related to the deterioration of butter fat,[2] vinegar,[3] rice bran,[4] sugar cane, cane juice,[5] and cane sugar.[6] The agencies concerned in the deterioration of the food products mentioned include (1) microörganisms (bacteria, yeasts, fungi, etc.); (2) enzymes (lipase, invertase, etc.); and (3) atmospheric factors (oxygen, moisture, and sunlight). In the present paper a fourth type of deterioration, resulting from internal chemical changes, will be considered.

In January, 1914, the late G. L. Spencer, of the Cuban American Sugar Company, called the attention of the author, during a visit at the sugar factory of Central Constancia, Cuba, to a peculiar type of deterioration that was taking place in tanks of stored molasses. The molasses, which was the final product obtained by the defecation process, was undergoing a constant, gradual loss in sucrose, although there were no apparent evidences of fermentation by yeasts or other biological agencies. The high concentration of the molasses was, in fact, so unfavorable to the growth of microörganisms that it seemed necessary to attribute the decomposition of the product to other causes. Samples of about 4 kg. each were accordingly drawn from two tanks of the deteriorating molasses and sent to the New York Sugar Trade Laboratory, where they were examined by the writer at intervals over a course of nine years. The examination was continued during the succeeding five years at the Bureau of Chemistry in Washington. The general analytical results obtained during the entire period are given in Table I.

Disregarding a few individual irregularities in the trend of the determinations—which can be explained by variations (see Note) in samples and imperfections in the methods of

analysis—the results of the analyses of the two samples of molasses show as a whole from year to year: (1) a progressive lowering in the polarization; (2) a constantly increasing loss of sucrose; (3) a slow, irregular increase in the percentage of invert sugar; (4) a constantly increasing loss in the total sugars after inversion; and (5) a constant increase in the percentage of organic non-sugars.

Note—There is a segregation of the insoluble solids in molasses upon standing, which is removed by stirring and mixing only with great difficulty. This produces a variation in all the analytical data, as is shown by the following results upon the top and bottom portions of a bottled molasses:

	WATER	SUCROSE	INVERT SUGAR	ASH	ORGANIC NON-SUGAR
	Per cent	Per cent	Per cent	Per cent	Per cent
Top	21.87	22.63	33.88	6.37	15.25
Bottom	20.38	20.44	32.29	10.23	16.66

Changes in Total Solids

In addition to the changes noted in Table I there was also observed a slight loss in the total solids of the two molasses. For the interval of ten and one-half years between September, 1917, and March, 1928, the following losses were noted in the total solids obtained by drying the molasses to constant weight in a vacuum oven at 70° C.:

	TOTAL SOLIDS IN MOLASSES	
	Molasses No. 1	Molasses No. 2
	Per cent	Per cent
September, 1917	75.59	76.80
March, 1928	74.98	75.82
Loss	0.61	0.98

In the same period molasses No. 1 lost by inversion 9.51 per cent sucrose (equivalent to 10.01 per cent invert sugar) and molasses No. 2 lost 12.63 per cent sucrose (equivalent to 13.29 per cent invert sugar). The calculated gain in the solids content, as a result of inversion, is 0.50 per cent in the case of molasses No. 1 and 0.66 per cent in the case of molasses No. 2. There was also probably a slight increase in weight of the solids as a result of the absorption of atmospheric oxygen by the unsaturated compounds of the molasses. In contrast with this increase in concentration of solids as a result of inversion and oxidation, there must also be considered a partial dilution of the molasses by the water which is split off

[1] Presented before the Division of Agricultural and Food Chemistry at the 76th Meeting of the American Chemical Society, St. Louis, Mo., April 16 to 19, 1928. Received December 21, 1928.

[2] Browne, *J. Am. Chem. Soc.*, **21**, 975 (1899); J. IND. ENG. CHEM., **7**, 30 (1915); **17**, 44 (1925).

[3] Browne, *J. Am. Chem. Soc.*, **25**, 27 (1903).

[4] Browne, *Ibid.*, **25**, 949 (1903).

[5] Browne, *Ibid.*, **28**, 453 (1906).

[6] Browne, Louisiana Agr. Expt. Sta., *Bull.* **91**, 103 (1907); *Louisiana Planter*, **54**, 281 (1915); **61**, 10 (1918); J. IND. ENG. CHEM., **10**, 178 (1918).

from the sugar molecules as a result of the dehydroxylation shortly to be described.

Unfortunately, the total solids of the molasses at the beginning of the experiment were determined, as was afterwards learned, by a faulty method of drying at too high a temperature, and the data are not available for ascertaining the total loss in solids for the whole fourteen-year period of the experiment. This total loss, in all probability, did not exceed 1.50 per cent. The samples of molasses were kept at room temperature in a dark place in large glass-stoppered bottles, so that there was no opportunity for the samples to dry out or to absorb moisture from the air. There was an almost imper-

lasses. This is attended by a marked evolution of carbon dioxide, which not only appears as froth upon the surface, but is also occluded in gas pockets at various depths of the tank. The insertion of a pole into the contents of the tank, under such conditions, will sometimes cause a sudden escape of gas from the hidden pockets with a violent ejection of stringy masses of molasses. The production of gas pockets in molasses obviously introduces a considerable error into the measurement of quantity, when this is based upon the level of liquid in the tank. Another evidence of the spontaneous decomposition of molasses in tanks is the occasional deposition of a granular, insoluble carbonaceous residue resembling

Table I—Changes in Composition of Cuban Molasses from Deterioration[a]

Time of Analysis	Molasses No. 1				Molasses No. 2			
	Polarization	Sucrose	Invert sugar	Total sugars as invert	Polarization	Sucrose	Invert sugar	Total sugars as invert
April, 1914	+24.86	31.30	19.10	52.04	+25.52	34.79	25.09	61.71
October, 1914	+23.54	30.73	18.74	51.09	+21.67	32.97	26.67	61.37
May, 1915	+22.33	30.00	18.19	49.77	+18.59	30.39	26.71	58.70
April, 1916	+21.34	29.74	18.84	50.14	+14.63	28.38	30.19	60.06
September, 1917	+19.80	28.45	19.93	49.88	+ 8.25	23.65	32.25	57.14
August, 1918	+18.26	25.81	20.66	47.83	+ 5.72	21.39	33.27	55.79
August, 1921	.....	24.93	20.93	47.17	.....	18.49	33.77	53.23
January, 1923	.....	25.13	21.07	47.52	.....	16.64	34.88	52.40
July, 1927	+11.84	20.98	21.00	43.08	− 5.20	12.97	34.43	48.08
March, 1928	.....	18.94	21.50	41.44	.....	11.02	35.60	47.20
Total change	−13.02	−12.36	+ 2.40	−10.60	−30.72	−23.77	+10.51	−14.51

[a] The author is indebted to C. A. Gamble, G. H. Hardin, and M. H. Wiley, of the New York Sugar Trade Laboratory, and V. Birckner, of the Bureau of Chemistry and Soils, for assistance in making these determinations.

ceptible evolution of carbon dioxide, which was sufficient, however, to create, during long periods of repose, a slight pressure of gas which escaped upon loosening the stoppers.

At the end of thirteen years of standing molasses No. 1 had an ash content of 8.54 per cent and a pH value of 5.9, and the molasses No. 2 an ash content of 6.50 per cent and a pH value of 5.3.

The decomposition of the molasses was attended by the formation of dark-colored organic non-sugars. At the time of the first analysis in 1914 the samples were easy to decolorize with lead subacetate solution, but as deterioration proceeded the clarified solutions became constantly darker in color, with the result that the polarization of the samples in 1928 could be obtained only in tubes of 50-mm. length.

A Chemical and Not a Biological Decomposition

Bacteriological examination of the samples, in 1914 and at various occasions until the final analysis in 1928, failed to reveal the presence of yeasts, molds, bacteria, and other microörganisms, which would indicate that the decomposition of the molasses must be ascribed to chemical and not to biological causes. This supposition is strengthened by the fact that the more concentrated molasses No. 2 showed the more rapid deterioration. The presence of toxic formic acid and formates in the deteriorating molasses might also possibly check the growth of microörganisms.

In the writer's opinion the deterioration of the two samples of molasses must be regarded as a very slow retarded type of what is sometimes known as the "hot-room" or "froth" fermentation of the sugarhouse. In this wrongly called fermentation thickly boiled molasses, when placed in the hot room for crystallization, begins to froth and give off carbon dioxide, formic acid, acetic acid, and pungent acrid fumes of unknown composition. Considerable heat is evolved, and if the action is particularly violent the molasses is finally converted into a black carbonaceous residue. This decomposition has long been recognized to be a spontaneous chemical change and not the result of the activity of microörganisms.

Of a similar character to the "hot-room fermentation" is the decomposition which is sometimes observed in tanks of mo-

that obtained in violent types of "hot-room fermentation." Similar changes have been observed by the author in bottled samples of molasses, which after long storage were found to be transformed into dark, porous masses resembling carbonized sugar. The insoluble carbonaceous residue obtained from such molasses is almost wholly dissolved by heating in solutions of sodium or potassium hydroxide, which would indicate that the material belongs to the so-called "humic acid" substances of high carbon content that are produced in certain decompositions of dextrose and other sugars.

Spontaneous decompositions of this type have also been observed in sealed tins of sterilized cane sirup and molasses. The oxygen of the air in the head space of tins of canned cane sirup is frequently found to be entirely replaced by carbon dioxide. The pressure of the carbon dioxide in such cans not only will produce the bulging condition of the ends, known as "swells," but it has been known on rare occasions to cause an explosion of the tin container.

Formation of Volatile Acids

Samples of the deteriorated molasses, when distilled in a current of steam, gave off with considerable frothing a small amount of carbon dioxide and an acid distillate which, after neutralizing with 0.1 N barium hydroxide solution and evaporating to dryness, left a residue that consisted almost entirely of barium acetate. There were obtained from 50 grams of molasses the following yields of volatile acids in two distillations with steam:[7]

	0.1 N Ba(OH)₂ Required for Neutralization	
	Molasses No. 1	Molasses No. 2
	Cc.	Cc.
First distillation, 225 cc.	83.90	32.83
Second distillation, 225 cc.	13.90	13.72
Sum	97.80	46.55
	Grams	Gram
Weight of barium salts in combined distillates	1.2490	0.5964
Calculated for barium acetate	1.2490	0.5945

[7] The writer is indebted to E. K. Nelson, of the Bureau of Chemistry and Soils, for making these determinations.

While the free volatile acids of the deteriorated molasses are thus shown to consist almost entirely of acetic acid, perceptible traces of formic acid were also proved to be present by the unmistakable reducing action of the liberated acids upon mercuric chloride, silver nitrate, and potassium permanganate.

The contents of the flasks, from which the two distillations of free volatile acids had been made, were acidified with 1 cc. of a sirupy solution of phosphoric acid in order to liberate any combined organic acids, and the distillation with steam was further continued. Only one distillation was made; there was required for neutralization 33.05 cc. of 0.1 N barium hydroxide for the 300 cc. of distillate from molasses No. 1 and 26.64 cc. of 0.1 N barium hydroxide for the 225 cc. of distillate from molasses No. 2. The actual and calculated weights of barium salts were as follows:

	Molasses No. 1	Molasses No. 2
	Gram	Gram
Weight of barium salts	0.3906	0.3262
Calculated for barium formate	0.3758	0.3029
Calculated for barium acetate	0.4221	0.3402

These weights are equivalent to a mixture of 68.03 per cent barium formate and 31.97 per cent barium acetate in the case of the salts from molasses No. 1 and 37.53 per cent barium formate and 62.47 per cent barium acetate in the case of the salts from molasses No. 2. The free acids, after liberation from the mixed barium salts, showed the presence of large amounts of formic acid, as was evident by the reducing action upon mercuric chloride, silver nitrate, and potassium permanganate. The distillations with steam were not carried to the final expulsion of all volatile acid decomposition products, so that the quantitative yields of acetic and formic acid cannot be calculated. The results indicate, however, that acetic and formic acids are both present in the two samples of deteriorated cane molasses. Acetic acid exists in greater amount and occurs in the molasses largely in the free state; formic acid is present in smaller amount and occurs in the molasses mostly in combination with calcium and other bases. In fact formic acid, owing to its greater chemical affinity, would tend to displace the other volatile and non-volatile organic acids of the molasses from their combinations. In addition to acetic and formic acids there was also obtained in the steam distillates of the molasses a small quantity of water-insoluble fatlike crystals of low melting point, the exact nature of which remains to be determined.

