



EDITORIALS

The Growth of Empire Chemically Speaking

WHEN Bishop Berkeley uttered his famous saying about the growth of empire being ever westward, he did not have the chemical industry in mind. Neither did James Hill, when he advised young men to seek their fortunes in the West and incidentally help build up business for the Northern Pacific Railway. But with the growth of population, wealth, and resources, many things moved in, both good and bad, including the chemist and the seeds of chemical industry. These seeds sprouted shortly before the turn of the century, and under the stimulus of western optimism, as well as foolhardiness that refuses to recognize defeat, this baby industry has grown to a robust size and now possesses the vigor and punch essential for healthy existence. A chemical empire has grown up west of the Rockies.

A number of fortuitous circumstances played their part in this rapid growth, of which the most important no doubt was the development of a large and cheap supply of petroleum and natural gas. This not only created the huge California refining and petroleum products industry, but it stabilized the acid industry, which, up to that time, had been dependent upon the requirements of the pioneer explosives works. It also occasioned a steady demand for caustic soda, justifying its western production on a large scale. Second in importance was the development of the paper industry of the Northwest, which created a large market for chlorine, this in turn stabilizing the manufacture of the caustic consumed by the petroleum industry. In 1936 the consumption of chlorine in the West amounted to 28,000 tons, and that of caustic soda to 40,000 tons. All of this chlorine and 90 per cent of the caustic were manufactured on the Coast, and all was sold in competition with eastern and foreign manufactured products. Additional caustic was produced and exported to the Orient approximately equal to the amount imported from the East.

As always follows, a large number of parallel activities came into existence—carbon black and alcohols from natural gas, ammonia from waste hydrogen, carbon tetrachloride and hydrochloric acid from surplus

chlorine. The waste waters from oil wells now give up their iodine and the bitters of the salt works, their bromine.

The growth of the fruit industry is responsible for numerous chemical and near-chemical operations—citric acid, pectin, essential oils, and extracts. The wine industry stands on its own feet. So also does the sugar industry. Directly dependent on horticulture is the insecticide industry and while a considerable portion of insecticidal demands are still supplied by eastern factories, consumption of western manufactured products is rapidly increasing. Hydrogenation of vegetable oils and fish oil is growing and alcohol fermented from molasses and fruit residues is well established.

Automobiles caused the building of good roads and they, in turn, stimulated the use of automobiles. This all led to the establishment of the tire industry and this, to the rubber industry in its broader aspect. Southern California is now the world's second largest producer of rubber goods, being second only to Akron, and neither of these rubber centers owes its existence to the proximity of its raw materials.

Roads, as well as building construction, called for Portland cement, which is now manufactured in large quantities throughout the West by sixteen separate companies. Tiles and ceramics are manufactured in quantity, and a considerable portion thereof is exported and sold in the East. Glass is mostly made for bottles and for local demand.

The soap industry has grown to large proportions. The fertilizer industry is not fully rounded out, but fish meal is manufactured up and down the Coast in large quantities and phosphoric acid in Montana and British Columbia, while potash is made from desert brines in California. Various important industrial chemicals are on the production list of a number of manufacturers, of which the most outstanding success has been the group of xanthates manufactured as flotation reagents by the Great Western Electrochemical Company.

Desert salts and nonmetallics—borax, potash, soda ash, etc.—are important items in the chemical balance sheet. Every chemist is familiar with the splendid work and commercial success of the American Potash

and Chemical Corporation, which at present does a world business. Likewise the Celite Company, now owned by Johns-Manville, built up a nation-wide business and is known to every chemical engineer through its filter aid and other products.

While metallurgy is usually associated with mining rather than chemistry, it is of interest that all electrolytic zinc produced in North America is manufactured in the West, including British Columbia, as is most of the copper, a large portion of the lead, all of the mercury, and some iron. Iron deposits of excellent grade and quantity exist in Southern California and Northern Mexico, but the absence of coking coal and limited demand have delayed the upbuilding of the steel industry. One blast furnace is in operation at Provo, Utah, using coke made from Utah coal, and steel plants are producing at San Francisco and Los Angeles, using imported pig iron and scrap and employing natural gas and petroleum for fuel. Several small concerns manufacture ferro alloys in electric furnaces.

The moving picture industry, while hardly to be viewed as a chemical industry, nevertheless has created a large demand for chemicals and chemical products, photographic and otherwise, including tons of hydrogen peroxide for the maintenance of the film colony's supply of blondes. A substantial portion of these requirements is supplied by western manufacture.

While the growth of the chemical industry in the West during the last few decades gives an impressive and even astounding picture, the developments which will probably take place during the next decade or two are even more important. Population and local requirements open manufacturing possibilities which did not exist even a few years ago, and the former freight penalty to eastern markets now becomes an equal advantage against eastern importation. Then there are large power projects, such as Boulder Dam, Bonneville, and Grand Coulee. These major developments, together with older hydroelectric and steam power plants, stand ready to deliver an enormous amount of power. These facilities were paid for either with private or government money. As this money is frozen, as the major item in cost of power is the capital charge, and as there is no market at present for all of the power that has been developed, it is reasonable to assume that there will be a constant lowering of rates—at least for large industrial consumers. Further, that a progressive reduction will take place until most or all of the power is sold, be this accomplished by political football tactics, or otherwise. At any rate, the basic heavy power-consuming industries should have an unusual opportunity to become established under favorable economic conditions. Raw material for almost every kind of manufacture is available somewhere in this vast western area, but in locating new factories, the dictates of sound engineering studies must be followed, and not the advice of en-

thusiastic real estate agents or optimistic local chambers of commerce. Synchronizing new undertakings with the development of actual needs is all important and a number of eastern manufacturers have their eyes on the West, studying from this point of view the question of establishing branch factories. Some have actually moved in ahead of time and operated at a loss for awhile in order to hold their position in the future growing market.

The western chemical empire will soon be a vital factor in the country's chemical economic balance, but in its development and growth it will take the usual toll among the plants which are based on inadequate research, are badly engineered, or are inadequately financed.

WALTER SCHMIDT

Comfortable Traveling

WE FIND interesting the comments of over 5000 passengers interviewed during a 240,000-mile investigation tour of 20 American and Canadian railroads on the subject of air-conditioned cars. About equal percentages criticized the cars as much too warm and much too cold, and the same ratio held for those who thought they were slightly too warm and slightly too cool. Eight per cent complained of stuffiness and 7 per cent of drafts, while 5 per cent noted unpleasant odors.

Some of the problems involved in cleaning the air are, of course, chemical. Odors is one of them, and there is a real need for a thorough and exhaustive study of the entire air-filtering problem. Odors are aggravated by humidity when it exceeds 60 per cent within the car. Tobacco smoke, dust, and moisture cause off-odors if the cooling coils are not cleaned frequently. The excessive use of disinfectants is a factor. Nicotine and other substances in the filters may produce odors.

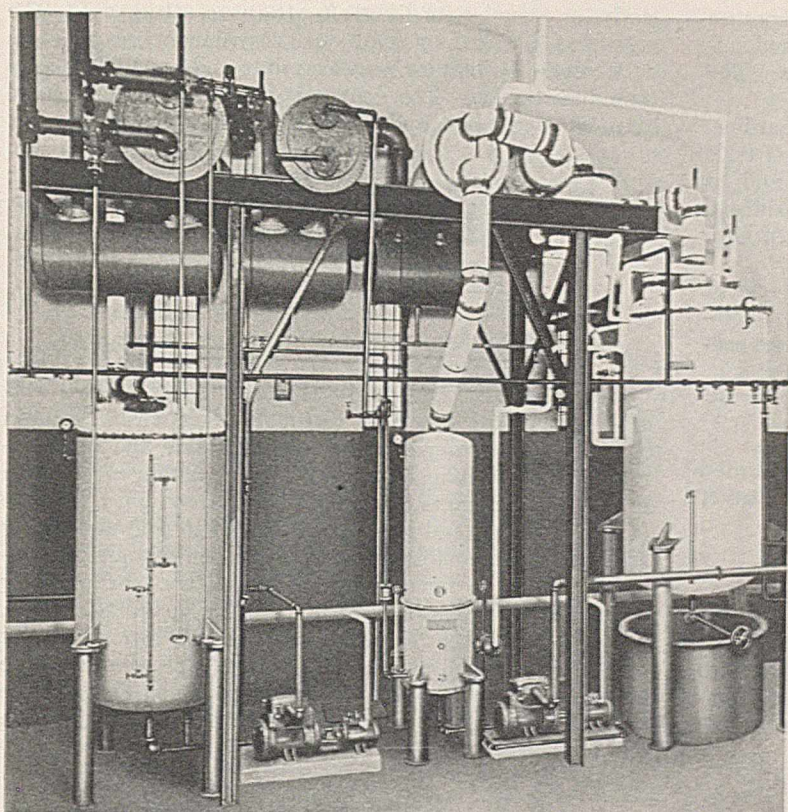
This seems to be a fruitful field for research, with by-products which are sure to be useful in many other industries. The problem will become more pressing as the rapidly increasing number of air-conditioned passenger cars climbs toward 100 per cent of the equipment, thereby introducing the whole traveling public to an experience entirely unheard of but a short time ago.

Science is many strides ahead of its application in most fields, but at times technology races on to the point where science is hard pressed.

It Has Been Said

We pay too much for the untrained service of politicians—too little for that of trained scientists.

Too many universities train men for the world that has passed. Classical education often stops with that period.



GLYCERIN DISTILLATION PLANT
Courtesy, Wurster and Sanger

GLYCEROL LIBERATION, RECOVERY, AND REFINING

ARTHUR GUILLAUDEU
 Swift & Company, Chicago, Ill.

The composition and purity of crude and refined glycerins are dependent upon the composition of the original glycerides, the methods by which the glycerol was liberated, and the purification methods used. This article discusses the compositions of some typical glycerides, flow sheets of soap manufacture, methods of treatment, and purification and concentration.

The various impurities affect the analytical results and complicate the calculation of the yields of factory operations. The *c. p.* grade is the final product and is one of the purest chemicals produced in large quantities.

GLYCEROL is the simplest trihydric alcohol. This statement indicates its composition, its structure, and many of its physical properties. It tells us that glycerol will appear in nature as esters united with one, two, or three acid radicals. It indicates that analyses can be made by oxidation or by esterification. Oxidation will yield aldehydes, acids, or mixtures of these two with one another and with alcoholic radicals. Fermentation will yield such products as trimethylene glycol. Dehydration is easily accomplished with the formation of acrolein. Glycerol reacts with alkalis to form glyceroxides. By heating in the presence of alkalis, ethers such as diglycerol are formed, from which glycerol is not easily regenerated.

Glycerides

Textbooks have spread the idea that the fats and oils are principally simple triglycerides or mixtures of simple triglycerides, with all three of the fatty radicals alike. Actually, their compositions are more complex. The following table shows the percentages of saturated fatty acids of some typical oils:

Acid	No. of C Atoms	Oil			
		Cotton-seed (2)	Corn (3)	Coco-nut (2)	Men-haden (4)
Caproic	6	--	--	0.5	--
Caprylic	8	--	--	9.5	--
Capric	10	--	--	4.5	--
Lauric	12	--	--	51.0	--
Myristic	14	--	--	18.5	9.2
Palmitic	16	23.4	7.9	7.5	22.7
Stearic	18	--	3.6	3.0	1.8

The percentages of unsaturated acids in the same samples of these oils are as follows:

No. of C Atoms	No. of Double Bonds	Oil			
		Cotton-seed (2)	Corn (3)	Coco-nut (2)	Men-haden (4)
18	1	23.0	46.3	5.0	24.9
18	2	53.6	41.6	1.0	
20	2 to 5	--	--	--	22.2
22	2 to 5	--	--	--	20.2

If we were dealing with a metallic alloy containing as many different elements as there are different acids in some of these oils, the effects of such differences would be very large. But, even when dealing with a homologous series of organic acids, the differences are important. For instance, the differences in length of chain between the acids of corn oil and those of cottonseed oil have important industrial significance upon the uses of the two oils.

The coconut oil group is characterized by the presence of short, saturated acids. The caproic, caprylic, and capric acids are advantageous for some soapmaking purposes, but

they are disadvantageous for the glycerin¹ refiner because their salts are too soluble. Although lauric acid predominates, it constitutes less than half of the total acids. The oil is by no means pure trilaurin.

The marine oils, including menhaden, herring, sardine, whale, seal, etc., are characterized by a wide variety of acids with from fourteen to twenty-four carbon atoms and as many as four or five double bonds. Being easily oxidized, these highly unsaturated acids add to the difficulties of both soapmaker and glycerin refiner.

Contrasting the compositions of these oils, it is evident that they are not entirely interchangeable, and that, wherever the length of chain is important, oils of one group cannot be freely substituted for those of a different group.

Typical Natural Glycerides

The component glycerides of a fat may be illustrated by the percentage composition of lard, as stated by Amberger and Wiesehahn (1):

Palmitodistearin	3	Oleopalmitostearin	11
Stearodipalmitin	2	Palmitodiolein	82
Oleodistearin	2		

Hilditch (3) summarized his researches on the constituent glycerides by saying that the tendency is for the glycerides to be as mixed as possible—that is, for the various acids to be distributed among the glycerol molecules in more or less even fashion.

Soapmaking

Most of the glycerin of commerce is set free by the soapmaking process. Soap kettles are usually from 12 to 20 feet in diameter and from 20 to 40 feet deep. They are heated by injected steam. Into such an open kettle the soap boiler will receive from 30,000 to 150,000 pounds of fats and oils during 2 to 5 hours, saponifying the fats as they come in with lyes which have been used previously on other batches for other parts of the process. Boiling is continued until practically all of the fat and all of the alkali have combined. The soap boiler will know in a general way the types of fats coming into the kettle, but he does not rely upon analyses of the fats or of the lyes to aid him in proportioning them. He judges the progress of the saponification by the appearance, the feel, and the taste of the mass.

After saponification is practically complete and the lye has been "killed" (i. e., approximately neutralized), salt is added and boiled through the mass. When the steam is turned off, the spent lye sinks and the soap floats. Each such boiling operation may be called a "change" because one lye is taken off and another one replaces it for the next operation. For small factories it

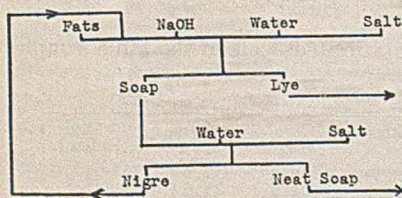


FIGURE 1. SIMPLE FLOW SHEET FOR SOAPMAKING

may be sufficient to use the flow sheet of Figure 1 and to follow the saponifying change with no more than a settling or finishing change to get the soap into acceptable form for the market. This is the final kettle operation on almost all boiled soaps. Its object is to leave the soap in a smooth, continuous, somewhat pasty condition in contrast to the broken,

curdy, or granular condition after the usual salting out. The nigre was so called by the French soapmakers because of its dark color. It contains less electrolyte and much more soap than does the lye. The neat soap, in turn, contains more soap, less electrolyte, and less water than either nigre or lye.

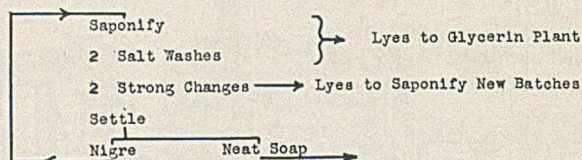


FIGURE 2. SECOND FLOW SHEET FOR SOAPMAKING

Larger factories will follow the saponifying change with other changes as shown in Figure 2. Salt washes contain only small percentages of sodium hydroxide and are separated from the soap by the salting-out action of common salt. Strong changes are much higher in sodium hydroxide (4 to 12 per cent) and correspondingly low in chloride. They are intended to complete the saponification and are particularly effective in removing coloring matters. Both strong changes and salt washes assist in removing suspended matter, glycerol, and other dissolved materials. When using this flow sheet, about 3 pounds of spent lye will be sent to the glycerin plant per pound of fat saponified. The average content of these lyes will be about 3 per cent glycerol with 5 to 15 per cent salt.

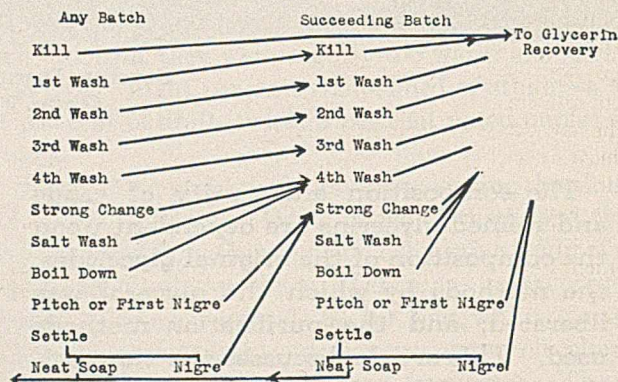


FIGURE 3. THIRD FLOW SHEET FOR SOAPMAKING

Other factories will profit by resorting to more complex flow sheets, such as the one in Figure 3. Arrows show the movement of the lyes as they progress from batch to batch. Fresh salt and water form the lye for the boil down. Fresh caustic and water form the lye for the strong change. These move, as indicated, countercurrent to the soap until, as spent first wash, they supply most of the alkali for the saponifying or killing change. They increase in percentage of glycerol and in impurities as they move from stage to stage, and increase in quantity by additions of condensed steam and water and of salt and caustic.

In this case there will be only 1 to 1.5 pounds of glycerin lye per pound of fat. There will be from 8 to 10 per cent of glycerol in the lye, with no more salt than in the previous case. Advantages of the flow sheet of Figure 3 include the improvement of the color and purity of the soap, a higher degree of saponification, and decreased charges for treatment and evaporation in the glycerin plant. The finished soap is more accurately adjusted by this process than by the others and carries no more alkali from the kettle. (Many of the troubles blamed on "strong soap" are due to entirely different causes.)

Other methods of liberating glycerol which should be mentioned include the Twitchell and the autoclave processes.

¹ The term "glycerol" is usually reserved for the pure trihydric alcohol, $C_3H_8(OH)_3$. Less pure material is usually termed "glycerin;" thus, the "dynamite glycerin" of commerce contains not less than 98.5 per cent glycerol.

The former calls for boiling the fats with water, sulfuric acid, and a catalyst at atmospheric pressure. The older autoclave process boiled the fats, under steam pressures of 80 to 160 pounds, with lime, magnesia, zinc oxide, or zinc dust. Autoclaves made of the newer alloys, using pressures up to 450 pounds per square inch, allow hydrolysis without catalyst. Both processes yield the glycerol in a so-called sweet water which carries much less inorganic compounds than do the soap lyes. The organic impurities will also be different in kinds and amounts from those present in soap lyes.

Glycerin Recovery and Refining

The glycerin refiner's problem includes the usual three manufacturing requirements. He must secure capacity, quality, and yield. To obtain capacity is usually a matter of having enough equipment and operating it enough hours, although other conditions will cause the capacity per hour to vary over a wide range. Quality is more difficult to obtain, and satisfactory yields are still more difficult.

To obtain the best quality, one should start with the selection of the raw material. Since the manufacture of glycerin is usually subsidiary to the main operation of making soap or fatty acids, the fats and oils are usually selected on the basis of their other qualities, and the conditions controlling the quality of the glycerin are less considered when purchasing the raw fats. The fat may have been separated from its accompanying animal or vegetable material by heat, pressure, or solvents, but in either case it will be accompanied by more or less nitrogenous material. Edible fats are refined in such fashion that this contamination is avoided. But for soapmaking purposes, the commercial fats and oils receive most of their purification in the kettle. The saponifying process, changing the fats from an oily acid phase to a water-soluble alkaline phase, sets free most of the impurities which accompanied the fats. Therefore, the lyes carry to the glycerin refinery various nitrogenous materials and the products of any oxidation or fermentation which the fats may have undergone. Again, the soap factory may be making a rosined soap, and some parts of the rosin lyes usually get into the glycerin plant in spite of all precautions.

Purification of Lyes

Before evaporation, the spent lyes must be treated to remove the soap, the traces of alkali, and the tarry and nitrogenous impurities. Strong oxidizing agents must be avoided. Reducing agents are useless. And the precipitants are not altogether effective to remove water-soluble acids and some other impurities. Simple treatment with aluminum sulfate and sodium hydroxide is customary. But to gain all of the possible advantages for both glycerin and soap manufacture, some factories resort to the following scheme of lye treatment:

Added	Precipitated
Lime, calcium chloride	Carbonates, bicarbonates, soaps
Ferrous sulfate, hydrochloric acid, air	Acids, nitrogenous and tarry materials
Sodium hydroxide, soda ash	Excess iron and calcium
Sulfuric acid	To liberate volatile acids

The alkaline lyes bring with them alkali-soluble materials which would have accompanied the fatty acids if the fats had been split with acids. They would then have accompanied the fatty acids instead of the glycerin. In some cases this difference in method of hydrolyzing makes all the difference between being able to recover the glycerin of inferior stocks at a profit and being unable to make it pay.

The treated lye is evaporated to a crude product contain-

ing about 80 per cent glycerin. During evaporation about 95 per cent of the salt separates. The following table illustrates the differences in the qualities of crude glycerins due to different percentages of raw materials:

	I	II	III
Gross acetin value (calcd. as glycerol)	82.54	79.18	56.47
Nonvolatile organic matter	1.16	3.45	14.55
Acetylizable value of nonvolatile organic matter	0.59	0.76	1.13
Ash	8.28	9.68	19.66
Alkalinity of ash (as Na ₂ O)	0.08	1.44	5.15

The factory which made crude glycerin I used coconut oil and a good grade of tallow. The second evidently used poorer stocks. Crude glycerin III was made from a highly acid stock which yields excellent soap but very impure glycerin lye. The following table shows the variation of the quality of the crudes when the same treatment was applied to lyes from different fats:

Fat	Non-volatile Organic Matter, %	Acetylizable Value of Nonvolatile Organic Matter, %
Hardened soybean oil	0.16	
Crude coconut oil	0.85	0.37
Tallow	1.07	0.40
Palm oil, raw	0.85	0.61
Palm oil, air-bleached	1.40	0.72
Yellow grease, raw	2.26	1.53
Yellow grease, washed	1.89	0.93
Olive oil foots	12.81	1.11
Rosin	10.36	

All of the percentages are on the basis of 80 per cent glycerol. The lyes from olive oil foots were so impure that they could not be concentrated to 80 per cent, but the resulting crude was calculated to that basis. Rosin yields no glycerol; therefore, the quoted percentage is that of the treated lyes concentrated as far as the glyceride lyes were concentrated to yield 80 per cent crude.

Crude glycerin produced from the sweet waters of the autoclave and the Twitchell processes is called "saponification" crude. Standard specifications for it require not less than 88 per cent glycerol, not more than 3 per cent ash, and not more than 3 per cent nonvolatile organic matter. Some saponification crudes may have as little as 0.5 per cent ash, and from 0.5 to 1.5 per cent nonvolatile organic matter, depending upon the quality of the fats, the method of hydrolyzing, and the chemicals used for treatment. When glycerin has been evaporated to crude, the recovery is said to have been completed, and the next step is the refining, principally by distillation and treatment with decolorizing carbon.

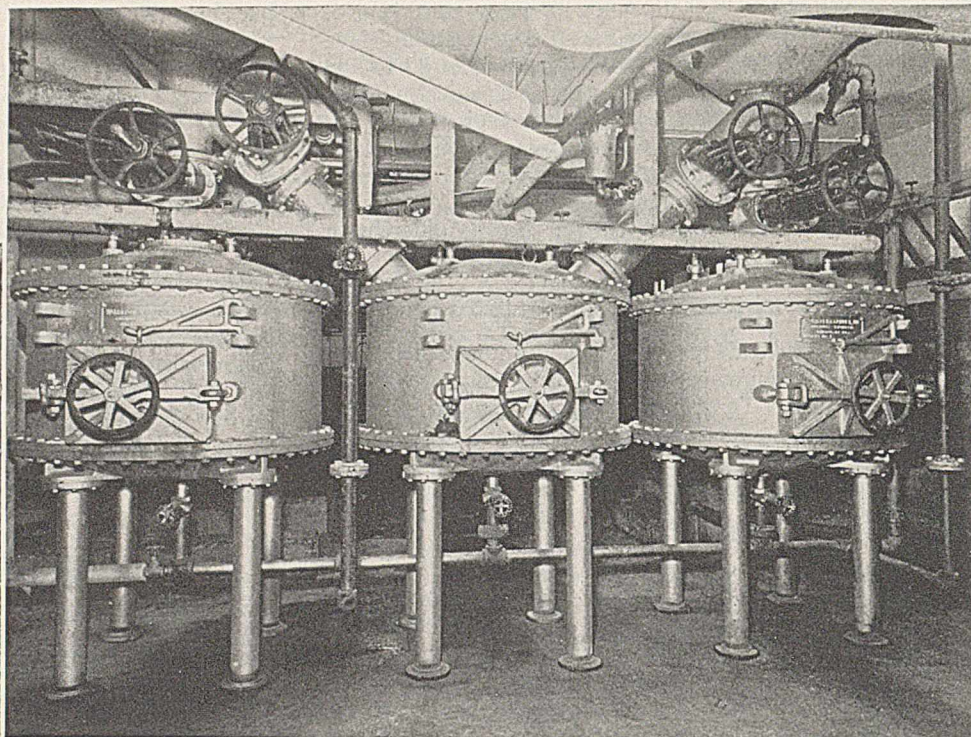
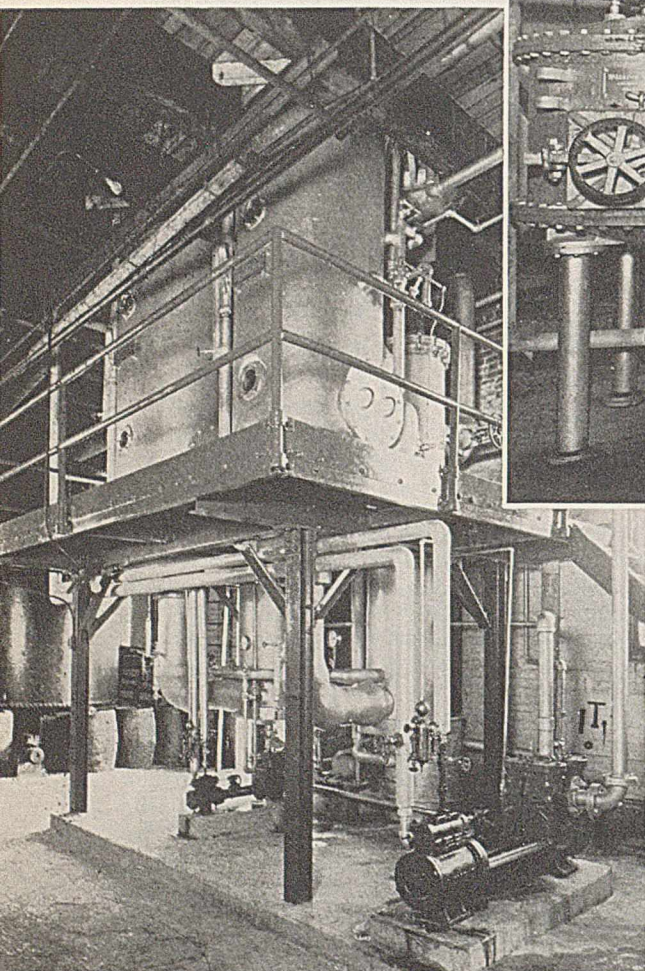
Glycerin Distillation

When the crude is fed to the still, sodium hydroxide is usually added to reduce the proportion of acids carried over by the injected steam. This increased alkalinity causes formation of polyglycerols which are less volatile than glycerol, which raise the boiling point, and which retain glycerol in the still, thus reducing the yield.

Conditions of distillation have a large influence upon quality and yield as well as capacity. The mass is viscous and liable to boil over if any of several conditions goes wrong. Too high temperature is destructive of glycerol and of quality. Certain types of crude glycerin can be distilled separately with success but foam tremendously if distilled together. Crudes are usually distilled on the alkaline side, but some distill much better when slightly acid.

On distillation, three principal fractions are made—heavy distillate, sweet water, and residue or foots. The heavy distillate should contain most of the glycerol. It should be free from acids and esters, from ash, from trimethylene glycol, and from polyglycerols. It should be easily concen-

2



SALT FILTERS OF DOUBLE-EFFECT SOAP LYE GLYCERIN EVAPORATOR

DOUBLE-EFFECT EVAPORATOR FOR TWITCHELL SWEET-WATER

External heating elements facilitate easy removal of calcium sulfate scale from tubes.

Courtesy, Wurster and Sanger

trated to the high-gravity grade, the principal specifications for which are given in the following table, along with those for the c. p. or U. S. P. grade, made from the once-distilled glycerin by redistillation and further treatment (in per cent):

	High Gravity	U. S. P.
Glycerol (minimum)	98.5	95.0
Ash (maximum)	0.10	0.007
Chloride (maximum)	0.01	
Acidity as Na ₂ O (maximum)	0.10	0.025

Occasionally batches of distilled glycerin will appear on the market which are unusual in their behavior. One lot of such distilled glycerin probably had been made from lyes of cottonseed soap stock. A portion of this had been distilled seven times without material improvement in color. It was dark red by transmitted light and green by reflected light. The cause of the color seemed to be actually distilling rather than entraining. However, a modified adsorption was worked out, after which one distillation produced a satisfactory color.

Trimethylene Glycol

The sweet water will include from 1 to 20 per cent of the glycerol distilled and may include most of the injected steam.

It also contains most of the acids which have volatilized and most of the trimethylene glycol. This trimethylene glycol is a nuisance to the glycerin refiner. It is much lighter than glycerol. It does not belong in the c. p. grade because it is not glycerol. The dynamite maker does not want it because its nitration products are unstable. In recent years there has been some demand for it as an anti-freeze. It should be kept to a minimum by preventing fermentation of either fats or lyes.

Glycerin Foots

The majority of the impurities of the crude remain in the still unvolatilized and form the feet. Soluble salts constitute most of this residue. Since the soap lye crude, as fed to the still, contains 8 or more per cent of ash and 1 or more per cent of organic impurities, a large amount of nonvolatile matter soon accumulates and sets a limit to the size of batch operations. Attempts to overcome this disadvantage by continuously drawing off portions of the still charge and removing the salts have met with considerable success; the feet is then distilled nearly to dryness in another still, and the residue is so low in glycerol that it can be discarded.

Treatment of Glycerin Feet

Economical recovery of glycerol from the feet has been attempted in many ways. One routine has been to return the feet for treatment with the new lye until the quality of the crude becomes so low that the distillation is too slow. Then, the feet from all of that crude is distilled separately and discarded. Meantime, the cycle is begun anew. Sometimes a system of separate treatment of the feet has been set up. The table which follows shows a series of steps by which some of the nonvolatile organic acids have been removed.

Added	Removed
Soda ash	Calcium carbonate
Sulfuric acid	Organic acids
Lime	Sulfate
Soda ash	Calcium carbonate

The essential step is acidification. The other steps are necessary supplements. The acid tar which rises is a possible source of caprylic and capric acids.

Various methods have been tried to regenerate the glycerol which, by dehydration, has formed polyglycerols. In general, the results have been unsatisfactory.

Analytical Difficulties

The responsibility for obtaining capacity and quality is more easily fulfilled than that of obtaining a satisfactory yield. Weights can be measured in the usual fashion. But analyses present the difficulties that glycerol cannot be sharply separated from the accompanying materials, that it is quite hygroscopic, and that it cannot be separated in a directly weighable form. If present as a mixture only with water, the percentage can be determined directly from the specific gravity or the refractive index. But in the complex mixtures in lyes, crudes, and especially in glycerin foots, resort must be had to oxidation or acetylation. Usually other materials are present which react to one or both methods. Distillation in steam under vacuum provides some of the most convincing figures. For accounting purposes, the bichromate method is usually preferred because it gives comparative figures, is less expensive and more speedy than the acetin method, and is generally applicable.

In determining yields, the first question is, "How much glycerol is to be charged?" If we start with the delivery of the fats to the kettles, complications arise at once. Neutral tallows, greases, and most vegetable oils yield about 10.5 per cent glycerol. If the fat has been hydrolyzed to the extent of, say, 20 per cent, we might expect to recover a maximum of 8.4 per cent. But the fats are triglycerides and they hydrolyze in steps, setting free acids and forming mono- and diglycerides as well as glycerol. The mono- and diglycerides accompany the rest of the fat and, on complete hydrolysis, the glycerol yield will be somewhat more than the calculated. A composite of fats gave the following results:

Free acid, as % oleic acid	22.6
Saponification value	193.3
Glycerol by calculation, %	8.11
Glycerol by direct analysis, %	8.89
Glycerol by experiment, %	9.08

The last item was obtained by saponifying 5 kg. (11 pounds) of the fat in an iron kettle with commercial sodium hydroxide, boiling by injected steam. Saponification was followed by two strong changes and two salt washes. The soap was left grained to avoid complications due to formation of nigre. All of the lyes were united, treated, and evaporated almost to the salting point before analysis. The soap, concentrated lyes, and filter cakes were weighed and analyzed to obtain the final glycerol figure.

The interpretation of analyses of the finished products may involve similar questions. Distilled glycerins are sold on the basis of their glycerol content as calculated from the specific gravity, but the less pure raw materials will yield some fractions of distillate which give contradictory analyses as the following percentage analysis of glycerol in a distilled glycerin shows:

By specific gravity	94.58
By bichromate oxidation	95.48
By acetylation	92.96

Calculations indicate the presence here of both trimethyl-ene glycol and polyglycerols, as well as glycerol and water.

Close fractional distillation and analyses of the fractions will show the correct composition. But for accounting purposes, this material has been charged into the plant on the bichromate analysis. Yet, it must be credited on the percentage calculated from the specific gravity. This causes the accounts to show a manufacturing loss which is actually due to the necessary methods of analysis.

A more extreme case, although usually not involving so many pounds of material, occurs in the glycerin foots. Here, the specific gravity method is not applicable because of the large proportions of salts and other impurities. Polyglycerols which do not volatilize in the still react to both bichromate and acetin analyses. For instance, a batch of foots which showed 34.18 per cent glycerol by the bichromate method and 19.94 per cent glycerol by acetylation, yielded on distillation only 5 per cent glycerol which needed to be redistilled before it was of salable quality.

Beside these complications of analysis, the manufacturing operations are made more difficult by the complete solubility of glycerol in water, by the many things which cause foaming and carry glycerol to the jet condensers and thus to the sewers, and by the usual results of corrosion and erosion. Recoveries of 90 per cent of the glycerol of the original fat as salable products are usually considered about as high as are economical, and many plants are content to recover only 70 to 80 per cent.

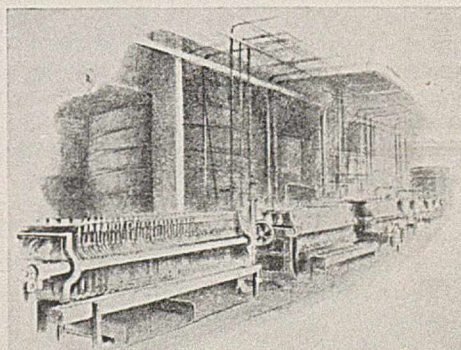
U. S. P. Glycerin, the Final Product

Although it is not profitable to obtain 100 per cent yields and although analyses of the cruder products require interpretation, the U. S. P. grade, in which most of the glycerol is sold, is one of the industrial chemicals produced in millions of pounds which properly deserves the title "chemically pure." Modern glycerin of this grade consists practically of 95 per cent glycerol and 5 per cent distilled water. The ash is reduced to a mere trace, and the other impurities are so slight that the most exacting test now applied is a color test after mixing with an equal volume of concentrated sulfuric acid. Even the present high standard should be surpassed by the increasing use of newer methods and newer equipment.

Literature Cited

- (1) Amberger and Wieseahn, *J. Soc. Chem. Eng.*, 43, B229 (1924).
- (2) Hilditch, T. P., "Industrial Chemistry of Fats and Waxes," pp. 139, 142, London, Ballière, Tindall & Cox, 1927.
- (3) Hilditch, T. P., *J. Soc. Chem. Ind.*, 54, 141 (1935).
- (4) Twitchell, E., *J. IND. ENG. CHEM.*, 9, 581-4 (1917).

RECEIVED February 12, 1937. Presented before the Chicago Local Section of the American Chemical Society, September 25, 1936.



Courtesy, CIBA

FILTER PASSES

Low-Temperature Carbonization of Bituminous Coal

Latest Developments in Germany and Great Britain

DAVID BROWNLIE

56 Grange Road, Ealing, London, W. 5, England

DURING the past two or three years there has been a sudden new interest in Germany in low-temperature carbonization of bituminous coal, largely because of the use of the tar for hydrogenation and of the solid fuel for operating automobiles by means of producer gas, instead of gasoline and oil. For this latter purpose high-grade, chemically reactive, low-volatile solid fuel is the primary requirement for the generators; Germany possesses no anthracite and charcoal is too expensive. Consequently a number of new German processes are at present being actively considered for the production from bituminous coal of hard, smokeless, reactive fuels with a low temperature of carbonization. There is also much interest in the use of such fuels for combustion in steam boiler and general heating plants, including the operation of retorts for low-temperature carbonization in direct conjunction with boiler furnaces.