Formation of Organic Non-Sugars of High Carbon Content

The production of organic non-sugars of high carbon content in sugar-cane molasses was indicated by the author[8] in 1919. The gradually increasing carbon content of the non-sugars of cane juice during the processes of manufacture is shown by the following abstract of analyses from this article:

Product	Organic Non-Sugars in Total Solids	Carbon in Non-Sugars
	Per cent	Per cent
Cane juice	4.22	28.27
Open-kettle molasses (sulfitation)	4.37	40.32
Cuban molasses (defecation)	12.38	48.17
Refinery blackstrap molasses	16.76	49.00

The percentages of carbon and hydrogen in some of the organic substances, which are known to occur in cane molasses, are as follows:

Compound	Formula	Carbon	Hydrogen
		Per cent	Per cent
Aspartic acid	$C_4H_7NO_4$	36.07	5.30
Asparagine	$C_4H_8N_2O_3$	36.39	6.11
Invert sugar	$(C_6H_{12}O_6)_2$	39.98	6.71
Aconitic acid	$C_6H_6O_6$	41.37	3.47
Sucrose	$C_{12}H_{22}O_{11}$	42.08	6.48
Gums	$(C_6H_{10}O_5)_n$	44.42	6.22

[8] Browne, *J. Am. Chem. Soc.*, **41**, 1432 (1919).

The value of 49 per cent carbon for the organic non-sugars of blackstrap molasses very clearly indicates the formation of products of considerably higher carbon content than that existing in the organic substances known to occur in cane molasses. There is thus very evidently a progressive splitting off of hydroxyl groups and hydrogen, in the form of water, from the residues of the sugar molecules in the molasses during the whole course of manufacture. This progressive dehydroxylation also continues after manufacture, more especially in molasses made by the lime clarification process, with the splitting off of carbon dioxide, formic acid, acetic acid, and other volatile decomposition products, and the formation of dark-colored compounds of higher carbon content, the effects being similar to those produced in the so-called "froth fermentation" and in the slow deterioration of molasses No. 1 and No. 2 as indicated in Table I.

Note—The author prefers the word "dehydroxylation" for the splitting off of hydroxyl groups in the form of water to the word "dehydration," which in its usual sense means the driving off of water already existing as such and not chemically combined.

Composition of Organic Non-Sugars

The proximate composition of the dried solids of the two molasses was as follows:

	Molasses No. 1	Molasses No. 2
	Per cent	Per cent
Invert sugar	28.67	46.95
Sucrose	25.26	14.54
Ash	11.39	8.57
Organic non-sugars (by difference)	34.68	29.94
Total	100.00	100.00

An elementary analysis[9] of the solids of the deteriorated molasses prepared by drying the molasses to constant weight over phosphorus pentoxide *in vacuo* at 70° C. gave the following results:

	Molasses No. 1	Molasses No. 2
	Per cent	Per cent
Carbon in dried solids	40.20	40.45
Hydrogen in dried solids	5.44	5.75

The calculated percentages of carbon in the two molasses belonging to invert sugar and sucrose subtracted from the total carbon in the dried solids gives the percentages of carbon belonging to the organic non-sugars.

	Molasses No. 1	Molasses No. 2
	Per cent	Per cent
Carbon in invert sugar ($C_6H_{12}O_6$)$_2$	11.47	18.78
Carbon in sucrose ($C_{12}H_{22}O_{11}$)	10.62	6.12
Total carbon in sugars of molasses	22.09	24.90
Residual carbon in organic non-sugars	18.11	15.55

The percentage of residual carbon, divided by the percentage of organic non-sugars and multiplied by 100, shows the percentage of carbon in the organic non-sugars of molasses No. 1 to be 52.22 per cent, and of molasses No. 2 to be 51.94 per cent. These values, it will be noted, are four units higher than the percentage of carbon in the organic non-sugars of recently made Cuban blackstrap molasses, which shows that the production of organic non-sugars of constantly increasing carbon content, as a result of continued dehydroxylation, is a characteristic of the type of molasses deterioration described in the present paper.

The calculated percentages of hydrogen belonging to the organic non-sugars of the two molasses were calculated as follows:

	Molasses No. 1	Molasses No. 2
	Per cent	Per cent
Hydrogen in invert sugar ($C_6H_{12}O_6$)$_2$	1.92	3.15
Hydrogen in sucrose ($C_{12}H_{22}O_{11}$)	1.64	0.94
Total hydrogen in sugars of molasses	3.56	4.09
Residual hydrogen in organic non-sugars	1.88	1.66

[9] The author is indebted to Max Phillips, of the Bureau of Chemistry and Soils, for making these determinations.

The percentage of residual hydrogen, divided by the percentage of organic non-sugars and multiplied by 100, shows the percentage of hydrogen in the organic non-sugars of molasses No. 1 to be 5.42 per cent and of molasses No. 2 to be 5.54 per cent.

The percentage of carbon in the total organic non-sugars of the deteriorated molasses is over 12 per cent higher, and that of hydrogen over 1 per cent lower, than the percentages of these elements in invert sugar. Since according to Table I there has been an actual conversion into organic non-sugars of the equivalent of 10.60 per cent invert sugar in molasses No. 1 and of 14.51 per cent invert sugar in molasses No. 2, there must have occurred during the fourteen years of storage, as previously indicated, a progressive dehydroxylation of the sugar molecules with the formation of organic non-sugars of higher carbon and lower hydrogen content. The possible explanation of these deteriorative changes with reference to two theories which have been proposed to explain the spontaneous decomposition of molasses known as "froth fermentation" will next be considered.

Glucic Acid Theory of Spontaneous Decomposition of Molasses

Many chemists who have examined molasses and the products which are produced by the action of alkaline solutions upon glucose and fructose have referred to the presence of an unstable substance that was first investigated by Peligot and for which Dumas proposed the name of "glucic acid." The sudden decomposition of this compound into carbon dioxide, formic acid, acetic acid, apoglucic acid, and humic acid, as well as into various unrecognized volatile substances of acrid odor, has been regarded by Prinsen-Geerligs and other authorities as the cause of the so-called "froth fermentation" of molasses and massecuites.

EARLY INVESTIGATIONS—The first attempt to isolate the acid compounds produced by the action of lime upon glucose was made in 1792 by Lovitz,[10] whose method was based upon the decomposition of the precipitated lead salts by means of sulfuric acid. Nothing definite, however, was accomplished in the identification of the products formed by the action of alkalies upon sugars until 1837, when Malaguti[11] reported the presence of formic and ulmic acids among the substances produced by the action of caustic potash upon sugar. In 1839 Peligot,[12] in investigating the substances produced by the action of lime upon glucose in water solution at ordinary temperature, noticed that the alkaline reaction gradually disappeared and the liquid turned to a dark yellow. Upon precipitating the calcium with an exact amount of oxalic acid, there was obtained a strongly acid solution, which left upon evaporation a non-crystalline, hygroscopic residue, which decomposed when heated to 100° C. The name "glucic acid" was proposed by Dumas for the product of this reaction. The lead salt of the acid gave a formula corresponding to $C_{24}H_{30}O_{15}.6PbO$. Peligot's analytical data, however, according to present values for atomic weights, correspond more closely to the formula $C_{24}H_{34}O_{17}.6PbO$.

By the action of lime upon glucose at a higher temperature Peligot observed a further cleavage of water from the reaction products, with the formation of a black amorphous material similar to the so-called ulmic acid and corresponding approximately to the formula $C_{24}H_{20}O_{10}$, for which Dumas proposed the name "melassic acid."

In 1840 Mulder[13] made further contributions to the nature of the humus-like decomposition products which are produced

from sugars by the action of acids and alkalies. He stated that Peligot's glucic acid, when its aqueous solutions are boiled in the air, is decomposed with brown discoloration into apoglucic acid (carbon content 54.10 per cent), to which the formula $C_{18}H_{22}O_{10}$ was assigned. According to Mulder, the additional cleavage of water from apoglucic acid produces substances of still higher carbon content (64 to 69 per cent carbon) to which the names "ulmin," "ulmic acid," "humin," and "humic acid" were assigned.

In a research published in 1858 Kawalier[14] reported having obtained glucic acid in thick sirupy form by the action of barium hydroxide upon glucose. The formula $C_{15}H_{26}O_{13}$ was assigned to the compound. Upon acidifying the products of this reaction with sulfuric acid and distilling, Kawalier obtained a so-called double formic-acetic acid which was probably only a mixture of these two named acids.

In 1870 Reichardt[15] subjected the nature of the products produced by the action of alkalies upon glucose to a further study. In addition to glucic acid, to which he assigned the formula $C_{24}H_{32}O_{18}$, Reichardt reported the presence of saccharumic acid, $C_{14}H_{12}O_8$, and an uninvestigated volatile substance. He stated that an aqueous solution of glucic acid, when heated, decomposed into apoglucic, formic, and acetic acids. He obtained glucic acid as a thick honey-like sirup of very hygroscopic character, easily soluble in water, less soluble in alcohol, and only slightly soluble in ether. Apoglucic acid, according to Reichardt, has the formula $C_{18}H_{16}O_8$.

The results thus far obtained in the laboratory upon glucic acid led certain chemists finally to the conclusion that this substance might also be produced in the sugar factory during the clarification of sugar beet and sugar-cane juices by means of lime. Mendes[16] in 1874 attributed the after-darkening of beet juice during saturation to glucic acid, which he thought to be present from the blue-violet coloration that salts of this acid are supposed to give with ferric iron in acid solution. Mendes found that the glucic acid made by Peligot's process gave the same coloration, while that obtained by Mulder's method produced no change in color, from which he concluded that the acids prepared by these two investigators were not identical but only isomers. Bodenbender[17] in 1875 and Kuthe[18] in 1881 also called attention to the presence of glucic acid in the clarified juices and molasses of the sugar beet.

In 1892 Prinsen-Geerligs[19] published analyses which showed the glucic acid content of sugar-cane molasses to vary from 0.31 to 7.29 per cent. In continuation of his work in the laboratory of the Sugar Experiment Station at Kajok-Teval, Java, Prinsen-Geerligs[20] stated that a solution of neutral calcium glucate, when warmed on the water bath, begins suddenly to foam with violence at about 85° C., giving off carbon dioxide, acetic acid, and gaseous products of an acrid odor, becoming strongly acid and darkening in color. If boiled in the free state with water or dilute acids, glucic acid was said to decompose at once with frothing into carbon dioxide, formic acid, acetic acid, apoglucic acid, and humic acid. For preventing the formation of glucic acid in cane juice clarification and the consequent troublesome "froth fermentation" of cane molasses, Prinsen-Geerligs recommended the avoidance of heat in the treatment of the alkaline solutions during saturation.

The experiments of Prinsen-Geerligs were repeated by

[10] Lovitz, *Crel's Annalen*, **1**, 292, 345 (1792).
[11] Malaguti, *Berzelius Jahresber.*, **1837**, 218.
[12] Peligot, *Ann.*, **30**, 76 (1839).
[13] Mulder, *Bull. sci. phys. et Nat. Neerlande*, **1840**, 1; abstracted in *Ann.*, **36**, 243 (1840).

[14] Kawalier, *Math. Naturwissenschaft, Sitzungsbericht der Wiener Akademie*, **30**, 122 (1858).
[15] Reichardt, *Z. Ver. Rübenzucker Ind.*, **20** (old series), 529 (1870).
[16] Mendes, *Ibid.*, **24** (old series), 420 (1874).
[17] Bodenbender, *Ibid.*, **25** (old series), 122 (1875).
[18] Kuthe, *Ibid.*, **31** (old series), 741 (1881).
[19] Prinsen-Geerligs, *Chem.-Ztg.*, **16**, R280 (1892).
[20] Prinsen-Geerligs, *Z. Ver. Rübenzucker Ind.*, **44** (old series), 297 (1894).

Herzfeld[21] and Claassen,[22] neither of whom was able to verify his conclusions as to the great instability of free glucic acid or its readily giving rise to carbon dioxide.

None of the experiments upon glucic acid thus far quoted reported the isolation of a pure crystalline compound of definite ascertainable properties, and one is therefore obliged to conclude that the many contradictions in the chemical literature upon the composition, reducing power, color reactions, and other properties of this substance are due to variations in the identity of the products examined.

WINTER'S GLUCIC ACID—The only investigation in the literature which records the isolation of a crystalline preparation of glucic acid is that of Winter,[23] but the product obtained by him was so unstable and impure that nothing definite could be ascertained regarding the chemical constitution of the compound.

Winter obtained by warming a 1 per cent invert-sugar solution with 0.5 per cent calcium oxide, previously slaked, at 66.5° C. a voluminous white precipitate, which after washing with limewater was decomposed with dilute sulfuric acid and extracted with ether. Evaporation of the ether extract yielded a small amount of a yellow sirup, which soon became filled with needle-shaped crystals. After being placed in a desiccator over sulfuric acid, the crystalline needles appeared in a few days to melt away and nothing was left in the sirup but some undeveloped crystals resembling cane sugar. After some time the sugar-like crystals also began to disappear with a darkening of color and a slight evolution of gas, which ceased only after the residue had solidified to a dark resinous mass. The latter upon distillation with water yielded carbon dioxide and formic acid, leaving behind a residue of brown flocks.

Winter's efforts to purify the substance by recrystallization from water, alcohol, ether, or chloroform were unsuccessful. An aqueous solution of the crystals reduced Fehling's solution in the cold and precipitated black silver immediately from silver nitrate. From these results Winter supposed the impure crystals that he had prepared to be those of the so-called glucic acid, which underwent on standing a slow transition into apoglucic acid and then further decomposed into carbon dioxide, formic acid, and other products.

A recent repetition of Winter's experiment by Nelson and Browne[24] under more carefully controlled conditions shows that the crystalline compound which he secured did not belong to the complex dark-colored products of high carbon content obtained by Peligot, Mulder, Reichardt, and other investigators, but was a substance of comparatively simple constitution. The crystals were those of a highly unstable unsaturated acid having the formula $C_3H_4O_3$ (C = 40.89 per cent, H = 4.58 per cent, molecular weight = 88) and appearing from its high reducing power, iodine absorption, neutralization value, and various other reactions to be hydroxyacrylic acid (CHOH:CHCOOH), which is also the enolic form of the semi-aldehyde of malonic acid. The precipitated calcium compound of this acid absorbed oxygen rapidly from the air with considerable evolution of heat and decomposition into formic acid and other products. The crystalline acid could be partially sublimed without decomposition but underwent upon heating a considerable degree of polymerization. It yielded formic and oxalic acids upon oxidation and decomposed spontaneously in the presence of organic impurities. No evidence could be found to confirm the supposition of Winter that his crystalline glucic acid undergoes a spontaneous decomposition into any such product as the apoglucic acid, described by Mulder, or into carbon dioxide, although abundant quantities of formic acid and of unidentified polymerization products were obtained.

The readiness with which Winter's glucic acid decomposes into formic acid leads to the conclusion that it is in all probability a parent substance of the formic acid which occurs in the sirups and molasses of cane-sugar factories, where the calcium hydroxide employed in clarification reacts with the reducing sugars of the juice. The instability of this unsaturated compound in the presence of atmospheric oxygen and in contact with accompanying organic impurities also leads to the supposition that it may play a prominent part in the spontaneous decomposition of sugar-cane molasses and that its polymerization or reaction products may constitute a source of some of the organic non-sugars that are produced during the manufacture and storage of cane molasses. The close relationship of hydroxyacrylic acid to acrylic acid and acrolein suggests that Winter's glucic acid may possibly be a parent substance of the acrolein which has been reported as present in the fermentation products of certain cane molasses, and which may possibly also give rise to some of the acrid fumes given off in the so-called "froth fermentation."

In the filtrate from the original calcium precipitate, from which Winter's glucic acid was obtained, are found a large number of other volatile and non-volatile decomposition products of dextrose. In addition to formic acid a considerable quantity of acetic acid was found. The latter occurs also in the two samples of deteriorated molasses, but the chemistry of its formation, which is probably the same in both cases, is not clearly understood. There are also undoubtedly present in the filtrate some of the many compounds obtained by Nef and his associates from the products resulting from the action of alkalies upon glucose. There are also present various dark-colored compounds of high carbon content, which are no doubt similar to the products obtained by Peligot, Mulder, Reichardt, and other investigators, and described by them as glucic acid. The evidence shows that the substances described in the literature by various authors under the name "glucic acid" were for the most part variable mixtures of unidentified compounds and that the products termed "glucic acid" varied greatly in properties and composition.

Amino Acid Theory of Spontaneous Decomposition of Molasses

Another more recent theory proposed for the spontaneous decomposition of molasses, corresponding to the "froth fermentation" type, is based upon the reaction between amino acids and reducing sugars. This reaction has been especially studied by Maillard,[25] from whose publications the following typical experiment with glucose and glycocoll is quoted:[26]

Place in a test tube 1 gram of pure glycocoll, 4 grams of pure glucose (anhydrous, crystallized from alcohol) and 3 to 4 cc. of water (this quantity of liquid being sufficient to dissolve the powdered ingredients) and set the tube in a hot water bath. Almost immediately after solution, the liquid begins to turn a light yellow color, which is usually quite perceptible after warming for about ten minutes. The coloration deepens with increasing rapidity, the mixture becoming a deep brown and acquiring at the same time a slightly thicker consistency. Small bubbles of gas then begin to be evolved, which form a froth and render the mass so porous that, if the mixture is allowed to remain without the addition of water, there is finally obtained a spongy voluminous residue of dark brown color and consisting of dry glistening plates. If a little water should be added before complete desiccation the evolution of gas continues for some time and there remains finally a dark brown amorphous material largely insoluble in water.

Maillard obtained the same result on warming other amino acids with other reducing sugars. The effects of the reaction

[21] Herzfeld, *Z. Ver. Rübenzucker Ind.*, **44** (old series), 612 (1894).
[22] Claassen, *Ibid.*, p. 613.
[23] Winter, *Ibid.*, p. 1049.
[24] Nelson and Browne, *J. Am. Chem. Soc.*, **51**, 830 (1929).
[25] Maillard, *Compt. rend.*, **153**, 1078 (1911); *Ibid.*, **154**, 66 (1912).
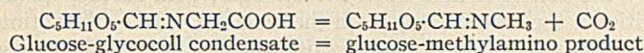[26] Maillard, *Ann. chim.*, **5**, 260 (1916).

resemble so markedly the behavior of the so-called "froth fermentation" of molasses that Lafar[27] in 1913 was led to propose the amino acid–reducing sugar reaction as the explanation of this sugarhouse phenomenon.

The amino acid–reducing sugar reaction has been investigated by a large number of chemists, who in general confirm the original conclusions of Maillard as to the character of the combination. In the case of glucose and glycocoll Maillard[28] suggests the following to be the first stage of the reaction:

$$C_5H_{11}O_5 \cdot CHO + H_2NCH_2COOH = C_5H_{11}O_5 \cdot CH:NCH_2COOH + H_2O$$

Glucose + glycocoll = glucose-glycocoll condensate
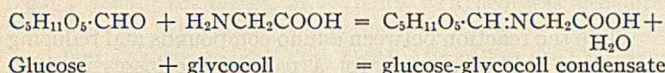
The instability of the glucose-glycocoll condensate is supposed to lead next to a rupture of the carboxyl group and the production of carbon dioxide:

$$C_5H_{11}O_5 \cdot CH:NCH_2COOH = C_5H_{11}O_5 \cdot CH:NCH_3 + CO_2$$

Glucose-glycocoll condensate = glucose-methylamino product

The glucose-methylamino product is also highly unstable and according to Maillard undergoes a loss of hydroxyl groups, a doubling of carbon linkages, and a further condensation with additional glucose, with the final production of a dark-colored nitrogenous residue of high carbon content consisting of substances variously designated as melanoidines, melanoidinic acids, nitrogenous humic substances, etc., and corresponding to formulas of the type $C_{16}H_{15}NO_6$ (found 58.85 per cent C).

Ripp,[29] who has investigated the formation of caramel-like substances by the action of glycocoll, alanine, glutamic acid, aspartic acid, and asparagin upon glucose and fructose, obtained dark-colored products similar to those described by Maillard. The product obtained from fructose and glycocoll corresponded to the formula $C_{12}H_{15}NO_6$ (found, 53.5 per cent C and 5.1 per cent N) and that from fructose and asparagin to $C_{12}H_{11}NO_4$ (found, 61.7 per cent C and 5.8 per cent N). Stoltzenberg[30] obtained for two dark coloring substances isolated from the alcohol precipitates of beet molasses formulas corresponding to $C_{20}H_{24}N_2O_9$ (found, 54.92 per cent C and 6.60 per cent N) and $C_{34}H_{40}N_2O_{15}$ (found, 57.16 per cent C and 3.8 per cent N).

COLLOIDS OF DETERIORATED MOLASSES—The colloidal material in the two samples of deteriorated molasses was determined[31] by diluting 20 grams of each molasses to a density of 20° Brix with distilled water. After warming the well-mixed diluted molasses upon the steam bath, a sufficient quantity of 95 per cent alcohol was slowly added until the mixture indicated 80 per cent of alcohol by weight, which caused the colloids to be thrown out as a flocculent precipitate. The alcohol-molasses mixture was maintained at a temperature of 70° C. for 15 minutes and then decanted through a filter (previously moistened with 80 per cent alcohol) supported in a hot-water funnel. When the liquor had drained away, the flocculated colloidal precipitate was dispersed in the original beaker in 25 cc. of warm water and again precipitated by adding 150 cc. of 95 per cent alcohol. The supernatant alcoholic solution was again decanted through the filter and the precipitate redispersed and reprecipitated by alcohol as before. After three dispersions and washings only traces of sugar were left in the precipitated colloids. The alcohol-washed precipitate was then removed from the filter paper into the beaker used for the precipitation and sufficient water added to redisperse all the colloids. The

[27] Lafar, Oesterr. ungar. Z. Zuckerind. Landw., **42**, 737 (1913).
[28] Maillard, Ann. chim., **5**, 280 (1916).
[29] Ripp, Z. Ver. deut. Zuckerind., **76**, 627 (1926).
[30] Stoltzenberg, Ber., **49**, 2021, 2675 (1916).
[31] The author is indebted to M. S. Badollet, of the Bureau of Chemistry and Soils, for these colloid investigations.

aqueous solution was then transferred to a platinum dish and dried to constant weight at 102° C. The following results were obtained upon the precipitated colloids of the two samples of molasses:

	MOLASSES No. 1	MOLASSES No. 2
	Per cent[a]	Per cent[a]
Total colloids	27.23	13.21
Ash in total colloids	5.56	2.16
Organic colloids by difference	21.67	11.05

[a] Per cent of water-free substance.

The organic colloids were 62.48 per cent of the organic non-sugars of molasses No. 1 and 36.91 per cent of the organic non-sugars of molasses No. 2. The elementary composition of the organic colloids of the two samples of molasses was as follows:

ORGANIC COLLOIDS OF:	CARBON	HYDROGEN	NITROGEN	OXYGEN
	Per cent	Per cent	Per cent	Per cent
Molasses No. 1	52.68	5.18	2.71	39.43
Molasses No. 2	50.61	4.59	2.90	41.90

The calculated approximate formula for the precipitated organic colloids of molasses No. 1 is $C_{23}H_{27}O_{13}N$ and of molasses No. 2, $C_{20}H_{22}O_{13}N$. The percentages of nitrogen are considerably lower than those obtained by other observers upon the colloidal substances isolated from sugar-beet molasses and upon the condensation products obtained by the condensation of fructose with glycocoll and asparagin. It will be noted that the carbon content of the colloids of the deteriorated molasses agrees very closely with the calculated carbon content of the organic non-sugars previously given.

The percentage of organic colloids in molasses No. 1 is almost twice that of molasses No. 2, and these differences, as might be supposed, have a very marked effect upon the physical properties of the two samples of molasses, as may be seen from the following determinations of viscosity and dye value:

	MOLASSES No. 1	MOLASSES No. 2
Viscosity at 55° C.	10.78 poises	3.53 poises
Dye value	13,348	5758

The viscosity measurements were made with a Bingham and Green viscometer. The dye value represents the weight of basic dye required to neutralize the electric charges of the colloid particles in a sample of diluted molasses, divided by the weight of solids in molasses taken and multiplied by 100,000, according to the method of Badollet and Paine.[32] The results for viscosity and dye value of molasses No. 1 are the highest ever obtained at the Bureau of Chemistry and Soils for a sugar-cane molasses.

PRODUCTS OF AMINO ACID–GLUCOSE REACTION—In two experiments conducted by Ambler[33] at the Bureau of Chemistry and Soils, in which (A) 2 grams alanine and 20 grams glucose in 50 cc. aqueous solution were heated to boiling 24 hours under a reflux condenser through which a slow stream of carbon dioxide-free air was passed, and (B) 2 grams alanine, 8 grams glucose, and 8 grams water were heated in a boiling-water bath, other conditions being the same as under (A), the following results were obtained:

EXPT.	ALANINE DESTROYED	GLUCOSE DESTROYED	RATIO ALANINE TO GLUCOSE		PRODUCTS OF DECOMPOSITION			
			Weight	Mols	CO2	Acetaldehyde	MELANOIDINS Insol.	Sol.
	Grams	Grams			Gram	Gram	Grams	Grams
A	0.50	4.226	1:8.45	1:4.2	0.0299	0.322	1.2346	1.6156
B	1.12	5.080	1:4.54	1:2.2	0.1018	0.105	2.9920	0.1464

[32] Badollet and Paine, Planter Sugar Mfr., **77**, 507 (1926).
[33] Ambler, IND. ENG. CHEM., **21**, 47 (1929).

With the more concentrated mixture B there was obtained a greater weight of glucose destroyed, a greater production of carbon dioxide, a greater production of insoluble melanoidins, and a much smaller production of soluble melanoidins. The molecular ratio of alanine destroyed to glucose destroyed is higher with the less concentrated mixture A, where the ratio of alanine taken to glucose taken was 1:10 instead of 1:4 as in Experiment B. No volatile acids were produced in this reaction, and it would seem necessary, therefore, to explain the occurrence of formic and acetic acids in the two deteriorated molasses to the breaking up of products formed by the action of the calcium hydroxide used in clarification upon the reducing sugars of the sugar-cane juice.