Low-temperature carbonization is a somewhat vague term, but roughly it means the carbonization of bituminous coal, generally at about 900–1200° F. (480–650° C.) and almost always by methods different from those of high-temperature carbonization in gas retorts and by-product ovens. The result is a relatively hard, reactive, smokeless fuel with about 10–12 per cent volatile matter content, which is superior in general properties to high-temperature-carbonization coke, especially for domestic and other purposes, including total gasification.

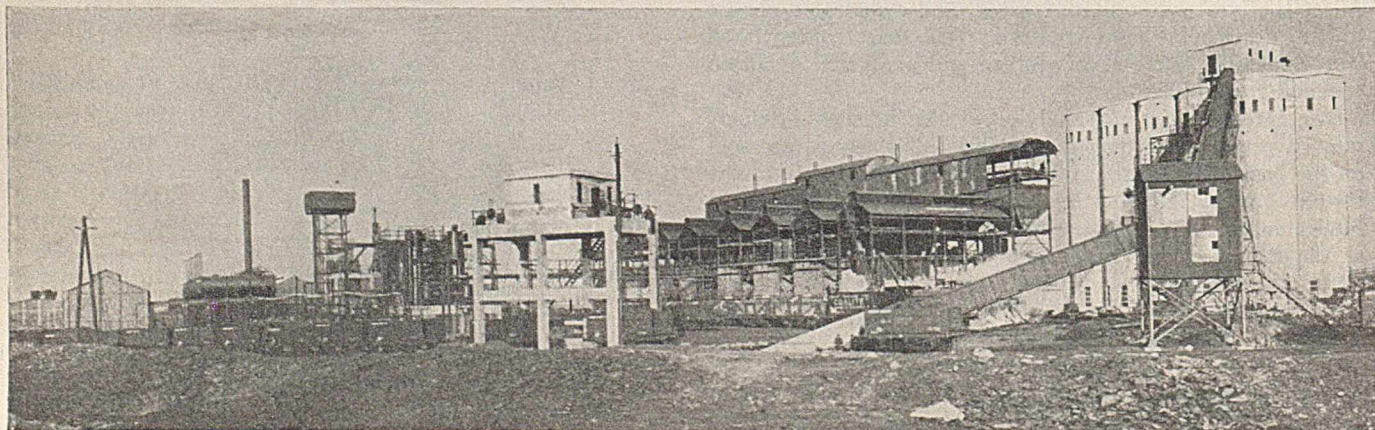
In general, what is popularly termed today "low-temperature carbonization" originated in Great Britain about

1890 with the work of Thomas Parker and the first of the long line of Coalite processes. The idea, however, that low-temperature carbonization of coal is relatively new is preposterous. For example, the town's gas industry, originated in Great Britain in 1805, operated for many years under conditions of low-temperature carbonization at not over about 1000° F. (540° C.), using intermittent cast-iron retorts.

Also there was for many years in extensive use in a number of countries, particularly the United States, Canada, Great Britain, France, and Germany, what was called the "coal-oil" industry. This term included the low-temperature carbonization of all kinds of material, such as torbanite, cannel, oil shale, and high-grade bituminous coal for the production of oil products. This flourishing development was killed by the commercial discovery of petroleum in 1857; another old-established carbonization industry which can be said to operate under low-temperature conditions is the treatment of lignite in Germany, dating primarily from 1850–1860 and the work of Edmund Rolle.

Low-temperature carbonization of bituminous coal in Germany has had a curious history. Until the World War it had virtually no existence, but the serious situation caused by the lack of liquid fuel resulted in the evolution of many different processes which operated on the principle of low-temperature carbonization of bituminous coal. Some of the most famous of these included the Fellner & Ziegler, the Kohlenscheidungs-Gesellschaft (K. S. G.), and the Thyssen, using externally heated, rotary cylindrical retorts, and the

NEW COALITE PLANT AT THE BOLSOVER COLLIERY, DERBYSHIRE



Dobbelstein, Plassmann, and Raffloer processes, operating on the principle of mechanical compression of the plastic swelling charge and using intricate and extremely ingenious types of retort. In addition, a number of combined low-temperature carbonization and partial or total gasification processes came into existence, which were operated by means of combined air and steam blast. However, by about 1925-1930 practically all of these processes went out of existence and for several years low-temperature carbonization was almost dead in Germany. Now there has been this new revival partly in connection with producer-gas-operated automobiles and the use of the tar for hydrogenation.

In Great Britain there has been continuous active interest in the subject for over twenty-five years, and at present about forty processes are more or less under consideration. Only one of these, however—Coalite—is operating on a large commercial scale, although a number of other interesting processes—notably the Hird, Salerno, and Maclaurin—have small plants at work.

In the present contribution an attempt will be made to give briefly the latest information concerning low-temperature carbonization of bituminous coal in Germany and Great Britain; reference will also be made to the Robinson Bindley synthetic liquid fuel process in Great Britain and the Pott Broche process in Germany for solvent and semihydrogenation action on bituminous coal.

The present interesting position of the British Coalite, Stephenson, and Suncole processes and the work of J. Stanley Morgan will be mentioned. Great attention has been given for a number of years to processes depending on the carbonization or heat treatment of pulverized coal and oil mixtures, of which the Stephenson is one example. Others are the Mitford or Cannock, Greenstreet, and Knowles processes, but this principle has so far made no commercial headway. Much stronger evidence is required before the general claim can be admitted that the carbonization of coal-oil mixtures gives more light oil and other fractions than if the coal and heavy oil were carbonized separately. Some of the statements that have been made in this connection are fantastic.

Also the total amount of coal carbonized in Great Britain under low-temperature conditions in 1935 (latest record available) was 327,112 long tons. There has been a slow rise for a number of years; in 1930 the figure was 204,464 tons, and over 85 per cent of this consumption represents one process—that is, the Coalite.

Seven or eight new German processes will be described, mostly dating from not later than 1932—that is, the B. T., Berg, Krupp-Lurgi, Hinselmann, Otto, Haken, and Koller-gas—as well as the present position in connection with two of the older processes—the Delkeskamp and a modification of the Pintsch in connection with the Weber process.

B. T. or Brennstoff-Technik Process

Franz Puening is the inventor of this process; he is a German fuel technologist, formerly with the Koppers Company, of Pittsburgh, and afterwards with the Brennstoff-Technik Gesellschaft, of Essen (Ruhr) which controls the process.

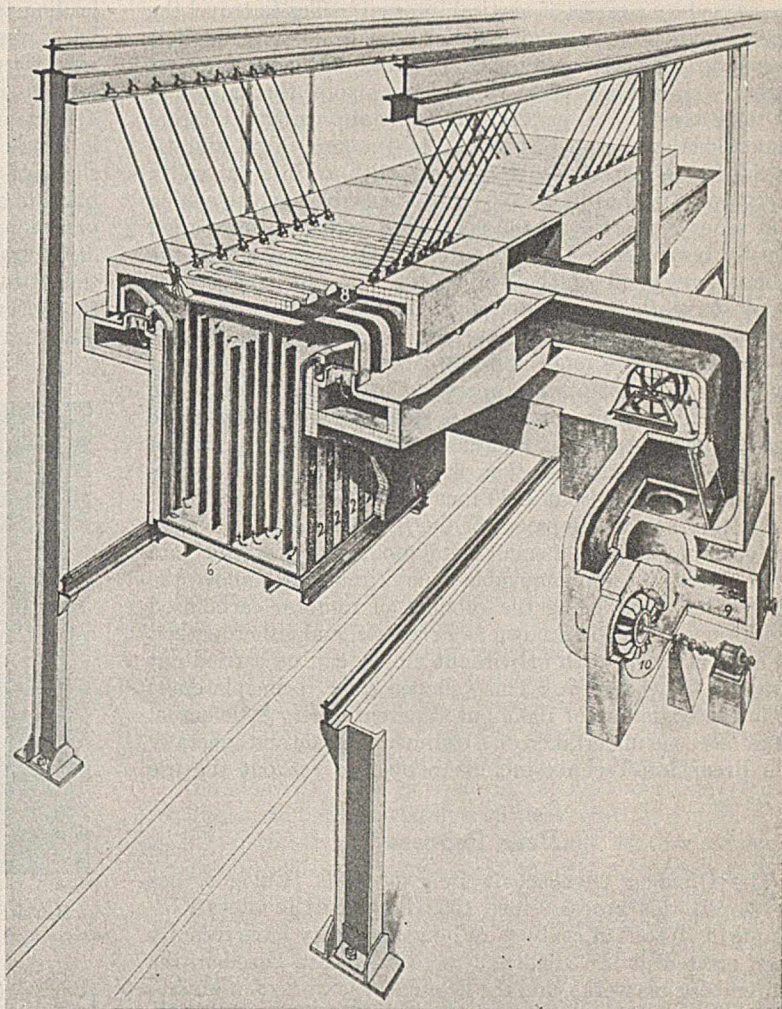


DIAGRAM OF BRENNSTOFF-TECHNIK APPARATUS

The retorts have moving side walls and the vertical baffles in the heating compartments provide uniform travel and distribution of the combustion gases.

Franz Puening has many United States patents of a lengthy and complicated character, involving a number of different designs of retorts or ovens for low-temperature carbonization. Essentially, however, the basic principle of most of them is the carbonization of bituminous coking coal in vertical, intermittent, externally heated, cast-iron carbonizing compartments of narrow width and rectangular plan, so arranged that one or both of the sides can be moved laterally by a somewhat complicated mechanical means to allow easy discharge of the residual carbonized fuel, even in the case of the most strongly swelling bituminous coking coal.

One general remedy for this difficulty of retort discharge is to blend the coking coal with noncoking coal, coke, or similar material and reduce the plasticity and degree of swelling, but apparently in the B. T. process the principle mainly adopted is to carbonize bituminous coal direct, irrespective of its plastic properties. After carbonization, the sides are moved laterally and the charge falls out, and a retort consists of an alternate series of carbonizing compartments and heating compartments supplied with combustion gases.

There are now two types of B. T. retort, one with non-moving walls for noncoking or slightly coking coal, and the other with moving walls for strongly coking coal.

Carbonization is carried out in both cases at about 1120° F. (600° C.), the heating compartments containing very hot combustion gases only and no flames, the burners being in adjoining flues; in each heating compartment the hot gases

are caused by a series of vertical internal baffles to travel the maximum distance and give uniform heating over the whole retort surface. Generally a B. T. retort unit consists of six carbonizing compartments which have a total throughput of 10 to 20 tons of coal per 24 hours; the approximate internal dimensions are 9.8 to 13.1 feet (3 to 4 meters) high, and 4.9 to 8.2 feet (1.5 to 2.5 meters) long, with an internal width of 2.3 to 5.1 inches (60 to 130 mm.), depending on the coking and other properties of the coal; the carbonization period usually lasts about 4 to 6 hours. Further, because of the lateral movement of the plates, the carbonizing compartments have the same internal width throughout; that is, they do not taper to facilitate the discharge, which feature is claimed to give more uniform carbonization. At present two large B. T. plants are operating in Germany along the lines of the main process. One is at the Delbrueck Schachte colliery in Upper Silesia and has a throughput of 10 tons of coal per 24 hours. The other plant is at a gas works in Berlin, and the throughput is 30 tons of coal per 24 hours.

Another new development of the B. T. process is to charge the coal into a series of small metal molds or boxes which are then placed in the nonmovable type of retort one above the other, the result being the product of uniform carbonized blocks of fuel which is known as *Formkoks*, and either method of carbonization, with or without molds, can be carried out with the same retorts. This "shaped coke" principle dates from the beginning of 1935, but apparently very little actual work has been undertaken on a commercial scale and generally the Brennstoff-Technik prefers to operate without the use of molds.

Berg Process

The Ofenbau Gesellschaft Berg of Kalk, Cologne, has developed this process since 1932 in several modifications. Plants of 10 tons of coal per 24 hours' capacity have recently been erected at the Heidenau gas works near Dresden, the Nuremberg gas works, and the Erlangen gas works; in March, 1937, another plant was completed at the Kaiserstuhl colliery near Dortmund (Ruhr).

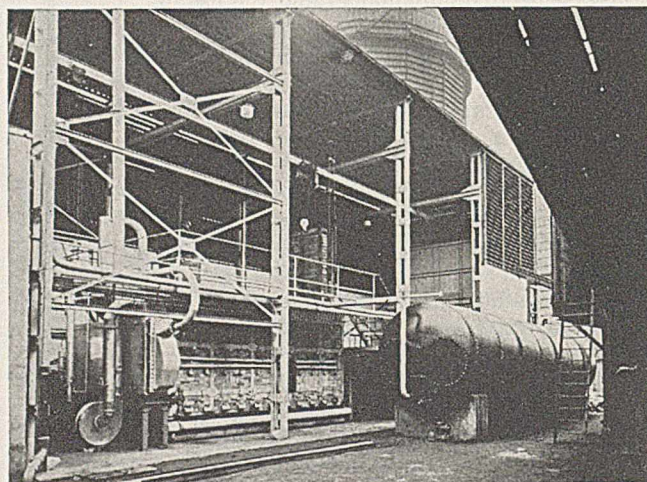
The Berg process consists essentially in the low-temperature carbonization of bituminous coking coal smalls in a series of molds which are made of shallow bottomless steel trays divided by transverse and longitudinal partitions to form small cells or molds which are filled with coal by hand. One tray is placed in a loose, flat metal plate, and, after charging, another is placed on the top, followed by a second tray with a plate, etc.; thus a pile of trays fits into a framework and forms a cage. By means of an overhead crane these cages are lifted in and out of vertical, externally heated, cast-iron rectangular retorts, divided transversely into a series of vertical compartments which fits the cage of trays.

The retort setting is externally heated by gas firing to about 840–930° F. (450–500° C.), and the operation is carried on until carbonization is complete. During heating, the plastic charge expands, developing considerable internal pressure in the molds, and forms coherent coked fuel in the form of small rectangular shapes, similar to carbonized briquets. The cages are then lifted out of the retort and replaced immediately by fresh cages of trays filled with raw coal, using the overhead conveyor; the operation of the retort setting is therefore continuous. After carbonization the hot cages are allowed to cool in the air, since the fuel cannot take fire when in the molds.

Each cage holds about 770 pounds (350 kg.) of coal; the carbonization period is approximately 4 hours so that each compartment of the retort setting, corresponding to one cage, has a throughput of 1 ton of coal per 24 hours. Since the complete retort setting has any number of carbonizing compartments, it has offtake pipes for the gases and vapors

leading to by-product recovery equipment; the setting can be heated with any desired quality of gas or, if necessary, with waste heat from adjoining high-temperature-carbonization gas retorts or coke ovens.

One modification of the Berg process for noncoking coal is to use a simple type of sheet metal container instead of the cage of trays; the container is filled by the charges and lifted in and out of the setting as described above. A third variation is especially intended for combined low-temperature carbonization of noncoking coal and combustion in conjunction with a steam boiler plant. For this purpose a simple type of vertical, continuous, externally heated, steel plate retort is used, operated adjacent to the boiler plant.



BERG PLANT AT THE HEIDENAU GASWORKS NEAR DRESDEN

The hot carbonized fuel is discharged direct from the bottom of the retort setting into a closed conveyor which takes it into closed hoppers in front of traveling grate stokers used for operating the boilers. By this means the fuel does not come into contact with the air and take fire, and little sensible heat is lost.

The general principle of separate low-temperature carbonization in conjunction with combustion chambers is claimed to have a number of practical advantages over the more usual method of combining the retort setting and the combustion chamber into one self-contained integral installation. Thus the retorts are operated independently of the boilers, and, since there is a considerable fuel reserve in both the retorts and the closed hoppers, the carbonization can be carried out under the best conditions without the difficulties represented by variations in steam demand and reductions in the efficiency of carbonization. On the other hand, separate retorts mean considerably more ground space and additional complications in the shape of the closed conveyors. So far as can be ascertained, no Berg plant of this type has been operated on a commercial scale.

Coalite Process

Great progress continues to be made with the Coalite process controlled by Low Temperature Carbonisation Ltd., of London. At present there are four large commercial plants in continuous operation, at Barugh (near Barnsley), the Askern Colliery (near Doncaster), the East Greenwich works of the South Metropolitan Gas Company (London), and the Bolsover Colliery (near Chesterfield); a total of approximately 10,000 long tons of coal is carbonized each week.

The present Coalite process consists in the low-temperature carbonization at about 1110° F. (600° C.) of washed

bituminous coking coal smalls in vertical, intermittent, externally heated, narrow-diameter, cylindrical, cast-iron or steel-alloy pipe retorts with 4 to 6 hours of carbonization.

Under these conditions 1 long ton of average bituminous coal, with 30 to 35 per cent volatile matter content, gives approximately 3 imperial gallons of crude light oil, 17 to 18 gallons of low-temperature tar (less 1 gallon of light oil fractionated), and 14 hundredweight (70 per cent) of graded low-temperature smokeless fuel (Coalite) of 10 to 12 per cent volatile matter content, in addition to a small amount of breeze. Further, there are 4000 to 6000 cubic feet of rich gas (600 to 700 B. t. u. per cubic foot) from which about 2 gallons of crude light oil are scrubbed. The basic principle involved is that the pipe retorts of narrow diameter resist the swelling action of the plastic charge and give internal compression to improve the quality of the smokeless fuel.

The new Bolsover plant began commercial operation in November, 1936, and consists of 288 retorts with a throughput of 500 long tons of coal per 24 hours; washed smalls (below 0.5 inch in size) are used which average 38 per cent volatile matter and about 12 per cent ash content. A large 2500-ton concrete storage bunker has been installed for blending purposes; it is divided into compartments for the different qualities of coal.

On March 9, 1937, it was announced that a fifth Coalite plant with complete by-product recovery equipment is to be erected in the South Wales area, with a capacity of 500 tons of coal per 24 hours (the same size as the Bolsover plant).

In view of the development of the Brennstoff-Technik process in Germany and the use of movable retort walls, it is interesting to recall that this method was adopted in 1919 by Low Temperature Carbonisation Ltd., in the form of special collapsible-plate retorts, invented by T. M. Davidson and operated on a large commercial scale at Barugh (near Barnsley) for several years.

These retorts were of the vertical, intermittent, externally fired, firebrick type; they had two vertical, perforated, movable iron plates inside at the center, forming two separate slabs of fuel between each retort wall and the corresponding plate. During carbonization these plates were extended to their maximum distance apart by means of a link mechanism fixed between them, so as to ensure compression of the plastic charge. On completion of carbonization, however, the link was operated and the plates were moved close together or collapsed, allowing the two slabs of fuel to fall out. However, this complicated but ingenious arrangement was eventually abandoned since it was too costly, and the original simple pipe type of retort was again used, with the addition of blending.

Delkeskamp Process

Because of the present importance of the carbonized briquetted type of fuel, attention has been again attracted in Germany to the Delkeskamp process, started about 1919 by the late Rudolf Delkeskamp.

This consisted mainly in the manufacture of briquets from coal, lignite, or any other material by using as a binder part of the material itself made into the true colloidal condition, followed by compression in briquet presses along the same lines as the manufacture of ordinary briquets with pitch or other binder.

When using coal for example, a small portion of the coal was pulverized and converted into the colloidal condition by long-continued grinding; the product so obtained was used as a binder in place of pitch or tar. These colloidal briquets could then be carbonized in any convenient type of retort, either with internal or external heating.

The position at the present time is somewhat obscure but, so far as can be understood, this interesting principle of mak-

ing briquets with a colloidal fuel binder has not been a commercial success and appears to have been abandoned. Also the Delkeskamp process is now under the control of the Deutsche Kollergenatoren und Ofenbau G., whose Kollergas process is described later in this paper; Karl Koller, a Hungarian engineer from Budapest, resident in Germany, was formerly associated with the Delkeskamp process.

The latest type of retort that has been evolved for the carbonization of any type of briquet, whether colloidal or otherwise, is somewhat complicated in character. It is a vertical, continuous, externally heated, cylindrical setting formed of a number of separate, small, narrow retorts or pipes 4.7 inches (120 mm.) in internal width, arranged in the form of a circle and constituting a composite retort with internal subdivisions, so that only a relatively small amount of briquets is treated in each of the pipe sections and thus breakage by the weight of the charge is avoided.

The carbonization temperature is 930° to 1110° F. (500° to 600° C.), and an experimental plant is said to be operating.

Haken Process

Attempts are being made in Germany by Kurd von Haken, a Russian oil technologist from Batum, now residing in Berlin, to redevelop the well-known principle of the carbonization and heat treatment of bituminous coal in the pulverized condition. This is an old idea that has been tried at intervals since about 1870, both in the United States and Great Britain; a large McEwen-Runge plant was operated on this principle for some time at the Lakeside Station, Milwaukee.

The Haken process consists in the carbonization of pulverized coal in suspension in a vertical retort or container by means of scrubbed gas on the internal heating principle, operating under a pressure of 15 to 20 atmospheres (220 to 294 pounds per square inch). It is claimed that under these conditions not only low-temperature carbonization but some degree of cracking and semihydrogenation results, with a consequent increase in the yield of light oil. A small experimental retort is stated to have been erected at a lignite mine in the Halle area, but this process is obviously in the early development stage and full details are not available.

Hinselmann Process

The Hinselmann Koksofenbau Gesellschaft, of Essen (Ruhr), the well-known by-product coke oven firm, controls this process; it is the invention of Otto Hellman, who developed a previous German low-temperature carbonization process on the tunnel oven principle, known as the Wibag but now abandoned.

Essentially the Hinselmann process is a special variety of tunnel oven process consisting in the low-temperature carbonization of bituminous coal of the coking variety in a series of cast-iron bottomless trays which are caused to slide through a horizontal externally heated retort or oven setting of complicated character. These trays are heavy, square, cast-iron plates about 3.20 inches (80 mm.) thick, which contain a large number of holes or perforations close together, in which small coal is placed. The trays are caused to travel one behind the other by means of a reciprocating piston device, through the oven setting which is arranged in a number of tiers of carbonizing compartments. Each of the latter has a smooth steel floor over which the trays slide, as well as very low steel sides and a steel roof. Heat is applied externally over the whole surface by means of gas firing.

As the trays travel, they are filled with coal from an overhead hopper, and the contents of each of the small compartments is gradually and progressively carbonized with considerable resistance to expansion of the charge, rising to a maximum temperature of 930° to 1110° F. (500° to 600° C.);

the gases and vapors evolved are taken off by means of suitable outlet pipes. At the end of the travel the coherent pieces of carbonized fuel are discharged in the shape of small cylinders. In general, the standard Hinselmann oven contains 3 to 6 tiers of these carbonizing pusher compartments—that is, 3 to 6 rows of the traveling cast-iron trays one above the other, with the corresponding externally heated flues and offtake pipes as well as recuperators.

A suitable scraper arrangement is now included for ensuring that each of the perforations in the trays is equally filled with coal; at one stage of the travel a series of cast-iron plates is placed on the top of the trays so as to increase the resistance to the expansion of the plastic charge and improve the quality of the carbonized fuel. At the end of the journey the trays pass out of the retort into the discharging portion of the setting, which has a perforated floor so that the carbonized shapes can be knocked downward through the floor of the bottomless tray; the empty trays pass on and are returned for recharging.

In February, 1937, at the Kaiserstuhl colliery, near Dortmund (Ruhr), a Hinselmann plant was completed with a capacity of 10 tons of coal per 24 hours; two smaller plants are being erected, one at the Breslau gasworks and the other at the Stuttgart gasworks. The experimental work was carried out in 1935 at the Viktoria colliery near Dortmund.

Kollergas Process

The Deutsche Kollergas- und Ofenbau Gesellschaft, of Berlin, is developing a low-temperature carbonization process known as the Kollergas; in basic principle it consists in the use of a vertical continuous retort heated by passing through the descending charge any suitable type of gas at the desired temperature of carbonization, such as 1000° F.

This company is a successor of the original Allgemeine Vergasungs Gesellschaft, of Berlin, which ceased business some time ago after having operated the A. V. G. processes. One of these processes consisted in the use of a simple type

of vertical cylindrical retort internally heated by passing gases through the charge at approximately 500° C. (930° F.), using waste combustion products from an adjoining furnace setting.

The other process, however, was of the combined carbonization and total gasification variety that is essentially a retort on the top of a producer gas generator in which the descending charge was carbonized in the upper part of the arrangement on its way to the generator below by the passage of the hot producer gas.

In general principle the present Kollergas retort is a vertical, mechanically continuous, cylindrical setting of comparatively wide diameter; in the center is a special inlet pipe device with upper louvers at the top passing up the charge for a certain distance from below to give uniform carbonization over the whole cross section of the charge.

Large-scale experimental work is being carried out at Spandau (near Berlin), and a considerable number of fuels have been investigated, including coal, lignite, lignite briquets, oil shale, and peat, as well as the special colloidal briquets of the Delkeskamp process.

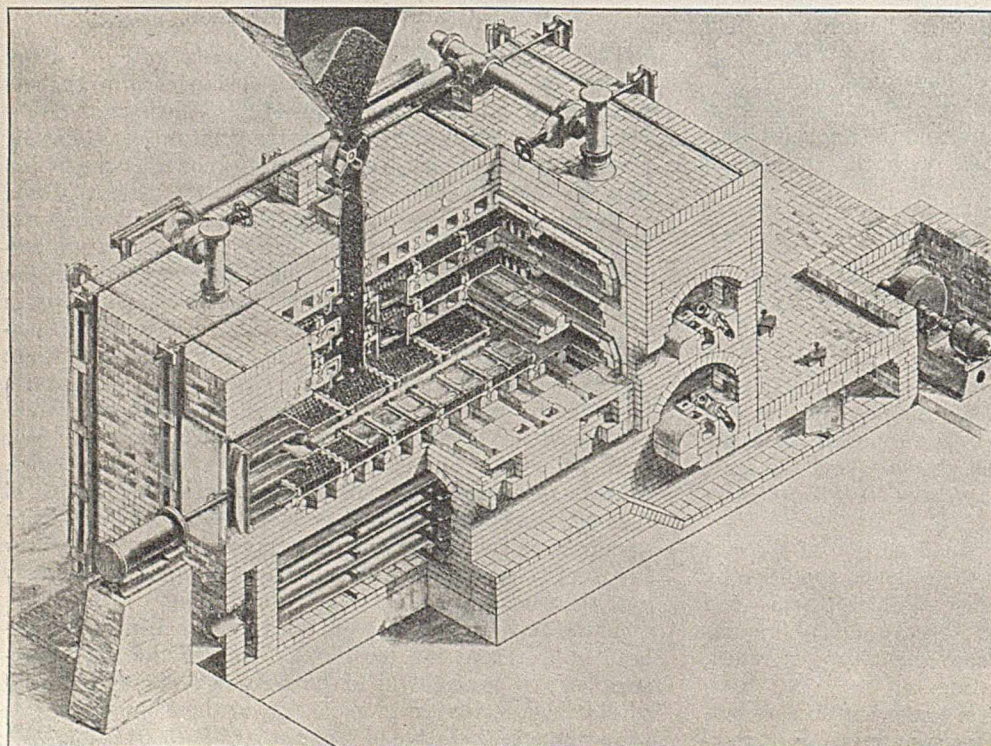
Krupp-Lurgi Process

This process was originated by the Friedrich Krupp A. G. of Essen about 1934, when a large-scale experimental retort was erected at the Helene colliery near Essen; with it is associated Fritz Muller, formerly in charge of the K. S. G. plant at Karnap-Ruhr. The Krupp-Lurgi process is also being developed commercially by the Lurgi Gesellschaft für Warmwirtschaft, Frankfurt, which has long been associated with low-temperature carbonization and operates another process known as the Lurgi, mainly used for lignite, with plants in both the United States and Canada. This process, however, operates along different lines; it has vertical continuous retorts with a louver arrangement in the charge, through which hot gases are passed to provide carbonization on the internal heating principle.

Essentially the Krupp-Lurgi process consists in the use of vertical, intermittent, externally heated steel retorts for the low-temperature carbonization of bituminous coking coal so that the swelling plastic charge is confined and considerable internal pressure develops to improve the quality of the fuel. The composite retort has a series of vertical, narrow, carbonizing compartments for the charge, alternating with heating compartments through which hot combustion gases are passed from gas burners; the whole arrangement is of metal, insulated on the outside, without brickwork.

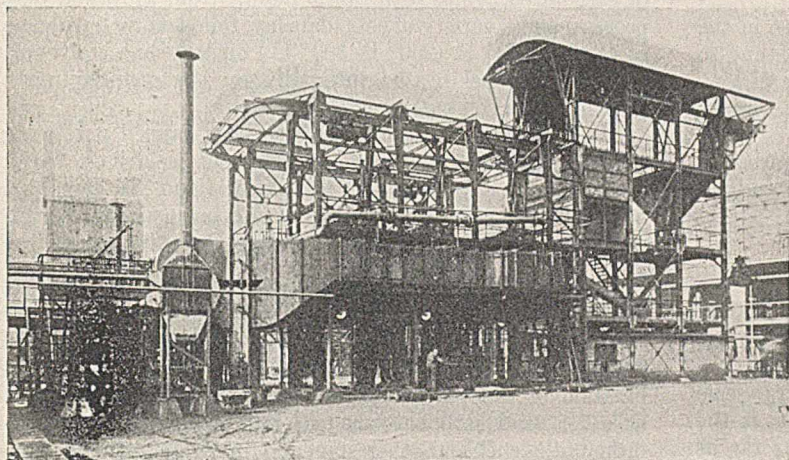
The coal is charged in from the top to the carbonization compartments, and, after completion of the heating, the residual smokeless fuel is discharged from the bottom; a vertical ram device can be provided if necessary on the top

DIAGRAM OF A THREE-TIER HINSELMANN LOW-TEMPERATURE CARBONIZATION OVEN



of the setting to assist the action. In contrast to the B. T. process, it is claimed that movable retort walls are not necessary.

In constructing the retorts, a special variety of heat-resistant Krupp steel is used, which is claimed to be proof against warping and deterioration, while the carbonization compartments have an interior width of 1.96 to 3.93 inches (50 to 100 mm.), depending on the type of coal. Further, the maximum temperature of carbonization is 1200° F.



KRUPP-LURGI PLANT AT THE AMALIE COLLIERY NEAR ESSEN

(650° C.), and presumably the heating period lasts about 4 to 6 hours. The setting is arranged so that no actual flames from the gas burners enter the alternate heating chambers but only the very hot gases from a separate combustion chamber.

The retort can be composed of any desired number of unit carbonizing compartments. Four Krupp-Lurgi plants have been erected in Germany, including the original experimental installation at the Helene colliery and another experimental plant operating in conjunction with a steam boiler at a power station, concerning which no information can be obtained. Neither of these plants is now operating since the development work has been completed.

Two commercial plants are running, one at the Amalie colliery in the Ruhr and the other at the well-known Heinitz colliery in the Saar. Each of these plants has a capacity of 35 tons of coal per 24 hours. Each plant consists of six composite retorts with six carbonizing compartments each, which are 6.5 feet (2 meters) long and 5.9 feet (1.8 meters) high; the internal width at Amalie is 3.5 inches (85 mm.) and at Heinitz 2.75 inches (70 mm.). The actual throughput of the Amalie plant varies between 35 and 40 tons of coal per 24 hours, and of the Heinitz plant, between 30 and 35 tons per 24 hours, because of the different qualities of coal used, including the moisture content.

These plants are operating without any mechanical pusher device at the top for discharging the solid fuel; this device will apparently not be required in most cases, depending mainly, however, on the degree of expansion of the coal in the plastic stage. The complete charge of a six-cell retort is 3307 pounds (1.15 metric tons), and the total yield of low-temperature fuel is approximately 80 per cent—that is, 16 hundredweight per ton (higher than the normal).

Further, the average yield obtained at the Amalie and the Heinitz collieries is about 8 per cent of tar by weight on the coal; the gas averages 110.0 cubic meters per metric ton, with a heating value of 843 B. t. u. per cubic foot (7500 kg.-cal. per cubic meter).

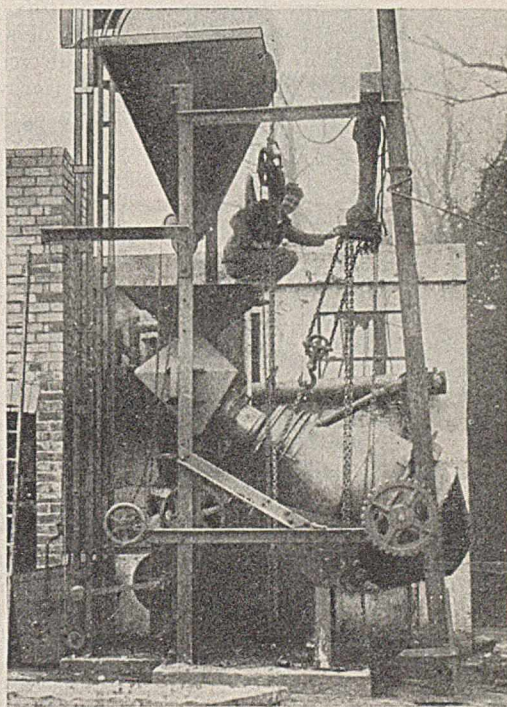
Morgan Processes

Considerable interest attaches to experimental work that has been carried out in England for several years by J. Stanley Morgan of Rodridge Hall, near Wingate (Durham), according to two general methods.

The first is intended for the operation of large water-tube boilers with traveling grate stokers. The method is to run the stokers of one boiler, for example, at about three times the normal speed so as to deliver incandescent coke from the end; this is approximately a low-temperature product with 10 to 12 per cent volatile matter content. This red-hot material is then mixed in a rotary mixer with raw coal in the proportion of 2 to 3 parts of coked fuel and 1 part of coal, so as to give rapid low-temperature carbonization in about 15 minutes, with treatment of the gases and vapors in a by-product plant. Then the coked fuel is burned on traveling grate stokers of adjoining boilers, together with the residual rich gas if necessary.

The mixing of coal or other products with incandescent solid material is an old idea, but the use of low-temperature fuel is new. This Morgan process has not yet reached the stage of actual operation on a boiler plant, the experimental work having been carried out on a small traveling grate operated in a setting without a boiler.

The second Morgan process is a new and ingenious method of partial gasification combined with low-temperature carbonization, using a special, rotary, closed container of cast



MORGAN EXPERIMENTAL ROTARY GENERATOR PLANT IN COURSE OF ERECTION AT RODRIDGE HALL, NEAR WINGATE, COUNTY DURHAM

The chain grate plant is in the building.

iron, lined inside with firebrick and something like a concrete mixer in appearance. This container is mounted on trunnions so that it can be tilted either backwards or forwards and is

also rotated at considerable speed by means of gearing, put in or out of action as desired.

The charge of coal is introduced and, after ignition, blown with a blast of air admitted at the bottom so as to form a charge of red-hot coke, the container being stationary. When the above stage has been reached, another charge of raw coal is added at the top and the container is rotated at considerable speed so as to mix the red-hot coke and raw coal completely. This results in rapid carbonization, with gases and vapors evolved, after which the container is stopped, blown again with air, and so on.

Under these circumstances there is a rapid increase in the amount of coke, and the container is stopped from time to time, tilted, and discharged; the very large volume of low-grade gas evolved is burned under boilers or other furnace settings along with the coke.

This process has not reached the commercial stage, although a large-scale carbonizing generator is being operated and the results are stated to be satisfactory.

Otto Process

The German firm of C. Otto, of Bochum (Westphalia), well known for its work in high- and medium-temperature coke-oven plants, has been working since early in 1935 on a process for low-temperature carbonization; two large-scale experimental retorts are understood to be operating at the Otto firebrick works at Dalhausen (Westphalia). As far as can be ascertained at present, no other Otto plant has yet been installed.

The process consists in the use of vertical, externally heated, intermittent firebrick retorts which are rectangular in cross section; they operate along the same general lines as the usual high-temperature carbonization retorts but have a

series of cast-iron divisions inside which divide the charge vertically and transversely into a series of relatively narrow layers. The object is to increase the rate of heat transmission on the same lines as a number of other processes—for example, the Illingworth in Great Britain.

These cast-iron devices are removable and interchangeable; the actual carbonizing temperature inside the retort does not exceed about 985°

F. (530° C.), although the temperature of the external heating flues can be considerably higher. Further, the carbonization of typical coking bituminous coal smalls takes about 4 hours, giving a smokeless fuel of 11 to 12 per cent volatile matter content when using "gasflame" bituminous coal with 30 per cent volatile matter.