The average elementary composition of the insoluble and soluble melanoidins, produced by the action of alanine upon glucose in the various experiments, is shown in the following table:

MELANOIDINS	CARBON Per cent	HYDROGEN Per cent	NITROGEN Per cent	OXYGEN Per cent
Insoluble (5 experiments)	62.14	5.61	3.68	28.57
Soluble (4 experiments)	57.00	5.08	3.04	34.88

The results of the experiments indicate that the soluble colloidal melanoidins, which are first formed in the amino acid–reducing sugar reaction, undergo a further dehydroxylation to insoluble colloidal compounds of higher carbon and nitrogen content. The conditions obtaining in the molasses during fourteen years' standing at ordinary room temperature are, of course, not strictly comparable with the conditions observed in the laboratory experiments. It should also be remarked that the organic colloids of the deteriorated molasses are not of a uniform character, but are mixtures of nitrogenous and non-nitrogenous ingredients, derived partly from the original sugar-cane juice and partly from decomposition products that were formed in the processes of manufacture and in the long after-period of storage.

The reaction between amino acids and reducing sugars undoubtedly plays some part, although probably a minor one, in the decomposition of sugar-cane molasses variously known as "froth" or "hot-room fermentation." Zerban[34] isolated from cane juice asparagin, glutamine, and tyrosine, the first two substances decomposing more or less completely during manufacture into aspartic and glutamic acids. The author[35] found the total nitrogen of a sample of "blackstrap" Louisiana molasses to be 0.467 per cent. The amino acid nitrogen was 0.1774 per cent, which is equivalent to 1.69 per cent aspartic acid, and the nitrogen in the form of amids of amino acids was 0.0672 per cent, which is equivalent to 0.32 per cent of asparagin. Ripp found that, while the reactivity of asparagin with glucose was 85.1 per cent, the reactivity of aspartic acid under similar conditions was only 9.1 per cent; the corresponding figures with fructose were found to be 52.3 per cent and 5.6 per cent, respectively. Ripp's results show that asparagin reacts about ten times more quickly with dextrose and fructose than does its decomposition product aspartic acid.

The reaction between the amino compounds and reducing sugars of sugar-cane juice is partially accomplished in the processes of manufacture. Comparative determinations of the amino nitrogen in fresh cane juice and blackstrap molasses, made by the author in Louisiana, indicated that nearly 40 per cent of the original amino substances had been destroyed in the various processes of clarification, evaporation, and boiling. That this destruction still proceeds in the final

molasses was indicated by a "ninhydrin" test made by Ambler[36] upon the two samples of Cuban molasses investigated in the present paper. The test was negative in both cases, which indicates a complete disappearance of amino compounds in the fourteen years during which the molasses had been kept. As Maillard[37] has shown, the amino acid–reducing sugar reaction can take place at ordinary temperature although with greatly reduced velocity.

Conclusion

While the reaction between amino compounds and reducing sugars no doubt accounts for a part of the losses in total sugars noted in Table I, the chief cause of the spontaneous deterioration of sugar-cane molasses would appear to be the reaction of unstable organic substances, originally produced by the action of lime upon invert sugar, with further quantities of the reducing sugars in the molasses. In confirmation of this explanation it may be said that it is more particularly the molasses obtained by the defecation process, especially where lime was used in excess, that show a susceptibility towards spontaneous decomposition. The cane sirups produced by a clarification with lime are also generally the ones that show after sterilization a spontaneous decomposition in the can. It should also be stated that the spontaneous destruction of sugars and the formation of organic nonsugars were still found to proceed in the two samples of deteriorated molasses after the disappearance of the "ninhydrin" reaction for amino compounds. Furthermore, the amino acid–reducing sugar reaction, as previously shown, fails to explain the formation of the considerable quantities of formic and acetic acids, which are particularly abundant in the cane sirup and molasses that have undergone spontaneous decomposition.

Although the general character of the deterioration products in the two samples of molasses is alike, the analytical results indicate certain well marked quantitative differences. In molasses No. 1 of higher ash and lower solid content, the inversion of sucrose was much less and the production of volatile acids and organic colloids much greater than was observed in the case of molasses No. 2. The combined volatile acids of molasses No. 1 contained an excess of formic acid and of molasses No. 2 an excess of acetic acid. It is hoped that a satisfactory correlation and explanation of these various differences may be established when other researches upon various phases of the spontaneous deteriorative changes in molasses have been completed.

36 Ambler, *Intern. Sugar J.*, **29**, 382 (1927).
37 Maillard, *Ann. chim.*, **5**, 275 (1916).

New Bureau of Mines Films

Work on the production of an educational motion picture film which will tell the story of alloy steels has been begun by the U. S. Bureau of Mines, in coöperation with a large alloy steel manufacturing concern which has appropriated $10,000 to meet the costs of production. Every step in the manufacture of alloy steels, whose remarkable hardness and durability have greatly advanced the progress of the manufacture of great numbers of useful products, will be visualized in the making of the film. The film is being made with a view to instructing the engineer and engineering student, and at the same time making the story plain to the layman.

"On the Firing Line, or the Story of the Spark Plug" is the title of a two-reel motion picture film recently prepared by the Bureau of Mines. The film shows the manufacture of the spark plug from the mining of the raw materials to the assembling of its completed parts, and concludes with a series of scenes intended to instruct the automobile user in the proper adjustment and care of the spark plug.

34 Zerban, 8th Intern. Cong. Pure Appl. Chem., Vol. VIII, p. 103.
35 Browne, La. Agr. Expt. Sta., *Bull.* **91**, 93 (1907). The nitrogen content of the two samples of deteriorating Cuban molasses investigated in the present paper was 0.662 per cent in the molasses from tank No. 1, and 0.631 per cent in the molasses from tank No. 2.

AMERICAN CONTEMPORARIES

Ernst Twitchell

ERNST TWITCHELL was born in Cincinnati, February 26, 1863. His father, Prof. Henry Twitchell, was recognized as an astronomer of superior rank, being for many years assistant astronomer with Prof. O. M. Mitchell at the Cincinnati Observatory. He contrived the first chronograph, the rude predecessor of one of the most important instruments in modern astronomy, and also invented a hydrometer and an acetimeter. He was a noted chemist and in later years became an optician of the highest authority. He was with General Mitchell as consulting engineer when he projected the line of the Mobile and Ohio Railroad and contributed much to its successful construction.

With such a father it is small wonder that his son should manifest the scientific bent. When we learn that his maternal grandparents came to America from Germany in 1850, when so many Germans were leaving their country on account of political disturbances, we realize that the teutonic traits of patience, thoroughness, and keen delight in study and research are Doctor Twitchell's by right of inheritance.

When he was still quite young his parents moved to Home City, a village on the Ohio River ten miles from Cincinnati. There he spent his early years, commuting to the city while attending Woodward High School and later the University of Cincinnati, from which he graduated in 1886 with the degree of B.S. It was under F. W. Clark and T. H. Norton that he laid the foundation of his future work.

His mother was left a widow with meager capital when her boys were still young; and upon Ernst, the oldest, fell a responsibility which probably deepened his serious character. When the financial strain became too heavy he obtained a position in Atlanta, Ga., and continued his studies on the side. He returned in the spring for the final examinations and graduated at the head of his class.

In 1886 he accepted a position with the Emery Candle Company as chemist and general manager, where he remained for upward of forty years. It was here that he discovered and perfected the process with which his name is identified at home and abroad. A company was organized under the name "The Twitchell Process Company," and Doctor Twitchell was made chairman of the board of directors, which position he held until 1925 when ill health forced him to retire from active business. This process of fat splitting by means of naphthalene stearosulfonic acid would never have been promoted by Doctor Twitchell, so his associates believe, had not other chemists, who were his friends, foreseen the financial possibility and urged him to do so. To Doctor Twitchell it was just the culmination of his experimental work and keen, active interest in research.

In 1915 his Alma Mater conferred upon him the honorary degree of doctor of science, and in 1917 he was presented with the Perkin Medal. Although best known internationally for the Twitchell process, Doctor Twitchell has made many other contributions to the knowledge of the chemistry of fats. His first contribution in 1891, giving his method for the determination of rosin in fatty acid mixtures from soaps, his very useful development of methods of determining the composition of mixtures of fatty acids, and his studies of the eutectics of mixtures of fatty acids to obtain proper crystallizations and separations are all of lasting importance.

Coming from a family of scientists, Doctor Twitchell turned naturally to chemistry as a vocation. His mind has not been wholly absorbed by science, as his library of several thousand volumes in various languages attests. Besides a diversified taste in literature, he has a keen appreciation of the best in music and art. He served his community for a number of years as member of the Board of Education. He has ever been fond of outdoor sports, and never happier than when on a fishing trip with his friends or shooting ducks along the southern shores.

Doctor Twitchell became a member of the AMERICAN CHEMICAL SOCIETY in 1892, the year in which the Chemical Society of Cincinnati and vicinity became affiliated with the national society. He served as president of the Cincinnati Section in 1896.

Though of a quiet and retiring disposition, Doctor Twitchell makes friends easily, as he is kind and understanding, having a personality that inspires confidence.

He is very fond of animals and usually had a pet cat in the laboratory who delighted in curling herself into his favorite chair at his desk; and oftentimes, rather than disturb her slumbers, he would pull up another chair.

Ernst Twitchell

A man who has never courted personal publicity, much of his life has been devoted to chemistry, and he has derived a full measure of pleasure and satisfaction in the accomplishment of those problems in science that lay closest to his heart. He has let his work speak to the world without turning the world's eye to himself. A man of deep thought, not given to haphazard experimentation, whose face lights up with a happy glow when an experiment successfully confirms the theories he has formulated, mobilized, and carefully constructed. With well-balanced mentality, he works slowly, carefully, thoroughly, and surely, preparing the advance like a general going forth to battle in taking all prior precaution against failure. A man of great works and simple modesty. When in his presence one is impressed by the greatness of his simplicity rather than by the magnitude of his work.

We are indebted for much of this characterization of Doctor Twitchell to his close associates in the field of chemistry, some of long standing and others who have been encouraged to carry into the world an inspiration to accomplish something which would prove worthy of their master, friend, and model. From the words of one, which is the tone of all, we quote: "My association with him left an impression which contributed much to the progress and happiness of my life. Among all men I ever knew, I do not know one who is as nearly faultless as he."

He keeps his associates' interest stimulated by informal talks about the latest scientific news or scientific speculation. He is ready and willing to help any man by sound advice and to point the way to betterment. He is easy of approach; even

the humblest laborer knows he can come to him for counsel. His dealings with others are marked by his love of honesty and justice, always fair, never taking advantage. When circumstances make it necessary to make an adverse decision, it is always tempered with a good will that breaches the gap.

He has been sought by many who regarded him as the master mind in the chemistry of oils and fats. When circumstances were against him, he quietly accepted the inevitable and proceeded to find a way to surmount the difficulty. His acceptance of facts and logical procedure was remarkable. A real scientist, whose work in the laboratory was paramount.

At home he spends many hours among his books. His wealth

of information upon any particular subject is always a source of wonder to those fortunate enough to be associated with him. Never secretive, all his associates knew what he wanted to accomplish and the progress that he made from time to time. His interest never waned and he was a fine instructor.

The writer wishes to add his personal testimony to the invariable helpfulness of his contacts with Doctor Twitchell. These were not in business association, but in quiet chats on the train years ago, conferences on welfare work in our industrial community, and personal calls in his home about one affair or another.

M. B. GRAFF

NOTES AND CORRESPONDENCE

Elements in Patent Law

Recently I have heard much of a new doctrine of patent law—the unpatentability of products of nature. It is not new, being just about forty years old; and I am sorry to say it is not law, being but a limber-worded phrase colliding head on with a statute more than twice as old and still going strong. My regret is because it is a neat, ready-to-use formula that I could employ occasionally, obviating mental wear and tear to that extent. It is proverbial that thinking between meals is a nuisance. All of which considerations likewise apply to a late syllogistic extension of the doctrine to the effect that all chemical elements are products of nature and therefore no element is patentable; an extension which now has judicial sanction in the tungsten decisions (see majority opinion, General Electric *v.* De Forest, 28 Fed. Rep. 641). In a still, small, entirely deferential voice I shall mention that any conclusion is not better than its premises; and that these premises need putty.

English is a great and wonderful language and becoming more so as the trade marks multiply. I believe it has 450,000 words already, with vacant places for a lot more, such as the epicene third person pronoun, rhymes for silver and month, a general word for both bull and cow, and one for both horse and mare, and so on. Likewise, there is room for a whole flock of new and definite words to supplement and help out overworked indefinite old ones. "Element" is a word that needs collaborators. We are "slaves of words" and some of our masters are sloppy. Jevons says all English words, except some chemical terms, have several meanings. I don't know them all; but as far as I have gone, I agree with him except as to the exception. "Nature" has many meanings; so many that it is really a "word of convenience;" a flexible word that means whatever is convenient. "Product" is another abused word; especially in patent matters, where it is quite often the wrong word in the right pew, or the right word in the wrong pew, or something like that—"product patents," for example. The statute does not mention "products" as patentable. The combination, "products of nature," sounds better than it means; which is to say, it doesn't mean much. A pearl is a "product of nature," and so, I think, is a cherry pie, since the girl who makes it is as much a part in the scheme of nature as an oyster.