Pintsch-Weber Process

The chief German process in the field of combined carbonization and combustion for the operation of water-tube

boilers with traveling grate stokers is that of the well-known firm of Julius Pintsch A. G., Berlin. This operates on the integral principle with the retort forming part of the boiler setting and the carbonization throughput varying according to the steam demands; the descending charge is carbonized at about 1000° F. (538° C.) by passing part of the very hot combustion gases through it in an upward direction.

It is now proposed to operate the Pintsch process with briquets made by the Weber process. Ludwig Weber's invention dates from 1927 and consists in briquetting lignite or carbonized lignite with sulfite liquor (from the wood pulp process) and a variety of colloidal clay, followed by hardening at 482° to 572° F. (250° to 300° C.) on traveling conveyors in a long tunnel heated internally on the countercurrent principle with combustion gas.

Much experimental work has also been carried out, using the Weber briquets direct for producer-gas-driven motor vehicles as well as for steam locomotives and rail cars, as a competitor to coal and ordinary lignite briquets made without a binder in high-pressure "sausage" extrusion presses.

Pott-Broche Process

The invention of Alfred Pott and Hans Broche, of the Stinnes colliery group at Essen, is understood to be a combination of the partial solution of coking bituminous coal or other solid carbonaceous material in Tetralin (tetrahydronaphthalene) and other solvents (including low-temperature tar phenols), and then hydrogenation of the extracted products left when the solvent has been driven off.

Details are not easy to obtain, but the solvent action with Tetralin appears to be carried out at 605° to 750° F. (320° to 400° C.) in closed containers; the extracted bituminous material is hydrogenated at 750° to 785° F. (400° to 420° C.) for 3 hours at 100 atmospheres (1420 pounds per square inch) pressure in the presence of a hydrogenating catalyst such as molybdic acid.

With average high-grade bituminous coal in the pulverized condition, it is claimed that approximately 70 per cent of the total weight dissolves in the Tetralin; the product obtained after driving off the solvent is more suitable for hydrogenation than the original raw coal.

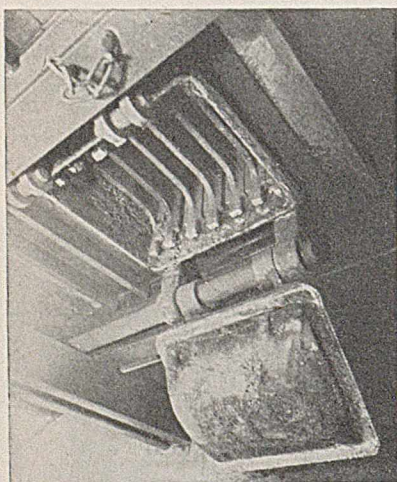
As far as can be determined, the action of the Tetralin is partially chemical and may be termed partial hydrogenation. Another claim is that the solid bituminous extract, which is almost entirely free from ash (less than 0.1 per cent), is suitable for use in Diesel engines after mixture with coal tar or other liquid fractions.

Recently a separate company was formed in Germany to develop the Pott-Broche process, in which the I. G. Farbenindustrie A.-G. is interested; a semicommercial plant with a capacity stated to be 48,000 tons of coal per annum is being or has been completed in the Ruhr, although information is lacking.

The main obstacle to the highly important pulverized coal engine or turbine has been ash, and the long-continued work of Walter Trent in this field with his Amalgam process is familiar. Still another claim in connection with the Pott-Broche process is that the extracted material from bituminous coal can be used direct in the solid pulverized condition for internal combustion engines or turbines because of the absence of ash. The Pott-Broche interests are stated to be associated in this connection with Pawlikowski and his work on the pulverized fuel engine, in which the I. G. Farbenindustrie A.-G. has long been interested.

Robinson Bindley Process

This process of synthetic liquid fuels from carbon monoxide-hydrogen mixtures at atmospheric pressure was



BOTTOM DISCHARGE DOOR OF THE RETORT OR CHAMBER OVEN OF THE OTTO PROCESS PLANT SHOWING THE VERTICAL PARTITIONS INSIDE THE RETORT

originated in 1932 and is controlled by Robinson Bindley Processes Ltd., of London. Generally a nickel (or cobalt) catalyst is used, and one of the main features is that the catalyst is supported in a framework of silica obtained by using special silicic acid esters. These are patented products made by Albright & Wilson Ltd., of Birmingham, and are utilized also for the protection of stonework and metal surfaces in electric ovens.

Another point is that blue water gas is used for the synthesis—that is, carbon monoxide and hydrogen in a 1 to 1 ratio; the gas is passed continuously through the nickel-silicon catalyst in containers maintained at about 374° to 410° F. (190° to 210° C.). The yield is stated to average 0.90 imperial gallon of crude oil per 1000 cubic feet of carbon monoxide-hydrogen mixture. It is a colorless product composed of a wide range of hydrocarbons from pentane up to wax, with 62.5 per cent distilling over up to 300° F. (150° C.). It is stated that the kerosene fractions can be converted into a range of lubricating oils by treatment with aluminum chloride to polymerize the olefins.

In comparison with the Fischer-Tropsch process, the main claims of the Robinson Bindley process are the superior strength and resistance of the catalyst and the better quality of the gasoline which has a higher octane figure and good anti-knock properties.

A small experimental plant, using 2000 hundredweight of gas mixture per 24 hours, has been operated since 1932 in buildings leased from the Epsom gasworks (near London), of the Wandsworth and District Company Ltd. In addition, a commercial plant is being erected at one of the collieries, near Coatbridge, of William Baird and Company Ltd., Glasgow; it should be completed at the end of 1937, with a capacity in the first section of 200,000 cubic feet of carbon monoxide-hydrogen mixture per 24 hours; some coke oven gas will also be used.

The scientific principles involved and the results obtained in connection with the Robinson Bindley process were described in British patents and in papers by Aicher, Myddleton, and Walker (1).

Stephenson Process

In a previous contribution (2) dealing with the carbonization of coal-oil mixtures, the writer gave a brief description of the Stephenson process, controlled by Coal and Allied Industries Ltd., of London, with a large-scale plant at Seaham Harbour, County Durham. At that time details were not available, but it was known that some form of carbonization of coal-oil mixtures was under consideration.

In the original British Patent (3) the process is described as the heat treatment of coal-oil mixtures under high pressure in long, horizontal, concentric steel tubes. Apparently this method has never been operated at Seaham Harbour, whatever may have been the case at the original small experimental plant at Slough, Windsor (near London), originally used for the Dvorkovitz process.

The process actually operated at Seaham Harbour and confirmed in recently published patents consists merely in heating a mixture of pulverized coal and oil in shallow steel trays, using a firebrick setting with externally heated steel containers into which the trays are passed, with the usual claim that heating of coal-oil mixtures results in a larger yield of light oil and lower boiling point fractions than would be the case if the coal and the heavy oil were heated separately.

Also the plant at Seaham Harbour, stated to have cost over £200,000 (\$1,000,000), does not seem to have reached the stage of continuous commercial operation; towards the end of 1936 it was partly destroyed by fire. It has since been

repaired but little success has been attained. At the beginning of January, 1937, a meeting of the shareholders of Coal and Allied Industries Ltd. was called to consider the voluntary winding up of the company because funds had become exhausted. Various expert reports have also been made on the possibilities of operating the plant at Seaham Harbour by some other carbonization process, but at present the position is obscure.

Some of Stephenson's more recent patents relate to the old idea of extracting unsaturated compounds, such as ethylenes, from rich gases for conversion into solvents, and also of obtaining such low-boiling compounds in the liquid condition by intensified refrigeration. At one time this principle also occupied the attention of Stanley Morgan and was operated on a commercial scale about twenty years ago by the Fellner & Zielger low-temperature carbonization process at Frankfurt, Germany; one of the products was liquefied, very low-boiling hydrocarbons sold under the name of Gasol for welding and similar purposes.

Suncole Process

What is now generally called the Suncole process in Great Britain is a modified L & N or Nielsen process, controlled by a company called British Coal Distillation Ltd., of London, which took over the L & N large-scale experimental plant at the New Lount colliery, near Leicester, formerly owned by L & N Leicestershire Ltd.

The L & N process, also known by a number of other names, consisted in the low-temperature carbonization of coal or other material in long, slightly inclined, mechanically continuous, rotary cylindrical retorts by internal heating of the charge; a heated gaseous medium at about 900° to 1000° F. (485° to 540° C.) passed through the charge on the counter-current principle.

After attracting public attention for a number of years, partly because of the formation of a considerable number of different companies in various countries, the L & N process was abandoned, and the only plant that ever seems to have been operated on a semicommercial scale (at the New Lount colliery) was taken over by the present company, British Coal Distillation Ltd.

The present process is the carbonization of cheap coal of high ash content in rotary cylindrical retorts with internal heating and direct passage of the very hot solid fuel into a solution of higher gravity than water, such as sodium chloride, with the claim that a considerable part of the ash is automatically separated by gravity flotation. The resulting smokeless fuel is then briquetted with a binder, such as pitch, and carbonized in a simple type of flat plate retort heated externally from underneath, with the formation of smokeless carbonized briquets, known as Suncole.

The main claim is that, because of the use of such cheap and inferior coal, the relatively costly method of operation represented by two carbonizations in succession, as well as briquetting, can be made a commercial proposition. However, except for the New Lount plant which is supposed to be able to carbonize 100 tons of coal per 24 hours, no Suncole plant has yet come into operation, although many statements have been made to the effect that a number of plants were to be erected in Canada.

Literature Cited

- (1) Aicher, Alfred, Myddleton, W. W., and Walker, James, *J. Soc. Chem. Ind.*, 54, 313-20T (1935); Myddleton, W. W., and Walker, James, *Ibid.*, 55, 121-4T (1936).
- (2) Brownlie, David, *IND. ENG. CHEM.*, 28, 629-35 (1936).
- (3) Stephenson, H. P., British Patent 431,063 (July 1, 1935).

TEXTILES GO CHEMICAL

JOSEPH F. X. HAROLD

W. M. Grosvenor Laboratories, Inc., New York, N. Y.

THE treatment of textile fibers with chemicals is probably as ancient as their earliest use. As a domestic art the use of textiles is so ancient that it is rooted in the most elemental words of our language. Even before the invention of the most primitive loom, chemically processed fabrics were probably employed. These were of the felted type which are still made by the nomads of the Gobi Desert. Wool fiber, pounded between stones wet with hot water to which wood fire ashes are added, makes a warm fabric to serve as clothing or headgear.

From the remotest time woven fabrics have been submitted, before or during use, in processing or laundering to the physical or chemical action of added auxiliary substances. Some oil, tallow, starch, or soap favored the spinning, weaving, finishing, or cleaning. These or a host of other substances endowed the final fabric or fibers with desirable weight, surface, feel, color, luster, or density, or they facilitated by their temporary presence the several operations of textile processing even if they were removed from the final fabric.

In many of these processes developed by long-practiced art, the fabric became a mere basket for the chemical. Back-filled cotton shirtings, especially those for the Oriental trade, artificial leather, oil skins, linoleum, and weighted silks contained more chemical than fiber.

In the chemical processing of textiles, many and varied are the objectives. The manufacturer may wish to remove an undesirable quality or to accentuate a good one. He may wish to make a cheap fabric imitate an expensive one. He may seek to endow an old fabric with a new quality it never before possessed. He may so process a fabric that its virtues are more enduring or more cheaply maintained in use. He may render its colors more insensitive to light and washing, or its area undiminished by influences which formerly shrank it enormously. He may make it wear better, remain uninjured by the conditions of adverse storage, and proof it against the several agencies that war upon its usefulness. Indeed, somewhat anomalously, he may usefully destroy it.

Etching

Quite an art of a series of textile arts is built upon the destruction of chemicalized fabrics. A fabric may be woven of cotton and woolen yarns, and the cotton carbonized out or the wool dissolved out by caustic soda, leaving open places in the fabric. Drawn work can thus be imitated. Weak sulfuric acid, harmless to wool, will completely destroy the cotton on dry heating. A 5 per cent solution of caustic soda at the boil will completely remove the wool and remain inert to the cotton. A fabric similarly constituted is adapted to patterned effects of any design (20). Resists, or protective chemicals, are first printed in designs upon the mixed wool and cotton fabric (12); then on the attack of acid or alkali these selected places remain and form a pattern. Beautiful transparent velvets made of rayon pile and pure silk ground (4) are etched in design with this method. Indeed, this so-called etched art is used for the complete destruction of the fabric. In the lace and embroidery art it is desirable to stitch cotton embroidery upon a background which is destructible. Cotton backgrounds are treated with dilute oxalic acid solution. Such impregnated fabrics have but a short life on storage, but, if used promptly as back-

grounds in the embroidery art, they are easily converted to an impalpable dust by being heated in an oven at a temperature that has little effect on the superimposed embroidery (25). Cheap silk, wool, and flame-proofed nitrocellulose fabrics are similarly used. The backgrounds are removed from the embroidery, not by heat but by solution in caustic soda, in the case of the nitrocellulose fabrics, by organic solvents also (16).

Somewhat allied to this etched art in which fibrous matter is dissolved is a series of processes relying on the partial solution and spread of cellulose or cellulose esters in fabrics with a view to cementing or stiffening the component of yarns or adjacent fabric layers (10). Certain salts in solution, such as zinc chloride, cuprammonium, calcium sulfocyanide, etc., dissolve cellulose. The partial or surface solution of a fabric leads to such processes, involving what might be called "autogenous impregnation" of the fabric with its own substance. The antetype method in this art was the Willesden process (39) as applied to tenting, canvas, etc. Here the fabric was coated with a cuprammonium solution which dissolved the surface cellulose and filled the treated face of the fabric with a continuous skin or membrane of cellulose. The copper was then removed by a careful treatment with acid or was left in the fabric to give the canvas a resistance to mildew while affording a pleasing color as well. Two fabrics thus treated could also be cemented together by the dissolved cellulose if the union was helped by effective pressure (14). Shirting materials requiring no starching have been made in this manner.

In the collar art, inventors have interposed a liner (28) consisting wholly or in part of cellulose acetate or other ester, and by the use of solvents of the ester have cemented the outer faces of the collar or imparted permanent stiffness to them. Other patentees have used soluble cellulosic elements in fabrics or yarns which, on aftertreatment with solvents, yielded strength, luster, or stiffness to the product (22).

In the paper cellulose industry, the solubilizing attack of salt solvents such as zinc chloride is used chiefly for their plasticizing effect. The most varied shapes of vulcanized

fiber can thus be made. Imitatively, cellulose knit fabrics that can be distorted readily without rupture may some day be similarly produced as hat frames or as supporting cores for articles shaped from the new synthetic resin plastics.

Proofing against Destruction or Damage

The proofing of textile fabrics against various destructive or damaging influences is accomplished by chemical means exclusively. Water- and spot-proofing materials are of the first consideration. Usually slight treatments with water-proofing materials secure spot-proofing, but with certain surfaces as in kerseys, water-proofing to the extent of making the fabrics water-tight will not secure the fabric from spotting in a light rain. The materials here used are generally fats, waxes, etc., applied in organic solvents, water emulsions in single baths, or aluminum salts and soap applied by the two-bath method. For stiffer fabrics and more severe requirements, resort is made to rubberizing treatments, plasticized lacquers, and oilskin formulas. Generally accepted standards are lacking in the trade, and, except for the textile technologist, the distinctions between shower-, rain-, and water-proofness are hazy (1). The protection against the moth is accomplished by certain botanical chemicals derived from the cube or derris root, silicofluorides, and certain synthetics that have proved of service (2). Mildew is under good control with

both inorganic and organic inhibitors. Some metallic salts were found to stimulate or stop the growth of spores according to the amount of metal present. It is known that certain materials used in finishing (the starches especially) afford breeding and feeding ground for spores, and that heat, dampness, and dark promote mildew.

Flame-proofing treatments involve chemical salts that give off flame-quenching vapors, that deliquesce, or that fuse readily and thus surround the fiber with an air-excluding film. Boric acid, borates, and ammonium salts such as the phosphate and sulfate, are of great value in this connection. Laundry-fast flame-proofing agents depend on insoluble stannates and tungstates for their effectiveness (36).

Many years ago a certain desirable stiffness and water-proof character were communicated to silk goods by weak solutions of gum dammar, copal, etc., in organic solvents. Now artificial resins of the vinyl, acrylate, phenol-formaldehyde, and urea-formaldehyde types are similarly employed. Some of these resins can be so employed below the amount necessary to secure water-proofness and are found to communicate a creaseless quality (44) to sheer goods, neckties, draperies, dress fabrics, linen garments, etc., without disturbing in any way the natural "hand" of the fabric.

Chemical dressings and impregnations of fabrics are frequently used where a complete filling of the texture is desired, where the fabric is to be rendered more dense and close-

woven in appearance without shrinking, or where a flat, smooth, and unbroken level is desired. Thus, assisted by printing and embossing machines, patent and artificial leathers are made. Here the web of the fabric is the base of compounds containing oxidizing oils, lacquer solutions, and fillers. Chemicals may substitute both starch and filler. Cellulose esters in organic solvents, alkali-soluble cellulose ethers (29), or viscose solutions may be used to impregnate or resurface the fabric. Shade cloth, wall-map stock, table cloth, and similar articles are thus made. By multiple passages through stannic chloride and sodium phosphate solutions, silk is weighted. Here there

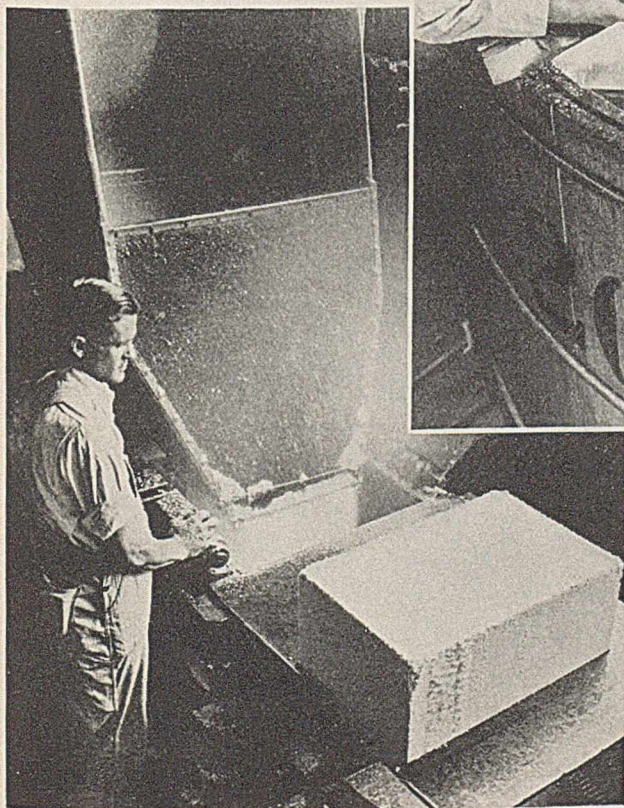
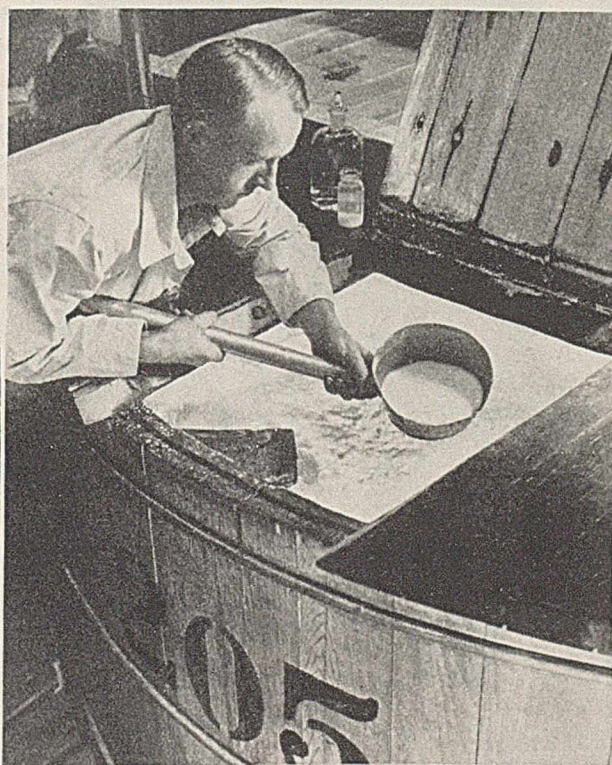
is no clogging of the mesh; the thread itself is weighted and expanded, and the improved appearance of the silk goods is due rather to this closing of the web than to the weighting itself.

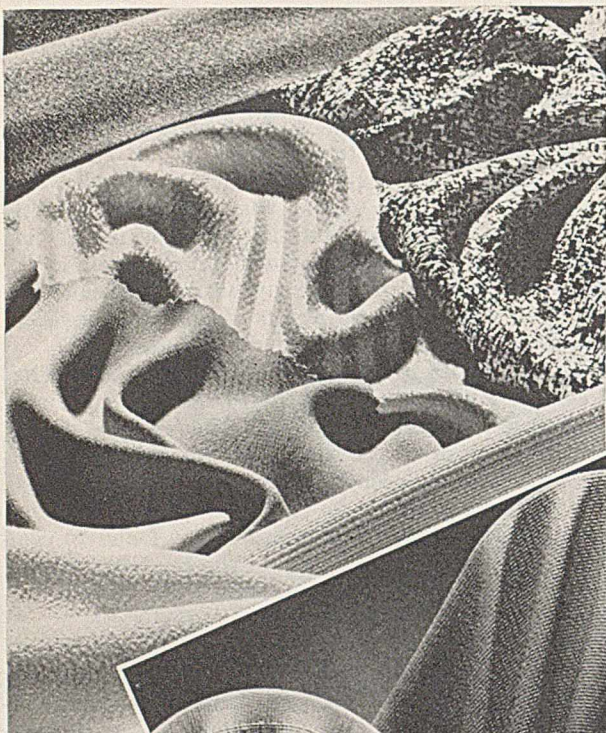
Beauty Treatments

Chemical treatments adding directly to the beauty of the fiber itself without any permanent addition of extraneous material were introduced by Mercer (32) or are implicit in his processes even if reduced to practice generations later. Mercer never saw mercerization. He noticed, however, the

(Right) WASHING FLAKED CELLULOSE ACETATE

(Below) PRESSED CAKE OF FLAKED CELLULOSE ACETATE





VARIED TEXTURES
FROM MANMADE
FIBERS



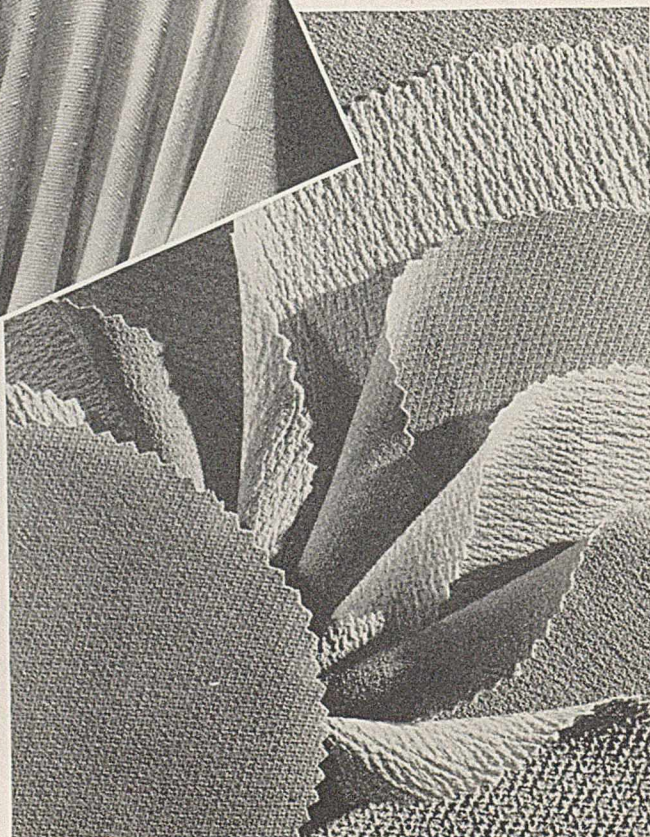
shrinkage induced by acid and alkaline treatments of cotton and the alteration in physical appearance of the individual fibers. Many years later Thomas and Prevost (42) devised means to prevent the shrinkage by tension, and Lowe (31) noticed the luster induced by caustic soda treatment under tension.

Later, with this past art as a guide, Swiss chemists (19) made exhaustive studies of the action of various acids on cotton goods at carefully controlled concentrations, temperatures, and times of reaction. Cellulose-dissolving salts were also studied in their effects. From this research came the well-known permanent or Swiss finish applied to fabrics of the type of organdie, batistes, etc., which require no starching but retain a trim stiffness throughout the life of the fabric. Similar processes applied to paper produce the so-called imitation parchment. Although these acid treatments are explained as producing "amylocellulose" because the fabric

under certain circumstances develops a material on the surface somewhat resembling the consistency and reactions of starch paste, this phrase is simply a statement of our ignorance in a formal but uninforming term. Now that the researches of Farr at the Boyce Thompson Institute (11) have shown the dual nature of cotton as a compound made up of a central chain of true cellulose particles cemented together by pectin-like matter, it is probable that these acid treatments represent a differential attack and that the pectin-like matter is liberated from the true cellulosic cores. It is probable also that to this disturbance of the quantitative relation of cementing material to the true cellulose or the structural rearrangement induced, the new properties of transparency and permanent stiffness are to be attributed.

To the future student of the history of chemistry it will probably appear as a marvel that, given the researches and discoveries of Mercer on cotton and the establishment of the industry of synthetic dyestuff within the same decade, so much advance has been made in the chemistry of dyestuffs and so little in our knowledge of the chemistry of fiber. The dyestuff industry is merely auxiliary to the textile industry.

Just before the Great War the value of textiles produced in America was one thousand times greater than that of the dyestuffs contributing to their use and sale. Yet the German dyestuff industry was the patron, support, and stimulus of practically all the organic research which gave that country its former primacy and leadership in chemistry. The skilled organic chemist could predict the synthetic or decomposition



products produced by the action of acids, alkalies, or reactive salts on the most complicated organic compounds. Yet the fibers of commerce were less recognized as chemically reactive entities than were the reagent bottles and were regarded, like the bottles, as mere recipients.

We know that the enclosing sericin of silk has to be removed to exhibit the full gloss of the fibroin beneath, although methods may yet be discovered for softening, modifying, and lustering the sericin so that this 30 per cent loss can be saved. We know that the sulfur-bearing compounds characteristic of wool are not necessary to its strength and structure, for careful treatment with cold caustic soda at 80° Tw. desulfurizes the fiber, yet gives it added strength and luster. The effect of tension in this treatment has not yet been studied. How much of the agglutinating matter surrounding the true cellulose in cotton can be removed and what advantages or new properties will reside in cotton so treated, we do not yet know. Yet these are elementary inquiries and are largely about matters of physical change. The use of the chemical entities of the fibers in their processing without destruction of form is almost unknown ground. The use of the amido groups in wool in "self-dyeing" with diazo dyes, the direct nitration of fabrics for filter cloths (35) or in the making of soluble lace backgrounds, and the combining of the acetate radical in cellulose acetate to form part of the dyestuff which colors it, constitute about all that has been done along this line and have led to commercial use only in the lace art.

The dyestuffs of today leave little to be desired. The cheapest of garments can be seen drying on the domestic clothes-lines of the country in full sunlight; a score of years ago no housewife would dare dry them except in the shade. Textile and testing associations have set standards and norms of fastness, wear, and resistance to shrinkage so that the just demands of the consumer can be met by the textile manufacturers.

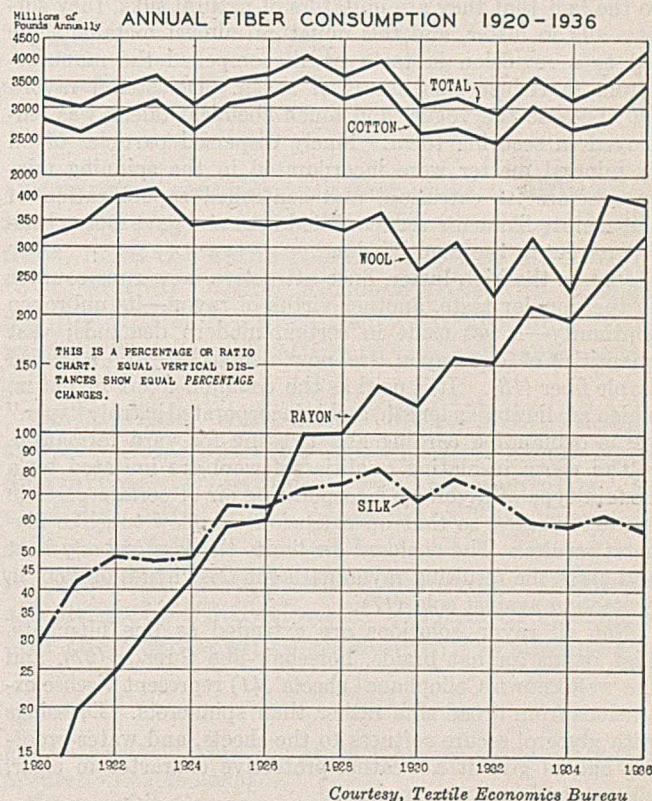
The dyestuff concerns have used their best scientists in perfecting textile auxiliaries as well as colors. Soap, that most important article of the dyehouse, has been improved upon, and better detergents and wetting-out agents are available which are insensitive, as soap is not, to acids and hard water (3, 8, 15, 23).

Artificial Fabrics

One of the objectives of the textile manufacturer may be to make a fabric look like the product of a more expensive fiber. As the cheapest of fibers, affording thus the best and most profitable differential, cotton goods have long been treated to look like linen, wool, or silk.

The mercerizing process induces a high luster in cotton goods. They are steeped in cold concentrated caustic soda and are kept under tension during the removal of the soda and drying. Acid lustering is also possible. A warm and woolen-like feel is imparted to cotton goods when treated with nitric acid at proper concentration and temperature (38), especially if the acid contains certain desirable additions. Not always is the cotton treated to have the aspect and feel of wool, but it is sometimes altered in order that it may dye like wool or that its chemical character may be so superficially changed that it resists the influence of the regular cotton dyestuffs. Cotton treated with protein bodies is called "animalized" (21) and dyes like wool. Cotton treated to resist dye is called "immunized" (5). Linen effects on cotton are not usually secured by chemical means (19) but are brought about by special spinning and fabric finishing to simulate the flatness and low twist of linen yarns. The same chemicals that produce the Swiss or permanent finish give cotton a wool-like feel, but their concentration is dissimilar and the degree of tension is markedly different during treatment (18, 24).

The chief triumph of chemistry as applied to the textile art is in the making of the synthetic fibers, rayon, and cellulose acetate fibers. Here cellulose or cellulose esters are reduced to thick, viscous solutions and in this condition extruded continuously through fine orifices and solidified by drying or coagulation. The first of these fibers was the nitro- or collodion silk of Chardonnet (6). It differs from



the others in being brought to perfection by the genius of the inventor, whereas the subsequently discovered rayons involved many fortunes in ruin before they were on a firm commercial basis of successful production. In the Chardonnet process a solution of nitrocellulose in organic solvents, after extrusion as a group of fine filaments, is solidified by warm air and, after denitrication by reducing agents, constitutes a regenerated cellulose from which all but traces of nitro compounds are completely removed. It is thus completely safe.

The viscose rayon (7) which makes up more than 80 per cent of the world's rayon production is made by converting spruce paper pulp to a soda cellulose and combining this with carbon disulfide to a viscous, molasses-like solution of cellulose xanthate—a cellulose ester. After proper ripening, this solution is similarly extruded through the fine orifices of a spinneret, a constellation of hairlike openings in a platinum plate, and the fine resulting filaments are led into an acid coagulating bath and thence wound onto reels, washed, and dried. The xanthate ester being thus decomposed, a continuous bundle of filaments of regenerated cellulose results. Cuprammonium or Bemberg (9) rayon derives from a viscous solution of cotton linters in the deep blue solution containing copper and ammonia known to the chemist as Schweitzer's reagent. Acid baths reprecipitate the dissolved cellulose as it is similarly extruded through spinnerets. It affords the finest filaments. Cellulose acetate fiber (34) differs from the other rayons in that it is not a regenerated cellulose but is filamented as an ester and is not thereafter hydrolyzed or saponified. Its dyeing properties are therefore sharply

different from the regenerated cellulose rayons, and it requires special treatment in the dye bath with regard to temperatures of dyeing and character of dye. Although it takes the basic dyes to a limited extent, it is usually dyed with special dyestuffs, insoluble in water but capable of being dispersed in an extremely fine state of division in aqueous dye liquors by the use of emulsifying agents.

While the rayons and acetate fibers owe their chief vogue to the fact that they are imitators of natural silks, they surpass silk in luster, and this unnatural almost metallic shine led to a revulsion in taste which compelled the manufacturers to reduce this excess of sheen. Delustered rayons (40) became the vogue, and much chemical talent was employed in securing them. Finely dispersed particles of oil or mineral matter were incorporated in the spinning mixture before its extrusion, and controlled saponification of the acetate filaments reduced the luster and gave more pleasant effects in the final fabrics.

Just as the high luster, once attractive, now runs counter to the popular taste, another virtue of rayon—its unbroken continuity—is set aside in certain modern demands; vast quantities of cut rayon are now demanded—the so-called staple fiber (13). It is used as the common fibers of nature which are limited in length, and is incorporated in truly "spun" yarns demanding carding and twisting for yarn formation.

The warm insulating qualities of wool are imitated by a certain type of rayon by incorporating air or certain gases in the rayon mass, so that on extrusion a hollow tubelike filament results. The enclosed air limits the loss of body heat and gives the resulting rayon garment the virtues of wool in protection against cold (17).

Not all rayon solutions are extruded as fine filaments. Flat bands for hat braids, horsehair-like threads (27), and the well-known Cellophane sheets (41) represent viscose extrusions from broad slits rather than spinnerets. Dressings with glycerol secure softness to the sheets, and water-proofing agents give it a weather-protective character in cigar, cigaret, and candy wrappings.

Artificial silk and wool, chemically (43) as well as physically imitative of the real article, are made by the extrusion of protein solutions through rayon spinning machines. Gelatin silk, artificial silk made from solutions of silk waste (33), and artificial wool from casein are the subjects of patents; the artificial wool has been rather recently promoted in Italy (26).

Chemical aftertreatments of rayons have been resorted to to increase their strength, and some of them have been given tensile strength much beyond that of natural silk (30). Unfortunately the elasticity is poor. The usefulness of a textile fiber demands both strength and elasticity.

Much is being done in developing fibers from synthetic resins that shall have the required strength and elasticity for enduring wear. It is highly probable that in the near future we shall have rayons that are truly synthetic, that do not require the destruction of wood or cotton fibers to make fibers, and that rely on no vegetable or animal sources but are chemical in all their phases of manufacture.

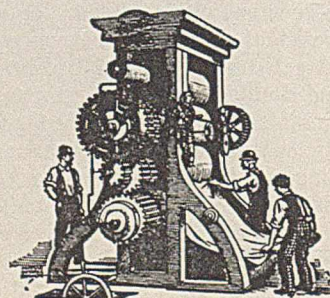
Near the turn of the century Ratignier and Pervilhac (37) devised a method of making continuously a web simulative of the woven fabric known as tulle, a sort of millinery veiling. Viscose or other rayon-making solution was poured upon a copper cylinder in which a mesh was deeply engraved. The cylinder rotated past a scraper knife and met a coagulating spray. On further turning, the weak but continuous net was doffed, carried off on a belt, washed, and dried. A good volume of business was done in the article. By suitable engraving of the cylinders the most attractive patterns in fabrics with lace and embroidery effects were possible, and by incorporating conductive graphite in the rayon mix-

ture the entire fabric could be plated until the textile was a firm, metallic mesh of any weight desired or of any metallic composition. One can well imagine the beauty of Irish or Valenciennes lace given the adornment of three or four contrasting metals and a new endurance and solidity for fire or window screens, wall dadoes, or wainscoting. When the ideal synthetic resin comes, there may be the suggestion of the fabric of the future, made on the instant, as fast as textiles are printed. It would need no loom with its troublesome tedious beaming, drawing in, arranging the box motion, or cutting the Jacquard cards. With the speed of the photo-engraver which the American hunger for news has rendered unsurpassed, milady's dress would not only boast of beauty but of the actuality of news itself. She would be clothed not merely in the *dernier cri* but in the 9 o'clock edition.