"Products of nature" made their debut in 1889 in the *Patent Office Gazette*. The syllabus of Commissioner Hall's decision in *ex parte* Latimer (46 O. G. 1638) says, "A product of nature * * * (is) * * * not such a patentable invention as is required by the statute." Hall's opinion did not carry this language; but some law clerk with the soul of a sloganeer, in digesting the decision, put it in the syllabus. Likely he evolved it from

his inner consciousness, as the Dutchman did his description of a giraffe. The syllabus also quoted a Supreme Court decision as an authority.

Mr. Hall decided that a particular fiber made from a particular pine needle was not made patentable as being the product of a certain new process; and that in a world full of fibers made from all sorts of vegetable sources by retting and the like, he could not grant a patent on every newly produced fiber; and, in detail, not one on fiber from *Pinus australis*. His point really was that there was no invention in picking out *Pinus australis*. Hall's opinion, which was fair and well reasoned, mentioned, but did not rely on, the Supreme Court decision in the wood paper case (American Wood Paper *v.* Fiber Disintegrating, 23 Wall 566; 1874). In the wood paper decision the court held that a particular cellulose was not patentable because a product of a particular process; and that the evidence did not show it differing in any identifiable way from prior cellulose. It was, therefore, not legally new. The court was not talking "products of nature."

Now, as most of us read syllabi and not decisions, the tradition grew up (*a*) that a product of nature is not patentable, and (*b*) that the Supreme Court had so decided in the wood paper cases. And this alleged doctrine of *ex parte* Latimer has had a profound influence on patent practice in and out of the Patent Office. In the Patent Office with forty years reiteration it has become somewhat of a dogma; it is deemed axiomatic. And a belief in it has crept into the courts. However, it will not stand analysis.

"Products of nature" per se carries no definite meaning, since nature produces a great variety of things and results. Paraphrased to "something existing in nature," the onus is thrown on "existing," which is as broad a word as we have. In much the same sense that Latimer's fiber existed in the pine needle, the Venus of Milo exists in any block of marble or an axe handle in any stick of hickory. Latimer isolated his fiber by removing its surroundings; and the same can be done in isolating the Venus or the axe handle. Paraphrasing again to say "something already existing as such in nature," the formula now becomes nearly true. Its accuracy is increased by changing "already existing" to "already known to be existing" since the statute (R. S., Sec. 9430, formerly 4886) makes knowledge of existence, rather than existence, the bar to patentability. But in so doing, "nature" can be thrown overboard as excess baggage.

The statute says, in part:

Any person who has invented or discovered any new and useful * * * manufacture or composition of matter * * * not known or used by others in this country * * * and not patented or

described in any printed publication * * * and not in public use or on sale within this country * * * may * * * obtain a patent.

In other words, under the statute prior existence, in nature or anywhere else, is no bar to patentability provided nobody knows it—if there is no use or sale or description in print or in a patent. If, however, *ex parte* Latimer is to be amended by removing the "nature" and the "product" and inserting the definitions of Section 9430, it might be perhaps as well to abandon *ex parte* Latimer and rely on Section 9430. This I recommend.

Reverting to the "chemical elements," the first duty of man is, of course, to get his definitions on straight. To any chemist the world "element" signifies several things. One is a particular substance of particular properties, existing as a material in a form in which it can be weighed, measured, tested, or bottled. This is a "free element." Another is an abstract mental concept; the finally indivisible; an "element in a state of combination." Mellor in his "Theoretical and Inorganic Chemistry" [Vol. I, p. 272 (1927)], in talking about hydrogen in the sense of the free element, says:

We really know nothing about the hydrogen as it is combined with oxygen in water. It is a fashion of speech to say the compound contains the element, or that the element occurs in or is present in the compound when the element can be obtained from the compound by suitable methods of decomposition.

"Potassium" in the free element sense is a particular soft white metal, generally kept under oil because of its tendency to excitement when wet. "Potassium" in this sense is not found in nature and is not likely to be—not in a damp climate, anyhow. But we also use the word "potassium" for the abstract conception K in KCl. What this K really is we know no more than Mellor knows of H, although the mathematicians are busy guessing. It is perhaps safe to assume that if KCl were a vapor at the ordinary temperature (which it is not) the K would form one end of the integral molecule KCl; perhaps to assume further that K is here a truncated or mutilated atom with one electron missing, this electron having migrated into the Cl system. It is quite certain, however, that in a bottle of KCl there are no sticks or blobs or grains of a light white metal taking fire with water. Nor are there in feldspar or in any other K compound in nature. Metallic "potassium" is merely one member of the series of K compounds and it is not their basis. Both KCl and the metal are articles as well as compositions; both are built up structures of molecules arranged in some way to form crystals.

Sir Humphrey Davy first made metallic potassium. He applied an electric current to a lump of caustic potash and obtained silvery white molten globules of metal. Taking advantage of Einstein's curved space-time relationships to become anachronistic and bring Davy up to date, it is obvious that he had transformed or reduced matter to a new condition or state; which is to say he had a new and patentable process. And his product was patentable under R.S. 9430, not because it was a product, but because it was a new thing; a new composition or a new manufacture, whichever you please, not known or used by others, not on sale or in public use, and not previously patented or described in any printed publication.

After the event, speculations on the constitution of K compounds were banal and irrelevant in view of Davy's amazing new thing, an inflammable metal which floated on water and took fire. Admitting for the argument that which is not true, that the metal was carved out of KOH as the Venus was carved, what of it? The metal was new.

To secure his rights in his metal under R.S. 9430, Davy would have to present a short description as a claim, giving identifying characteristics by which the metal could be certainly recognized. So to speak, he would have to put its finger prints on file. This was necessary both to differentiate from old materials outside Davy's monopoly and to establish his rights in the event of an infringing metal appearing. The utility of the identifying characteristic Davy might have chosen was of no importance whatever. A finger print merely serves to show that John Smith is not somebody else. Davy might have identified his metal by the fact of its firing when wet; and it would be quite immaterial whether Davy regarded the property as merely a nuisance or thought it might be valuable in fireworks. And I can imagine Davy's surprise if somebody had argued inflammability was inherent in his starting material, caustic potash.

All of which is presented as more or less of a parable, perhaps a bit parabolic. I do not wish to discuss ductile tungsten or its relation either to the "element" W or to the compound WO_3. Legally that is a closed matter, though the law points are open for discussion. Nor do I wish to express any opinion as to any injustice which may have been done Mr. Coolidge, of Schenectady.

Better luck to the men who actually make metallic hafnium or illinium.

724 Ninth St.,   K. P. McElroy
Washington, D. C.

Patents and Court Procedure

Editor of Industrial and Engineering Chemistry:

I am very glad to see in your editorial columns certain comments on our patent system. Those in your April, 1929, issue are particularly pertinent.

As to an unofficial court within any industry, I am frankly skeptical. It is in line with many other suggestions (and some experiments) looking towards improvements in our judicial system. We have in many states compulsory or optional arbitration systems which operate somewhat along the lines of your suggestion. My own rather limited experience leads me to think such systems do not operate very well.

The problems involved in settling any dispute are fundamental ones that must be solved regardless of the system of trial. We must first of all define the issues to be tried. Theoretically this is done in a lawsuit by the pleadings—that is, the complaint and the answer. Having defined the questions involved, we then seek to find out what the facts are. This is done by the evidence presented to the court. The lawyers then present the law applicable to the case as they see it, or perhaps I should say, as they choose to see it. The court then decides what the facts are and in what manner the law applies to this state of facts.

In any dispute involving any legal question the only orderly way to proceed is: (a) to state the question, (b) determine the facts, (c) determine the law applicable to the facts, (d) apply the law to the facts, and (e) thus decide the question. We may believe that we can simplify our procedure by eliminating steps (c) and (d), and the average engineer or chemist shares in the general public impression that cases should be decided on their "merits" and not upon "precedents." As a matter of fact steps (c) and (d) cannot be eliminated. We can substitute something else for what we now regard as law, but, broadly considered, law is merely a rule of action and we must have some rule. If none exists we must make one before we can decide the case. The proposal to try cases on their merits instead of upon precedents merely means that we will leave the decision to some referee or board of referees, who can decide however they see fit. In other words, we substitute the judgment of the referee or referees for the formal rules of law. Personally I would prefer to have cases decided upon established and settled rules of law rather than upon rules made to suit the case. Where we can depend with reasonable certainty upon established rules, we can in some measure predict results. If we are to leave the matter wholly to the judgment of the referee, it becomes a matter of solving a personal equation, which is always difficult.

In any event the fundamentals of deciding legal questions cannot be changed by merely changing the method of procedure. The issues must be defined, the facts ascertained, the rules applicable to the situation ascertained (or assumed), and these rules must be applied to the facts. The only possible improvement lies in cheapening the cost of litigation by changes in procedure. We may define the issues more directly by agreement, but there is nothing to prevent our doing this in a lawsuit under our present practice and the cost of the pleadings is small. The present equity rules are quite definite in saying that "the technical forms of pleading in equity are abolished." (Rule 18)
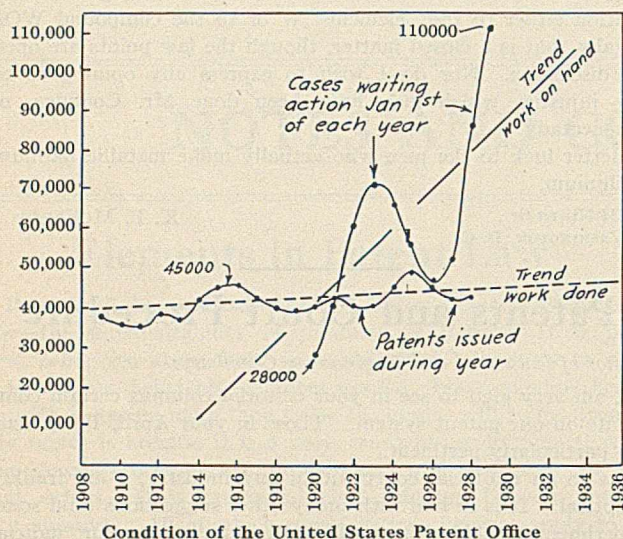
Condition of the United States Patent Office

As to ascertaining the facts. In a lawsuit we are bound by the rules of evidence. Certain kinds of evidence are admissible and certain kinds are not. Certain non-judicial tribunals and commissions are proud of the fact that they ignore these rules of evidence, and the ascertainment of facts by such tribunals becomes a sort of "catch as catch can" affair. I do not think that this expedites matters. The rules of evidence as applied by a court shorten the trial, keep the evidence within bounds, and make for economy. Some experience with non-judicial tribunals leads me to think that the rules of evidence, applied in a broad-minded way by an experienced equity judge—and they so apply them—are our greatest time and money saver. For example, we exclude hearsay. The rule is subject to many wise exceptions but is based primarily upon the broad principle that we cannot testify to facts merely because someone has told us they are facts. If we ignore this rule we are led into a mass of testimony which has little or no probative value, and this certainly does not shorten or cheapen trials. The same is true of our other rules of evidence. It has taken five hundred years to work them out. They are the result of the experience in tens of thousands of cases, and although they gradually change as conditions change they are all based upon long experience and are designed to get at the real facts by the shortest and surest route. I doubt if any body of men can materially improve them. Admitting this, I do not see how we can materially shorten the actual time of trial. We should bear in mind that under our present system we can and do present cases on an agreed state of facts without testimony. There is no reason to think that the parties to an arbitration trial will be any more (or less) ready to do this.

As I see it, we cannot reasonably hope to develop and set up a new system. Moreover, I do not see any more logic in setting up a new judicial system than there is in setting up a new chemical system. Our knowledge of chemistry has grown from small beginnings. We have, for example, named the elements as we discovered them. The system of nomenclature is awkward and illogical. Why not forget the present names and

rename the elements according to their atomic weights or according to their physical properties? For example, why not rename them so that their symbols would form a coherent and expressive system easily memorized and applied? Suppose the American Bar Association were to agitate this matter, pointing out that the whole system of chemistry is based on an outgrown system of nomenclature which hangs like a millstone about the neck of the industries of the country, and were to suggest that a committee of lawyers be appointed to investigate the whole subject of chemistry and see what could be done to put it on its feet?

The above questions are not asked for the purpose of indicating that I think that the chemists have problems of their own with which they may keep abundantly busy, leaving litigation to the lawyers. On the contrary, as I shall point out, I think meddlers are God's greatest gift to mankind. These questions are asked to give point to the answer which applies with equal force to our legal system. We cannot scrap any system which is established without destroying its "going value." Our system of law has grown side by side with our system of chemistry. We have in both systems an extensive bibliography which represents an enormous outlay of money and expresses and preserves an enormous amount of human effort and thought. No lawyer would ever expect the chemists to make a fresh start. Chemistry seeks hourly to expand and develop along lines leading back to the days of the alchemists. Law seeks to develop and expand along lines leading back to Charlemagne and the towns of the Hanseatic League. Both systems do expand and develop, not by the scrapping of the advantages they have gained, but by preserving and consolidating these advantages.