Literature Cited

- (1) Am. Assoc. Textile Chemists and Colorists, Yearbook 1935-6, page 155.
- (2) Back, E. A., U. S. Dept. Agr., *Farmer's Bull.* 1353 (1923).
- (3) Bertsch, H., U. S. Patents 1,993,431 (March 5, 1935); 2,007,492 (July 9, 1935).
- (4) Cadgene and Jeandros, *Ibid.*, 1,513,370 (Oct. 28, 1924).
- (5) Cassella, German Patent 346,883 (1923).
- (6) Chardonnet, French Patent 165,349 (1885).
- (7) Cross, Bevan, and Beadle, British Patent 8700 (1892).
- (8) Daimler and Platz, U. S. Patent 1,881,172 (Oct. 4, 1932).
- (9) Despaissis, French Patent 203,741 (1890).
- (10) Dreyfus, C., U. S. Patent 1,828,397 (Oct. 20, 1931).
- (11) Farr, *Am. Dyestuff Repr.*, March 22, 1937.
- (12) Gieseler, H., U. S. Patent 1,425,520 (Aug. 15, 1922).
- (13) Girard, French Patent 438,131 (March 7, 1912).
- (14) Göncz, C. de, U. S. Patent 1,661,880 (March 6, 1928).
- (15) Guenther and Hausmann, *Ibid.*, 1,932,180 (Oct. 24, 1933).
- (16) Harold, J. F. X., *Ibid.*, 1,835,866 (Dec. 8, 1931).
- (17) Hartogs, German Patent 247,418 (July 13, 1911).
- (18) Heberlein, U. S. Patents 1,392,264-5 (Sept. 27, 1921).
- (19) *Ibid.*, 1,439,512-21 (Dec. 12, 1922).
- (20) Jegler, French Patent 318,427 (June 24, 1902).
- (21) *J. Soc. Dyers Colourists*, May 2, 1892, page 83.
- (22) Kennedy, A. L., U. S. Patent 590,842 (Sept. 28, 1897).
- (23) Killeffer, D. H., *IND. ENG. CHEM.*, 25, 138-40 (1933).
- (24) Klausner, O., U. S. Patent 1,285,738 (Nov. 26, 1918).
- (25) Krüsi, J., *Ibid.*, 337,687 (March 9, 1886).
- (26) Lanital, *Am. Dyestuff Repr.*, 25, 538 (1936).
- (27) Lehner, F., U. S. Patent 680,719 (Aug. 20, 1901).
- (28) Liebowitz, B., *Ibid.*, 1,968,409-10 (July 31, 1934).
- (29) Lilienfeld, L., *Ibid.*, 1,188,376 (June 10, 1916).
- (30) *Ibid.*, 1,989,099 (Jan. 29, 1935).
- (31) Lowe, British Patent 4452 (1890).
- (32) Mercer, *Ibid.*, 13,296 (1850).
- (33) Millar, A., U. S. Patent 611,814 (Oct. 4, 1898).
- (34) Mork, Little, and Walker, *Ibid.*, 712,200 (Oct. 28, 1902).
- (35) Newton, British Patent 1770 (1893).
- (36) Perkin, *8th Intern. Congr. Applied Chemistry*, 28, 119 (1912).
- (37) Ratignier and Pervilhac, French Patent 384,934 (1908).
- (38) Schwartz, C., U. S. Patents 1,400,380-1 (Dec. 13, 1921).
- (39) Scoffern, British Patent 1744 (1859).
- (40) Singmaster, J., U. S. Patent 1,725,742 (Aug. 20, 1929).
- (41) Société anon. cellophane, British Patent 159,868 (April 19, 1922).
- (42) Thomas and Prevost, German Patent 97,664 (July 30, 1898).
- (43) Todtenhaupt, F., U. S. Patent 836,788 (Nov. 27, 1906).
- (44) Tootal Broadhurst Lee Co., Ltd., Barrett, F. L., and Foulds, R. P., British Patent 200,881 (April 13, 1922).

RECEIVED March 5, 1937.



Permeability of Organic Polysulfide Resins to Hydrogen

THERON P. SAGER

National Bureau of Standards, Washington, D. C.

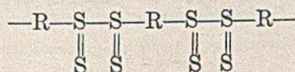
The ability of films of organic materials to impede the passage of gases is important in connection with balloon and airship fabrics, where thin films and large surfaces are encountered. The tendency for hydrogen and helium to diffuse readily through rubber has been the incentive for the study of a large number of film-forming materials. Among these the product resulting from the reaction between dichloroethane and sodium polysulfide attracted particular interest since it not only exhibited a high impedance to hydrogen but possessed other desirable physical characteristics as well. A more comprehensive study indicates that other products, resulting from

the general reaction between organic dihalides having $-\text{CH}_2\text{Cl}$ terminals, and metallic polysulfides, have the same relatively low permeability to hydrogen. Data indicate that the lowest permeabilities are obtained with products containing 4 atoms of sulfur in the primary molecule.

Comparison with films of natural rubber shows that for both the disulfide and tetrasulfide derivatives, a much lower permeability is obtained with these products. The permeabilities of fabrics coated with both derivatives indicate the same relative behavior. Factors affecting the limitations of weights of coatings and the permeability to helium are discussed.

A CHARACTERISTIC of balloon and airship fabrics which is of prime importance is that they shall be gas-tight or nearly so. The inherent tendency of hydrogen and of the more costly gas helium to diffuse through thin membranes of rubber provides the incentive for the study of the behavior of a large number of film-forming materials in a search for a more satisfactory material. Considering all of the requirements involved in this application, the permeability of the group of synthetic polymers which are characterized by elastic extensibility has been of particular interest.

The general reaction between organic dihalides with $-\text{CH}_2\text{Cl}$ terminals and inorganic polysulfides yields products which in many cases are characterized as rubber-like. Martin and Patrick (3, 4) suggested that the structure of the polysulfide resins is that of long-chain polymers in which the radicals are connected through disulfide linkages and represented as $-\text{R}-\text{S}-\text{S}-\text{R}-\text{S}-\text{S}-\text{R}-$. According to their hypothesis, any additional sulfur in the material in excess of that required to provide the disulfide linkages is believed to be coordinately linked to the sulfur comprising the disulfide linkages. The structure is represented as



with the added possibility that the coordinately linked sulfur may be in a *trans* rather than a *cis* arrangement. The radical may be derived from ethylene or one of its homologs, or it may be obtained from a reactant containing an ether group, a sulfide group, or an unsaturated group. It is of interest particularly in connection with the present discussion that certain of these products exhibit elasticity both when the amount of sulfur is confined to that representing the disul-

fide linkages and when the primary molecule contains sulfur in excess of these linkages.

What is often given as the specific example of the formation of this type of plastic is the product obtained when the reactants are dichloroethane and sodium polysulfide. Shortly after the addition of this material to the growing list of synthetic plastics, a compound containing this material was applied to a closely woven fabric by calendaring. The weight of coating was 5.2 ounces per square yard (176 grams per square meter). The permeability to hydrogen of this fabric was found to be 0.014 cubic foot per square yard (0.5 liter per square meter) per 24 hours. The low permeability of this material can be appreciated more fully when it is stated that a fabric coated with the same weight of a rubber compound would have a permeability of as much as twenty times this value.

There were, however, several objections to the use of the polyethylene polysulfide product for this purpose. This material cannot be dispersed in suitable solvents and does not therefore adapt itself easily to application in the form of a plurality of thin films to fabric. A somewhat less important objection is its distinctive and unpleasant odor which made it undesirable for use on gas-cell fabric aboard an airship. With the extension of this general reaction to include other organic dihalides and the production of materials which are capable of being dispersed in solvents to form cements, their utility was greatly enhanced and their laboratory investigation rendered comparatively simple. The odor of these products is, moreover, much less offensive.

Experimental Method

The materials were prepared in a manner similar to the preparation of rubber cements; the resins were masticated on a differential speed mill and the compounding ingredients were

added on the mill. The compounds contained 10 parts of zinc oxide and 0.1 to 0.2 part of such accelerators as tetramethylthiuram disulfide and benzothiazyl disulfide. Thin cements were prepared by dispersing the compounds in β -trichloroethane. In the preparation of films unsupported by fabric, the cements were applied to regenerated cellulose sheeting which had not been coated with any moisture-proofing composition (5). After being cured in dry heat for 50 minutes at 130° C. (266° F.), the uncoated surface of the regenerated cellulose was moistened with water. The polysulfide films could then be removed without any appreciable deformation. In the preparation of coated fabrics, the cements were applied to closely woven balloon cloth by means of a small spreading machine. The curing conditions were the same as for the unsupported films.

The permeabilities were determined by means of a gas interferometer of the Rayleigh type. The apparatus and conditions of test have been previously described (1).

Permeabilities of Films Unsupported by Fabric

Table I presents the permeabilities to hydrogen obtained with unsupported films of different thicknesses. The organic polysulfide products represent the disulfide and tetrasulfide derivatives obtained from the reaction between 2, 2'-dichloroethyl ether and sodium polysulfide. Values obtained with rubber films of approximately corresponding thicknesses are included for comparison.

TABLE I. PERMEABILITIES TO HYDROGEN OF UNSUPPORTED FILMS

	Av. Thickness		Permeability		Specific Permeability
	Cm.	In.	L./sq. m./24 hr.	Cu. ft./sq. yd./24 hr.	
Disulfide derivative	0.030	0.012	0.6	0.018	12.5
	0.025	0.010	0.8	0.024	13.8
	0.017	0.007	1.4	0.041	16.2
	0.015	0.006	1.5	0.044	14.6
	0.011	0.004	2.2	0.065	16.8
Tetrasulfide derivative	0.033	0.013	0.2	0.006	4.5
	0.024	0.010	0.4	0.012	6.6
	0.019	0.008	0.6	0.018	7.9
	0.016	0.006	0.8	0.024	8.8
	0.009	0.004	1.2	0.036	7.5
Rubber	0.030	0.012	10.0	0.295	208
	0.025	0.010	14.2	0.419	246
	0.018	0.007	20.0	0.590	250

The results indicated sufficient uniformity to warrant the calculation of what may be called the "specific permeability," or the volume of gas passing through a unit area of a material of unit thickness in unit time. This was calculated by means of the equation:

$$P = Vd/At$$

where P = specific permeability
 V = hydrogen volume, cc.
 d = thickness, cm.
 A = area, sq. cm.
 t = time, min.

The values for the specific permeability of rubber are in close agreement with those obtained by Kayser (2) and Edwards and Pickering (1). The values obtained with both the disulfide and tetrasulfide derivatives are much lower than those with corresponding thicknesses of rubber, and those of the tetrasulfide product are consistently lower than those of the disulfide derivative.

Although the specific permeabilities of the disulfide and tetrasulfide derivatives are of the same order of magnitude, they are not constant. This would appear to indicate that permeability in the case of these materials is not a linear function of the thickness. A possible explanation for this deviation is that the permeabilities were determined with a slight excess of pressure on the hydrogen side of the test specimen (30 mm. of water) which in the case of thin films may have produced a small undeterminable reduction in thickness while under test.

Permeabilities of Coated Fabrics

It was previously observed that the permeability of a given weight of rubber of definite area is greatly decreased when it is spread on a corresponding area of cloth (1). It has also been noted that the thread count of the cloth exerts an influence (6). The permeabilities of fabrics of different thread counts, coated with the same weight of rubber, become lower as the thread count increases. The values given in Figure 1 represent the permeabilities obtained on a fabric coated with different weights of the two polysulfide resins which were employed in the determinations of the permeabilities of unsupported films. The cloth employed was that designated as HH balloon cloth, a square-woven cotton fabric with a thread count of 120 in both directions; the average weight of a square yard was 2.05 ounces.

The results indicate the same relative difference in the permeabilities of the two derivatives as was obtained in the examination of the unsupported films.

The effect of the supporting fabric upon the permeability is apparent when comparison is made with the values obtained for unsupported films given in Table I. For example, a film of the tetrasulfide derivative with a thickness of 0.009 cm. (0.004 inch) weighs about 4.6 ounces per square yard. When unsupported by fabric, this film has a permeability of 0.035 cubic foot per square yard per 24 hours. If this same weight of material is applied to fabric, the permeability of the coated fabric will be (according to Figure 1) about 0.008 cubic foot. Likewise, a film of the disulfide derivative 0.011 cm. (0.004 inch) in thickness weighs about 4.2 ounces per square yard and has a permeability, when unsupported, of 0.064 cubic foot. When applied to fabric, the permeability of the coated fabric is about 0.035 cubic foot.

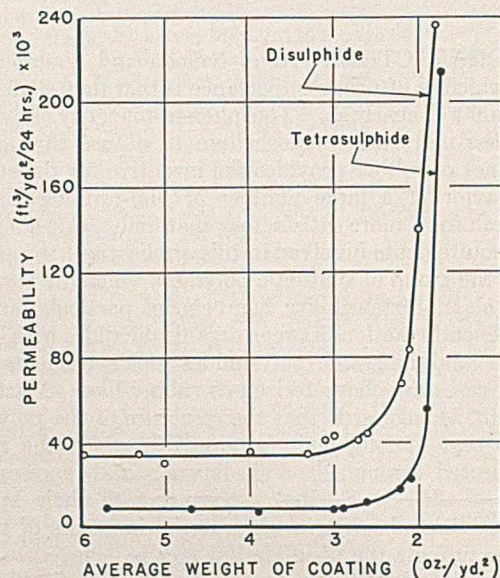


FIGURE 1. PERMEABILITIES OBTAINED ON A FABRIC COATED WITH DIFFERENT WEIGHTS OF TWO POLYSULFIDE RESINS

The specific gravity of the compound containing the disulfide derivative is 1.426 and that containing the tetrasulfide derivative is 1.547. The covering power of these compounds is not, therefore, as high as that of a corresponding compound of rubber, the specific gravity of which would be about 0.995. It is for this reason that, in the case of both derivatives, an abrupt increase in permeability occurs with decrease in weight of coating below about 2.6 ounces. As the weight of material applied becomes less, it becomes in-

creasingly difficult to cover the threads of the cloth uniformly with a continuous film. As the film becomes thinner, it is probable that fibers of the fabric will protrude through the film, thus affording channels for leakage.

That the permeabilities become practically constant within the range shown in Figure 1 would appear to be explainable on the basis of the difference in the permeabilities of films attached to fabric and those which are unsupported. Within the range shown in Figure 1, the permeability of the impregnated fabric and the thin film overlying it, represented by a weight of coating of about 2.8 ounces per square yard, is apparently the controlling factor in the behavior of fabrics carrying higher weights of coatings. In accordance with this view the permeability of a coated fabric would be lowered further only when the thickness of the overlying film became sufficiently great as to have a permeability lower than that of the raw fabric plus 2.8 ounces of coating. A fabric was prepared on which the total weight of coating was the equivalent of 15.5 ounces per square yard. The permeability of this fabric proved to be 0.003 cubic foot per square yard per 24 hours, a value considerably lower than those in the practically constant range in Figure 1. The amount of overlying film in excess of the 2.8 ounces per square yard representing the minimum constant value was 12.7 ounces, which corresponds approximately to a thickness of 0.029 cm. Comparison of the permeability obtained with this fabric with that of an unsupported film of about this same thickness indicates fairly close agreement. The behavior of a resin film overlying a base fabric coated with rubber is also explainable on this basis. The weight of rubber applied to the raw fabric was about 0.6 ounce per square yard. The permeability of a fabric coated with this weight of rubber is so high as to be negligible in its impedance value. The rubberized fabric was coated with 4.6 ounces per square yard of the tetrasulfide derivative. The permeability of the complete fabric was found to be 0.038 cubic foot per square yard per 24 hours, a value which is again in close agreement with that of an unsupported film of a thickness corresponding to this weight.

Effect of Pigmentation

It was to be expected that the addition of pigments to compounds containing polysulfide resins would raise the limits of weights of coatings with which very low permeabilities are obtainable, since the presence of pigments decreases the covering power. However, for a given weight of coating the addition of moderate amounts of carbon black did not produce a pronounced lowering of the permeability. This is indicated in Table II.

TABLE II. EFFECT OF CARBON BLACK UPON PERMEABILITY OF TETRASULFIDE DERIVATIVE

Formulas:	100	100	100	100	100
Tetrasulfide derivative	10	10	10	10	10
Zinc oxide	10	10	10	10	10
Carbon black	15	10	5	2	0
Weight of coating, oz./sq. yd.	3.2	3.4	3.0	3.4	3.4
Permeability, cu. ft./sq. yd./24 hr.	0.029	0.023	0.021	0.012	0.010

Permeability to Helium

Because of the accuracy with which the permeability to hydrogen can be determined, this gas is customarily employed in determining the permeability of balloon fabrics. Since helium is employed in lighter-than-air craft in this country as the lifting gas, it is of interest to note the relation between hydrogen and helium permeabilities of a polysulfide resin. A few measurements made on fabrics coated with different weights of coatings on fabric are as follows:

Helium	Hydrogen	Ratio, Helium to Hydrogen
Cu. ft./sq. yd./24 hr.		
0.006	0.009	0.66
0.011	0.017	0.64
0.014	0.023	0.60
0.009	0.013	0.66
		Average 0.64

The average ratio is in close agreement with that found previously for rubber (1).

Mechanism of Permeation

In a report which is largely concerned with the practical application of a material, the nature of the data does not warrant definite conclusions regarding the mechanism of permeation. It is possible that the passage of a gas through a material may be simply filtration through intermolecular spacings or, in highly permeable substances, an actual porosity, or it may take place by a process of adsorption of the gas on the surface followed by diffusion through the material. Under practical conditions, particularly with the heterogeneous compositions widely employed, both mechanisms may function. The behavior of the organic polysulfide resins may perhaps be explainable with either. In these resins the sulfur atoms are enormously large compared to the other constituents of the molecule. They are, in effect, linear polymers of sulfur atoms. From the viewpoint of simple mechanical phenomena, the intermolecular spacings of substances containing such large amounts of sulfur must be small and a high degree of impedance might be anticipated. The lower permeability of the derivative containing the greater amount of sulfur might be attributed to a greater structural density in this substance. On the other hand, these materials would be expected to be inert compared to a material such as rubber and hence would offer much less solvent action towards hydrogen. Concerning the relative behavior of the disulfide and tetrasulfide derivatives, it is to be expected that, as the ratio of the sulfur atoms to the remainder of the molecule is altered, changes in solubility relations would result which would be reflected in the relative permeabilities of these substances.

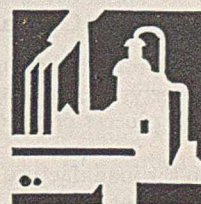
Acknowledgment

The information reported here was obtained in the course of an investigation conducted for the Bureau of Aeronautics, United States Navy Department. The interest of this organization and particularly that of Commander Garland Fulton is gratefully acknowledged.

Literature Cited

- (1) Edwards, J. D., and Pickering, S. F., *Bur. Standards, Technol. Paper 11* (1918); *Sci. Paper 16*, 327-62 (1920).
- (2) Kayser, H., *Wied. Ann.*, 43, 544 (1891).
- (3) Martin, S. M., Jr., and Patrick, J. C., *IND. ENG. CHEM.*, 28, 1144-9 (1936).
- (4) Patrick, J. C., *Trans. Faraday Soc.*, 32, No. 177, Part 1, 347-57 (1936); *Rubber Chem. Tech.*, 9, 373-82 (1936).
- (5) Sager, T. P., *IND. ENG. CHEM., Anal. Ed.*, 9, 156 (1937).
- (6) Sager, T. P., *J. Research Natl. Bur. Standards*, 13, 879-85 (1934).

RECEIVED May 18, 1937. Presented as part of the Symposium on Organic Plastics before the Division of Paint and Varnish Chemistry at the 93rd Meeting of the American Chemical Society, Chapel Hill, N. C., April 12 to 15, 1937. Publication approved by the Director, National Bureau of Standards.





FILTERING

In order to safeguard against possible dirt and dust particles entering the material, the plastic colloid is forced under 3000 pounds hydraulic pressure through a fine 250-mesh wire screen and cloth filtering medium. After this operation the filtered plastic is returned to a machine similar to the regular mixing machine where it is further mixed under vacuum to remove some of the excess solvent (alcohol).

Pigments, Lakes, and Other Coloring Materials in Plastics

J. H. CLEWELL AND H. W. PAINE

E. I. du Pont de Nemours & Company, Inc., Arlington, N. J.

THE appearance of a plastic article is one of the important incentives to its use. As a consequence the obtaining of decorative effects assumes great importance. The proper selection of coloring materials to obtain various tints and shades of color, and the combination of two or more colors of plastics to produce mottled effects and designs, together with suitable methods of accomplishing the incorporation of the colors into the plastic, constitute a large portion of the problem of the plastics manufacturer.

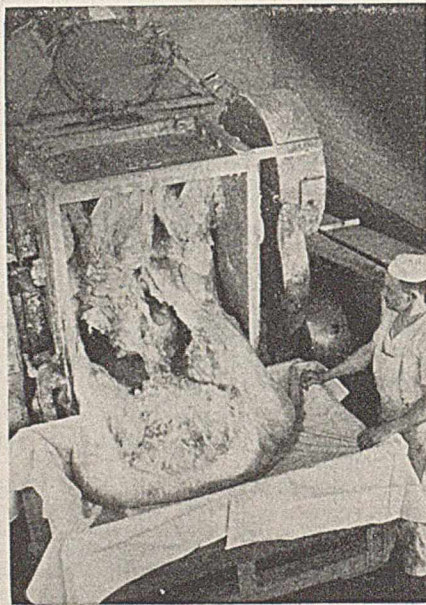
The general subject of coloring plastics has been treated by Peacock and Kienle (2). The purpose of this paper is to discuss briefly the color problems confronting the pyroxylin plastics manufacturer, with brief comments on cellulose acetate and methyl methacrylate.

By pyroxylin plastics are meant those which are known in the trade as "Pyralin," "Celluloid," "Fiberloid," "Nixonoid," and the like, sold generally in the form of sheets, rods, and tubes.

Manufacturing Operations

In order to present the problems of the colorist in the pyroxylin plastic field properly, it is necessary first to outline the various steps in the process of producing these plastics (3).

The pyroxylin used in the manufacture of plastics is usually nitrated to a nitrogen content of about 11 per cent, corre-



MIXING

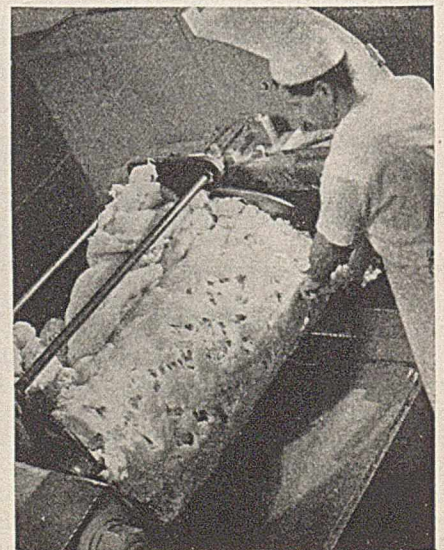
On this machine the material has been thoroughly mixed into a plastic or colloid form and is being loaded into a carrier where it will be taken to the next operation. Again, every precaution is taken against dust and dirt particles.

sponding approximately to the dinitrate. This variety of pyroxylin yields plastics of better toughness than the higher nitrates without any serious decrease in water resistance. Camphor is generally used as the plasticizer since it yields a product of the maximum toughness combined with the maximum rigidity. Other plasticizers, such as tricresyl phosphate, triacetin, dibutyl phthalate, and others, have been and are employed at times, but camphor remains the standard.

After nitration and thorough washing and stabilization by boiling water, the pyroxylin is partly freed from water by pumping denatured ethyl alcohol through a

ROLLING

Huge calendar rollers are used to blend and work together thoroughly all the various materials that go into the manufacture of Pyralin, as well as to remove additional solvent (alcohol). Color is also added at this operation and the coloring material is carefully dispersed and worked into the plastic colloid.



pressed mass or "cake." These cakes are charged into a Werner and Pfeiderer kneading mixer where the pyroxylin is broken up, and the camphor, pigments, and additional alcohol are added if necessary. The mixing is continued until the pyroxylin is completely dispersed in the camphor-alcohol mixture to form a rather soft, doughlike colloid¹ which is then filtered by hydraulic pressure through muslin and a wire cloth supported on a perforated metal plate. If desired, the filtered colloid can be returned to the Werner and Pfeiderer kneading mixer provided with a vacuum attachment, and the excess alcohol needed for accomplishing the filtering can be distilled off and recovered.

The colloid is then sent to mixing rolls where it is worked or masticated to remove further solvent; at the same time the solvent content is kept homogeneous since any portions with a lower solvent content than the mass surrounding them will be brittle in the finished product. On the rolls the colloid is finally shaped into rectangular slabs about 0.5 inch thick.

A stack of these slabs is then placed on a grooved steel plate and transferred to the chase of a hydraulic press. Pressure is applied and steam or hot water circulated through the bottom and top plates of the press. The combination of heat and pressure welds the mass into a solid, substantially homogeneous condition.

The pressed block is then placed on a planer, and sheets, rods, or other shapes are sliced from it with the use of a knife or a die.

The colloid may also be taken from the rolls and placed in a hydraulic or screw stuffer and extruded into the form of rods or tubes.

The sheets, rods, and tubes at the end of these operations contain up to about 10 per cent volatile solvent which must be removed by a seasoning treatment usually consisting of hanging in a room at slightly elevated temperature.

Coloring Materials

Pigments and soluble colors may be added during either the mixing or the rolling operation. The question of where these coloring ingredients are to be added will be determined largely by practical considerations. If a large quantity of pigment is to be used, it is better to add it at the mixing stage before the pyroxylin is colloided. This prevents the dusting of the powder and facilitates its complete and rapid dispersion. If only small quantities of coloring ingredients are to be used,

The process of manufacturing pyroxylin plastics is outlined with reference to methods of incorporating coloring ingredients and of securing varicolored and pearlescent effects. Factors in the selection and use of coloring materials include the natural color of the plastic base, its impurities, particularly those of metallic nature which appear to catalyze discoloration, any stabilizing or decomposing action of the plastic base upon coloring materials, the effects of high temperatures during manufacture, and effects of sunlight upon the finished material.

A coloring material satisfactory in pyroxylin plastic may be unsatisfactory in cellulose acetate plastic and vice versa. The chemical character of a coloring material offers some indication of its suitability, but nothing short of actual tests gives a conclusive answer. Artificial light sources frequently give misleading indications in fading tests. The suitability of coloring materials of various chemical types is discussed.

It is often more convenient to add them during the rolling operation. The working of the plastic in the mixer and on the rolls provides internal friction which is very effective for accomplishing dispersion of pigment aggregates. If, however, the pigment aggregates are gritty or horny in texture, it is necessary to provide an additional process to secure dispersion. This may consist of a preliminary grinding of the pigment in oil, plasticizer, or solvent in a suitable mill, such as a ball mill or a three-roll ink mill, or it may consist merely of rolling the pigment into a small portion of very stiff pyroxylin colloid to provide the necessary friction to accomplish dispersion. The mixture of colloid and dispersed color is then usually softened with solvent before incorporation into the larger mass. The obtaining of proper dispersion is of prime importance, since the presence of any undispersed pigment results in failure to obtain its full coloring value; as a consequence the finished article will not be of standard hue or depth. Undispersed pigment also results in a speckled or gritty appearance.

Soluble colors are ordinarily added in solution. Methanol is usually the most suitable since it dissolves the greatest range of colors of any solvent. Toluene, however, is a solvent for the oil-soluble

type of color and plasticizer (4), and is sometimes employed as the color solvent. The dye solution is usually added to the colloid at the rolling stage although practical considerations may dictate the suitability of adding it at the mixing stage. The use of the solution method of adding dyes provides a perfect method of accomplishing their dispersion. Dyes which are soluble in the plastic medium retain their full transparency and can be used for obtaining the most highly transparent effects. Dyes which are not soluble in the plastic medium but are soluble to an extent in methanol, such as certain of the acid and direct dyes, can be employed also to obtain a lesser degree of transparency provided the concentration is not too great. Dispersion of dyes in dry form into a plastic medium which is not a solvent for the dye generally results in impairment of the transparency since the dispersion is not sufficient and the particle size is too large.

Color Development and Matching

The development of new color effects in plastics presents a complex problem. Assuming that the base material is truly transparent, then transparent as well as translucent and opaque products may be made, according to whether

¹ The term "colloid" is used here to designate a jelly-like mass.

pigment is used and how much. Assuming a base material which is free from characteristic color, then any hue, in any shade or tint, can be obtained through the use of proper quantities of suitable coloring materials. If a colored transparent material is desired, either a dye or one of the transparent pigments is selected. Translucent and opaque colored effects are obtained either by colored pigments, by



POLISHING

The straightening operation takes place after the material has been taken from the seasoning vaults. Pyralin in sheet form is placed in hydraulic presses and, under heat and pressure, these sheets are completely straightened so they will lie flat. This operation also puts a polish on the sheet of Pyralin.

white pigments with dyestuff, or by mixtures of all three. Theoretically any color effect may be possible, but in practice certain limitations must be recognized.

In the first place, the natural color of the plastic medium—e. g., the slightly yellowish cast of an uncolored pyroxylin plastic—has a marked effect on the color of the finished product and must be taken into account in developing a new color. In producing plastics resembling glass, it is customary to add a small amount of blue-violet to neutralize this yellowish color. A slightly grayish cast results but is not objectionable if the thickness of the material produced is not too great. If the plastic medium is definitely dark at the beginning, it is impossible to obtain products of brilliant color from it.

In this connection it is interesting that some of the recently developed resins, particularly polymethyl methacrylate, possess the highest clarity and are completely free from color, so that even extremely thick layers are water-clear. Such resins obviously lend themselves to the widest range of colorations.

In the second place, no coloring material should be used which is not both adequately fast to light and unaffected by the chemical nature of the plastic itself, the solvents and plasticizers used, and the temperatures to which the plastic is subjected in manufacturing operations.

The permanence of color in a colored plastic depends to a large extent upon the stability of the plastic itself. This is especially true in very light transparent and translucent tints. The presence of metallic contamination is in many cases the source of serious color difficulties, such as discoloration by sunlight which is accelerated catalytically by the impurity. Manufacturers have gone to great expense to eliminate such impurities in order to improve the stability of the product; in so doing they have at the same time definitely improved the transparency, through elimination of the serious clouding of the plastic which in many cases is also due to metallic impurities. In some plastics the greatest stability is observed at a certain optimum degree of acidity or al-

kalinity. Pyroxylin plastics are most stable when they are slightly on the acid side. If an attempt is made to neutralize this acidity, as through the addition of alkaline substances, discoloration results. The same is true, although to a lesser degree, of moderate acidification beyond the optimum, which is likely to result in a further increase in contamination of the plastic by contact with metals.

The high temperatures (about 150° F.) to which the pyroxylin plastics are subjected during the mixing, rolling, and pressing operations, and the prolonged exposure to moderately high temperatures in the course of seasoning, are destructive to certain dyes, particularly many of the triphenylmethane and azo groups, although by no means to all of these.

Advantage may be taken of the fact that the very nature of the plastic is in some cases the means of stabilizing a coloring material. A good example is Prussian blue (ferric ferrocyanide blue) as used in nitrocellulose plastics. This pigment is stable in acid and oxidizing media but unstable in alkaline and reducing media. Nitrocellulose is slightly acid and has a slight but definite oxidizing action. Prussian blue has thus been found to be one of the most stable colors for use in nitrocellulose, resisting all of the influences of the manufacturing processes to which these plastics are subjected and also long periods of exposure to direct sunlight. However, if nitrocellulose sheeting tinted with Prussian blue is sandwiched between two glass plates for the manufacture of safety glass and the resulting safety glass is exposed to sunlight, the blue tint of the plastic fades. If the glass is broken, admitting moisture and air to the plastic, the blue color returns. This seems to indicate that sunlight has a reducing effect in the absence of oxygen.



SHEETING

After the material has been removed from the baking press, where it has been welded into one solid block on an iron base, the huge block, 24 × 56 × 6 inches, is placed on a sheeting machine and each piece of Pyralin is sheeted or planed to the desired thickness.

In many other plastics Prussian blue is not permanent. In cellulose acetate it fades badly, perhaps as a result of the fact that cellulose acetate as ordinarily prepared is seldom on the acid side of neutrality. Cellulose acetate is also possibly somewhat reducing in character.

With many other coloring materials the reverse is true; that is, they are fugitive in nitrocellulose plastics but permanent in cellulose acetate plastics.

In the manufacture of variegated effects, stripes, mottles, etc., or when two sheets of dissimilar color are to be welded together by the application of heat and pressure, the further requirement arises that the dyestuff used shall not diffuse or bleed from one colored area into another. In general, the degree of solubility of a dyestuff in the plastic is a measure

of its tendency to bleed. Insoluble coloring materials, of course, do not bleed at all.

Selection of Coloring Materials

It is essential that the plant chemist or color matcher should have at hand an assortment of coloring materials from which he can safely make a selection when called upon to duplicate any desired shade. Every color on this list should be absolutely permanent, but this is not entirely possible, especially with coloring materials of great brilliancy. Any limitation in the permanence of the colors used must be thoroughly understood so that the resulting colored product will not fail to have a degree of permanence satisfactory for the use for which it is intended.

Soluble dyestuffs are largely used, particularly in obtaining transparent effects and in the formulation of the brightest colors, but frequently they lack permanence. This is most likely to be true of those that give the most brilliant colors. To meet a demand for brilliant color effects, the colorist must comb the field in order to obtain dyestuffs that are most nearly permanent. Little has been published concerning the behavior of coloring materials in plastic media, and the search for fast colors must therefore frequently be a matter of cut and try. Within a single group or family of dyestuffs one member may be fast and another fugitive under the conditions of use, and the reason why one or more individuals in a group presents an unusual degree of permanence is not thoroughly understood.

A knowledge of the constitution and chemical properties of a dyestuff or pigment is no doubt of considerable advantage in judging in advance its suitability for coloring plastics, but by no means does it always give an answer to the question of whether it will fit a given requirement. The color chemist must combine his knowledge of the chemistry of the substance with an actual test of its use in his plastic, subjecting it to processes as nearly as possible the same as those to which the commercial batch will be subjected during manufacturing operations and subsequent use. Testing for fastness to sunlight is best accomplished by actual exposure to sunshine, preferably in the extreme southern part of the country where the actinic strength of the sun's rays does not vary so widely between winter and summer. The various artificial testing lamps are of assistance in many cases but are not thoroughly reliable in testing coloring materials in plastics.

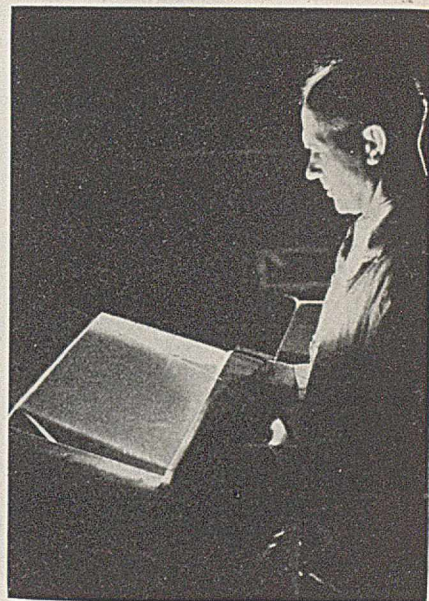
Of all the available dyestuffs, the familiar triphenylmethane basic colors are the brightest. They can readily be dispersed in the plastic. They have good solubility in alcohol but the disadvantage of poor resistance to sunlight. However, some brilliant color effects can be obtained only with the use of dyestuffs of this class. The azo colors as a group are somewhat faster to light, and they are used to a considerable extent in both nitrocellulose and cellulose acetate plastics. But it has been the general observation that many of the azo colors tend to discolor as a result of the heat to which the nitrocellulose plastics are subjected during the process of manufacture. Many, however, are sufficiently permanent to be satisfactory. The sodium salts of the sulfonic acid derivatives lack ready solubility in alcohol, and it has been found preferable to take advantage of the better solubility obtained by combining the sulfonic acid derivative of the dye with certain organic bases. Oil-soluble dyestuffs in this group are sometimes designated as color bases; they are soluble in toluene and esters as well as in alcohol. They are of value in coloring varnishes and lacquers and in plastics of certain types, but the use of oil-soluble colors is to be avoided if bleeding is objectionable. Many of the anthraquinone and alizarin groups, as well as some of

the vat dyes, are of great value in obtaining plastics of fast color.

Transparent insoluble pigments are those which, when dispersed into the plastic by mixing or rolling, produce a transparent or nearly transparent colored effect. This class includes Prussian blue, certain of the vat dyes such as indanthrene blues and violets, and a number of lakes precipitated in alumina hydrate such as alizarin lakes and some of the lakes of azo dyes. Many of these colors, unless used in too great concentration, do not noticeably impair the clearness of the plastic; their use in too high a concentration results in some cloudiness. The fastness to sunlight of some of these is superior to that of the soluble colors.

INSPECTION

The sheets are given a preliminary inspection, after which they are sent to heated concrete vaults where practically all the remaining solvent is removed. The curing period of these sheets depends largely on the thickness of the particular sheet and the use to which it is to be put by the fabricator. In the manufacture of dice the "Pyralin" material is cut from solid blocks in square rods 50 inches long, $\frac{3}{4}$ inch wide, and $\frac{3}{4}$ inch deep. These rods are then ready for dice fabrication.