Assuming that we cannot start any new system of law or make radical changes in our judicial system, the main question then is, what can we do? And by "we" I mean the lawyers, the chemists, and everyone else. In the first place, we can be intensely dissatisfied with what we have. Let us all meddle whenever we can with anything we object to. Nine times out of ten our objections will arise from ignorance or prejudice, but that tenth time is what counts. Let the chemists become as vociferous as they like about the lawyers and the law. The more they holler, the more likely we are to get somewhere.

Take the Patent Office. It now has some 106,000 applications awaiting action. The enclosed graph tells the story of the operations of the Patent Office for the last twenty years. On January 1, 1920, this office had awaiting action by the examiners about 30,000 applications. This was admitted by all concerned to be an excessive amount in view of the fact that only about 40,000 applications were issued per year. By 1923 the number of pending applications had doubled. On January 1, 1926, the number had been reduced to about 45,000, but during the last three years it has again increased to an approximate value of 106,000. This is extremely interesting, but to my mind the production curve is far more interesting. This curve, showing the number of patents issued, has, except for the year 1925, hung in the narrow zone between 35,000 and 45,000 patents a year. Making reasonable allowances for variations, we can reasonably say that the Patent Office has increased its output from 40,000 to 45,000 patents or about 12.5 per cent in twenty years. During this time the number of cases filed has increased at least 50 per cent, probably much more than this. It is obvious that the Patent Office is in a very bad condition and that it is constantly getting worse.

In considering the Patent Office it is usual to consider simply what must be done to clear up the work now in arrears and to put it in condition to carry the load now imposed and future loads which will be imposed on it. This, of course, must be done, but a mere improvement in the capacity of the Patent Office is not to my mind an entire answer to the problem. The Patent Office is an entirely negative institution. The broad idea that it might

be a positive instrument of service has apparently never been developed. It is substantially self-supporting. The inventors pay the bill and get very little for their money. We seek to get minor reforms—a little more money or a few more men. Sometimes we get them and more often we do not. I am intensely disappointed in President Hoover. As Secretary of Commerce he had the Patent Office for years and he left it deeper in the mud than when he took it.

What is needed is not a few men or a little money, but a new vision of the office's capabilities. The patent system is not a pauper seeking alms from industry. The patent system *is* industry. It should render service. This does not mean merely a reasonable service according to its present plan, but a wider and more diversified service in ways which it has never attempted. Those of us who are close to the problem marvel that Congress will not give us more money and men. Is it not possible that the Patent Office gets all that it deserves? What has it to point to in the way of achievement in the last twenty years that would warrant better rewards?

Obviously it should do its work as now laid out and it should be given the personnel and money to make this possible. As long, however, as it merely does this work, it will still be merely a bureau, a temporary refuge for the aspiring patent lawyer, and a haven of refuge for the incompetent. Given a wider vision and some reasonable aspirations and hopes, it may become a real institution and a positive force for industrial progress. It can be made such a force and kept self-sustaining or nearly so. Industry has never asked the Government to subsidize the Patent Office. The Government has readily paid enormous sums in the interests of agriculture, but industry has pretty much fought its own battles. Agriculture is today a pauper economically considered, and yet we continue to spend vast sums on service to agriculture. Industry is the backbone of our prosperity and yet we allow the Patent Office, one of the most vital factors of our progress, to sink into its present condition. This is industry's problem, not the problem of the patent lawyer, who gets along nicely in spite of, and perhaps on account of, the present appalling conditions.

Consider now our courts. Patent cases are tried in the district courts of the United States. The district judges are one and all exceptional men, men of fine caliber, and of large experience. Congress dumps into these courts the garbage of prohibition. It provides no more judges and no additional machinery. It demands that an exceptionally able jurist spend his days listening to bootlegging cases, with the result that the ordinary civil cases, including patent cases, cannot be heard for many long months. In this respect, I am most agreeably surprised at President Hoover. He has discovered that our judicial machinery is not running smoothly and he intends to find out why. He need not investigate very deeply to find out. In spite of the present condition of the Patent Office, I am just foolish enough to think that the President may do something about the courts.

Of course, finding out what is the matter and inducing our collection of best minds now in Congress to do something about it are two entirely distinct matters. I understand that the lawyers are well represented in Congress and the chemists are not, and it may be that there is no hope, but we may give faith temporary triumphs over experience even in such matters as this—which brings me to the real meat in this rather discursive letter. What we need is not different courts or different procedure, but to see that what we now have operates with reasonable certainty and efficiency. The lawyers all know this, but the lawyers are not the men who are paying the bills. When England some years ago cleaned its judicial stables, it was not the lawyers but the business men that did it. And they did a good job. Justice is cheap and speedy in England, and little thanks to the lawyers. So Mister Editor keep hollering. I am not at all sure you know exactly what you are hollering for, but that makes no difference. When a baby hollers loud enough and long enough people satisfy him. They may assume that he is hungry when he suffers from an open safety pin, but eventually he gets fixed up. The meek may inherit the earth, but this waiting for inheritances is slow work.

Ford W. Harris

471 Chamber of Commerce Bldg.
Los Angeles, Calif.
April 11, 1929

BOOK REVIEWS

An Etymological Dictionary of Chemistry and Mineralogy. By Dorothy and Kenneth C. Bailey. 308 + viii pages. Longmans, Green & Company, New York, 1929. Price, $10.00.

It is a pleasure to review a dictionary that has been prepared in an accurate and workmanlike manner, as this one has been. It is a collection of about 10,000 terms, of which approximately two-thirds are chemical. The authors explain that the difficulty of drawing a dividing line between chemical and mineralogical terms led them to include the latter.

As the name implies, the aim of the dictionary is primarily etymological, the brief definitions serving the purpose rather than identifying the words clearly than of giving an exhaustive explanation of their meanings. Rock names and most trade names have been omitted, and very few phrases have been included. Space has also been economized by entering only one or two words of a group having a common derivation. Accordingly, it must not be expected that the book should serve as a handbook of chemical information; nevertheless, it will prove convenient for desk use. Many empirical formulas are given.

The work will naturally appeal most to those interested in the origin of words. The etymologies are taken from a variety of sources, in many cases the original articles. A large number of the terms, probably more than half, are not in the Oxford Dictionary. Examination of a portion of the terms under A yielded the following interesting results: Of the mineral names examined 29 are derived from Greek, 18 from place names, 13 from names of individuals, 2 from Latin, and 4 from scattering sources. Of the chemical names, 37 are from the names of plants and 3 from

those of animals; of the remainder, 33 are from Latin, 16 from Greek, 19 from Greek and Latin mixed, and 14 scattering. The fact that Greek etymologies are given in Roman as well as Greek letters is probably a sign of the times; one may expect that in the future Greek words will be written in Roman letters altogether in works intended for non-classical readers.

The number of English chemical dictionaries in the true sense has been increasing steadily in recent years, and the Etymological Dictionary is a notable addition to the list.—Austin M. Patterson

Nobel—Dynamite and Peace. By Ragnar Sohlman and Henrik Schuck. Translated by Brian and Beatrix Lunn. 353 pages. Cosmopolitan Book Corporation, New York, 1929. Price, $5.00.

On opening this book, one would expect to find an ordinary biography, but instead of being simply that of Alfred Nobel it is also the story of his very remarkable family—a family of inventors and idealists. The first chapter gives a most interesting account of Alfred Nobel's personality and characteristics. The second and third chapters deal mainly with his family, and in particular with his father, Immanuel Nobel, and his elder brothers, Robert and Ludwig. All of these men were inventors and idealists, so that Alfred Nobel came by his inventive genius probably as an inheritance. His father, Immanuel, while living in Russia, was the inventor of submarine mines and also of the hot-water system of heating buildings. They were also engineers of high repute and had much to do with the development of munitions in Russia in the early part of the nineteenth century.

Nobel is perhaps best known for his invention of dynamite, but he was the first to produce nitroglycerin on a large scale, and it was the large number of accidents which occurred during its manufacture, transportation, and handling that led him to seek a safer explosive which would still have the valuable properties of nitroglycerin. However, perhaps his greatest invention is that of a detonator to bring about the explosion of the less sensitive dynamite, and to those familiar with the industry his discovery of blasting gelatin made by the combination of nitroglycerin and nitrocellulose was nearly as important.

The book will prove extremely interesting to all readers, but particularly to those who have had contact with the industry of which Nobel was the founder. The authors are to be congratulated in bringing together material which could not be obtained in any other way and which could only be obtained in piecemeal from the literature of the past.

I cannot close this review without calling attention to the very remarkable examples of Nobel's poetry, which appear in Chapter X, entitled "Eternal Idealist," and although the world has reaped great benefit from him as a scientist, it has probably lost much from the fact that he decided to follow science rather than the call of the poet. Chapter XI is devoted to his connection with the peace movement, and the final chapter to his remarkable will, under which the marvelous foundation for the encouragement of science, art, and peace, by which his name will be carried on for generations, was established. Among the numerous appendixes is given a list of the recipients of the Nobel prizes.

Mr. Hoover has said, "Science is the base upon which is reared the civilization of today," and this fact is amply demonstrated by the perusal of this most interesting book.

There are two slight errors in the book, which should be noted. One is the use of the name "Nobel" instead of "Soberro," bottom line on page 106; and a typographical error of "Uobel" for "Nobel," on page 162.—CHAS. L. REESE

1928 Year Book of the American Association of Textile Chemists and Colorists. 308 pages. Published for the Association by Howes Publishing Company, Inc., 90 Williams St., New York, N. Y.

This little volume holds within its pages valuable information to the textile man, particularly to the man interested in dyes, and it should find a place on the desk of every dyehouse manager.

Not only are all the year's activities of this association described in full, giving a detailed report of each section in the country with names of eminent members and topics of different papers, but there is also technical information for the textile chemist and dyehouse man. This information is in the form of outlines of research committees, details of various tests, up-to-date standards, fastness of color, mill methods, and several chemical treatments submitted by dyehouse and textile experts. There is also a list of approximately three thousand American-made dyes giving chemical classification; this is arranged in three different lists—one alphabetical, another by Colour Index number, and the last by Schultz color numbers.

Of further interest is the alphabetical as well as the geographical enrolment of members of the American Association of Textile Chemists and Colorists, giving name, address, and business connection of each.—W. O. MITSCHERLING

The Biochemistry of the Amino Acids. By H. H. MITCHELL AND T. S. HAMILTON. A. C. S. Monograph 48. 618 pages. The Chemical Catalog Company, Inc., New York, 1929. Price, $9.50.

It is generally conceded that a reviewer should not be enthusiastic. In fact, too frequently he honestly cannot be. Yet, it would be indeed difficult for one not to be enthusiastic after having reviewed Mitchell and Hamilton's contribution—enthusiastic for those who had the foresight to launch the excellent monographic series under the auspices of the AMERICAN CHEMICAL SOCIETY, and equally enthusiastic over the collation of material in book form so excellently presented in "The Biochemistry of the Amino Acids."

The material is presented in ten chapters starting with the Physical and Chemical Properties of the Amino Acids, and their determinations, followed logically by the discussion of the Liberation of the Amino Acids in the Intestinal Tract. After these are two chapters on General Amino Acid Metabolism and one on Special Phases of Amino Acid Metabolism. The last-named chapter is divided in the general topics of arginine, histidine, cystine, and the metabolism of sulfur, tyrosine and phenylalanine, and tryptophane. Under the discussion of epinephrine it is unfortunate that credit is not given to Abel in the isolation of the

substance, although later the authors do quote liberally from Abel on the physiologic action of epinephrine. The section on thyroxine includes the most recent work. While the authors show that Harrington's yield of thyroxine from the fresh gland was greater than that of Kendall's, they have not brought out the fact that Harrington was fortunate in using glands having high thyroxine content, and that Kendall's method also yields high results with thyroid glands of equally high thyroxine content. Of significant interest is Chapter VIII on the Specific Dynamic Effect of Amino Acids, in which are included also collateral subjects. Then follow the last two interesting chapters on the Endogenous Catabolism and the Nutritive Values of Proteins and the Protein Values of Foods in Nutrition.

The book itself is a review of such an ever expanding subject that it could serve for an extended seminar course. It is replete with references and contains an adequate index. For those interested in current developments in the field of proteins, it should find a ready reception. Like all books of this nature, it will need frequent revision to keep it up to date. In the opinion of the reviewer, however, this would be well worth the effort.—PAUL N. LEECH

Gas Chemists' Handbook. 3rd edition. 795 pages. Published by the American Gas Association, 420 Lexington Ave., New York, N. Y. Price, $7.00.

The 1929 edition of this handbook contains 795 pages as compared with the 608 pages in the 1922 edition, and represents a much improved volume for the use of chemists engaged in the laboratory work of gas companies and in associated activities concerned with the raw materials, products, impurities removed, and the miscellaneous materials associated with the manufacture, distribution, and utilization of industrial gases.

In general, the methods given for coal, coke, paint materials, lubricants, refractories, cement, steel and zinc-coated materials are the standards of the American Society for Testing Materials, while the other methods have been revised to conform as far as possible with these standards. Other revisions have usually been made in general accordance with the recommendations of committees of the American Gas Association. Chapter II, Part I, on Illuminating Gas, has been entirely rewritten to double its former size, and in its 225 pages given an up-to-date presentation of the art of fuel gas analysis, and a long list of references to books and other published matter relative to the analysis and properties of gases. Chapter IV, on Miscellaneous Analyses, has been enlarged from 233 pages to 285 pages and covers analytical methods for water, solder, bearing metals, brass and bronze, pipe deposits, lime and ferrous metals, in addition to those already mentioned. However, as in many books of this kind, some subjects could be more broadly treated and more interpretations of results might be given.

The tables of the previous edition have been replaced in some cases with those containing the latest data and some helpful additions have been made.

Improvements in the character of type for titles and subheadings and other helpful aids have resulted in a much improved book of reference.—R. B. HARPER

Chemisches Fachwörterbuch für Wissenschaft, Technik, Industrie und Handel. Band I—Deutsch-Englisch-Französisch. By A. W. MAYER. 826 pages. Verlag von Otto Spamer, Leipzig, 1929. Price, bound, 75 marks; paper, 70 marks.

Intended not only for the scientist but also for the business man and the technical and industrial chemist, this polyglot dictionary gives equivalents, in the languages concerned, for the special professional terms and phrases for manufacturing processes, special machinery, apparatus, products, etc. Particular attention has been paid to popular chemical terms and professional chemical phraseology. To prevent possible doubts as to the meaning of words, the chemical formulas or explanations (in German in the present volume; in proposed Volumes II and III they are to be in English and French, respectively) are given wherever deemed necessary. A dictionary of this character deserves a cordial welcome.

Although unusually complete within its scope, the reviewer must note the following omissions: Ammonal (an explosive); Alit, Arndsche Legierung, Duraluminium, Ferrotherm, Invar, Kupferron, Lautal, Manganin, Nialit, Nichrom, Nichrotherm, Si-Guss, Silumin (alloys); Leunasalpeter, Norgesalpeter, Rhenaniaphosphat (fertilizers); Blaugas, Dawsongas; Aquadag, Oildag, Voltolöl (lubricants); Anon, Depanol, Dissolvan, Pyranton, Tetra (solvents); Ambroid, Diatomit (insulating materials); and Hopcalit (a catalyst).—ALBERT R. MERZ

MARKET REPORT—MAY, 1929

FIRST-HAND PRICES FOR CHEMICALS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET ON MAY 15

Newer Chemicals

Acetaldehyde, drums, lc-l., wks...lb.	.18½
Acetaldol, 50-gal. drums.........lb.	.27
Acetylene tetrachloride, *see* Tetrachloroethane	
Aldol, c/l., wks...............lb.	.27
Amyl furoate, 1-lb. tins.........lb.	5.00
Butyl carbitol, *see* Diethylene glycol monobutyl ether	
Cellosolve, *see* Ethylene glycol monobutyl ether	
Furoate, tech., 50-gal. drums. .lb.	.50
Carbitol, *see* Diethylene glycol monomethyl ether	
Cellosolve, *see* Ethylene glycol monoethyl ether	
Acetate, *see* Ethylene glycol monoethyl ether acetate	
Cellulose acetate, 50-lb. kegs.....lb.	1.25
Crotonaldehyde, 50-gal. drums...lb.	.32
Dichloroethylether, 50-gal. drums.lb.	.05
Diethylene glycol, drums.......lb.	.10
Monobutyl ether, drums.......lb.	.28
Monoethyl ether, drums.......lb.	.13
Monomethyl ether, 50-gal. drums, c/l...............lb.	.15
Diethylene oxide, 50-gal. drums..lb.	
Dioxan, *see* Diethylene oxide	
Diphenyl, c/l...............lb.	.40
Ethyl acetoacetate, 50-gal. drums...............gal.	.65
Carbonate, 90%, 50-gal. drums...............gal.	1.85
Chlorocarbonate, 50-gal. drums ....gal.	.35
Ether, absolute, 50-gal. drums...lb.	.50
Furoate, 1-lb. tins...........lb.	5.00
Ethylene chlorhydrin, 40-, 50-, 90-gal. drums...............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.	.20
Monomethyl ether, drums...lb.	.20
Oxide, cyl...............lb.	2.00
Furfuramide (tech.), 100-lb. drums.lb.	.30
Furfuryl acetate, 1-lb. tins.......lb.	5.00
Alcohol, 100-lb. drums........lb.	.50
Furoic acid (tech.), 100-lb. drums.lb.	.50
Helium, 1-liter bot...........liter	25.00
Lead dithiofuroate, 100-lb. drums.lb.	1.00
Magnesium peroxide, 100-lb. cs...lb.	1.25
Methyl acetate, drums........gal.	.95
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.	.35
Propyl furoate, 1-lb. tins........lb.	5.00
Strontium peroxide, 100-lb. drums.lb.	1.25
Sulfuryl chloride, 600-lb. drums, crude...............lb.	.10
Distilled...............lb.	.35
Tetrachloroethane, 50-gal drums..lb.	.09
Trichloroethylene, 50-gal. drums..lb.	.10
Triethanolamine, 50-gal. drums...lb.	.55
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., bbls........lb.	.36
Acetic anhydride, 92–95%, cbys..lb.	.29
Acetone, C. P., drums, wks......lb.	.15
Acetophenetidine, bbls..........lb.	1.40
Acid, acetic, 28%, c/l. bbls....100 lbs.	4.13
56%, c/l. bbls.........100 lbs.	7.35
Glacial, c/l. bbls......100 lbs.	13.68
Acetylsalicylic, bbls..........lb.	.85
Anthranilic, 99–100%, drums...lb.	.98
Benzoic, tech., bbls..........lb.	.57
Boric, bbls.................lb.	.05¾
Butyric, 60%, pure, 5-lb. bot...lb.	.55
Chloroacetic, mono-, bbls., wks..lb.	.21
Di-, cbys...............lb.	1.00
Tri-, bbls...............lb.	2.50
Chlorosulfonic, drums, wks....lb.	.05
Chromic, pure, 98%, drums... .lb.	.21
Cinnamic, 5-lb. cans.........lb.	3.25
Citric, U. S. P., kegs, bbls..... lb.	.46
Cresylic, pale, drums.........gal.	.72
Formic, 85%, cbys., N. Y.....lb.	.11
Gallic, U. S. P., bbls.........lb.	.74
Glycerophosphoric, 25%, 1-lb. bot...............lb.	1.40
H, bbls., wks...............lb.	.68
Hydriodic, 10%, U. S. P., 5-lb. bot...............lb.	.67
Hydrobromic, 48%, cbys., wks..lb.	.45
Hydrochloric, 20°, tanks, wks. ....100 lbs.	1.10
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.	.04¼
66%, light, bbls., wks.......lb.	.26
Mixed, tanks, wks........N unit	.07
S unit	.01
Molybdic, 85%, kegs.........lb.	1.25
Naphthionic, tech., bbls.......lb	nom.
Nitric, C. P., cbys...........lb.	.12
Nitric, 38°, c/l. cbys., wks. ....100 lbs.	5.00
Oxalic, bbls., wks...........lb.	.11
Phosphate, bulk...........ton	10.00
Phosphoric, 50%, cbys.......lb.	.08
Picramic, bbls...............lb.	.65
Picric, bbls., c/l............lb.	.30
Pyrogallic, tech., bbls........lb.	.86
Salicylic, tech., bbls..........lb.	.37
Stearic, d. p., bbls., c/l.......lb.	.14½
Sulfanilic, 250-lb. bbls........lb.	.15
Sulfuric, 66°, c/l. cbys., wks. ....100 lbs.	1.35
66°, tanks, wks...........ton	15.50
60°, tanks, wks...........ton	11.00
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.	.35
Tartaric, U. S. P., cryst., bbls...lb.	.38
Tungstic, kegs.............lb.	1.00
Valeric, C. P., 10-lb. bot......lb.	2.50
Alcohol, U. S. P., 190 proof, bbls. ....gal.	2.69½
Amyl, 10%, Imp. drums......gal.	1.75
Butyl, drums, c/l., wks.......lb.	.17¾
Cologne spirit, bbls..........gal.	2.67
Denatured, No. 5, comp. denat., c/l. drums...............gal.	.49
No. 1, comp. denat., drums.gal.	.50
Isoamyl, drums...........gal.	3.50
Isobutyl, ref., drums........lb.	1.00
Isopropyl, ref., drums........gal.	1.00
Propyl, ref., drums.........lb.	1.00
Wood, *see* Methanol	
Alpha-naphthol, bbls.........lb.	.65
Alpha-naphthylamine, bbls......lb.	.32
Alum, ammonia, lump, bbls., wks. ....100 lbs.	3.25
Chrome, casks, wks.......100 lbs.	5.25
Potash, lump, bbls., wks..100 lbs.	3.00
Soda, bbls., wks........100 lbs.	3.75
Aluminum, metal, N. Y.........lb.	.240
Aluminum chloride, anhyd., drums ....lb.	.35
Aluminum stearate, 100-lb. bbl...lb.	.23
Aluminum sulfate, comm'l, bags, wks...............100 lbs.	1.40
Iron-free, bags, wks.....100 lbs.	1.95
Aminoazobenzene, 100-lb. kegs...lb.	1.15
Ammonia, anhydrous, cyl., wks...lb.	.14
Ammonia water, 26°, drums, wks..lb.	.03
Ammonium acetate, kegs.......lb.	.34
Bifluoride, bbls.............lb.	.21
Bromide, 50-lb. boxes........lb.	.48
Carbonate, tech., casks.......lb.	.09
Chloride, gray, bbls......100 lbs.	5.40
Lump, casks.............lb.	.11
Iodide, 25-lb. jars...........lb.	5.20
Nitrate, tech., cryst., bbls.....lb.	.06
Oxalate, kegs..............lb.	.35
Persulfate, cases............lb.	.31
Phosphate, dibasic, tech., bbls...lb.	.13
Sulfate, bulk, wks........100 lbs.	2.30
Thiocyanate, tech., kegs.......lb.	.40
Amyl acetate, tech., drums......gal.	1.65
Aniline oil, drums............lb.	.15¼
Anthracene, 80–85%, casks, wks..lb.	.60
Anthraquinone, subl., bbls.......lb.	.85
Antimony, metal.............lb.	.09½
Antimony chloride, anhyd., drums ....lb.	.17
Oxide, bbls...............lb.	.09½
Salt, dom., bbls............lb.	.26
Sulfide, crimson, bbls........lb.	.25
Golden, bbls.............lb.	.16
Vermilion, bbls...........lb.	.38
Tartrolactate, bbls..........lb.	.45
Argols, red powder, bbls.......lb.	.08
Arsenic, metal, kegs..........lb.	.50
Red, kegs, cases...........lb.	.09
White, c/l. kegs...........lb.	.03¾
Asbestine, bulk, c/l...........ton	15.00
Barium carbonate, bbls., bags, wks...............ton	58.00
Chloride, bags, wks.........ton	65.00
Dioxide, bbls..............lb.	.12
Hydroxide, bbls............lb.	.04¾
Nitrate, casks.............lb.	.08¼
Barium sulfocyanate, 400-lb. bbls. ....lb.	.27
Barytes, floated, 350-lb. bbls., wks. ....ton	23.00
Benzaldehyde, tech., drums.....lb.	.65
F. F. C., cbys.............lb.	1.40
U. S. P., cbys.............lb.	1.15
Benzene, pure, tanks, mills......gal.	.23
Benzidine base, bbls..........lb.	.70
Benzoyl chloride, cbys.........lb.	1.00
Benzyl acetate, cbys..........lb.	1.30
Alcohol, 5-liter bot.........lb.	1.40
Chloride, tech., drums.......lb.	.25
Beta-naphthol, bbls...........lb.	.24
Beta-naphthylamine, bbls.......lb.	.63
Bismuth, metal, cases.........lb.	1.70
Bismuth, nitrate, 25-lb. jars.....lb.	1.80
Oxychloride, boxes.........lb.	3.10
Subnitrate, U. S. P., 25-lb. jars.lb.	2.05
Blanc fixe, dry, bbls..........ton	80.00
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.	.10½
British gum, com., c/l......100 lbs.	4.37
Bromine, bot..............lb.	.45
Bromobenzene, drums........lb.	.50
Bromoform, 5-lb. bot.........lb.	1.65
Butylacetate, 100-gal. drums....gal.	1.35
Cadmium bromide, 50-lb. jars....lb.	1.20
Cadmium, metal, boxes........lb.	.65
Cadmium sulfide, cs...........lb.	1.00
Caffeine, U. S. P., 5-lb. cans.....lb.	2.80
Calcium acetate, bags......100 lbs.	4.50
Arsenate, bbls.............lb.	.07
Carbide, drums............lb.	.05
Chloride, drums, wks........ton	20.00
Cyanide, 100-lb. drums......lb.	.30
Lactate, tech., bbls..........lb.	.35