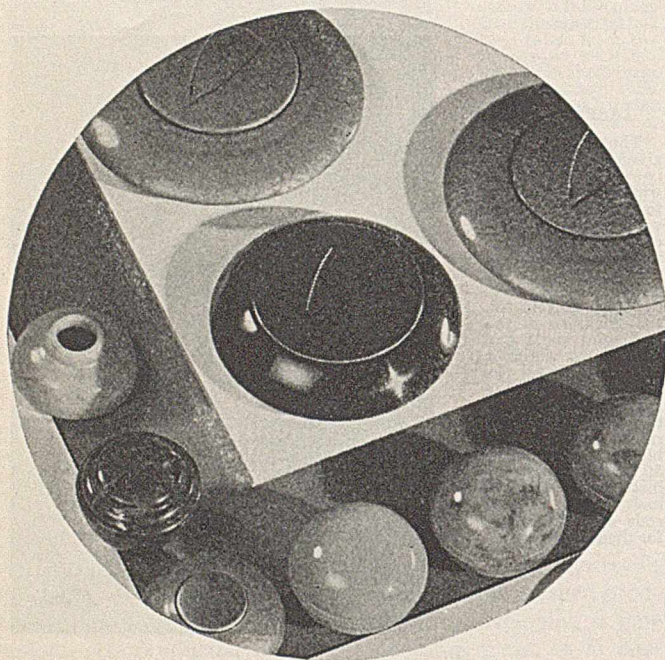


The list of opaque pigments contains many excellent examples, from which a selection must be made to fit the particular case in hand. Zinc oxide, for example, is excellent in plastics of many types and is a standard white pigment for use in the coloring of pyroxylin plastics, in which it has a stabilizing effect without any tendency to promote hydrolysis. But it cannot be used in cellulose acetate because it promotes hydrolysis, with the formation of zinc acetate, a corresponding loss of opacity, and a deterioration of the plastic. Titanium dioxide has come into general use in plastics and has the advantages of greater hiding power and an inertness that permits its use in media susceptible to hydrolysis.

Cadmium and chromium colors furnish abundant examples of oranges, yellows, and reds, and are very permanent. Ultramarine, a translucent pigment, furnishes a satisfactory blue. Cobalt blue is very permanent, but expensive and rather dull. The blue lakes, if prepared from the triphenylmethane blues, are fugitive except when used in high concentrations. Some of the alizarin blue lakes are moderately fast. Blacks offer no particular difficulty; lampblack, ivory black, and carbon black all serve particular purposes. But it should be noted that absolute jet black cannot be obtained in plastics except through the use of the soluble nigrosines, which have the disadvantage of a tendency to bleed yellow in certain media. The earth colors, including siennas, umbers, and ochers, are completely permanent and are widely used in the coloring of plastics, although their dispersion presents some difficulty.

Designs and Mottled Effects

Frequently an important part of the color development is the combining of two or more differently colored portions of plastic to obtain designs or mottles. Much ingenuity is frequently necessary to work out these combinations, and a high degree of skill is required in their actual manufacture. We see the results in many of the familiar articles of commerce—for example, variegated fountain pen designs, plastic toilet sets, buttons and buckles, costume jewelry, radio parts, toys, novelties, umbrella handles and tips, scuffless heel covers, slide type fasteners, toothbrush handles, bathroom fittings, optical frames, and dentures.



HORN BUTTONS AND GEAR-SHIFT KNOBS PRODUCED WITH "PLASTACELE" CELLULOSE ACETATE MOLDING POWDER

In the early development of plastics many natural substances were imitated, including tortoise shell, ivory grain, onyx, horn, mother-of-pearl, jade, and various wood grains. In many of these cases the combining of one or more differently colored plastics constituted an essential part of the process.

Tortoise shell imitation is made by combining amber and brown. The two colored plastics, while in a soft condition, retaining a considerable portion of the volatile solvent, are passed together repeatedly through mixing rolls whereby they blend and flow together to give the characteristic shell markings.

Grained ivory is made by stacking thin sheets of ivory colored soft plastic (the successive sheets contain slightly different amounts of pigment), cutting the pile of sheets so obtained into sections, and turning each section at right angles so that the upper surface shows the desired grain. The sections are clamped together and consolidated in a hydraulic press with the application of heat, resulting in a new block from which sheets of grained ivory are sliced. By slicing this grained block into thin sheets, stacking the sheets, and repressing, a block is obtained that shows the ivory grain with a pleasing cross grain or moiré grain considered to imitate natural ivory more closely. Another method of obtaining an ivory grain is to roll out slabs of the two slightly different colored ivory plastics, place the slabs one on the other, and calender them

through the rolls to about a quarter of the original thickness. The long resulting slab is cut in two, one part is laid on the other, and the calendering is repeated. This is done several times until the grain is of the proper thickness. The final slab is then cut into sections and repressed so that the grain is at the top of the new block, and from this sheets are sliced.

Mosaic effects are obtained merely by cutting soft sheets of plastics into small pieces and reconsolidating in the hydraulic press into a block from which sheets are sliced.

By combining various of these operations, numerous unusual effects are obtained. For example, two colors are first grained according to one of the methods outlined and the resulting sheets are cut into small pieces and repressed.

Plastics with a pearly sheen can be made by a patented process and are much in demand in certain lines; their production of these is an interesting and important branch of the art of coloring plastics. The material for imparting the sheen may be the so-called *essence d'orient*, the brilliant coating obtained from the scales of certain fish. The particles are colorless, nearly transparent, and extremely small, and possess a beautiful luster. When suspended in a protective colloid, such as a pyroxylin dispersion, the brilliancy is permanent. *Essence d'orient* has been used extensively in the past for imparting the luster to artificial pearls but in recent years has come into extensive use in the manufacture of pearl plastics. Synthetic pearl essences are also used, particularly crystallized mercurous chloride and crystallized lead carbonate. Metallic powders, especially aluminum, are also used; although they are gray compared to either the natural or synthetic pearl essences, they possess considerable luster, and a small enough particle size can be obtained to give effects in the plastic in which the individual particles are not easily detected.

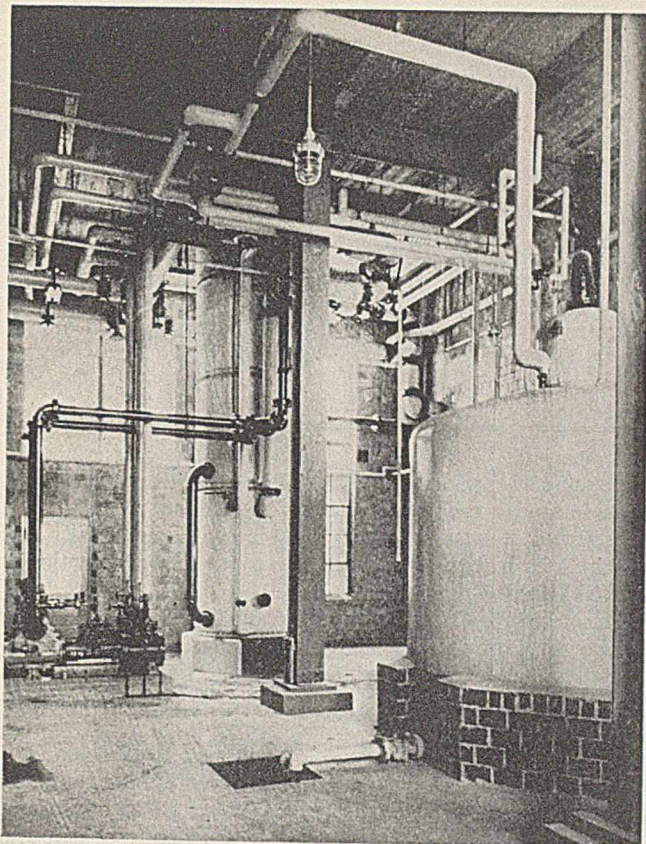
Any of these lustrous pigments incorporated into plastic in the mixing process fails to show its full effect because of the indiscriminate arrangement of the particles. To bring out their full values, these particles must be oriented. The principle of orienting lustrous particles contained in a plastic was enunciated in the Higgins patents (1). The process involves the incorporation of the pearl essence or other lustrous particles into the plastic while in a softened condition, resulting from the presence of an excess of solvent, and extruding the plastic carefully through an orifice. The resulting slab can then be cut into irregular pieces, stacked into the chase of a hydraulic press, and consolidated by the application of heat and pressure into a block from which sheets are sliced. These sheets present a very fair imitation of mother-of-pearl without, however, any iridescence.

The manufacture of rods for use in the fountain pen industry presents the difficulty of arranging the oriented plastic so that the orientation is distributed approximately evenly around the rod. This may be done by producing small cubes of the oriented pearl plastic material and repressing them in a hydraulic press into a block from which rods are cut.

Literature Cited

- (1) Higgins, U. S. Patents 1,539,084 (May 26, 1925); 1,606,030 (Nov. 9, 1926); 1,607,622-4 (Nov. 23, 1926).
- (2) Peacock, W. H., and Kienle, R. H., *Modern Plastics*, 14, 63 (Oct., 1936).
- (3) Sproxtton, Foster, *J. Soc. Chem. Ind.*, 52, supplement, S-12 (May 19, 1933); Boehmer, G. H., *Modern Plastics*, 12, 48-9 (Sept., 1934); Stark, C., *Nitrocellulose*, 7, 121 (1936).
- (4) Wood, U. S. Patent 1,966,329 (July 10, 1934).

RECEIVED May 11, 1937. Presented as part of the Symposium on Organic Plastics before the Division of Paint and Varnish Chemistry at the 93rd Meeting of the American Chemical Society, Chapel Hill, N. C., April 12 to 15, 1937.



DOUBLER STILL WITH BEER STILL IN THE BACKGROUND

WHISKY VERDIGRIS ANALYSIS

ROBERT H. BAKER AND CHARLES BARKENBUS
University of Kentucky, Lexington, Ky.

IN THE manufacture of whisky from the fermentation mass or beer, the mixture is distilled through a beer still into a tank called the "singling tank." The crude, so-called low wines contain about 50 per cent alcohol and are further fractionated by distilling through the doubler. The first and middle fractions are run directly into the whisky well; the last fraction or tails, containing about 10 to 35 per cent alcohol, is run back into the singling tank to be mixed with the next run from the beer still.

As the concentration of alcohol falls in the doubler a white, insoluble, fatlike material appears in the trial box. Although most of this goes back into the singling tank, some collects in the condenser and is partially dissolved and washed out by the higher alcoholic content of the next distillation. This appears in the heads or foreshots of the next distillation and is colored a distinct green. This part of the insoluble material goes directly into the whisky well and dissolves in the strong alcohol present. Thus a part of the original volatile fatty material collects in the singling tank, and part finds its way into the whisky. The trade calls this material "verdigris" which is an unfortunate name since it has no connection with the verdigris of commerce. For lack of a better name, it will be called "whisky verdigris" in this article.

The amount of this material is small in comparison to the volume of alcohol produced. Probably 250 grams per 30,000 liters of high wines would be a fair approximation, although no exact figures are available and would be very difficult to obtain. Of this amount only a part is washed into the whisky well and dissolved. In addition, some is probably in solution in the distillate when the alcoholic content is high.

The exact nature of the so-called congeners of whisky is not known since they occur in such small amounts; nevertheless they are the deciding factor in the flavor or taste that a whisky

will have. An analysis of this fatty material would at least indicate the nature of some of the congeners, although no exact figures could be given.

Only one reference to this material has been found in the literature. Allen (2) states that the foreshots of a distillation when diluted with water produce turbidity, and finally oily globules appear. A cursory examination of this oil showed that part of it could be distilled. Although the nonvolatile material consisted chiefly of fatty acids, the volatile portion contained acids, esters, and unsaponifiable material, and had a most intolerable odor. It is remarkable that no complete analysis has ever been made because it is present at all distilleries and offers a method of determining qualitatively some of the congeners in whisky.

Through the courtesy of W. T. Black, a former graduate student at the University of Kentucky, approximately 350 grams of the whisky verdigris were obtained. About half of the sample came from the singling tank and the other half from the trial box of the doubler. This sample would not be a true picture of the material dissolving in the whisky, but it seems reasonable to expect that the variation in composition would be small.

Experimental Procedure

Three hundred thirty-seven grams of the wet, pasty, whisky verdigris were extracted by centrifuging with 2.5 liters of ether in twenty-one portions. Eighty-two grams of dry, ether-insoluble material remained as a green fluffy solid.

The green ether solution was extracted with 2 N potassium hydroxide, and from this soap solution 25.5 grams of dry acids were obtained which were solid at room temperature.

The ether phase, upon drying and evaporating, yielded a brown oil containing about 0.1 gram of suspended cupric oxide which was removed by centrifuging. The oil, after drying over sulfuric acid, weighed 90.1 grams. From the quantity of cupric

TABLE I. ANALYTICAL DATA ON REDISTILLED FRACTIONS

Fraction No.	Temp. at 2 Mm. ° C.	Weight Grams	Mean Mol. Wt.	Iodine No. (Hanus)	Unsatd. Esters ^a	Ethyl Oleate	Ethyl Linolate	Ethyl Esters			Unsaponifiable Matter
								Ethyl Caprate	Ethyl Laurate	Ethyl Palmitate	
1	75-90	5.1	221	9.2	0.44	0.32	0.12	2.83	1.83
2	115-133	3.9	259	11.5	0.43	0.31	0.12	..	1.92	1.55	..
3	138-146	20.1	296	24.3	4.65	3.34	1.31	15.45	..
4	148-150	9.4	298	37.6	3.36	2.42	0.94	6.04	..
5	150-152	4.1	308	43.3	1.69	1.22	0.47	2.41	..
6	152-156	16.5	309	92.5	14.50	10.44	4.06	2.00	..
7	156-158	9.6	314	117.5	9.3	6.70	2.60	0.30	..
8	158-162	3.9	320	105.8	3.9	2.81	1.09
9	Residue	1.1	349	93.1	1.1	0.79	0.31
10	Residue (preliminary distn.)	9.2	7.5	5.40	2.10	0.10	1.6 ^b
Total		82.9	33.75	13.12	2.83	3.75	27.85	1.6
Per cent		40.79	15.82	3.42	4.53	33.59	1.94

^a The iodine number 105 was used in these calculations.

^b Expressed as from this fraction rather than as distributed throughout the samples.

oxide obtained, it was evident that the ether-soluble cupric salts were negligible.

The total weight of the dried fractions was 197.6 grams, a weight loss of 41.3 per cent due chiefly to water. The composition given in Table II was calculated from this quantity.

Neutral Ether-Soluble Fraction

Preliminary experiments indicated the presence of a large amount of ethyl esters and the complete absence of glyceryl esters. Constants were determined as follows: iodine number, 61.5 (Hanus); saponification number, 187.9; unsaponifiable matter, 1.94 per cent.

Preliminary distillation of 85 grams of this fraction at 2 mm. yielded 74.3 grams of oil which were cut into six fractions distilling over a range of 98° to 180° C., and 9.2 grams of an oily residue. Redistillation of these fractions into eight volatile and one nonvolatile fraction at 2 mm. is summarized with the analytical data in Table I.

The various fractions were saponified with aqueous potassium hydroxide, and the soap solutions were distilled until the iodoform reaction was negative. These alcohol distillates were combined for the determination of higher alcohols. The soaps were then extracted with ether, and these extracts were combined for the investigation of the unsaponifiable matter.

FRACTION 1 yielded acids melting at 20° to 21° C., and with a neutral equivalent of 187. A 2-gram fraction was hydrogenated with the Adams catalyst to render the unsaturated acids nonvolatile (5), and was steam-distilled. Barium salts were prepared from the steam distillate, and they were crystallized from water according to Allen (1). Beginning with the most insoluble crystals, the percentages of barium were as follows: 25.42, 25.77, 27.65, 28.15, 28.69. Barium laurate and caprate require, respectively, 25.64

and 28.65 per cent. Inasmuch as the two extremes check closely, the saturated esters are expressed as laurate and caprate.

FRACTION 2 was not analyzed since it was small, and attempts to isolate acids lower than palmitic in fraction 3 proved impossible.

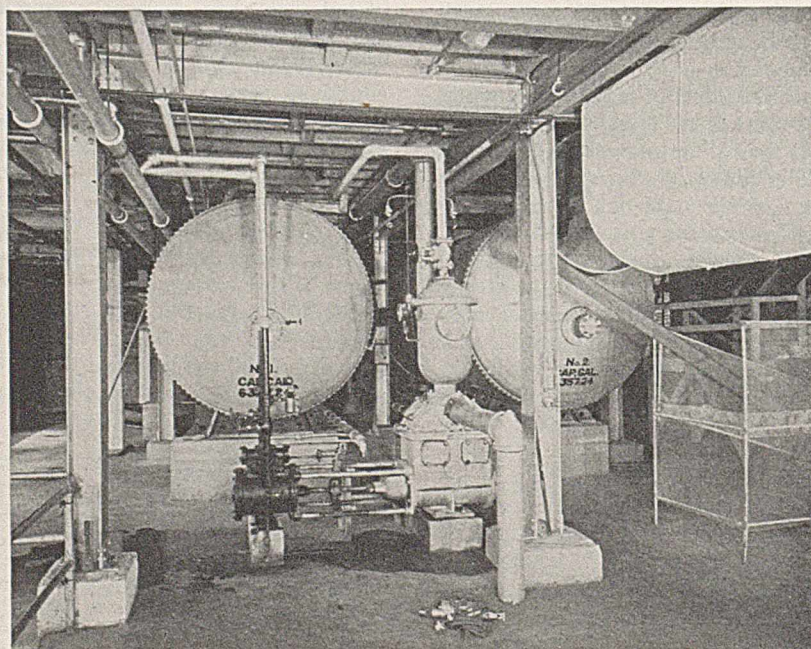
FRACTIONS 3, 4, 5, 6, and 10 invariably yielded palmitic as the only saturated acid by crystallization from alcohol (4). Throughout the investigation palmitic acid was characterized by its melting point of 62.5 ± 0.2° C. and its neutral equivalent of 256.3 ± 1.0.

FRACTIONS 7 and 8 were combined and their acids subjected to the lead salt-ether separation according to Jamieson (8), except that the ether-insoluble salts were removed and washed by centrifuging. This yielded 0.15 gram of palmitic acid and 6.23 grams of liquid acids, neutral equivalent 283 and iodine No. 115. The unsaturated acids were brominated according to Baughman and Jamieson (3). No hexabromide was obtained, but crystals from petroleum ether proved to be linolic acid tetrabromide, melting at 113° to 114° C., and analysis of the noncrystalline residue from the mother liquor gave 39.40 per cent bromine. Tetrabromide and dibromide require, respectively, 53.33 and 36.18 per cent bromine; hence a more saturated acid than linolic is present and is regarded as oleic. The iodine number of the liquid acids, 115,

calculated to ethyl esters, 105, was used in calculating the distribution of oleate and linolate in the fractions of Table I.

ALCOHOLS. Although the alcohol distillates from all fractions gave positive iodoform tests, it was desirable to identify ethyl alcohol positively; hence it was salted out of the saponification distillate from 7 grams of fraction 6 and formed a 3,5-dinitrobenzoate which melted at 91.5° C.

Fusel oil was determined in the combined distillates by the method of Peniman, Smith, and



Courtesy, Old Lewis Hunter Distillery Company

Lawshe (12). Using the synthetic standard and vanillin, the concentration calculated to the neutral ether-soluble fraction was 0.154 per cent.

UNSAPOFIABLE MATTER. The ether extracts of the soap solutions upon evaporation yielded 1.4 grams of a viscous oil having somewhat the odor of corn. It contained no nitrogen or sulfur and gave negative tests for sterols, alcohols, aldehydes, ketones, and unsaturated compounds, although a slight coloration was produced when it was treated with strong sulfuric acid. Repeated crystallization from alcohol yielded 0.2 gram of an odorless, white, waxy solid, melting at 42.5° C. and insoluble in and giving no coloration with cold concentrated sulfuric acid. Since the quantity was small and the purity questionable, it was not analyzed, but was considered to be a hydrocarbon.

Free Acids

Constants were determined as follows: weight, 25.5 grams; iodine number, 51.68; neutral equivalent, 268.2.

Separation by the lead salt-ether method as previously described yielded 8.88 grams of liquid acids (iodine number, 114) and 13.86 grams of solid acids (neutral equivalent, 258.3; iodine number, 5.09). The liquid acids were assumed to be of the same character as those obtained from the ester fractions. The solid acids after one crystallization from alcohol proved to be palmitic, melting point 62° to 62.5° C., and neutral equivalent 256.4. The calculated distribution of the free acids in per cent is palmitic 54.74, oleic 32.60, linolic 12.66.

Ether-Insoluble Material

This fraction had an ash content of 30.3 per cent, which was analyzed as follows: cupric oxide, 26.25; ferric oxide, 23.87; silica, 31.90 per cent.

Seventy-nine grams of the green solid were digested on the steam bath with 6 N sulfuric acid, cooled, and filtered. The clear blue filtrate was distilled and required less than 1 cc. of 0.1 N alkali for neutralization; hence only traces of water-soluble volatile acids were present. The filter cake upon extraction with ether yielded 29 grams of solid acids (iodine number, 3.90), which were considered to be saturated. Crystallization from alcohol yielded pure palmitic acid, melting point, 62.3° to 62.8° C., and neutral equivalent, 256.1.

The green solid when leached with hot alcohol was dissolved, leaving a brown solid. Upon filtering and cooling, the alcohol solution deposited green crystals; hence the palmitic acid is considered to be held as a cupric salt.

Discussion of Results

The higher fatty acids and their derivatives found in whisky verdigris without doubt originate mainly in the corn (3) which makes up from 60 to 89 per cent of the total grain used in making Bourbon whisky from which the sample was obtained. The corn oil alone does not offer an explanation of the presence of laurate and caprate esters, although Hilger (6) reported the free acids to be present in fusel oil. The occurrence of the various fatty acids and their derivatives in the beer is easily understood, but their presence in the distillate is more difficult to explain. Although it is known that the higher fatty acids are volatile in steam, or at least volatile in steam containing the vapors of more volatile acids, it must be remembered that this is not purely a steam distillation. In support of the evidence of Arnold, cited by Lewkowitsch (9), the writers were able to isolate 0.2 gram of pure palmitic acid from 3000 cc. of steam distillate from the acids of fraction 3 of the ether-soluble material.

It is possible that the acids distill and cling to the copper condenser, and that partial salt formation (11) and esterification take place there. The majority of the esters are probably formed in the beer, and many other possibilities are obvious although none appears to explain satisfactorily the

absence of stearic acid or its derivatives. Although this acid has been reported in fusel oil (6), the writers were unable to find any indication of its presence in whisky verdigris.

The absence of the cupric salts of the unsaturated acids is easily correlated with the generally higher solubilities of the salts of liquid acids in organic solvents.

The presence of silica and iron oxide in the ash was not understood until it was learned that the singling tank from which part of the sample was removed had been regularly charged with spring water while the sample was being collected. Neither of these substances could reasonably be expected to pass through the doubler.

Whisky verdigris has a strong odor of green whisky and may be said to be yeasty; although none of the substances mentioned by Hochwalt and others (7) were found, their hydrogenation process may owe part of its effectiveness to the reduction of the unsaturated derivatives which otherwise become rancid.

A cursory survey of the literature revealed no definite information as to the copper content of whisky; however, Lythgoe, Berry, and Hall (10) state that copper was present in 10 per cent of the distilled beverages intended for sale in Massachusetts, and Wood (14), quoting Hayes, states that new spirits from copper stills are likely to be contaminated with that metal. Hayes believes that this copper is deposited upon aging.

TABLE II. ANALYSIS OF WHISKY VERDIGRIS SAMPLE ON A DRY BASIS

Ethyl caprate	1.56%	Copper	2.70%
Ethyl laurate	2.07	Silica	4.03
Ethyl palmitate	15.32	Iron oxide	3.03
Ethyl oleate	18.60	Palmitic acid held as green ether-insol. salt	28.80
Ethyl linolate	7.11	Ether-sol. unsaponifiable matter, chiefly hydrocarbons	0.88
Palmitic acid	7.06	Fusel oil	0.07
Oleic acid	4.20	Total	97.12
Linolic acid	1.69		

The highest value found by Valaer and Frazier (13) for the nonvolatile acids in new whisky was 2.4 grams per 100 liters. In 197.6 grams of dry whisky verdigris 25.5 grams of free acids have been found; hence if the sample is homogeneous, it may be calculated that about 1000 liters will be required to contain the sample, or that new whisky contains 0.02 per cent of this material. Since the congeners are usually represented at 0.25 to 0.50 per cent, it is evident that all of the congeners have not been accounted for.

Literature Cited

- (1) Allen, "Commercial Organic Analysis," 4th ed., Vol. I, p. 517, Philadelphia, P. Blakiston's Son & Co., 1909.
- (2) Allen, *J. Soc. Chem. Ind.*, 10, 305 (1891).
- (3) Baughman and Jamieson, *J. Am. Chem. Soc.*, 43, 2696 (1921).
- (4) Brown and Stoner, *Ibid.*, 59, 3 (1937).
- (5) Hilditch and Sleightholme, *Biochem. J.*, 24, 1101 (1930).
- (6) Hilger, *Chem. Zentr.*, 1894, I, 981.
- (7) Hochwalt, Thomas, and Dybdal, *IND. ENG. CHEM.*, 27, 1404 (1935).
- (8) Jamieson, "Vegetable Fats and Oils," p. 351, A. C. S. Monograph 58, New York, Chemical Catalog Co., 1932.
- (9) Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats, and Waxes," 5th ed., Vol. I, p. 418, London, Macmillan Co., 1913.
- (10) Lythgoe, Berry, and Hall, *Boston Med. Surg. J.*, 194, 984-8 (1926).
- (11) Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. III, p. 101, London, Longmans, Green & Co., 1923.
- (12) Penniman, Smith, and Lawshe, *IND. ENG. CHEM., Anal. Ed.*, 9, 91 (1937).
- (13) Valaer and Frazier, *IND. ENG. CHEM.*, 28, 92 (1936).
- (14) Wood, "Dispensatory of the United States of America," 13th ed., p. 835, Philadelphia, J. B. Lippincott, 1875.

Development of P_2O_5 Insolubility

W. H. MACINTIRE, L. J. HARDIN, F. D. OLDHAM,
AND J. W. HAMMOND

The University of Tennessee Agricultural
Experiment Station,¹ Knoxville, Tenn.

Ammoniation of superphosphates and incorporation of dolomite have given rise to the serious economic problem of phosphate degradation when large piles of the processed fertilizers are aged. Engendered basic phosphates have been assumed to be the cause for the development of P_2O_5 insolubility. The fluoride content of superphosphates has been ignored as a causal factor.

The formation of fluorapatite in non-acid-forming phosphatic fertilizers is advanced as an explanation for decreases in P_2O_5 availability. Component fluorides, introduced into phosphatic mixtures by either superphosphates or calcic materials, induced citrate insolubility, whereas that effect was not induced in parallel mixtures devoid of fluorides. When mixed moist with tricalcium phosphate, in 1 to 12 proportion, pulverulent calcium fluoride soon lost its petrographic identity and the mixtures registered characteristic properties of apatite by chemical and Neubauer tests. When acidulated with either H_2SO_4 or H_3PO_4 , the behavior of the synthetic fluorapatite corresponded to that of natural apatite, and the liberated calcium fluoride was of submicroscopic dimensions. Different types of dicalcium and tricalcium phosphates reacted with different types of calcium fluoride in variant degree during citrate digestions. It was concluded that the development of citrate insolubility, attributable to fluorapatite formation, will occur not only during the curing of processed superphosphates, but also during their analysis.

THE composition and reactivities of calcium silicate slags from the rock phosphate reduction furnaces at Wilson Dam were reported in a study of their adaptability, in lieu of limestone, for admixing with concentrated superphosphates at the point of usage (10). A high citrate-insoluble P_2O_5 content developed when the moistened mixtures of those slags with phosphatic fertilizers were aged. It was postulated that the calcium fluoride content of the slags caused the formation of fluorapatite, $3Ca_5(PO_4)_2 \cdot CaF_2$, in the slag-phosphate mixtures of 2 to 1 proportion during aging.

The present contribution represents a study of the role of calcium fluoride in causing citrate insolubility during the aging of mixtures of superphosphates and calcic materials and during the analytical digestion of various phosphatic mixtures in ammonium citrate. Particular objectives were to determine whether synthesis of fluorapatite develops during the aging of the phosphatic mixtures and whether the presence of calcium fluoride induces citrate insolubility during the analysis of processed superphosphates. Tables I to VII deal with calcium fluoride as a causal factor in the development of citrate-insoluble P_2O_5 during the aging of solid phosphatic mixtures. Tables VIII to X deal with the P_2O_5 transitions that ensue only during the actual analysis of the immediate mixtures and suspensions.

Experimental Technic

All phosphomolybdate precipitations were made by 30-minute, cold, agitated digestions and suction filtrations through cellulose mats on Shimer filters, as previously described (12). The A. O. A. C. method for citrate insolubility (1) was followed, with constant inclusion of a 9-cm. pulped filter, since comparative studies in several laboratories had shown the advantages of this modification reported by Jacob, Rader, and Tremearne (3). The only other departure was the washing of insoluble residues with an electrolyte, as previously described (9), and the substitution of centrifuging for filtration of all systems where either di- or tribasic phosphates were the starting materials. The centrifuging technic was particularly efficacious for those systems in which silica hydrosols were developed during digestion. One-gram charges of initial materials were used throughout, except as noted. All fluorine determinations were made by the method of Willard and Winter (16).

P_2O_5 Transitions in Solid Mixtures of Superphosphate and Calcic Materials

MIXTURES CONTAINING FLUORIDE-FREE SUPERPHOSPHATE. The first concentrated superphosphate used was a fluoride-free product, made by decomposing Appalachian marble with a pyrolytically produced H_3PO_4 (8). Five of the calcic materials were also devoid of fluorides, and six of the seven mixtures of Table I were therefore fluoride-free. The only material that introduced component fluorides was the Wilson Dam slag, which contained 6.5 per cent calcium fluoride.

¹ This study was conducted under the auspices of the Tennessee Valley Authority, Chemical Engineering Division.

in Phosphatic Mixtures

The Formation of Fluorapatite as Its Cause

The seven mixtures were brought to a common initial moisture content of 6.67 per cent, gently compacted, and aged in closed containers for 35- and 75-day periods.

Six of the calcic materials reduced the water-soluble P_2O_5 content of the mixtures to a level of 1 to 2 per cent during the first 35 days, whereas the Wilson Dam slag completely eliminated that content. After 75 days negligible P_2O_5 insolubility had been developed by the additions of limestone and of cement slag. Only the Wilson Dam slag mixture produced an increase in citrate insolubility not removable by immediate repetition of the ammonium citrate digestion of the residue from the first digestion. It has been pointed out (10, 11, 15) that single digestions of such mixtures of superphosphate and liming materials are inadequate to effect complete removal of the engendered basic phosphates. The solvent capacity of the citrate solution was reduced by the common-ion effect (2, 4, 15) and also by the decided alkalinity induced in the citrate solution by its solvent action upon unreacted fractions of the added calcic materials (10).

The Wilson Dam slag was the only addition that showed citrate insolubility for the 35-day period. This cannot be attributed solely to formation of either tricalcium phosphate or hydroxyapatite, since that effect was not induced by the other six calcic materials. The failure of the three types of calcium silicate to induce citrate insolubility in mixtures with the fluoride-free triple superphosphate (T. S. P.) indicate that the calcium fluoride content of the Wilson Dam slag was the cause for the development of P_2O_5 insolubility in its mixtures, either during the aging of the mixtures or during their analysis.

The moisture, added and also generated, of the two carbonate systems was either dispelled or fixed as water of hydration in the dicalcium phosphate produced in the solid mixtures, whereas a considerable part of the moisture of the siliceous systems was retained through the hydration of the silicon dioxide liberated from the added calcium silicates.

MIXTURES CONTAINING FLUORIDE-FREE SUPERPHOSPHATE AND CALCIUM FLUORIDE. A constant addition of pulverulent c. p. calcium fluoride, equivalent to 8 per cent of the superphosphate, was included as replacement of an equal weight of each calcic material in the six moist systems of Table II that corresponded in other respects to those of Table I.

The substantial decreases in water-soluble P_2O_5 , formation of dibasic phosphates, divergent effects of added carbonates and silicates upon final moisture content, and marked enhancement of citrate-insoluble P_2O_5 in the Wilson Dam slag mixtures of Table II were in harmony with the results obtained for the previous mixtures of

Table I. Again, only the system that contained Wilson Dam slag gave a definite and persistent increase in citrate-insoluble P_2O_5 content for the 35-day period and further increases thereafter.

The mechanical additions of finely divided calcium fluoride functioned differently from the disseminated calcium fluoride content of the Wilson Dam slag. The reason for this variation will be developed in consideration of the findings embodied in subsequent tables. It should be noted, however, that 97.4 per cent of the fluoride component of the slag and all of the calcium silicate content were dissolved during digestion by the citrate solution in contrast to the low solubility of the calcium fluoride in ammonium citrate and the still lower solubility when calcium silicate was also present.

The results of Table III were obtained by a mechanical addition of calcium fluoride in another form. The superphosphate and the calcium silicate of these mixtures were likewise fluoride-free. Both mixtures contained a pulverized eutectic calcium silicate-calcium fluoride melt that contained 38.2 per cent of calcium fluoride, corresponding to 7.93 per cent of the charges of phosphate, and were identical except for the amounts of water incorporated.

TABLE I. P_2O_5 TRANSITIONS IN WETTED AND AGED MIXTURES OF FLUORINE-FREE TRIPLE SUPERPHOSPHATE AND C. P. MONOCALCIUM PHOSPHATE WITH FLUORINE-FREE CALCIUM CARBONATES AND SILICATES AND FLUORIDE-CONTAINING SLAGS

Mixture Components	Period Parts Days	Mois- ture %	Total		P_2O_5 Value		Insol.	
			Found	Calcd.	Water-Sol. Found	Calcd. ^a	Found	Calcd.
CaCO ₃ , c. p.	80	0.21	19.5	19.3	1.2	19.0	None	None
Triple superphosphate ^b	40							
H ₂ O	8	0.06						
CaSiO ₃ , c. p.	100	1.52	17.8	17.5	1.6	17.2	None	None
Triple superphosphate ^b	50							
H ₂ O	10	5.12						
CaSiO ₃ , c. p.	80	6.68	18.0	17.8	1.5	17.5	None	None
CaH ₄ (PO ₃) ₂ , c. p.	40							
H ₂ O	8	6.58						
Limestone	400	0.44	18.7	18.7	1.3	18.4	None	None
Triple superphosphate ^b	200							
H ₂ O	40	0.10						
Dicalcium silicate	400	2.61	17.5	17.7	1.5	17.4	None	None
Triple superphosphate ^b	200							
H ₂ O	40	3.08						
Atlas Cement Co. slag ^b	400	1.76	17.9	17.7	2.25	17.4	None	None
Triple superphosphate ^b	200							
H ₂ O	40	1.16						
Wilson Dam slag ^d	400	3.59	18.7	18.7	Trace	18.6	7.35 ^e	0.84/ ^f
Triple superphosphate ^b	200							
H ₂ O	40	2.80						

^a If no reaction had ensued.

^b Fluorine-free.

^c No citrate-insol. after second digestion.

^d Contained 6.50 per cent CaF₂.

^e Second and third digestions gave 2.65 and 0.95 per cent.

^f Amount calculated from citrate-insol. P_2O_5 content of slag.

^g Second and third digestions gave 4.65 and 1.05 per cent.

TABLE II. INFLUENCE OF CALCIUM FLUORIDE ADDITIONS UPON P_2O_5 TRANSITIONS IN WETTED AND AGED MIXTURES OF FLUORINE-FREE TRIPLE SUPERPHOSPHATE WITH FLUORINE-FREE CALCIUM CARBONATES AND SILICATES AND FLUORINE-CONTAINING SLAGS

Mixture Components	Period Days	Loss in Wt. Grams	Moisture %	Total P_2O_5		P_2O_5 Value Water-Sol.		Citrate-insol.		
				Found %	Calcd. %	Found %	Calcd. ^a %	Found %	Calcd. %	
CaCO ₃ , c. p.	75	76.8	14.2	0.27	19.75	19.70	1.50	19.50	None	None
T. S. P. ^b		40.0								
CaF ₂		3.2								
H ₂ O		8.0								
CaSiO ₃ , c. p.	75	76.8	+2.0	6.64	18.15	18.00	1.50	17.60	None	None
T. S. P. ^b		40.0								
CaF ₂		3.2								
H ₂ O		8.0								
Limestone	75	76.8	8.0	0.26	18.85	18.65	1.55	18.33	None	None
T. S. P. ^b		40.0								
CaF ₂		3.2								
H ₂ O		8.0								
Dicalcium silicate ^b	75	76.8	3.0	3.03	17.70	18.04	1.60	17.75	None	None
T. S. P. ^b		40.0								
CaF ₂		3.2								
H ₂ O		8.0								
Atlas Cement slag ^b	75	76.8	5.0	1.52	17.95	18.23	7.75	17.86	None	None
T. S. P. ^b		40.0								
CaF ₂		3.2								
H ₂ O		8.0								
Wilson Dam slag ^c	75	76.8	6.6	1.79	18.90	19.33	1.90	18.12	4.58	0.88 ^d
T. S. P. ^b		40.0								
CaF ₂		3.2								
H ₂ O		8.0								

^a If no transition had ensued.

^b Fluoride-free.

^c Contained 6.5 per cent CaF₂.

^d Amount computed from citrate-insoluble P_2O_5 content of slag.

^e At the end of a 100-day period the first, second, and third digestions gave respective values of 6.45, 3.75, and 2.25 per cent.

TABLE III. P_2O_5 TRANSITIONS IN MOISTENED AND AGED MIXTURES OF FLUORINE-FREE TRIPLE SUPERPHOSPHATE WITH CALCIUM SILICATE SUPPLEMENTED BY A FUSED EUTECTIC MIXTURE OF CALCIUM SILICATE AND CALCIUM FLUORIDE^a

Original components	Final Moisture %	P_2O_5 after 35 Days	
		Water-sol. %	Citrate-insol. %
T. S. P. (F ₂ -free) ^b	8.82	1.75	Trace
CaSiO ₃			
CaSiO ₃ -CaF ₂ melt			
H ₂ O			
T. S. P. (F ₂ -free) ^b	9.26	Trace	Trace
CaSiO ₃			
CaSiO ₃ -CaF ₂ melt			
H ₂ O			

^a The mechanical mixture of CaSiO₃ and CaF₂ simulated the composition of the Wilson Dam slag.

^b Containing 55.0% water-soluble and no citrate-insoluble P_2O_5 .

After a 35-day aging period in closed containers at room temperature, the initial water-soluble P_2O_5 contents had practically disappeared, and no citrate-insoluble content was registered. Apparently the pulverulent c. p. calcium silicate reacted with the superphosphate to produce mixtures so dry as to preclude activity of the fluoride-silicate melt. The ready solubility of engendered dicalcium phosphates and calcium silicate residues and the resultant concentration of calcium salts also served to protect the eutectic melt from solvent action of the citrate solution during analytical digestion. The results of Table II and III, with those of Table I, demonstrate the distinction between the reactivity of the dispersed content of component fluoride and that of mechanical incorporations of calcium fluoride in mixtures so rich in calcic materials.

MIXTURES OF SUPERPHOSPHATES CONTAINING FLUORIDES. The superphosphate used in the mixtures with c. p. calcium silicate and with cement slag (Table IV) differed from the fluoride-free product used in Tables I, II, and III. This superphosphate was obtained by the acidulation of brown Tennessee phosphate rock with H_3PO_4 and contained fluorine equivalent to 3.35 per cent of calcium fluoride.

Formation of citrate-insoluble P_2O_5 was registered by each

of the three calcic admixtures after 35 days. The fluoride content of the superphosphate was derived from the phosphate rock and was in such chemical and physical state as to admit of its reaction with the neutralized superphosphate of the three mixtures, either during aging or during analysis. Hence, when either the superphosphate or the calcic material contained fluoride components, the persistent citrate insolubility that developed in their mixtures exceeded any of the completely removable insolubility that was in evidence in the aged fluoride-free mixtures after a single digestion.

INFLUENCE OF TEMPERATURE ON ACTIVITY OF FLUORIDES. The admixing of 200 pounds of limestone or of dolomite with 1800 pounds of superphosphate, as such or with included supplements, may be taken to be representative of commercial practice. Such partial neutralization of a superphosphate could not produce tribasic phosphates to account for the increases in citrate insolubility that actually occur.

The seven mixtures of the first group of Table V were made with a fluoride-free concentrated superphosphate diluted with additions of calcium sulfate and ground quartz before incorporation of the seven liming supplements. Each mixture was brought to a moisture content of 6 per cent and then divided into two equal portions. One portion was placed in a glass container, compacted, and aged for 6 days at room temperature; the other was aged at 65° C. The second series of seven pairs was an exact duplication of the first series, except for the substitution of a commercial superphosphate that contained fluorine equivalent to 3.62 per cent calcium fluoride.

Computed to compensate for losses in weight attributable to carbon dioxide and water, the results of Table V show the changes in contents of water-soluble and citrate-insoluble P_2O_5 for the fourteen systems of each series. The accelerative effect of the higher temperature is registered by the greater

TABLE IV. P_2O_5 TRANSITIONS IN AGED MIXTURES OF COMMERCIAL TRIPLE SUPERPHOSPHATE WITH C. P. CALCIUM SILICATE AND WITH CEMENT SLAG

Original components	Final Moisture %	P_2O_5 after 35 Days	
		Water-sol. %	Citrate-insol. ^a %
T. S. P. ^b	1.13	1.00	3.00
Atlas Cement slag ^c			
H ₂ O			
T. S. P. ^b	7.34	Trace	11.10
CaSiO ₃			
H ₂ O			
T. S. P. ^b	8.59	Trace	9.00
CaSiO ₃			
H ₂ O			

^a Determined values calculated to basis of original T. S. P. component, which had an initial citrate-insoluble content of 1.55 per cent P_2O_5 .

^b Contained 3.35 per cent CaF₂.

^c Fluoride-free.

decreases in water-soluble P₂O₅ contents for each of the four-teen comparisons.

In the first series fluorides were present only in the two systems that contained the two separates of Wilson Dam slag, and those systems gave an indication of increased citrate insolubility only when aged at 65° C. The mixtures of the

aging at room temperature, the initial P₂O₅ insolubility of 6.75 per cent had increased to 36.24.

The heated and aged, moistened phosphate-fluoride mixtures showed a marked physical transformation, an altered apparent density, and a clear supernatant citrate extract; none of these phenomena occurred with the dry control mixture. Similar results took place when the systems were heated only overnight.

The aged moistened mixture of the homemade phosphate and c. p. calcium fluoride of Table VI was also used for the determination of P₂O₅ uptake by rye seedlings, following the Neubauer technic, for six conditions and with two soils. The uptake from the moistened, heated, and aged mixture of tricalcium phosphate and calcium fluoride was uniformly only about half that shown by the corresponding heated dry mixture of those two solids.

Since no appreciable change in the solubility of

TABLE V. INFLUENCE OF TEMPERATURE ELEVATION UPON THE TENDENCY OF COMPONENT CALCIUM FLUORIDE TO PRODUCE CITRATE INSOLUBILITY IN MIXTURES OF 9 PARTS OF PHOSPHATES WITH 1 PART OF LIMING MATERIAL DURING A 6-DAY AGING PERIOD

Components of Mixtures ^a			Water-Soluble Portion			P ₂ O ₅ Values Citrate-Insoluble			Gain in Citrate-Insol.	
Phosphate	Liming Material ^b	Mesh	Initial %	Portion cured		Initial %	Portion cured		at room temp. %	at 65° C. %
				at room temp. %	at 65° C. %		at room temp. %	at 65° C. %		
Fluoride-free T. S. P., CaSO ₄ , and quartz	CaCO ₃ , c. p.	325	15.32	2.27	0.50	None	None	None	None	None
	Limestone	325		2.50	1.00	None	None	None	None	None
	Limestone	20-40		12.43	2.25	None	None	Trace	None	None
	Dolomite	325		6.10	1.05	None	None	None	None	None
	Dolomite	30-40		10.76	7.20	None	None	None	None	None
	Wilson Dam slag	325		4.40	1.30	0.14	Trace	0.43	-0.14	0.29
Wilson Dam slag	20-40	8.42	3.25	0.14	0.06	0.20	-0.08	0.06		
Commercial standard superphosphate ^c	CaCO ₃ , c. p.	325	11.97	2.50	1.10	1.35	1.35	2.24	None	0.89
	Limestone	325		2.80	1.00	1.35	1.40	2.03	0.05	0.68
	Limestone	20-40		11.10	3.50	1.35	1.27	2.09	-0.08	0.82
	Dolomite	325		9.80	2.90	1.35	1.37	1.85	0.02	0.50
	Dolomite	30-40		11.45	9.52	1.35	1.27	1.37	-0.08	0.02
	Wilson Dam slag	325		11.50	1.40	1.49	1.39	1.70	-0.10	0.21
Wilson Dam slag	20-40	11.90	7.50	1.49	1.58	1.59	0.09	0.10		

^a All mixtures were of an initial moisture content of 6 per cent; phosphates were 35 mesh.
^b The Wilson Dam slag contained fluorine equivalent to 6.5% CaF₂; the other liming materials were fluoride-free.
^c Contained fluorine equivalent to 3.69% CaF₂.

commercial superphosphate showed no indication of the formation of citrate-insoluble compounds during the 6-day aging at room temperature; that formation was shown, however, by the parallel series which was aged at 65° C., especially by the mixtures that contained the more soluble liming materials. Hence, when aged at 65° C. for 6 days, component fluorides increased the citrate insolubility.

The reaction that develops citrate insolubility without an excess of alkalinizing material is not rapid in dry mixtures, and prolonged aging of the heated systems of Table V would undoubtedly have registered greater values.

Fluorapatite Formation through Reaction between Solid Mixtures of Tricalcium Phosphate and Calcium Fluoride

Keenen (6) showed that elevation in temperature and aging are dominant factors in the development of high citrate insolubility in ammoniated superphosphates, and postulated the formation of tricalcium phosphate "of entirely different chemical and physical behavior from mineral rock phosphate." Jacob and Ross (4) concluded that "the citrate solubility of tricalcium phosphate in a mixed fertilizer may be considerably lower than that of the pure salt."

Since the fluoride content of superphosphate has not been considered as a causal factor in the decrease in solubility of the P₂O₅ content of processed and aged superphosphates, conditions were imposed to determine whether fluorapatite will develop in intimate mixtures of tricalcium phosphate and calcium fluoride.

The data of Table VI show that little change in the solubility of the tricalcium phosphate monohydrate occurred when it was heated at 65° C., alone and in dry mixtures with calcium fluoride in a 12 to 1 proportion. In contrast, a 4.4 fold increase in P₂O₅-insoluble content was registered by the 6-day heating of the moistened mixture. Supplemental mixtures showed that 91 per cent of this 6-day effect occurred overnight. Mere moist contact of another tricalcium phosphate and fluoride overnight at room temperature caused a threefold increase in citrate insolubility. After 60-day

the triphosphate monohydrate occurred during the digestion of the heated dry mixture of phosphate and calcium fluoride, in contrast to the marked increase shown by solid-phase moistened mixtures maintained at 65° C., it is clear that a chemical transition took place during the aging period. The only change possible for the mixture of the triphosphate and fluoride would be the combination:



Microscopic examination showed distinctly divergent refractive properties for the final mixtures. The calcium fluo-

TABLE VI. FORMATION OF APATITE IN MIXTURES OF LABORATORY-PREPARED TRICALCIUM PHOSPHATE WITH C. P. CALCIUM FLUORIDE AFTER AGING AT 65° C.

Condition	Mixture Original components	Grams	Citrate-Insol. P ₂ O ₅	
			After 6 days	After 20 days
			As % of Ca ₃ (PO ₄) ₂ component	
Dry	Ca ₃ (PO ₄) ₂ ·H ₂ O alone	..	7.50 ^a	8.25
Moist	Ca ₃ (PO ₄) ₂ ·H ₂ O alone	..	7.82	...
Dry	Ca ₃ (PO ₄) ₂ ·H ₂ O	23.8	7.86	7.59 ^b
	CaF ₂	2.0		
Moist	Ca ₃ (PO ₄) ₂ ·H ₂ O	23.8	34.69 ^c	36.05
	CaF ₂	2.0	26.29 ^d	29.81 ^d
			17.78 ^e	20.32 ^e
Dry	c. p. tricalcium phosphate ^f	23.8	23.88 ^g	...
	CaF ₂	2.0		
Moist	c. p. tricalcium phosphate ^{f,h}	23.8	27.25 ^g	29.25
	CaF ₂	2.0		

^a Initial citrate-insoluble P₂O₅ value of 6.75%.
^b Heating period, 35 days.
^c Citrate-insoluble P₂O₅ values obtained from an identical moistened mixture, after aging overnight at room temperature and at 65° C., were 17.00 and 32.25 per cent, respectively.
^d Residue from first ammonium citrate digestion, redigested.
^e Residue from second ammonium citrate digestion, redigested.
^f A purchased product, representative of solid solutions of phosphates, rather than a true Ca₃(PO₄)₂.
^g Initial citrate-insoluble P₂O₅ value of 20.00%.
^h Substitution of trimagnesium phosphate for tricalcium phosphate in this mixture gave no change in citrate-insoluble P₂O₅ value after heating at 65° C. for 6 days.
ⁱ Substitution of CaCO₃ for CaF₂ in this mixture gave no change in citrate-insoluble P₂O₅ value after heating at 65° C. for 6 days.

ride continued as such in the dry mixture, whereas the fluoride lost its petrographic identity in the moistened mixtures of the laboratory-prepared phosphate.

When portions of the aged, dry, and heated mixture of tricalcium phosphate monohydrate and calcium fluoride were acidulated with H_2SO_4 and with H_3PO_4 , the original fluoride crystals remained unchanged. But when the aged moistened mixture was likewise acidulated, neither treatment reproduced identifiable crystals of calcium fluoride—a result in accord with that found for commercial superphosphates.

The c. p. tricalcium phosphate compound, of indeterminate components, showed a high initial citrate insolubility of 20 per cent, and enhancement of its citrate insolubility after contact with calcium fluoride was only a third of that registered by the laboratory product, $Ca_3(PO_4)_2 \cdot H_2O$, which contained CaO and P_2O_5 in exact theoretical ratio. When the c. p. calcium fluoride of the moistened c. p. triphosphate mixture was replaced by calcium carbonate at the same 1 to 12 ratio, no change in P_2O_5 solubility occurred after 6 days of aging at $65^\circ C$. When moistened mixtures of trimagnesium phosphate and c. p. calcium fluoride in the 1 to 12 proportion were similarly aged, the calcium fluoride had no effect upon P_2O_5 solubility.

Citrate solubility of partially defluorinated fused white and brown rock phosphates was also decreased by moist contact with calcium fluoride when solid mixtures of 12.9 to 1 proportion were aged for 6 days at $65^\circ C$. Comparative citrate digestions of the unheated and unaged control mixtures demonstrated, however, that the determined increases in P_2O_5 insolubility had developed largely during the citrate digestions.

Fluorapatite Formation in Aqueous Suspensions of Tricalcium Phosphate and Calcium Fluoride

Although increased citrate insolubility was induced by digestion of aqueous suspensions of tricalcium phosphate alone at $65^\circ C$., the presence of a small amount of calcium fluoride caused further P_2O_5 insolubility. A 1-hour aqueous digestion of a 1-gram charge of the laboratory-prepared tricalcium phosphate alone and with an addition of 0.085 gram of calcium fluoride gave citrate insolubility increases of 75 and 193 per cent, respectively.

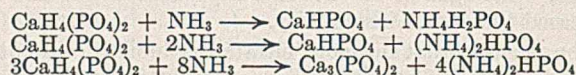
The synthesis of fluorapatite was also indicated by a 39 per cent increase in citrate insolubility that developed in filtered residues from agitated 18-hour suspensions of 12 parts

tricalcium phosphate and 1 part calcium fluoride in carbonated water saturated at $8^\circ C$. The same technic was used for three systems that contained a 0.5-gram charge of tricalcium phosphate alone, with 0.5 gram of c. p. calcium carbonate, and with 0.5 gram of Wilson Dam slag. The inclusion of the calcium carbonate gave a residue that registered an increased citrate insolubility of 86 per cent; the inclusion of the Wilson Dam silicate-fluoride slag caused 147 per cent increase.

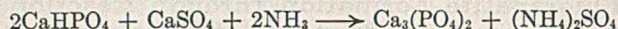
Ammoniation of Fluoride-Free Superphosphate in Mixtures with Limestone and Calcium Fluoride

Citrate insolubility is also encountered in the ammoniation of superphosphates. Keenen (6) demonstrated that the degree of ammoniation and development of citrate-insoluble P_2O_5 are closely related; in a recent contribution (7) he treated the problem of citrate insolubility that develops in ammoniated superphosphates that contain dolomite supplements. This aspect was considered in the four systems of Table VII which were exposed immediately to an atmosphere of ammonia.

The fluoride-free concentrated superphosphate of two mixtures was first diluted by admixture of an equal amount of calcium sulfate dihydrate and further diluted with two parts of 100-mesh limestone to one part of the superphosphate-calcium sulfate mixture. Pulverulent calcium fluoride was then added to one of the mixtures. The third system contained only the fluoride-free superphosphate and limestone. Calcium fluoride (c. p.) was included in the fourth mixture. Upon immediate ammoniation, the phosphate transition of mixtures devoid of sulfates would ensue substantially in the order of



The system that contained calcium sulfate would undergo further change, according to the equation,



In the four ammoniated systems of Table VII, complete P_2O_5 transitions were inhibited by the drying effect and the surface coatings incident to the formation of dicalcium phosphates by absorption of ammonia, and were further restricted by the surface effect of the dry limestone.

In these systems, as in those of Table II, the quickly attained high concentration of calcium salts in the citrate solution precluded any production of solute fluoride from the incorporated solid. Hence, no indication of fluorapatite was adduced, either during the curing period of 75 days at room temperature or during the analytical digestion of the fluoride-fortified systems.

As supplemental to the foregoing (Table VII), portions of an ammoniated fluoride-free monocalcium phosphate were aged 6 days at room temperature and at $65^\circ C$. No citrate insolubility developed in either of these two fluoride-free mixtures. Similar mixtures were made with a commercial standard superphosphate that contained 4.31 per cent calcium fluoride. No increase in citrate-insoluble P_2O_5 developed in the mixture aged at room temperature; an increase of 1.90 per cent took place in the mixture aged at $65^\circ C$.

TABLE VII. INFLUENCE OF CALCIUM FLUORIDE AND SULFATE ADDITIONS UPON P_2O_5 TRANSITIONS IN MIXTURES OF TRIPLE SUPERPHOSPHATE WITH LIMESTONE DURING 35- AND 75-DAY PERIODS, IN PRESENCE OF MOISTURE VAPOR AND GASEOUS AMMONIA^a

Mixture Components	Parts	Period Days	Moisture %	Value after Aging P_2O_5				Insol. %
				Total		Water-sol.		
			Found %	Calcd. %	Found %	Calcd. ^b %		
T. S. P. ^c	50	35	3.77	9.10	8.7	2.1	8.5	None
$CaSO_4 \cdot 2H_2O$, c. p.	50	75	8.48	8.60	8.7	1.03	..	Trace
Limestone	200							
T. S. P. ^c	50	35	4.16	9.04	8.7	2.70	8.5	None
$CaSO_4 \cdot 2H_2O$, c. p.	50	75	8.13	8.80	8.7	1.13	..	Trace
CaF_2	8							
Limestone	192							
T. S. P. ^c	100	35	4.66	17.1	16.8	10.65	16.5	None
Limestone	200	75	7.91	17.2	17.3	6.65	..	0.13
T. S. P. ^c	100	35	4.98	16.95	16.8	10.50	16.5	None
CaF_2	8	75	7.96	17.40	17.5	6.45	..	0.10
Limestone	192							

^a The mixtures were placed under a bell jar with a 400-cc. beaker filled with concentrated NH_4OH .

^b If no reaction had ensued.

^c Fluoride-free product.

The results of Tables I to VII demonstrate that the effect of component fluorides caused the development of citrate insolubility, when such fluorides were introduced into the several phosphatic mixtures through the use of either commercial superphosphates or Wilson Dam slag, an increased effect being induced by elevation of temperature. The separate introductions of calcium fluoride were inactivated by the added calcic materials or by ammoniation. Although petrographic examination, diminution of citrate solubility, and Neubauer tests indicated the formation of fluorapatite in both cold and warmed mixtures of tricalcium phosphate and calcium fluoride, the increases in the citrate-insoluble P_2O_5 content of the superphosphate mixtures were shown solely by ammonium citrate digestions. Hence, it was not known to what extent the degradation was induced prior to citrate digestion and during that digestion.

Activity of Various Forms of Calcium Fluoride during Citrate Digestions of Their Mixtures with Tricalcium Phosphates

The extent to which the postulated formation of fluorapatite may occur during ammonium citrate digestion was determined for mixtures of tricalcium phosphate with the three calcium fluorides of variant form and solubility—precipitated c. p. calcium fluoride, pulverized fluorspar, and the component of the slag. The c. p. tricalcium phosphate of Table VIII showed a citrate-insoluble P_2O_5 content three times that of the laboratory-prepared material and a calcium fluoride content of 0.17 per cent, as against 0.04 per cent for the homemade tricalcium phosphate of Tables VI and VIII. Citrate digestions of 1-gram charges of the Wilson Dam slag showed that 97.4 per cent of its 6.5 per cent calcium fluoride content was readily dissolved, along with the large proportion of calcium silicate. The same treatment dissolved 14.60 per cent calcium fluoride from c. p. calcium fluoride of 92.19 per cent purity; only 1.15 per cent was dissolved from a 94.54 per cent fluorspar.

The solids of the several systems of Table VIII were in contact only during the citrate digestions. No increase of citrate-insoluble P_2O_5 occurred when the combined charges of c. p. tricalcium phosphate and either c. p. calcium fluoride, or fluorspar, were subjected to immediate digestions with ammonium citrate. A marked increase did occur, however, when the combined charges of tricalcium phosphate and slag were digested. But since the solvent capacity of the citrate solution (10) was diminished by the dissolving of the calcium silicate of the slag, a control mixture of 0.9 gram of fluoride-free calcium silicate and 1 gram of triphosphate was included. This fluoride-free control gave an insoluble P_2O_5 value 3 per cent less than that induced by the Wilson Dam slag.

In the other five-unit group of Table VIII, where the more soluble tricalcium phosphate monohydrate was used, both of the fluoride supplements caused a decided increase in the citrate insolubility of the more soluble tricalcium phosphate. That result can be construed as indicating a twofold effect—synthesis of fluorapatite and a repressive effect of salts of a common ion during digestion. Although the more soluble calcium fluoride may have enhanced the common-ion effect, it also supplied a larger quantity of solute calcium fluoride to combine with the basic phosphate. Furthermore, the repressive effect upon P_2O_5 solubility that was exerted by the augmented concentration of calcium salts derived from the calcium silicate equivalent of the Wilson Dam slag was made still more repressive by the charge of Wilson Dam slag with its fluoride content. As previously pointed out, however, the removal of the common-ion effect by repetitions of citrate digestions will eliminate the increases in citrate insolubility induced by the fluoride-free carbonates and silicates of

TABLE VIII. EFFECT OF CALCIUM FLUORIDES UPON SOLUBILITY OF TRICALCIUM PHOSPHATES^a DURING AMMONIUM CITRATE DIGESTIONS

Components ^b Included with Phosphates during 1-Hr. Digestions with Ammonium Citrate at 65° C. ^c	Citrate-Insol. P_2O_5 Developed by:	
	c. p. tricalcium phosphate ^d	Lab. product $Ca_3(PO_4)_2 \cdot H_2O^e$
	Per cent ^f	Per cent ^f
Components Digested Simultaneously		
None	20.00 ^g	6.75
Precipitated CaF_2	20.40	21.50
Pulverized fluorspar	20.00	13.75
200-mesh Wilson Dam slag	31.73 ^h	30.35 ^h
c. p. $CaSiO_3$ equivalent of Wilson Dam slag	28.75 ⁱ	26.75
Components Added after 1-Hr. 65° C. Digestion of Phosphate Alone, Followed by Further 1-Hr. Digestion of Mixtures		
Precipitated CaF_2	21.50	23.75
1/2 charges of CaF_2 and phosphate	16.50	6.25
200-mesh Wilson Dam slag	23.35 ^h	16.65 ^h
c. p. $CaSiO_3$ equivalent of Wilson Dam slag	22.66	14.75
Components Subjected to 1-Hr. 65° C. Digestion before Addition of Phosphates, Followed by Further 1-Hr. Digestion of Mixtures		
Precipitated CaF_2	25.40	23.75
1/2 charges of CaF_2 and phosphate	19.60	15.00
200-mesh Wilson Dam slag	33.10 ^h	34.85 ^h
c. p. $CaSiO_3$ equivalent of Wilson Dam slag	29.50	27.75

^a A purchased c. p. chemical and a laboratory product.

^b Constant charge of 1 gram of each component, except as specified.

^c The ammonium citrate extracts were separated from the solids by centrifuging, instead of filtering, because of the retarding effect of SiO_2 , and the residues were protected against peptization by washing with ammonium citrate (9).

^d Contained 0.17 per cent CaF_2 .

^e Contained 0.04 per cent CaF_2 .

^f Expressed as content of phosphatic component.

^g Charge of 0.5 gram gave 14.76 per cent.

^h After correction for the 1.40 per cent citrate-insoluble content of slag.

ⁱ Charges of 0.5 gram of phosphate and $CaSiO_3$ gave 25.60 per cent.

calcium. This, however, is not true for the citrate insolubility that develops during citrate digestions of immediate mixtures of basic phosphates and calcium fluoride, nor is it true of the insolubility that develops when unsupplemented moist mixtures of solid phases of tricalcium phosphates and calcium fluoride are aged.

When the laboratory product was digested alone for 1 hour and then supplemented with a 1-gram charge of c. p. calcium fluoride and the citrate digestion continued for 1 hour, the resultant citrate insolubility exceeded that obtained by the 1-hour simultaneous digestions of the same components. To a less extent this was true of the less soluble c. p. tricalcium phosphate. But when the more soluble phosphate was dissolved alone, and additions of either the Wilson Dam slag or its calcium silicate equivalent were then introduced, the insolubility values were materially less than those found when the corresponding pairs of solids were digested simultaneously. Minimal citrate-insoluble P_2O_5 values, or maximal solubilities, were shown by the 0.5-gram charges of both phosphates.

When the digestion of each fluoride material preceded the introduction of the phosphate, the ammonium citrate became saturated with calcium fluoride. In seven of the eight systems the resultant insolubilities exceeded those of corresponding systems where digestion of the phosphate preceded the addition of the fluoride materials. The lowest citrate-insoluble values of this group were also registered by the use of 0.5-gram charges. In addition to the greater solvent capacity of the standard volume of citrate for a reduced charge of calcium solids, an opposing factor was involved. The determined ratio of solute calcium fluoride to phosphate addition in the 0.5-gram systems was almost twice that extant in the 1-gram systems; greater opportunity for synthesis of fluorapatite was thus afforded in the 0.5-gram systems.

TABLE IX. CITRATE-INSOLUBLE P_2O_5 PRODUCED DURING AMMONIUM CITRATE DIGESTION OF MIXTURES OF CALCIUM PHOSPHATES WITH THE CALCIUM FLUORIDE AND SILICATES

Materials ^a	Citrate-Insol. P_2O_5 , ^b %
c. p. monocalcium phosphate ^c plus:	
Slag	3.25
CaSiO ₃ + CaF ₂ mixture ^d	Trace
c. p. dicalcium phosphate ^e plus:	
Alone	4.00
CaSiO ₃	8.75
CaF ₂ + CaSiO ₃	11.75
CaF ₂ + CaSiO ₃ + iron silicate	10.00
CaF ₂ + CaSiO ₃ + aluminum silicate	9.75
Wilson Dam slag	15.85 ^f
Wilson Dam slag, 0.5-gram charge of each component	6.10
c. p. tricalcium phosphate ^e plus:	
Alone	20.00
Alone, 0.5-gram charge	14.76
CaSiO ₃	30.63
CaSiO ₃ , 0.5-gram charge of each component	25.60
CaF ₂ + CaSiO ₃	30.00
CaF ₂ + CaSiO ₃ + iron silicate	25.50
CaF ₂ + CaSiO ₃ + aluminum silicate	27.75
Wilson Dam slag	31.73 ^f
Wilson Dam slag, 0.5-gram charge of each component	28.86 ^f

^a Constant charges of 1 gram phosphate and also of each calcic supplement or mixture, except as noted: CaSiO₃ + CaF₂ mixture contained equal parts; 0.16 gram ferric silicate and 0.08 gram aluminum silicate added where these materials are specified.

^b P_2O_5 expressed as per cent of 1-gram phosphate charge.
^c The mono- and dicalcium phosphate residues were washed with water, but the tricalcium phosphate residues were washed with ammonium citrate solution; clear solutions were obtained.

^d 93.5% CaSiO₃, 6.5% CaF₂, to simulate analysis of calcium silicate slag.
^e After correction for the 1.40 per cent citrate-insoluble content of the slag.

P_2O_5 Insolubility Induced during Citrate Digestion of Phosphate Mixtures with Calcium Fluorides

Table IX gives data on several combinations of solid components subjected to immediate digestions with ammonium citrate at 65° C. In the mixture of c. p. monocalcium phosphate with Wilson Dam slag, the calcium silicate content of which was in excess of the amount requisite for complete transition of the monocalcium to tricalcium phosphate, more than 3 per cent of citrate-insoluble P_2O_5 was produced. This did not occur, however, when the calcium silicate slag was replaced by c. p. calcium silicate and 1 gram of precipitated calcium fluoride. Hence repression of the reactivity of the 65-mg. calcium fluoride content of the slag by the concomitant calcium silicate content was less than the repressive effect exerted by the c. p. calcium silicate upon the reactivity of the calcium fluoride.

The c. p. calcium silicate effected an increase in the citrate-insoluble P_2O_5 value of c. p. dicalcium phosphate, but still further increases occurred in each system that contained c. p. calcium fluoride. The maximal effect was registered by the full charge of fluoride-rich Wilson Dam slag. The make-up systems that simulated the slag were not so active as the slag.

In the third series of Table IX, inclusion of an equal amount of calcium silicate caused an increase in the P_2O_5 insolubility for the 1-gram charges of the c. p. tricalcium phosphate, with no further effect by the supplements of c. p. calcium fluoride. Digestion of mixtures of calcium silicate and c. p. calcium fluoride and prior digestions of the calcium fluoride, followed by addition of the calcium silicate, demonstrate that the silicate caused a decrease of more than 80 per cent in the solvent action of the citrate extract towards the fluoride. The fluoride effect was indicated, however, by the dispersed calcium fluoride content of the supplement of Wilson Dam slag in both the 1- and 0.5-gram systems.

Variant Reactivity of Dicalcium Phosphates towards Calcium Fluorides in Citrate Digestions

Transition of water-soluble P_2O_5 to dibasic phosphates is the principal effect in either ammoniated or dolomite-treated superphosphates. Reactions can extend beyond that point, but full transitions are not desired in commercial ammoniation and they are not so readily induced by limestone and dolomite in solid mixtures or even in aqueous suspensions (11, 13, 14, 15). Dibasic phosphates possess varying solubilities, however, depending upon the mode of preparation, fluorine content, and degree of hydration.

The data of Table X show that dicalcium phosphates behave differently towards additions of different types of calcium fluorides during the citrate digestion. The purchased c. p. material was presumably a precipitated product that contained 0.29 per cent of calcium fluoride; the University of Tennessee material was substantially an anhydrous fluoride-free material devoid of tricalcium phosphate. The disparity between the initial citrate insolubilities of the two products might be attributed to the occurrence of tricalcium phosphate and reactant calcium fluoride in one product and their absence from the other.

TABLE X. REACTIVITY OF DICALCIUM PHOSPHATES, SHOWN BY CITRATE-INSOLUBLE P_2O_5 ENGENDERED DURING ANALYSIS OF THEIR IMMEDIATE MIXTURES WITH CALCIUM FLUORIDES^b

	P_2O_5 , %
c. p. dicalcium phosphate, alone ^d	4.00
Univ. of Tenn. dicalcium phosphate, alone ^e	0.15
c. p. dicalcium phosphate + CaF ₂	6.25
Univ. of Tenn. dicalcium phosphate + CaF ₂	0.70
c. p. dicalcium phosphate + fluorspar	4.50
Univ. of Tenn. dicalcium phosphate + fluorspar	Trace
Wilson Dam slag, alone	1.40
c. p. dicalcium phosphate + Wilson Dam slag	15.85 ^f
Univ. of Tenn. dicalcium phosphate + Wilson Dam slag	2.85 ^f
c. p. dicalcium phosphate digested in ammonium citrate 1 hour at 65° C.; CaF ₂ added; digested 1 hour more at 65° C.	5.88
Same treatment, using Wilson Dam slag	12.98
Same treatment, using 0.5-gram charge of each component	7.76
Univ. of Tenn. dicalcium phosphate digested in ammonium citrate 1 hour at 65° C.; CaF ₂ added; digested 1 hour more at 65° C.	Trace
Same treatment using Wilson Dam slag	7.35
Same treatment using 0.5-gram charge of each component	1.10
c. p. CaF ₂ digested in ammonium citrate 1 hour at 65° C.; c. p. dicalcium phosphate added; digested 1 hour more at 65° C.	8.25
c. p. CaF ₂ and same treatment with U. T. dicalcium phosphate	Trace

^a 1-hour digestions with 100 ml. ammonium citrate at 65° for 1 hour.

^b Constant charges of 1 gram of each component.

^c P_2O_5 expressed as per cent of the 1-gram phosphate charge.

^d Contained 0.29 per cent CaF₂ capable of producing approximately 1.5 per cent P_2O_5 as $3Ca_3(PO_4)_2 \cdot CaF_2$.

^e Fluoride-free.

^f After correction for the 1.40 per cent citrate-insoluble P_2O_5 content of the slag.

Additions of both c. p. calcium fluoride and fluorspar engendered much greater citrate insolubility during the citrate digestions of the c. p. dicalcium phosphate than in those of the laboratory product. The greater solubility of the pulverulent type of calcium fluoride was also reflected in the greater citrate-insoluble value induced by it. There was also a decided disparity between the amounts of citrate-in-

soluble P_2O_5 engendered in the simultaneous digestions of the two types of dicalcium phosphates with equal charges of Wilson Dam slag.

In the predigestions of both the 1- and 0.5-gram charges of two phosphates with subsequent additions of either calcium fluoride or Wilson Dam slag, the c. p. material developed greater citrate insolubilities. With prior digestions of c. p. calcium fluoride and subsequent inclusions of the phosphates, the citrate-insoluble P_2O_5 content of the c. p. material increased twofold, whereas the laboratory product showed no increase.

In each of the last four comparisons of Table X, maximal citrate insolubility was caused by the Wilson Dam slag, which imparted alkalinity to a solution enriched in calcium citrate and containing free ammonia. These conditions are conducive to the formation of tricalcium phosphates and, from their reaction with calcium fluoride, to the formation of fluorapatite, $3Ca_3(PO_4)_2 \cdot CaF_2$, as in Table VI. The citrate solution became quite alkaline upon digestion with carbonates and silicates of calcium and emitted a distinctly ammoniacal odor. The actual loss of ammonia was small, however, as determined by the ammonia content of the citrate solution before and after 1-hour $65^\circ C.$ digestions, alone and with 1-gram charges of calcium carbonate and silicate.

Analysis and Evaluation of Data

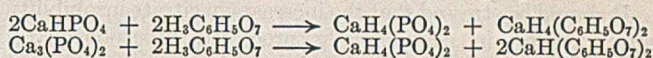
Since monocalcium phosphate and calcium fluoride do not combine in a system that contains an excess of hydrogen ions, the presence of the fluoride can have no effect upon citrate insolubility in fully acidulated superphosphates. Laboratory experiments confirmed this fact. Evidence of the fluoride effect appears, however, during the curing of superphosphates partially neutralized by ammoniation or by incorporated liming materials. In commercial manures such neutralizing treatments usually fall considerably short of changing all the free acid and monocalcium phosphate contents to dicalcium phosphate. Nevertheless, the curing of large piles of such partially neutralized superphosphates frequently develops sufficient "reversion" to cause economic loss to the manufacturer. Even though the added basic material is insufficient to effect full conversion of the bulk of water-soluble P_2O_5 to di-forms, there may be focal occurrences of basic phosphate. This behavior was demonstrated by the partially neutralized phosphate-fluoride systems of Table V and is in accord with the recent contribution by Keenen (7).