Nitrate, bbls. ....ton	52.00
Phosphate, monobas., bbls.....lb.	.07
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.	.60
Camphor, monobrom, cs........lb.	1.85
Caramel, bbls. ....gal.	.63
Carbazole, bbls. ....lb.	.15
Carbon, activated, drums.......lb.	.05
Carbon bisulfide, drums........lb.	.05½
Carbon black, cases............lb.	.10
Carbon dioxide, liq., cyl........lb.	.06
Carbon tetrachloride, drums......lb.	.07
Casein, stand. gr., bbls.........lb.	.14½
Cellulose acetate, kegs.........lb.	1.25
Cerium oxalate, kegs...........lb.	.32
Charcoal, willow, powd., bbls...lb.	.06
China clay, imp., bags......100 lbs.	15.00
Chloral hydrate, drums........lb.	.70
Chloramine, U. S. P., 5-lb. bot..lb.	1.75
Chlorine, liq., c/l., cyl........lb.	.04½
Chlorobenzene, mono-, drums...lb.	.09
Chloroform, tech., drums.......lb.	.20
Chromium acetate, 20° soln., bbls..lb.	.05½
Coal tar, tanks, bbls., wks......gal.	.07
Cobalt, metal, kegs............lb.	2.50
Cobalt oxide, bbls. ....lb.	2.10
Cod-liver oil, bbls. ....bbl.	39.50
Collodion, drums.............lb.	.23
Copperas, c/l., bulk............ton	13.00
Copper, metal, elec........100 lbs.	18.00
Copper carbonate, bbls.........lb.	.19
Chloride, bbls. ....lb.	.25
Cyanide, drums..............lb.	.55
Oxide, red, bbls. ....lb.	.18
Sulfate, c/l., bbls........100 lbs.	6.00
Cotton, soluble, bbls...........lb.	.40
Cream tartar, bbls.............lb.	.27¾
Cyanamide, bulk, N. Y. ....Ammon. unit	1.67½
Diaminophenol, kegs...........lb.	3.80
Dianisidine, kegs..............lb.	3.00
Dibutylphthalate, drums, wks...lb.	.29½
Diethylaniline, drums..........lb.	.55
Diethylene glycol, l. c. l. lots, drums.....................lb.	.11
Carload lots, drums...........lb.	.10
Diethyl phthalate, drums.......lb.	.24
Diethyl sulfate, tech., drums.....lb.	.20
Dimethylaniline, drums........lb.	.30
Dimethylsulfate, drums........lb.	.45
Dinitrobenzene, drums.........lb.	.15½
Dinitrochlorobenzene, bbls......lb.	.15
Dinitronaphthalene, bbls........lb.	.35
Dinitrophenol, bbls............lb.	.31
Diphenylamine, bbls...........lb.	.45
Diphenylguanidine, bbls........lb.	.36
Epsom salt, tech., bbls., c/l., N. Y. ....100 lbs.	1.70
Ether, nitrous, bot............lb.	.90
Ether, U. S. P., drums.........lb.	.38
Ethyl acetate, 85%, drums.....gal.	.95
Bromide, drums..............lb.	.55
Chloride, drums.............lb.	.22
Methyl ketone, drums.........lb.	.30
Ethylbenzylaniline, 300-lb. drums.lb.	1.05
Ethylene dichloride, tanks......lb.	.05
Chlorohydrin, anhyd., drums...lb.	.75
Glycol, c/l., wks.............lb.	.25
Ethyl ether, drums, cars....gal.	1.79
Feldspar, bulk...............ton	20.00
Ferric chloride, tech., bbls......lb.	.07
Ferrous chloride, cryst., bbls.....lb.	.05
Ferrous sulfide, bbls........100 lbs.	2.50
Fluorspar, 98%, bags..........ton	41.00
Formaldehyde, bbls............lb.	.09½
Formaniline, drums...........lb.	.38
Fuller's earth, bags, c/l., mines..ton	15.00
Furfural, 500-lb. drums., c/l....lb.	.17½
Glauber's salt, bbls........100 lbs.	.70
Glucose, 70%, bags, dry...100 lbs.	3.14
Glycerol, C. P., drums.........lb.	.15
G salt, bbls. ....lb.	.50
Hexamethylenetetramine, tech., drums...................lb.	.62
Hydrogen peroxide, 25 vol., bbls. ..lb.	.06½
Hydroquinone, kegs...........lb.	1.25
Indigo, 20%, paste, bbls.......lb.	.15
Iodine, crude, 200-lb. kgs......lb.	4.20
Iodine, resubl., jars...........lb.	4.65
Iodoform, bot...............lb.	6.00
Iridium, metal...............oz.	280.00

Kieselguhr, bags.............ton	60.00
Lead, metal...............100 lbs.	7.00
Lead acetate, bbls., white.......lb.	.13
Arsenate, bbls...............lb.	.13
Oxide, litharge, bbls..........lb.	.08½
Peroxide, drums.............lb.	.25
Red, bbls. ....lb.	.09½
Sulfate, bbls. ....lb.	.08¾
White, basic carb., bbls.......lb.	.09
Lime, hydrated, bbls........100 lbs.	.85
Lime, live, chemical, bbls., wks. ....100 lbs.	1.05
Limestone, ground, bags, wks....ton	4.50
Lithium carbonate, 100-lb. kgs...lb.	1.45
Lithopone, bbls...............lb.	.05¾
Magnesite, crude.............ton	36.00
Calcined, 500-lb. bbls., wks....ton	48.00
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.	.08
Dioxide, 80%, bbls...........ton	80.00
Sulfate, casks...............lb.	.08
Mercury bichloride, cryst., 25 lbs...lb.	1.58
Mercury, flasks, 75 lbs........flask	123.00
Meta-nitroaniline, bbls.........lb.	.72
Meta-phenylenediamine, bbls....lb.	.84
Meta-toluylenediamine, bbls.....lb.	.70
Methanol, pure, drums........gal.	.67
Denaturing grade, tanks......gal.	.60
Methyl acetone, drums........gal.	.83
Salicylate, cases.............lb.	.42
Methyl chloride, cylinders......lb.	.55
Michler's ketone, bbls..........lb.	3.00
Monoethylaniline, drums.......lb.	1.05
Naphtha, solvent, tanks........gal.	.35
Naphthalene, flake, bbls........lb.	.05
Nickel, metal................lb.	.35
Nickel salt, single, bbls.........lb.	.13
Double, bbls. ....lb.	.13
Niter cake, bulk..............ton	13.00
Nitrobenzene, drums..........lb.	.10¼
Oil, castor, No. 1..............lb.	.13
China wood, bbls............lb.	.14¾
Coconut, Ceylon, tanks.......lb.	.08½
Cod, N. F., tanks............gal.	.60
Corn, crude, tanks, mills......lb.	.08¼
Cottonseed, crude, tanks......lb.	.08½
Lard, edible, bbls............lb.	.15¾
Linseed, bbls. ....lb.	.106
Menhaden, crude, tanks......gal.	.52
Neat's-foot, pure, bbls........lb.	.15
Oleo, No. 1, bbls.............lb.	.11½
Olive oil, denat., bbls.........gal.	1.25
Foots, bbls. ....lb.	.10¼
Palm, Lagos, casks...........lb.	.08¾
Peanut, crude, bbls..........lb.	nom.
Perilla, bbls. ....lb.	.16
Rapeseed, bbls., English......gal.	.88
Red, bbls. ....lb.	.11⅛
Soy bean, crude, bbls.........lb.	.12
Sperm, 38°, bbls.............gal.	.84
Whale, bbls., natural, winter..gal.	.78
Ortho-aminophenol, kegs.......lb.	2.20
Ortho-anisidine, drums........lb.	2.50
Ortho-dichlorobenzene, drums...lb.	.08
Ortho-nitrochlorobenzene, drums ...lb.	.32
Ortho-nitrophenol, bbls........lb.	.85
Ortho-nitrotoluene, drums......lb.	.17
Ortho-toluidine, drums........lb.	.27
Palladium, metal.............oz.	46.80
Para-aminophenol, kegs........lb.	1.15
Para-dichlorobenzene..........lb.	.17
Para-formaldehyde, cases.......lb.	.40
Paraldehyde, tech., drums......lb.	.26
Para-nitroaniline, drums.......lb.	.48
Para-nitrochlorobenzene, drums ...lb.	.25
Para-nitrophenol, bbls.........lb.	.50
Para-nitrosodimethylaniline, bbls. ....lb.	.92
Para-nitrotoluene, drums.......lb.	.30
Para-phenylenediamine, bbls....lb.	1.15
Para-toluidine, bbls...........lb.	.40
Paris Green, 250-lb. kegs.......lb.	.25
Phenol, drums..............lb.	.13¼
Phenolphthalein, drums........lb.	1.10
Phenylethyl alcohol, 1-lb. bot....lb.	7.00
Phosphorus, red, cases.........lb.	.60
Phosphorus trichloride, cyl......lb.	.35
Phthalic anhydride, bbls........lb.	.18

Platinum, metal..............oz.	68.00
Potash, caustic, drums.........lb.	.07½
Potassium acetate, kegs........lb.	.29
Bicarbonate, casks...........lb.	.13
Bichromate, casks...........lb.	.09¼
Binoxalate, bbls.............lb.	.16
Bromate, cs. ....lb.	.35
Carbonate, 80–85%, calc., casks ....lb.	.05½
Chlorate, kegs..............lb.	.08½
Chloride....................ton	34.55
Cyanide, cases..............lb.	.55
Meta-bisulfite, bbls..........lb.	.12
Permanganate, drums........lb.	.16
Prussiate, red, casks.........lb.	.39
Yellow, casks...............lb.	.18½
Titanium oxalate, bbls.........lb.	.21
Pyridine, drums.............gal.	1.75
Quinine bisulfate, 100 oz........oz.	.40
Sulfate, 100-oz. cans.........oz.	.40
Resorcinol, tech., kegs.........lb.	1.20
Rochelle salt, bbls., U. S. P......lb.	.23
R salt, bbls. ....lb.	.45
Saccharin, cans..............lb.	1.75
Salt cake, bulk...............ton	19.00
Saltpeter, gran., bbls..........lb.	.06½
Silica, ref., bags.............ton	22.00
Silver nitrate, 16-oz. bot........oz.	.40¼
Soda ash, 58%, light, bags, contract, wks...........100 lbs.	1.32
Soda, caustic, 76%, solid, drums, contract, wks..........100 lbs.	2.90
Sodium acetate, bbls...........lb.	.05½
Benzoate, bbls..............lb.	.50
Bicarbonate, bbls........100 lbs.	2.25
Bichromate, casks...........lb.	.07½
Bisulfite, bbls...............lb.	.04
Bromide, bbls. ....lb.	.42
Carbonate, sal soda, bbls...100 lbs.	1.30
Chlorate, kegs..............lb.	.06½
Chloride, bags..............ton	12.00
Cyanide, cases..............lb.	.18
Fluoride, bbls...............lb.	.08¼
Metallic, drums, 12¼-lb. bricks ....lb.	.27
Naphthionate, bbls...........lb.	.55
Nitrate, crude, bags, N. Y. ....100 lbs.	2.22½
Nitrite, bbls................lb.	.08
Perborate, bbls..............lb.	.20
Peroxide, cases..............lb.	.27
Phosphate, trisodium..........lb.	.04
Picramate, kegs.............lb.	.69
Prussiate, bbls..............lb.	.12
Silicate, drums, tanks, 40° ....100 lbs.	1.65
Silicofluoride, bbls...........lb.	.05¼
Stannate, bbls..............lb.	.41¾
Sulfate, anhyd., bbls..........lb.	.02¼
Sulfide, cryst., bbls..........lb.	.02½
Solid, 60%................lb.	.03¼
Sulfocyanide, bbls...........lb.	.40
Thiosulfate, reg., cryst., bbls...lb.	.02½
Tungstate, kegs.............lb.	.70
Strontium carbonate, bbls.......lb.	.07¼
Nitrate, bbls. ....lb.	.09
Strychnine alkaloid, 100 oz., powder.....................oz.	.46
Sulfate, powder.............oz.	.38
Sulfur, bulk, mines, wks........ton	18.00
Sulfur chloride, red, drums......lb.	.05
Yellow, drums..............lb.	.03½
Sulfur dioxide, commercial, cyl...lb.	.08
Sulfuryl chloride, drums........lb.	.10
Thiocarbanilid, bbls...........lb.	.22
Tin, Amer., stand............lb.	.43⅞
Tin bichloride, 50% sol., bbls....lb.	.14½
Oxide, bbls. ....lb.	.56
Titanium oxide, bbls., wks......lb.	.40
Toluene, tanks..............gal.	.40
Tribromophenol, cases.........lb.	1.10
Triphenylguanidine, drums......lb.	.65
Triphenyl phosphate, bbls.......lb.	.70
Tungsten..............WO₃ unit	15.50
Urea, pure, cases............lb.	.25
Whiting, bags...............ton	18.00
Xylene, 5°, drums, mills.......gal.	.40
Xylidine, drums.............lb.	.38
Zinc, metal, N. Y.........100 lbs.	6.90
Zinc ammonium chloride, bbls....lb.	.05½
Chloride, granulated, drums....lb.	.06¼
Oxide, Amer., bbls..........lb.	.07¾
Stearate, bbls. ....lb.	.25
Zinc dust, bbls., kegs, c/l.......lb.	.08½