The second transition step, whereby added liming materials induce the formation of tricalcium phosphates, has been dealt with in previous contributions (13, 14, 15), and the effect of increase in temperature was shown to be accelerative, even in small bulk (14). Such localized occurrences of triphosphate may react with component calcium fluoride to form fluorapatite as in Table VI. When concentrated superphosphates are diluted with liming materials to obtain a product with a P_2O_5 content of 16 per cent or less, a great many localized formations of basic phosphates ensue. When a superphosphate is diluted with limestone rather than dolomite and then aged, the cumulative fluoride effect is especially evident. It was shown, in mixtures of 500 pounds of concentrated superphosphate with 1000 pounds of wetted limestone, that the citrate-insoluble P_2O_5 content of the mixture was 1.00 per cent after 24 hours and 1.24 per cent after 6 weeks (11). After the 35-mesh reserve sample of that pile had stood for 2 years, the citrate-insoluble content had increased to 8.4 per cent. In contrast, the dolomite mixture gave citrate insolubilities of 1.10, 1.19, and 1.50 per cent for the 24-hour, 6-week, and 2-year periods, respectively.

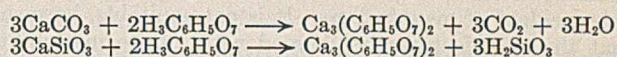
Undecomposed limestone residues also induce a marked rise in the pH value of the citrate solution (10, 15), the

common-ion effect, and a decided decrease in the solvent capacity of the extractant. Formation of more basic and less soluble phosphates, as well as fluorapatite, may therefore take place during the citrate digestion.

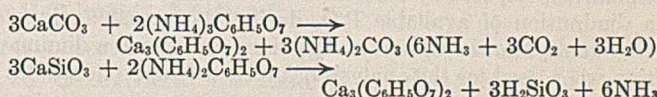
The solvent capacity of the "neutral" citrate solvent (1) of 1.09 specific gravity is derived from its hydrolysis. When the potentially acidic "neutral" citrate solution is used for the digestion of the water-insoluble portions of unaltered superphosphates, the solvent capacity of the citrate is not measurably diminished. Even when considerable percentages of the di- and tricalcium phosphates are present, they will be dissolved when the proportions of charge to volume of solvent permit, as indicated by the following equations:



But when phosphatic mixtures contain either calcium carbonate or silicate, these readily soluble neutralizing materials are quickly decomposed by the hydrolyzed citrate solution,



or by the indicated exchange reactions,



that develop a citrate solution of greatly increased pH value (10, 15). A common result of these reactions is the development of a high concentration of calcium citrate and the advent of the common-ion effect. Jacob and Ross (4) and MacIntire and Shuey (15) showed this effect to be appreciable, dolomite being decidedly less active than limestone.

Jacob and Ross (4) included the relatively insoluble fluorspar among the calcium salts added to citrate digestions of tricalcium phosphate and found that the natural fluoride exerted a solubility depression comparable to that induced by relatively soluble calcium compounds. They concluded, however, that "the decrease in solubility is not due to any change in the chemical nature of the chemical phosphate, but simply to the effect of other compounds in depressing its solubility." That depressive effect was likewise distinctly in evidence in the present systems that contained large proportions of the readily soluble carbonates and silicates of calcium. But 1-hour ammonium citrate digestions at $65^\circ C.$ of a 1-gram charge of the natural calcium fluoride alone showed a solubility of only 1.15 per cent that was reduced 80 per cent by an equal charge of either calcium carbonate or silicate. A similar digestion of the c. p. calcium fluoride dissolved 8.72 per cent calcium fluoride. Both values were obtained by means of fluorine determinations rather than by losses in weight. The higher value imparted a common salt concentration only one-twelfth of that derived by the citrate solution from the dissolved charges of the carbonate and silicates of calcium. But the data of Table VIII demonstrate conclusively that the citrate insolubility engendered by the small amount of calcium fluoride dissolved from the slightly soluble fluoride far exceeds that engendered by the high concentration of calcium citrate derived from the readily dissolved silicate. Hence, an effect beyond that of the common salt was involved.

Karandeeff (5) showed that calcium metasilicates and calcium fluoride do not combine chemically, and microscopic examinations of the Wilson Dam slag revealed these two compounds as separate components. In spite of the predominant concomitant occurrence of calcium silicate, the fluoride content of the Wilson Dam slag was almost completely dissolved and was decidedly reactant towards basic phosphates. This behavior is attributed to the wide distribution of this fluxing

halide in the mass of the calcium silicate of the slag and the extensive surface afforded by the liberated calcium fluoride when the calcium silicate framework of the slag is dissolved by the citrate solution.

The reaction between the more basic phosphates and calcium fluoride induced experimentally in the solid mixtures, in aqueous suspensions, in carbonated water suspensions, and in ammonium citrate solution-suspensions, gave a persistent citrate insolubility not found for the basic phosphatic mixtures devoid of fluorides. Component calcium fluoride may therefore be considered as a potent factor in the development of citrate insolubility in ammoniated superphosphates and in those with which liming materials are incorporated.

It should be stressed that the increases in citrate insolubility may develop in commercially processed superphosphates not only during the curing period, but also during the actual analysis of the finished product. The citrate insolubility that develops during curing of superphosphates rendered nonacid forming, or those ammoniated, may be considered an inescapable incident of manufacture. It is not equitable, however, that the manufacturer be charged with citrate insolubility that is developed during the imposition of analytical technic. Conditions imposed by the analytical technic should not cause a diminution of available P_2O_5 during the actual analysis. Apparently, however, citrate digestions cause such a diminution when used for the analysis of processed superphosphates

that contain fluorides and considerable proportions of basic phosphates.

Literature Cited

- (1) Assoc. Official Agr. Chem., Methods of Analysis, 1930.
- (2) Jacob, K. D., Rader, L. F., Marshall, H. L., and Beeson, K. C., *IND. ENG. CHEM., Anal. Ed.*, 4, 25 (1932).
- (3) Jacob, K. D., Rader, L. F., and Tremearne, T. H., *J. Assoc. Official Agr. Chem.*, 19, 449 (1936).
- (4) Jacob, K. D., and Ross, W. H., *J. Am. Soc. Agron.*, 23, 771 (1931).
- (5) Karandeeff, B., *Z. anorg. Chem.*, 68, 188 (1910).
- (6) Keenen, F. G., *IND. ENG. CHEM.*, 22, 1378 (1930).
- (7) *Ibid.*, 29, 197 (1937).
- (8) MacIntire, W. H., U. S. Patent 2,067,538 (1937).
- (9) MacIntire, W. H., and Hardin, L. J., *J. Assoc. Official Agr. Chem.*, 18, 297 (1935).
- (10) MacIntire, W. H., Hardin, L. J., and Oldham, F. D., *IND. ENG. CHEM.*, 28, 48 (1936).
- (11) *Ibid.*, 28, 711 (1936).
- (12) MacIntire, W. H., Jones, R. M., and Hardin, L. J., *J. Assoc. Official Agr. Chem.*, 18, 301 (1935).
- (13) MacIntire, W. H., and Shaw, W. M., *IND. ENG. CHEM.*, 24, 1401 (1932).
- (14) MacIntire, W. H., and Shaw, W. M., *J. Am. Soc. Agron.*, 26, 656 (1934).
- (15) MacIntire, W. H., and Shuey, G. A., *IND. ENG. CHEM.*, 24, 933 (1932).
- (16) Willard, H. H., and Winter, O. B., *IND. ENG. CHEM., Anal. Ed.*, 5, 7 (1933).

RECEIVED March 1, 1937.

Fertilizer from Rock Phosphate¹

Conversion by Fusion and Treatment with Water Vapor

FOR some time it has been known that when finely ground rock phosphate is heated in an oxidizing atmosphere and in the presence of sufficient silica and water vapor, fluorine is volatilized from the material. Under suitable conditions the fluorine content may be reduced from an initial value of over 3.0 per cent to a final value of less than 0.1 per cent. When the defluorinated product is quickly cooled, the phosphate is nearly all available as plant food.

Jacob and his co-workers in the United States Bureau of Chemistry and Soils studied this process on a small scale (3, 4, 5, 6). With rock phosphate containing 4 to 12 per cent silica, they found that upwards of 95 per cent of the fluorine was volatilized and 80 per cent or more of the phosphate was converted into the citrate-soluble condition by heating small charges of 40-mesh material in the presence of water vapor for 30 minutes at approximately 1400° C. These investigators demonstrated that water vapor and silica together promote the defluorination of rock phosphate.

Attempts are being made, both in this country and abroad, to develop practical means of using the calcination process on a larger scale (1, 7). There are several difficulties to be overcome. One of the worst arises from the fact that the tempera-

HARRY A. CURTIS, RAYMOND L. COPSON,
EARL H. BROWN, AND GORDON R. POLE
Tennessee Valley Authority, Wilson Dam, Ala.

ture required is just below that at which the phosphate fuses. Incipient fusion gives rise to mechanical difficulties in handling the pasty mass. Rock phosphates have a softening range rather than a sharp melting point, and they vary considerably in fusing temperature, depending on the proportions of the several impurities present. Consequently the temperature must be under very close control by the operator at all times.

In the investigation a number of attempts were made at first to calcine rock phosphate in an experimental oil-fired rotary kiln, approximately 15 inches inside diameter and 20 feet long. The combustion of the oil was relied upon to produce the water vapor necessary for the reaction. However, the results were not equal to those obtained in small-scale work. For example, when a rock phosphate containing 6 to 9 per cent silica was calcined at a maximum temperature of 1400° to 1450° C. and at a feed rate such that the total time in the kiln was approximately one hour, the fluorine volatilization varied from 50 to 70 per cent, and the conversion to citrate-soluble phosphate varied from 20 to 40 per cent. Even when the time in the kiln was doubled, either by decreasing the rate of feed or by putting the product back through the kiln a second time, the fluorine volatilization did not exceed 75 per cent, and the conversion to citrate-soluble phosphate did not exceed 50 per cent. In these experiments the rock phosphate was ground to pass a 40-mesh sieve and was moistened with water and fed to the kiln as a stiff mud, to avoid dust losses.

¹ The term "rock phosphate" is used to distinguish the amorphous phosphates, such as occur in the deposits in Tennessee and Florida, from the "mineral phosphates" of definite chemical compositions, such as fluorapatite, phosphorite, etc.

The experimental conditions were varied considerably from those just stated, without improvement in the results. When coarser material was used, the reaction was much slower. When temperatures within the softening range were used, the material became plastic and formed rings in the kiln. The use of steam to atomize the oil, or the addition of small quantities of superheated steam to the atmosphere in the kiln, did not improve the results noticeably.

Preliminary Fusion Experiments

During the experiments on calcination in the rotary kiln, a few samples of fused material were obtained. The product from one run at approximately 1450° C. contained rounded particles about 1/8 inch in diameter, which apparently had been fused. These were separated by hand; on analysis it was found that the sample contained only 0.5 per cent fluorine, and that 74 per cent of the P₂O₅ was citrate soluble. Another sample of fused material collected from the wall of the kiln was found to contain only 0.14 per cent fluorine.

In one set of preliminary experiments, finely ground rock phosphate was mixed with water, molded into rods approximately 5/8 inch in diameter, and dried. The rods were held in the flame of an oxyhydrogen torch, and the molten material was allowed to drop directly into water. The products contained 0.2 per cent fluorine or less, corresponding to over 93 per cent volatilization, and 86 per cent of the P₂O₅ was citrate soluble. This result was surprising, in view of the short time during which the phosphate was in a fused condition. Apparently the reaction was very rapid at the high temperature and at the high water vapor concentration of the oxyhydrogen flame.

Other preliminary experiments were made in which rock phosphate was fused in refractory crucibles and also in a small cylindrical furnace having a capacity of about 5.5 pounds. Oxygen-hydrocarbon gas flames were used in these experiments. The temperatures varied from 1500° to 1600° C., and the time of fusion from 20 to 60 minutes. The products contained from 0.5 to 0.03 per cent fluorine, and 72 to 86 per cent of the P₂O₅ was citrate soluble.

Small-Scale Fusions in Indirect-Arc Furnace

In order to investigate the conditions necessary for rapid volatilization of fluorine from fused rock phosphate, a small

indirect electric arc furnace was adopted for small-scale experiments. The furnace was a Detroit rocking electric furnace type GM. The furnace was modified as shown in Figure 1. A pipe manifold was mounted on the furnace, through which steam or gas could be forced into the molten material. The furnace was operated at 20 to 25 kw., using 1.5-inch graphite electrodes. A 20-pound charge of rock phosphate could

Because of practical difficulties encountered in attempting to defluorinate rock phosphate by treatment with water vapor at temperatures below the fusion range of the rock, the possibility of defluorinating fused rock phosphate was investigated. Small-scale experiments indicated that fluorine could be removed from rock phosphate at temperatures 50° to 170° C. above its melting point, that contact with water vapor was necessary for rapid defluorination, and that combustion gases from hydrocarbon fuels might be used to supply the water vapor. Products containing approximately 0.1 per cent fluorine, 30 per cent total P₂O₅, and 26 per cent citrate-soluble P₂O₅ were obtained.

Three different semiworks furnaces, oil-fired, were built and operated to determine necessary conditions, fuel consumption, life of refractories, and character of product. Results obtained in the small-scale tests and in the semiworks furnaces are summarized in this paper.

be fused in about one hour, starting with a cold furnace. In all of the experiments described here, the indirect-arc furnace was lined with a silica refractory. The normal operation of the furnace was as follows:

A charge of lump rock phosphate was dumped into the hot furnace, and the arc started. During the period of fusing the charge, the openings from the gas manifold were kept above the charge. After fusion was complete and the desired temperature reached, steam or other gas was started through the manifold and the furnace rotated so as to bring the gas openings to the bottom of the molten charge. The gas was forced through the molten rock for the predetermined time. In order to prevent the melt from solidifying around the openings from the gas manifold, and thus cutting off the gas flow, it was customary to heat the molten rock to a temperature 100° C. or more above its fusion point. The furnace was then rotated so as to bring the openings above the melt, the gas flow interrupted, and the melt poured out. The melt was either blown into pellets by a blast of air or was quenched in water. An optical pyrometer was used to measure the temperature in the furnace at intervals and the temperature of the fused product as it was poured from the furnace. The arc was shut off during the measurement of temperature within the furnace.

The composition of the rock phosphates used in the experiments is shown in Table I. Sample 1 is representative of the material fused in the indirect-arc furnace.

The products were analyzed for total P₂O₅, citrate-insoluble P₂O₅, and fluorine. Fluorine was determined in all samples by the Willard and Winter method. The citrate-insoluble P₂O₅ was determined by the official neutral ammonium citrate method, using 1.0 gram of sample to 100 cc. of citrate solution, and with the addition of filter paper pulp (2). All samples for analysis were ground to pass an 80-mesh sieve. It was necessary to adopt a standard fineness, since it was found that the

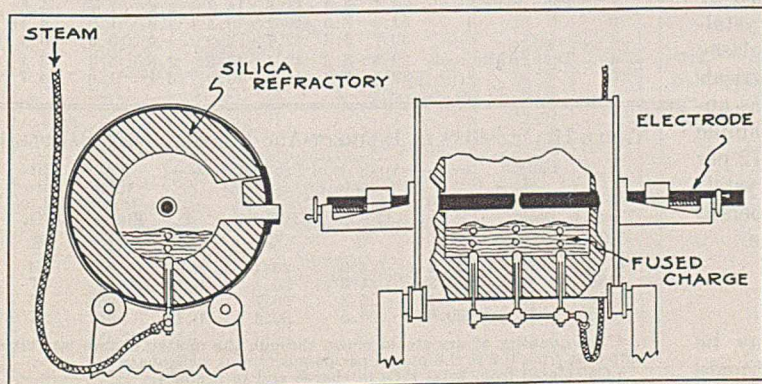


FIGURE 1. INDIRECT-ARC FURNACE

citrate solubility of the P_2O_5 , determined by the indicated procedure, varied with the fineness of the sample, and that the finer the sample, the greater was the citrate solubility.

When rock phosphate was fused for 60 minutes in the indirect-arc furnace, with no control of the furnace atmosphere, the product contained about 1.9 per cent fluorine. When nitrogen saturated with water vapor was introduced over the melt in the furnace, the fluorine removal was only slightly improved, since the products contained about 1.2 per cent fluorine, after treatment for 60 minutes. Likewise, bubbling a rapid stream of dry air or nitrogen through the melt for 15 to 20 minutes resulted in unsatisfactory removal of fluorine, the products containing from 1.8 to 2.2 per cent fluorine.

However, when dry steam was bubbled through the molten phosphate at such a rate as to agitate the melt violently, thereby giving good contact, volatilization of most of the fluorine was accomplished readily. During the steam blow, acrid fumes were emitted from the charge.

Table II gives the results of several experiments in which steam was blown through the molten phosphate; the data in each case are the average of two duplicate experiments. The fluorine in the products varied from 0.30 to 0.12 per cent, and the citrate solubility of the P_2O_5 from 84 to 87 per cent. No appreciable volatilization of P_2O_5 was observed during the experiments. The fact that the total P_2O_5 in the products was lower than in the rock phosphate charged was evidently due to solution of some of the silica refractory by the molten charge.

It was found possible to blow the molten product into small pellets by means of an air blast, as the melt was poured from the furnace. The size of the pellets could be varied within wide limits by regulating the pressure of the air blast. The fluorine content and the citrate solubility of the P_2O_5 were about the same, whether the melt was blown with air or was quenched in water. When air-blown, the product consisted of small, dark green, glassy spheres; when quenched in water, it disintegrated into pieces approximately $1/8$ inch in size.

Photomicrographs of thin sections of the defluorinated phosphate are shown in Figure 2. The sample of Figure 2A contained 0.14 per cent fluorine, and 83 per cent of the P_2O_5 was citrate soluble. The major constituent was identified by its optical properties as α -tricalcium phosphate (δ), crystallized in random orientation. A small amount of a glassy material, with a refractive index close to that of the α -tricalcium phosphate (1.58 to 1.59), was also present; it was apparently a calcium-aluminum-iron silicate glass. The sample of Figure 2B contained 0.42 per cent fluorine, and only 72 per cent of the P_2O_5 was citrate soluble. In this case the crystals of tricalcium phosphate were smaller and were interspersed with fibrous crystals which apparently were fluorapatite.

Rotary Kiln

These experiments demonstrated that fluorine may be volatilized rapidly from molten rock phosphate when intimate contact with water vapor is provided.

Since the rotary kiln was available in which the calcination experiments had been made as described, it was decided to try to fuse rock phosphate in this kiln. The kiln was lined with silica refractory brick and was fired with 28° to 32° A. P. I. gas oil atomized with compressed air. The rock phosphate fed to the kiln was sized to pass a 2-mesh and be retained on a 20-mesh sieve. With material of this size there was little trouble with formation of rings in the kiln.

The molten product was quenched in water, and the quenching apparatus was arranged so that the steam generated was drawn back into the kiln.

A test run lasting 18 days was made in the rotary kiln. The average composition of the feed is given as sample 2 in Table I. The average composition of the product is shown in Table III, where the results of this run are summarized. On the average, 92 per cent of the fluorine was volatilized, and 83 per cent of the P_2O_5 was converted to the citrate-soluble condition. The oil consumption averaged 5.7 pounds per pound of available P_2O_5 produced; this figure was excessive since the heat losses from the kiln were large and since no attempt was made to recover heat from the flue gases.

After 18 days it was necessary to stop operation because the silica brick lining of the kiln had been badly attacked by the molten phosphate, and the steel shell of the kiln had become so hot that there was danger of serious warping.

Tilting Converter Furnace

A semiworks furnace was built in which superheated steam could be blown through the molten phosphate, as shown in Figure 3. This furnace was similar to the small, indirect-arc furnace except that it was oil-fired. The chamber of the furnace was cylindrical, and it was mounted on trunnions so that it could be rotated about its horizontal axis. A single opening in the furnace shell was used both for charging and



FIGURE 2. PHOTOGRAPH OF THIN SECTIONS OF FUSED PHOSPHATE TAKEN WITH TRANSMITTED LIGHT AND CROSSED NICOLS ($\times 75$)

A. 0.14 per cent fluorine

B. 0.42 per cent fluorine

TABLE I. ANALYSES OF ROCK PHOSPHATES USED

Sample No.	Material	Analysis, %						Ignition loss
		P_2O_5	F	CaO	SiO_2	Fe_2O_3	Al_2O_3	
1	Tenn. brown rock	30.7	3.3	41.8	14.3	2.4	1.4	5.6
2		32.9	3.5	46.1	9.5	2.9	1.3	4.1
3		30.7	3.3	42.7	9.9	3.5	3.5	3.4
4	Tenn. white rock	29.6	3.3	42.1	13.5	2.8	2.3	3.1
5		29.6	3.3	44.0	13.0	3.1	1.6	4.7

TABLE II. FUSIONS IN INDIRECT-ARC FURNACE WITH SAMPLE 1

Temp. $^\circ$ C.	Length of Steam Blow ^a Min.	Analysis of Product				Volatilization of Fluorine %	Citrate Sol. of P_2O_5 %
		Total P_2O_5 %	Citrate-sol. P_2O_5 %	SiO_2^b %	F %		
1550	15	28.7	24.0	25.1	0.30	90	84
1580	17	28.3	24.5	26.1	0.18	94	87
1610	15	30.4	25.8	20.7	0.12	96	85
1630	17	30.6	26.5	20.4	0.12	96	87

^a The quantity of dry steam blown through the molten charge was estimated at from 0.4 to 0.8 pound per pound of rock phosphate.

^b Calculated from total P_2O_5 in charge and in product.

TABLE III. AVERAGE RESULTS OBTAINED IN SEMIWORKS FURNACES

Rock Phosphate No.	Type of Furnace	Type of Charging	Duration of Test Days	Temperature ° C.	Production Rate Per hour Lb.	Production Rate Per batch Lb.	Analysis of Product			Oil ^a Consumption			
							Total P ₂ O ₅ %	SiO ₂ %	F %	Citrate soly. of P ₂ O ₅ %	Per hour Lb.	Per lb. of product Lb.	Per lb. of available P ₂ O ₅ Lb.
2	Rotary kiln	Continuous	18	1510	65	...	30.8	19.2	0.25	83	94	1.45	5.7
3	Converter ^b	Batch	9	1520	80	640	29.8	17.5	0.34	80	90	1.12	4.7 ^c
4	Hearth	Batch	8	1540	110	715	31.5	14.8	0.19	85	108	0.98	3.7
5	Hearth	Continuous	8	1540	191	...	30.2	17.0	0.47	70	80	0.42	2.0

^a Gas oil, 28° to 32° A. P. I.

^b Superheated steam blown through melt for 5 minutes during each 8-hour cycle; quantity of steam estimated at 0.06 pound per pound of rock phosphate.

^c Does not include oil for superheater.

for pouring out the molten product by tilting the furnace. A pipe manifold was mounted along the side of the furnace, through which superheated steam could be introduced. The openings from this manifold were maintained above the level of the melt during charging and fusing, and the furnace was rotated so as to bring them at the bottom of the bath during the steam blow.

The furnace was heated by two oil burners, located at opposite ends of the combustion chamber, and two regenerators were provided for recovering part of the heat from the flue gases. The burners were used alternately; the hot flue gases passed through one regenerator and the air for combustion was preheated in the other, in the usual manner for such furnaces.

An oil-fired superheater was provided for superheating the steam. Flexible pipe connections were used between the superheater and the fusion furnace.

The furnace was lined throughout with silica refractory, with the exception of the pouring spout which was lined with zircon brick. The regenerators were constructed of high-grade fire clay refractories.

This furnace could produce 1.0 to 1.7 tons of fused rock phosphate per day, when charging 1-inch lump rock. On the average, over 90 per cent of the fluorine was volatilized, and 80 per cent of the P₂O₅ in the product was citrate soluble, when the melt was blown with superheated steam for 5 minutes. However, the time required for fusing the charge was excessively long, indicating low rates of heat transfer. It was also necessary to reheat the charge after the steam blow to make it sufficiently fluid for pouring. Thus the steam blow occupied only 5 minutes out of an average operating cycle of 8 hours. Although it is probable that the operation can be improved, the results so far obtained indicate an excessively high oil consumption in this type of furnace. The average results of a 9-day run are given in Table III.

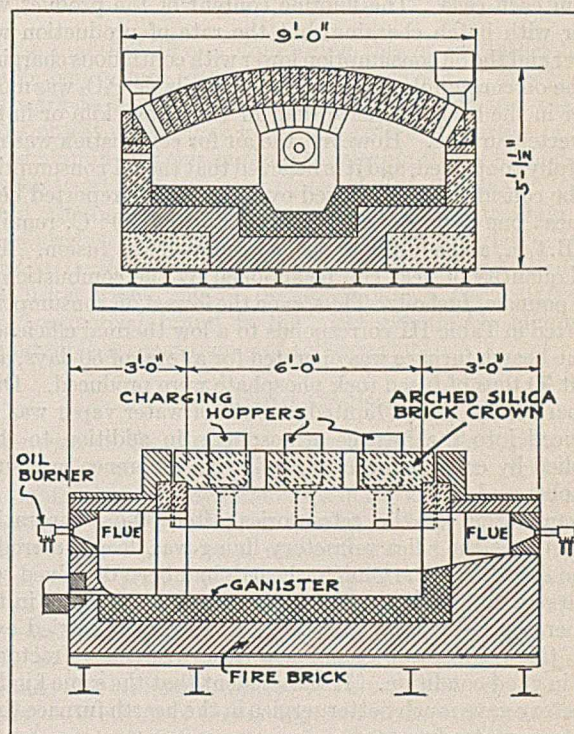


FIGURE 4. HEARTH FURNACE

The life of refractories in the converter furnace was found to be very short. Thus, a 9-inch silica refractory lining had a life of only 14 days of continuous operation. The attack of the molten phosphate on the refractory lining probably was increased as a result of the agitation of the charge in this type of furnace.

Hearth Furnace

The third type of furnace was a regenerative, oil-fired furnace, having two hearths on which the charge was melted. This furnace is shown in Figure 4. Silica refractories were used for the crown and side walls. The hearths were constructed of tamped ganister, on a firebrick base. The furnace was heated by two oil burners located at opposite ends of the combustion chamber. The burners were used alternately, the hot flue gases passing through one regenerator and the air for combustion being preheated in the other, as in the converter furnace. The regenerators are not shown in the drawing.

Rock phosphate was supplied to the furnace through the hoppers shown in Figure 4. The feed was between 1 and 1/4 inch in size. As the rock phosphate fused, it flowed into the central trough of the furnace in which it collected and from

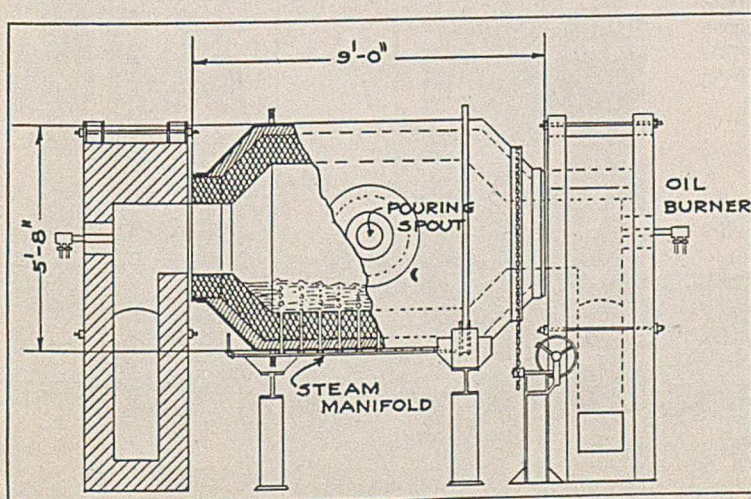


FIGURE 3. CONVERTER FURNACE

which it was tapped at intervals. The fused phosphate was quenched by means of a high-pressure water jet and sprays.

The furnace was operated with both continuous and batch charging. In the first case the hoppers were maintained full of rock phosphate which descended continuously into the furnace as the material on the hearths melted. The fused product was tapped from the furnace at intervals of about 5 hours. In the second case a batch was charged into the furnace, and was melted and tapped before a second charge was introduced. With batch charging the interval between taps averaged about 6.5 hours.

The results obtained with each type of operation are summarized in Table III; the data are the average for an 8-day run in each case. The fluorine content of the product was lower with batch charging, but the rate of production was higher and the oil consumption lower with continuous charging.

The oil consumption per pound of available P_2O_5 was much lower in the hearth furnace than in the rotary kiln or in the converter furnace. However, the air for combustion was not carefully controlled, and it is believed that the oil consumption can be considerably decreased over the figures reported here. To heat one pound of rock phosphate to $1550^\circ C.$ requires 540 B. t. u., and additional heat is required for fusion. The total quantity of heat can be supplied by the combustion of 0.04 pound of fuel oil. Thus, even the lowest oil consumption reported in Table III corresponds to a low thermal efficiency.

The hearth furnace was operated for a total of 50 days, and about 70 tons of fused rock phosphate were produced. During part of the time a limited amount of water vapor was introduced into the furnace atmosphere, in addition to that supplied by combustion of the oil. No difference in results was observed.

Examination of the refractories after 50-day operation showed that the silica refractory lining was deeply corroded at the flux line. The ganister hearth had been dissolved to a depth of 2 to 3 inches. The top two courses of brick in the regenerator checkers were glazed, owing to dust carried over from the combustion chamber. Otherwise the refractories were in good condition. It was evident that the same kind of refractory gave much better service in the hearth furnace than in the converter furnace.

Conclusions

1. Fluorine was volatilized readily from fused rock phosphate at temperatures above $1500^\circ C.$ and in the presence of

water vapor. When dry steam was bubbled through the molten phosphate, from 5 to 15 minutes were sufficient for volatilization of over 90 per cent of the fluorine, and for conversion of over 80 per cent of the P_2O_5 to the citrate-soluble condition. No addition of silica over that present in the rock phosphate was required.

2. Rock phosphate was fused and defluorinated in an oil-fired furnace in which water vapor was supplied only by combustion of the oil. In the hearth furnace the time required for fusion and defluorination was approximately 5 to 6.5 hours.

3. Refractories were severely attacked by molten rock phosphate. Most of the experience so far has been with silica refractory, and this has not given satisfactory length of service. The attack on the refractories was much less in the hearth furnace than in the rotary kiln or the converter furnace; in the latter, corrosion of the refractories probably was increased by the agitation of the molten charge.

4. If the refractory problem can be solved, either by use of better refractories or by improvements in furnace design, it appears probable that available phosphate can be produced cheaply by fusion and treatment by water vapor. The lowest oil consumption was 2.0 pounds per pound of available P_2O_5 produced, and a considerably lower figure should be possible.

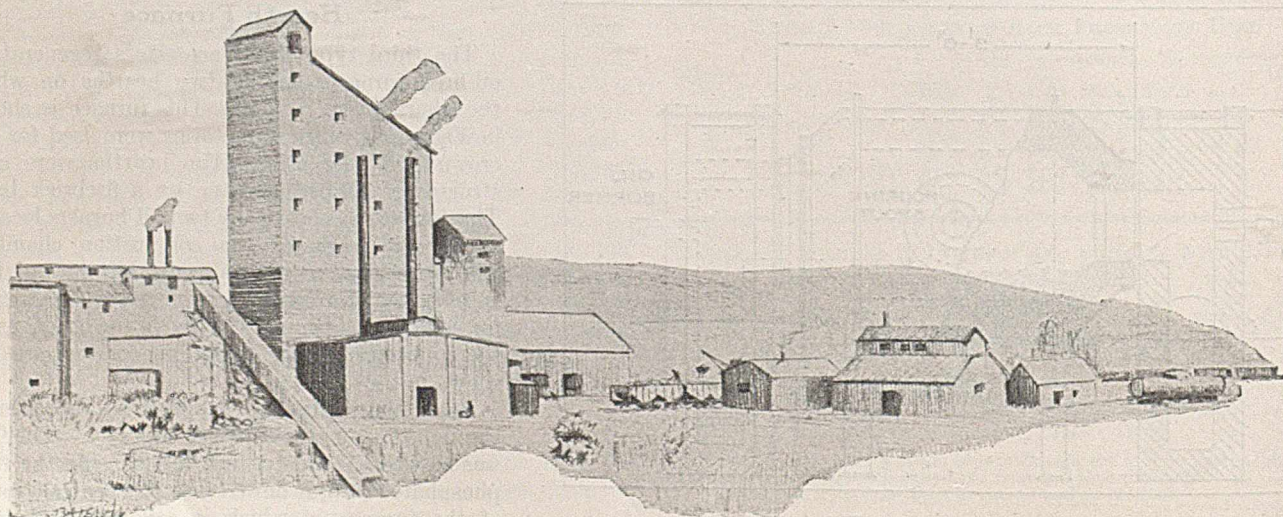
Acknowledgment

The authors are indebted to other members of the staff of the T. V. A. Chemical Engineering Laboratory at Wilson Dam for assistance in obtaining the data presented in this paper.

Literature Cited

- (1) Caldwell, U. S. Patent 1,902,832 (March 28, 1933).
- (2) Jacob, Rader, and Tremearne, *J. Assoc. Official Agr. Chem.*, 19, 449-70 (1936).
- (3) Marshall, Reynolds, Jacob, and Rader, *IND. ENG. CHEM.*, 27, 205-9 (1935).
- (4) Reynolds, Jacob, Marshall, and Rader, *Ibid.*, 27, 87-91 (1935).
- (5) Reynolds, Jacob, and Rader, *Ibid.*, 26, 406-12 (1934).
- (6) Reynolds, Marshall, Jacob, and Rader, *Ibid.*, 28, 678-82 (1936).
- (7) St. Jacques, *IND. ENG. CHEM., News Ed.*, 15, 29-30 (1937).
- (8) Schneiderhohn, *Mitt. Kaiser-Wilhelm Inst. Eisenforsch. Düsseldorf*, 14, 34-6 (1932).

RECEIVED April 17, 1937. Presented before the Division of Agricultural and Food Chemistry at the 93rd Meeting of the American Chemical Society, Chapel Hill, N. C., April 12 to 15, 1937.



Removal of Undesirable Constituents from Tobacco Smoke

R. B. DERR, A. H. RIESMEYER,
AND R. B. UNANGST

Aluminum Research Laboratories,
Aluminum Company of America,
New Kensington, Pa.

MANY investigators have studied the constituents of smoke which pass from a cigaret or pipe into the smoker's respiratory system. From this work it is well known that tobacco smoke contains nicotine, carbon dioxide, carbon monoxide, ammonia, aldehydes, and a number of organic tarry compounds. Although there has been disagreement as to the degree of harm resulting from the assimilation of these constituents into the body, it is generally conceded that nicotine, ammonia, and tarry matter are present in amounts which could be irritating or which would have the greatest physiological effects.

Most investigations have been concerned with the nicotine content of the smoke, but substantially no data are available

on the practicability of minimizing this or any other undesirable compound. Because of the lack of this information the work to be described was undertaken. It had the primary object of employing the adsorptive properties of activated alumina for this purpose by placing this highly adsorptive material in the stem of pipe and cigaret holders. (Activated alumina is a highly adsorptive granular aluminum oxide produced by Aluminum Company of America.) Other sorptive materials were investigated also, and as a result the conclusion which will be developed is: A fresh cigaret of any commercial brand is the most practicable eliminator of undesirable constituents of tobacco smoke.

Puffing Device

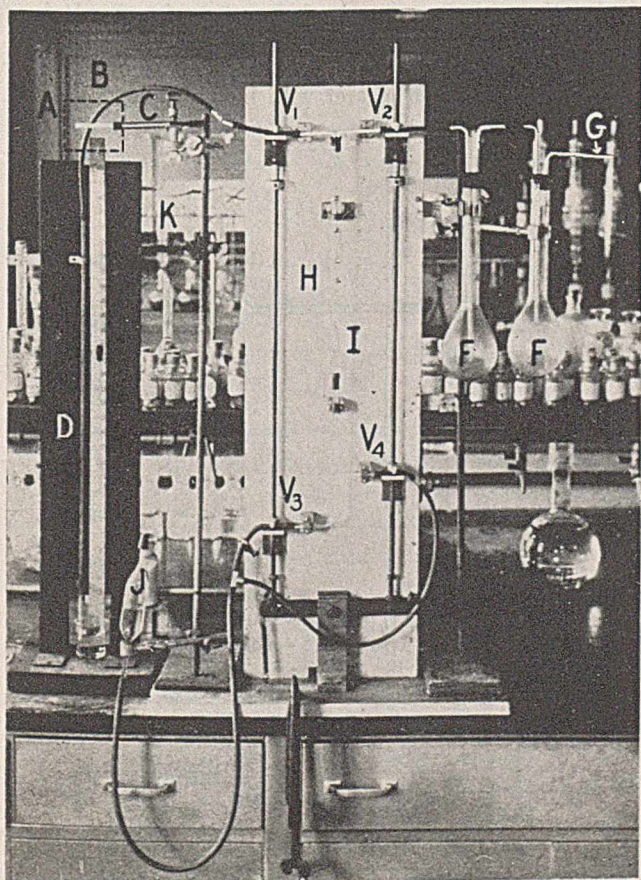
A review of the literature shows considerable variations in the quantity of nicotine present in tobacco smoke, and this is undoubtedly caused by differences in the smoking procedures. Therefore, the first problem was the selection of a puffing device with which normal smoking could be simulated and which would permit consistent duplication of results. The use of a partial vacuum as a means of drawing the puff and a mechanically rotated valve for controlling the duration of puff, as employed by Jensen and Haley (4), was rejected because of insufficient control of volume and velocity. Obviously, the effects of these important items would be accentuated by the slightly increased resistance introduced by a sorptive smoke filter. The smoking device selected was constructed substantially as shown in Figure 2 of the article by Bradford, Harlan, and Hanmer (2):

This device permits the drawing of a definite volume of air at a uniform rate and in a definite period. The volume is controlled by a measured quantity of water flowing from a buret. The puff is terminated sharply by a ground-glass float which serves as a quick-operating valve as it sinks to the constriction at the bottom of the buret. Moreover, the duration of puff may be adjusted accurately by constricting the water outlet so that the desired period elapses between the start of fall and the click of the float as it reaches the bottom of the buret.

• • • • •

FIGURE 1. PUFFING DEVICE

- A = cigaret
- B = shield for cigaret (not shown)
- C = cigaret holder with cigaret filter
- D = water gage manometer
- V₁ = puff inlet valve
- V₂ = puff outlet valve to nicotine recovery flasks
- V₃ = water outflow valve open during intake puff
- V₄ = water inflow valve open during outflow of puff
- F = Kjeldahl flasks
- G = exit to atmosphere or to Norris bulb
- H = buret for measuring puff volume
- I = ground-glass float which terminates puff; small glass hook on top permits ready removal for cleaning
- J = water leveler
- K = adjustable top support for leveler bulb
- L = bottom support for leveler bulb



The original train consisted of a cigaret supported horizontally by a holder capable of receiving the sorbent material under investigation. The cigaret was surrounded by a shield to minimize the effects of air currents. The bit of the holder was connected to a Y, one arm of which led to a vacuum indicator and the other to a Kjeldahl flask, followed by two Milligan scrubbers containing dilute hydrochloric acid. Smoke from the lighted cigaret was drawn through this train by the above puffing device, and the efficiency of the sorbent in the holder was determined by comparing the quantity of materials retained in it to that which passed to the secondary scrubbers.

Special mention should be made of the joint at the tip of the holder and the cigaret to be smoked because other investigators have considered it necessary to employ special means of sealing to prevent leakage. The tip of the holder employed in this work was designed so as to contact 0.95 cm. ($\frac{3}{8}$ inch) of the length of the cigaret to be smoked, and it tapered, in this length, from about 0.86 to 0.80 cm. in diameter. The standard cigarets fitted into this tip with very slight compression. Moreover the cigaret butted against a small shoulder at the base of the tip. For all practical purposes this butt contact, together with the slight contact at the side, prevented leakage of air.

After trying out the assembled equipment, it was observed that the actual flow of air through the cigaret did not cease in exactly the period indicated by the fall of water in the smoking device. This difference became greater with increasing resistance introduced by the sorbent in the holder, and it was especially noticeable when the sorbent had accumulated tar and nicotine. Because this lag introduced the objection which has been made to the vacuum smoking devices, the puffing apparatus was placed between the cigaret holder and the scrubbers.

Substantially all of the nicotine was recovered in the first dry flask, and two dry flasks (Figure 1) were sufficient to collect all of the nicotine when puffs up to 30-cc. volume were used. With the larger puff the dry flasks were supplemented with a small Norris bulb containing dilute hydrochloric acid and alcohol. This modified arrangement caused a direct and more positive flow through the cigaret as is the case in natural smoking. Moreover the effect of gradually increasing resistance could be readily eliminated merely by opening the restriction in the outflow water line until the glass float dropped in the desired puff period. The operation of the equipment arranged in this manner was somewhat more cumbersome than that used by Bradford because the water level had to be adjusted manually and also because it necessitated the thorough washing of the entire system with hot dilute sodium hydroxide solution to recover the nicotine passed. These modifications, however, seem justified by the uniformity of the results obtained with sorbents offering varying resistance.

Selection of Velocity and Volume of Puff

The smoking habits of several individuals were determined by Pfyl (5), who concluded that a 40-cc. puff, lasting 2 seconds and drawn twice a minute, approximated the average. Bradford et al. (1) arbitrarily selected a 35-cc. puff lasting 2 seconds and drawn once a minute; Jensen and Haley (4) smoked by applying a partial vacuum, equivalent to 15.25 inches (38.74 cm.) of water below atmospheric pressure, for a period of 1.6 seconds and with an interval of 6.1 seconds between puffs. They indicated that the volume of air was 20 cc. per puff.

In order to check the volume of puff, an apparatus similar to Pfyl's was set up as shown in Figure 2. Care was taken to seat the individual under test in a comfortable position and with the measuring buret out of view. The subject was requested to take small, average, and large puffs, and the respective volumes were observed and recorded. The results from ten different smokers indicated the range of a small puff to be 20 to 30 cc., an average puff 25 to 35 cc., and a large puff 35 to 50 cc. The total averaged 32 cc. Observations of the duration of puff indicated an average between 1.5 and 2 seconds. Also observations of frequency indicated that two puffs per minute most closely approximated the habits of individuals taking average puffs. Certainly one puff in 15 seconds or less is too frequent, and one puff per minute is much too infrequent.

No doubt an examination of the habits of many more individuals would be of interest, but this was sufficient to show

that the volume varied widely even with the same subject and that data of general application should cover at least a range of velocities.

Cigarets Used for Smoking

Six commercial brands of cigarets were used in the tests. Each brand was transferred from the original package to a chamber maintained at 60 per cent relative humidity. They were retained in this atmosphere for at least 7 days prior to test. The characteristics of each brand were determined under a particular condition of smoking, but a single brand was selected for the major tests.

The nicotine contents of the six brands, determined by the official silicotungstic acid method (1) and based upon the weight of the cigarets saturated at 60 per cent relative humidity, are as follows:

Brand	% Nicotine	Brand	% Nicotine
A	1.83	D	2.23
B	2.15	E	2.16
C	1.95	F	2.05

Effect of Volume and Duration of Puff on Quantity of Nicotine Passed

For the determination of the quantity of nicotine passed to a smoker's mouth, ten cigarets were smoked using several volumes of puffs. In these tests brand A cigarets, containing 1.83 per cent nicotine, was employed. The total nicotine recovered from the absorption train was determined and related to the variables of the respective experiments as summarized in Table I.

The most striking point in Table I is the large increase in the quantity of nicotine that will pass to the smoker's respiratory system as the volume of the puff is increased. This relation is also shown in the last column by the increasing ratio of nicotine in the smoke to the nicotine in the tobacco smoked. As would be anticipated, the average period of smoking a cigaret decreases with increasing volume of puff when employing the same frequency and duration of puff. It is of interest to note, however, that the decreased period is not proportional to the increase in volume; as a result, more air is required to smoke a cigaret with increasing puff volume.

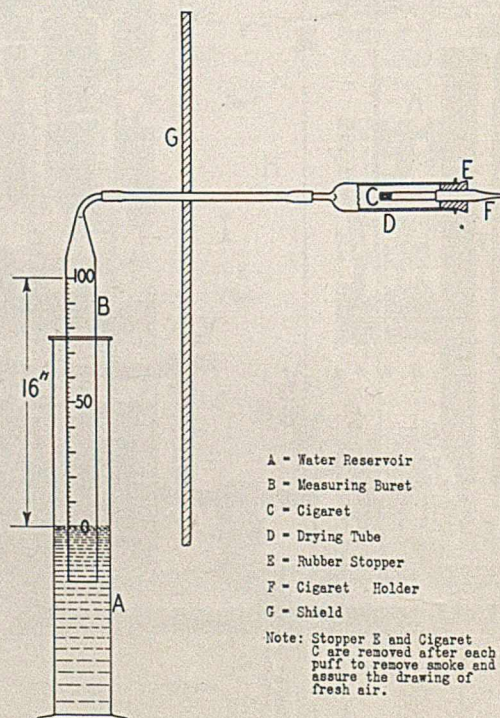


FIGURE 2. APPARATUS FOR DETERMINING VOLUME OF PUFF

Thus, the smoker who takes a small puff will take a longer period to smoke a cigaret, a lesser volume of puffed air will be required to consume it, and much less nicotine will pass to the respiratory system per cigaret smoked.

In view of the above results, it is not surprising that there is difficulty in reconciling the work of different investigators who have employed various volumes, velocities, and frequencies as has been previously indicated. In this connection Bradford (3) makes the statement that "correlation of the smoke results of different investigators and on many types of cigarets is facilitated when the yield of smoke constituents in a given volume of smoke is calculated." This relation is shown in column 10 of Table I where the total volume of the puffs drawn under the different conditions is related to the nicotine passed per gram of tobacco smoked. Surprisingly, within the range of normal puffing, a unit volume of smoke contains substantially a uniform quantity of nicotine, and this is in accord with the above statement. Nevertheless, inasmuch as the total volume required to smoke a cigaret varies with the conditions employed, any correlation in this manner will give no information concerning the quantity of nicotine entering the smoker's mouth. Moreover, the statement does not appear to be true when small puffs and low velocities are employed.

Efficiency of Sorbents for Nicotine Removal

For the initial experiments on the removal of nicotine from smoke, a small cartridge 3.8 cm. (1.5 inches) long and 0.56 cm. (0.22 inch) in diameter was filled with 8-14 mesh activated alumina and then fitted into the cigaret holder so that all of the smoke passed through the sorbent. The initial puffs were 40 cc. in volume, lasted 2 seconds, and were drawn twice every minute. Because the efficiency of removal of nicotine was so low, the puff volume was reduced to 20 cc. to note whether improvements would result from lower velocities. With this relatively small puff the nicotine removal was increased to 36 per cent of the total which entered the holder. In another test the particle size of the adsorbent was reduced to 14-20 mesh, but this made no improvement.

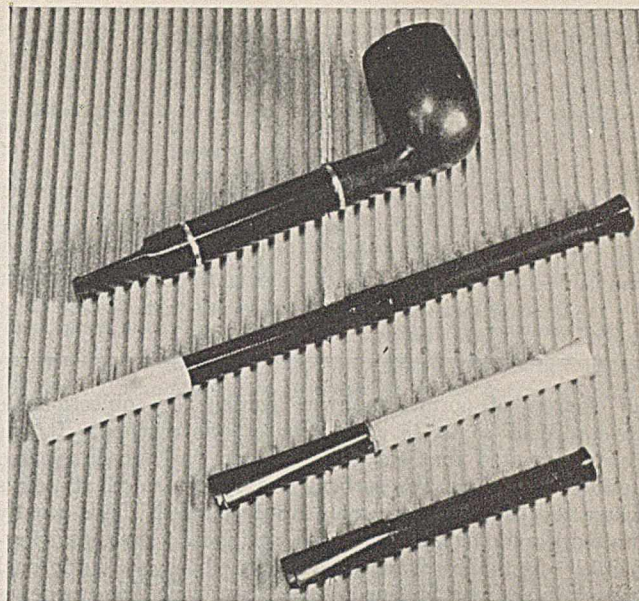


FIGURE 3. CONSTRUCTION OF HOLDERS FOR PIPE AND CIGARET FILTERS

Several modifications were then made in the shape of the cartridge so as to accommodate a greater quantity of sorbent. First, a cartridge 5.1 cm. (2 inches) long and 0.71 cm. (0.28 inch) in diameter was employed, the puff volume was reduced to 15 cc., drawn in 1.5 seconds, and the sorbent was reduced to 20-30 mesh. Under these conditions the efficiencies of two well-known adsorbents, activated alumina and silica gel, were compared with the inert porous materials pumice and calcined alumina. As shown in Table II, 40 to 43 per cent of the nicotine was removed by the adsorbents; the inert filters removed only 29 to 32 per cent under comparable conditions.

Because the above results were not especially promising, a rather extreme holder capable of retaining a bed of adsorbent 9.5 cm. (3.75 inches) long and 0.71 cm. (0.28 inch) in diameter was tried. In the experiments with this holder, satisfactory removal of nicotine was effected. The resistance to flow, however, was initially equivalent to about 12.7 cm. (5 inches) of water. This resistance increased only slightly during the smoking of the first ten cigarets; but after smoking 15 to

TABLE I. EFFECT OF VOLUME AND DURATION OF PUFF ON QUANTITY OF NICOTINE PASSED TO SMOKER'S MOUTH

Vol- ume Cc.	Puff Dura- tion		Av. Pe- riod per Cigaret Min.	Av. Vol. per Cigaret Cc.	Tobacco Smoked Grams	Wt. of Butts Grams	Nicotine Passed			Ratio Nicotine in Smoke to Nicotine in Tobacco Smoked
	Cc./sec.	Sec.					Total Mg.	Per g. tobacco smoked Mg.	Per g. tobacco smoked per cc. air puffed Mg. $\times 10^{-3}$	
15	1.5	10	12.0	375	8.505	2.625	18.2	2.14	5.72	0.117
20	2.0	10	11.0	460	8.743	2.586	27.5	3.15	6.85	0.172
30	2.0	15	9.5	600	8.922	2.655	36.4	4.08	6.82	0.223
40	2.0	20	8.5	720	8.476	2.511	43.2	5.09	7.07	0.280

TABLE II. EFFICIENCY OF NICOTINE SORBENTS AS INFLUENCED BY PUFF VOLUME AND DIMENSIONS OF SORBENT BED

Expt. No.	Puff		Kind ^a	Mesh	Sor bent		Wt. of Tobacco Smoked Grams	Resistance		Nicotine			Efficiency %	
	Vol. Cc.	Time Sec.			Weight Grams	Length Cm.		Diam. Cm.	Initial Cm. of water	Final	Passed Mg.	Sorbed Mg.		Total Mg.
1	40	2.0	A	8-14	0.833	3.8	0.56	8.588	36.8	3.9	40.7	10.0
2	20	2.0	A	8-14	0.876	3.8	0.56	8.912	17.7	10.0	27.7	36.1
3	20	2.0	A	14-20	1.000	3.8	0.56	8.411	15.2
4	15	1.5	A	20-30	1.940	5.1	0.71	8.818	10.6	13.9	10.8	8.2	19.0	43.0
5	15	1.5	C	20-30	1.850	5.1	0.71	8.712	7.6	10.1	12.8	6.0	18.8	31.9
6	15	1.5	P	20-30	0.840	5.1	0.71	7.891	7.8	7.6	12.6	5.1	17.7	28.8
7	15	1.5	S	20-30	1.084	5.1	0.71	8.947	8.1	13.1	10.7	7.2	17.9	40.2
8	15	1.5	A	20-30	3.581	9.5	0.71	9.065	11.9	12.9	4.7	11.7	16.4	71.2
9	20	2.0	C	20-30	3.550	9.5	0.71	8.391	11.4	13.9	11.2	15.8	27.0	58.5
10	20	2.0	A	20-30	3.716	9.5	0.71	8.736	15.7	20.7	7.6	20.8	27.8	75.0
12	30	2.0	A	20-30	3.622	9.5	0.71	9.068	19.0	21.5	15.3	21.4	36.7	58.3
13	40	2.0	A	20-30	3.623	9.5	0.71	8.514	24.0	27.1	17.7	22.3	40.0	56.8
14	15	1.5	A	20-30	2.604	5.6	0.76	8.714	7.6	7.6	13.5	5.5	19.0	28.0
15	20	2.0	A	20-30	5.205	5.1	1.11	8.284	15.5	9.1	24.6	37.0

^a A = activated alumina; C = calcined alumina; P = pumice; S = silica gel.

TABLE III. EFFECT OF VOLUME OF PUFF AND LENGTH OF FILTER IN SORPTION OF NICOTINE BY BRAND A CIGARET FILTERS

Expt. No.	Vol. of 2-Sec. Puff Cc.	Cigaret Filter Length ^a Cm.	Wt. of Tobacco Smoked Grams	Resistance ^b Cm. of water		Nicotine			Efficiency %
				Initial	Final	Passed	Sorbed	Total	
1	20	6.95	8.626	8.9	10.2	12.5	14.9	27.4	54.4
2	30	6.95	8.922	12.7	14.0	21.2	15.2	36.4	41.8
3	40	6.95	7.704	15.2	18.4	26.6	13.6	40.2	33.8
4	30	3.48	8.081	12.2	13.3	26.7	8.4	35.1	23.9
2	30	6.95	8.922	12.7	14.0	21.2	15.2	36.4	41.8
6	30	10.43	8.089	12.7	16.5	17.2	18.2	35.4	51.4
7	30	13.90	9.310	15.2	18.4	13.4	19.1	32.5	58.8

^a The length of a standard size cigarette is 6.95 cm. (2.75 inches).

^b The resistance of a lighted cigarette with no filter is about 6.5 cm. with a 30-cc. puff.

20 cigarettes of normal moisture content, an objectionable resistance of 35 to 45 cm. of water was reached. It was generally noted that the tarry matter was not distributed uniformly through the sorbent but concentrated at points where the particles were more firmly packed. This greatly limited the life of the longer bed, and from a practical viewpoint it offsets the advantage of higher efficiency. Additional tests with the inert calcined alumina and with larger volumes per puff show somewhat lower efficiencies, but in each case the actual amount of nicotine removed appeared to be related to the resistance and the accumulation of tar at certain cross sections.

Several other modifications of the holders were also tried out as indicated by experiments 14 and 15, Table II. These show that decreasing the resistance by increasing the diameter materially reduces the efficiency. Thus it seems conclusive that the removal of nicotine and tarry matter is related to the effectiveness of filtration and that granular materials of this type have little possibility of meeting with favor among smokers concerned with minimizing the compounds inhaled with tobacco smoke.

Cigaret as a Filter for Nicotine Removal

Inasmuch as efficient filtration appeared necessary for the removal of nicotine from smoke, the use of a cigarette for this purpose seemed to have special merit. Obviously the tobacco in commercial cigarettes is uniformly compacted; thus the fibers should readily take up the high-boiling constituents, such as nicotine and tarry matter, which would condense above the temperatures of normal tobacco smoke. The use of tobacco in different containers in pipe stems has been suggested, but no popularity for it developed because cumbersome and objectionable operations were involved in charging and especially in discharging the soggy, saturated material. A cigarette has the advantages of being always available to the cigarette smoker, it can be readily placed in a holder, and presumably it could easily be removed. The main items of interest then were: Does a cigarette have sufficient rigidity to withstand handling to and from the holder, and how effective is a cigarette for the purpose? No information of this type is available.

A cigarette holder capable of receiving a cigarette as a filter and of supporting a second cigarette to be smoked was constructed of aluminum. The dimensions were such as to permit the filter to fit loosely into the tubing and to be held in position by the tip and bit of the holder. At least one end

contacted the filter so as to cause the smoke from the lighted cigarette to pass through the cigarette filter.

Brand A cigarettes were smoked using 20-, 30-, and 40-cc. puffs, lasting 2 seconds and drawn every 28 seconds. After smoking ten cigarettes, the nicotine that passed the holder and that retained by the filter were determined separately. The nicotine originally present in the cigarette filter, as determined by analyses of cigarettes from the same package, was subtracted from the total found in the filter, and the result was recorded as the nicotine sorbed. Because of the uniform nicotine content of the cigarettes and the

accuracy of the analytical procedure, the total nicotine accounted for is in very good agreement with that previously found when puffs of corresponding volumes were taken.

The results summarized in Table III show that 54 per cent of the nicotine was removed when a small puff was employed and that the percentage of nicotine sorbed decreased as the volume of the puff increased. Nevertheless, throughout the range of normal puffing very satisfactory removal of nicotine was accomplished.

Additional results in Table III show the efficiency of a half, one, one and a half, and two cigarettes as filters when using puffs of 30-cc. volume. These tests show that the efficiency of removal of nicotine increases with increasing length of the filter.

Six commercial brands of cigarettes were then smoked while employing a cigarette of the corresponding brand as a filter. The results, summarized in Table IV, show that 33 to 42 per cent of the nicotine present in the smoke is removed when using the 30-cc. puff, lasting 2 seconds. It appears that the variation in efficiency is related to the quantity of nicotine in the cigarettes smoked and to the compactness of the filter, as indicated by the resistance to flow.

TABLE IV. SORPTION OF NICOTINE BY SIX COMMERCIAL BRANDS OF CIGARETS AS FILTERS WHEN SMOKING CORRESPONDING BRANDS

Cigaret Filter Brand	Filter Length Cm.	Wt. of Tobacco Smoked Grams	Resistance Cm. of water		Nicotine			Efficiency %
			Initial	Final	Passed	Sorbed	Total	
A	6.95	8.922	12.7	14.0	21.2	15.2	36.4	41.8
B	6.95	8.014	11.4	12.0	26.3	14.0	40.3	34.7
C	6.95	8.785	12.0	12.7	27.1	17.2	44.3	38.8
D	6.95	8.115	10.7	12.0	28.2	16.9	45.1	37.5
E	6.95	8.469	12.2	18.2	25.7	17.1	42.8	40.0
F	6.95	8.947	10.2	15.2	24.7	12.4	37.1	33.4

Special Smoking Tests

Three additional variables which are occasionally encountered were briefly investigated. These results, as summarized in Table V, indicate the following:

1. A dry cigarette used as a filter removes nicotine less effectively than a fresh cigarette. After smoking a number of cigarettes, the tobacco in the filter should take up moisture and become as efficient as a fresh cigarette.

2. A fresh cigarette used as a filter in a non-metallic holder which retains heat appears to absorb less nicotine than the same filter used in a metal holder. The metallic holder dissipates heat more readily, and the smoke leaving the holder is cooler.

3. When dried cigarettes are smoked, a greater percentage of

TABLE V. SPECIAL SMOKING TESTS

Smoking Conditions ^a	Tobacco Smoked Grams	Wt. of Butts Grams	Wt. of Cigaret Filter Grams	Resistance Cm. of water		Nicotine			Efficiency %
				Initial	Final	Passed	Sorbed	Total	
A	8.088	2.237	0.934	10.2	11.4	24.5	8.3	32.8	25.3
B	8.318	2.452	1.078	10.7	12.7	22.6	12.9	35.5	36.3
C	7.994	2.442	1.082	10.7	12.0	28.2	22.0	50.2	43.8

^a All puffs were of 30-cc. volume, lasting 2 seconds, and drawn every 28 seconds. A, brand A cigarette dried over activated alumina was used as a filter; B, fresh brand A cigarette filter in holder having low thermal conductivity; C, cigarettes smoked were dried over activated alumina.

the nicotine in the tobacco smoked passes into the smoker's mouth; e. g., the total passed was 50.2 mg. as compared to about 36 mg. when smoking similar cigarettes saturated at 60 per cent relative humidity. No doubt this behavior is related to the more rapid burning of dry cigarettes, which is shown either by the reduction of the average smoking period from 9.5 to 7.5 minutes or the correspondingly reduced volume of air (660 to 480 cc.) required to smoke a cigarette. It is of special interest that the normally saturated cigarette filter took up an increased quantity of nicotine; to a large extent this compensated for the greater quantity passed with the smoke.

Useful Life of a Cigarette Filter

Generally, in measuring the efficiencies of the various sorbents, only ten cigarettes were smoked per test. With the granular sorbents it had been found that the resistance increased gradually as the smoke from a greater number of cigarettes was passed through the sorbent; and, as the resistance increased, the percentage removal of nicotine increased. Thus the minimum efficiency was measured in smoking the first ten cigarettes. With the cigarette filter, however, it was found that the resistance did not materially increase until the filter became substantially saturated with moisture and tarry matter. This degree of saturation was attained after passing the smoke from between thirty and forty cigarettes through the same filter. To show this behavior, several tests are recorded in Table VI in which one and two cigarettes were used as filters, and the cigarettes were smoked to the normal 1.27-cm. (0.5-inch) butts. Also a further test is included in which the cigarettes were smoked to 2.54-cm. (1-inch) butts.

A smoker will find no objection to a resistance to flow as high as 25 to 30 cm. of water, and this resistance was not exceeded during the continuous smoking of thirty cigarettes. The life is indicated, however, in test A where the resistance increased sharply to 36 cm. during the smoking of the thirty-sixth cigarette.

The over-all efficiency of nicotine removal is shown to be 43.9 per cent for a single cigarette filter and a total of 64.6 per cent for two cigarettes in tandem. Because of the slightly greater average resistance these figures are slightly higher than were obtained with the initial tests on ten cigarettes. It is worthy of note that with the two cigarettes in tandem the first adsorbed 40.6 and the second 24.0 per cent of the total nicotine. This suggests that the residual nicotine and tarry mist is more finely divided and thus more difficult to absorb. If this is true, it seems logical to conclude that the quantity of nicotine taken up in the respiratory system will be reduced much more than is indicated by the figures given.

When the cigarettes were smoked only to 2.54-cm. butts, the total nicotine entering the holder was about 17 per cent

less per cigarette than was obtained when smoking to 1.27-cm. butts. However on the basis of grams of tobacco actually smoked, substantially the average quantity of nicotine entered the holder.

Nicotine Content of Butts

The cigarette butts from a number of experiments were analyzed to determine the relative percentage of nicotine absorbed. The results summarized in Table VII show that the butts contained an average of 2.13 per cent nicotine as compared to 1.83 per cent in the original cigarettes. Thus, on the average, ten butts retained about 8 mg. of nicotine, whereas the nicotine in the tobacco smoked contained about 160 mg. If due allowance is made for the retention of moisture, etc., by the butts, it may be concluded that between 5 and 8 per cent of the nicotine in the tobacco smoked is retained by the butts.

TABLE VII. NICOTINE CONTENT OF 1.27-CM. BUTTS

Puffing Conditions	Weight ^a of Ten Butts		Total Nicotine	Nicotine in Butts	
	Vol. Cc.	Time Sec.			Grams
15	1.5	2.619	51.6	1.98	
20	2.0	2.611	56.4	2.16	
30	2.0	2.762	60.4	2.18	
30	2.0	2.655	57.5	2.16	
30	2.0	2.320	50.4	2.17	
Av.				2.593	2.13

^a All cigarettes were smoked to between 1.27 and 1.5 cm. except where specific mention is made of more exact lengths of butts. The burning tips of the butts were pinched off with tweezers and discarded with the ash. The weight of butts represents the residual unburned tobacco plus some moisture, tar, and nicotine absorbed from the smoke which passed. It is not possible to proportion length and weight of cigarette to length and weight of butt, because the heavier cigarettes, being more tightly packed, retain more moisture, etc. The proportionate increase in the butts varied from 5 up to about 20 per cent. In general, the weight of butts has been shown merely to indicate uniformity.

Pipe Smoking with a Cigarette Filter

Smoking a pipe mechanically proved to be quite different from smoking a cigarette. Tobacco in a pipe cannot be kept lighted by any of the puffing conditions used with a cigarette. Careful observation of the habits of a pipe smoker reveals that, in lighting a pipe, between eight and fifteen short rapid puffs are drawn within 20 to 30 seconds. Subsequently, longer puffs are taken at intervals of 10 to 20 seconds but these are interspersed with short puffs at intervals of 3 to 5 seconds. If the interval extends to 30 seconds for several consecutive puffs, the fire becomes extinguished even though the tobacco is frequently compacted. Because of these variations it is

difficult to select any standard of volume or frequency which will duplicate the habits of a pipe smoker. The task was accomplished, however, with the robot smoker by first puffing as rapidly as the water level could be raised and lowered and, after the tobacco was well lighted, employing a 30-cc. puff, lasting 2 seconds and drawn every 10 seconds.

Three pipefuls of tobacco were smoked with a pipe having a stem suited for receiving a full-size standard cigarette. A popular brand of pipe tobacco containing 1.8 per cent nicotine was smoked with a brand A cigarette in the pipe stem. The gross and net weights of

TABLE VI. EFFICIENCIES OF CIGARETTE FILTERS USED UP TO THE SATURATION POINT

Expt. No. ^a	No. of Cigarettes Smoked	Tobacco Smoked Grams	Wt. of Butts Grams	Resistance		Passed Nicotine Mg.	Nicotine Sorbed Mg.	Total Mg.	Efficiency %
				Initial Cm. of water	Final Cm. of water				
A	10	8.036	2.440	10.2	13.2	23.5	61.4	146.0	43.9
	10	8.783	2.496	..	13.2	28.8			
	10	8.722	2.415	..	20.8	21.1			
	6	5.190	1.245	..	36.0	11.2			
Total	36	30.731	8.596			84.6			
B	10	8.335	2.528	11.4	14.0	14.0	{ 42.8 ^b } { 25.3 ^c }	104.5	64.6
	10	7.985	2.601	..	15.7	13.5			
	10	8.402	2.611	..	22.0	9.9			
Total	30	24.722	7.740			37.4			
C	10	7.189	3.846	12.1	13.2	17.7	34.0	88.1	38.6
	10	7.093	3.674	..	14.5	18.5			
	10	6.750	3.576	..	17.0	17.9			
Total	30	21.032	11.096			54.1			

^a In each test 30-cc. puffs lasting 2 seconds and drawn every 28 seconds were employed. A, cigarettes smoked to 1.27-cm. butts, 1 cigarette as filter; B, cigarettes smoked to 1.27-cm. butts, 2 cigarettes as filter; C, cigarettes smoked to 2.54-cm. butts, 1 cigarette as filter.

^b First cigarette filter.

^c Second cigarette filter.

tobacco smoked were 6.6 and 5.4 grams, respectively. The nicotine content of the net weight of tobacco smoked was 97.2 mg. The nicotine recovered in the cigaret filter was 42.3 mg., and that which passed the filter was 10.5 mg. Thus, without the filter, 54.4 per cent of the nicotine in the tobacco would have passed to the smoker's mouth, but with the cigaret filter 80 per cent of the nicotine in the smoke stream was absorbed. It is of further interest that the weight of the cigaret filter increased from 1.08 to 2.27 grams, and this shows a large accumulation of moisture and other undesirable compounds.

A practical comparison with mechanical pipe smoking was then made to note whether the conditions approached personal habits. In this test a gross weight of 10 grams of tobacco was smoked in five pipefuls. The nicotine taken up by the cigaret filter was found to be 61.5 mg. In proportion to the gross weights the mechanical smoker would have taken up 64 mg. of nicotine. This is excellent duplication and seems to justify the conclusion that a cigaret filter will prevent at least 75 per cent of the nicotine in pipe smoke from entering the smoker's mouth.

The great efficiency of nicotine removal from pipe smoke is logical because pipe smoke contains much more moisture than cigaret smoke. The moisture condenses and is taken up rapidly by the filter, thus assisting in the removal of nicotine. In this connection it should be noted that a cigaret filter becomes saturated after smoking four to five pipefuls (about 10 grams) of tobacco, whereas 35 to 40 cigarets (net, 30 to 35 grams) may be smoked before saturation is reached.

Construction of Stems for Filters

On first thought it would appear that a stem suited for holding a full-size cigaret filter would be large and inartistic. However, by taking advantage of construction possibilities, a full-size cigaret may be placed in the stem of a pipe or cigaret holder without suggestion either of massiveness or of what is actually being accomplished. For example, a cigaret holder of vest pocket size, 9.5 cm. (3.75 inches) long and 0.95 cm. ($\frac{3}{8}$ inch) in diameter, is adequate for a single cigaret filter. A holder 17.8 cm. (7 inches) long will hold two cigaret filters in tandem. Likewise a pipe stem 11.4 cm. (4.5 inches) long, which approximates the average

length of stem, may be well adapted to hold one cigaret filter. Typical examples are illustrated in Figure 3.

Taste of Filtered Smoke

Realizing that tobacco manufacturers have spent great effort in producing blends with pleasing aroma, it is obvious that this important item requires some consideration. The main objection to granular sorbent filters is that, when employed in sufficient quantities to be effective, a flat tasteless smoke results unless an artificial flavor is added to the sorbent. The cigaret filter imparts a slight mildness, but the taste of characteristic blends remains readily distinguishable. The most notable comment offered by individuals, who have used a cigaret filter for several days and then again started with the favorite brand without the filter, is that the unfiltered smoke had a slight bite which previously had not been observed.

An important change is noted in the smoke from a pipe. Obviously the removal of so much moisture, nicotine, and tar reduces the intensity of the flavor of pipe smoke. The real flavor of the smoke, however, is not altered and to many pipe smokers the mildness as well as the complete elimination of strong tobacco extract from the smoker's mouth will have special appeal.

A comment which has been offered by the uninitiated is that, if the "kick" (nicotine) is removed, there will be no satisfaction in smoking. The writers are not qualified to answer this from a physiological viewpoint but, from observation of those using a cigaret filter, it can be stated that the smoker does not use more cigarets per day to supply the deficiency of nicotine which enters the system. Thus it appears that the taste and operations of smoking, rather than nicotine, provide the real satisfaction for the smoker.

Literature Cited

- (1) Assoc. Official Agr. Chem., Methods of Analysis, 3rd ed., 1930.
- (2) Bradford, Harlan, and Hanmer, *IND. ENG. CHEM.*, 28, 836-9 (1936).
- (3) Bradford, Harlow, Harlan, and Hanmer, *Ibid.*, 29, 45-50 (1937).
- (4) Jensen and Haley, *J. Agr. Research*, 51, 267-75 (1935).
- (5) Pfyl, *Z. Untersuch. Lebensm.*, 66, 501-24 (Nov., 1933).

RECEIVED March 5, 1937



THE ALCHEMIST

By Gregor Rabinovitch

In No. 79 of his series of Alchemical and Historical Reproductions, Mr. Berolzheimer again brings us a new artist, a modern.

Gregor Rabinovitch, etcher, wood engraver, and lithographer was born in St. Petersburg in 1884. He pursued his art studies in St. Petersburg, Munich, and Paris, and since 1914 has been living in Switzerland.

This is the first of a number of originals in which the alchemical emanation takes the form of a beautiful female.

• • •

A detailed list of Reproductions Nos. 1 to 60 appeared in our issue of January, 1936, page 129, and the list of Nos. 61 to 82 appeared in January, 1937, page 74, where also will be found Reproduction No. 73. Reproduction No. 74 appears on page 166, February issue, No. 75 on page 345, March issue, No. 76 on page 459, April issue, No. 77 on page 554, May issue, and No. 78 on page 710, June issue.

GLUCONIC ACID PRODUCTION

Development of Inoculum and Composition of Fermentation Solution for Gluconic Acid Production by Submerged Mold Growths under Increased Air Pressure

A. J. MOYER, P. A. WELLS, J. J. STUBBS,
H. T. HERRICK, AND O. E. MAY
Industrial Farm Products Research Division,
Bureau of Chemistry and Soils, Washington, D. C.

IN THE course of developing a process for the production of gluconic acid by mold fermentation suitable for large-scale operation, it became apparent that one of the major problems would be that of obtaining spores in the large quantities required for inoculation of the solutions to be fermented. An almost unlimited number of asexual generations of yeasts and bacteria can be developed when submerged in a single lot of culture medium. On the other hand, fungi of the genera *Aspergillus* and *Penicillium* form a mycelial mat on the surface of either liquid or solid media which produces a single crop of spores. These mature over a period of 2 to 8 days, depending to some extent on the nature of the culture medium.

The purpose of this study was to effect economy in the production of the spore-bearing mycelium, to produce a highly active inoculum, and to determine some effects of variation of the medium composition on the rate of fermentation of glucose to gluconic acid.

Materials and Methods

In studying the conversion of glucose to gluconic acid by mold fungi, the authors used four organisms: *Penicillium luteum purpurogenum* (2), *P. chrysogenum*, strain 5034.11 (3, 4, 5), *Aspergillus ficuum*, strain 142 (4), and *A. niger*, strain 67 (6), which were selected because of their outstanding ability to cause rapid fermentation. These four organisms differ markedly, however, in their ability to produce the large quantities of spores necessary for inoculation purposes. *A. niger*, strain 67, was most satisfactory for the abundant production of spores and was therefore selected for this experimental work.

The fermentation was conducted in rotary aluminum drums, previously described (1). This equipment represents a close approach to apparatus which is believed to be suitable

Improvements have been made in the development of the inoculum and the composition of the solution to be fermented for the production of gluconic acid by submerged mold growths under increased air pressure in rotary drums. The first improvement of the inoculum was the selection of a new fungus, *Aspergillus niger*, strain 67, which not only readily produces large quantities of spores but also effects a rapid fermentation; the second improvement was the germination of these spores under conditions which make possible economies in the amount of inoculum and decrease the fermentation period. The composition of the solution to be fermented, such as glucose concentration, amount of calcium carbonate present, and nitrogen sources, have a pronounced effect upon the duration of the fermentation period.

for large-scale industrial operation.

The fermentation liquors were inoculated with two different types of material—i. e., with ungerminated spores and with spores which had undergone an intermediate treatment designed to bring about rapid germination and growth within a period of 20 to 46 hours.

Except as otherwise noted, the formulas for the nutrient solutions for the production of spores, for the germination of spores, and for the solutions to be fermented, were as follows:

Medium A, for growth of spore-bearing mycelium: glucose 91.5 grams; $\text{NH}_4\text{-NO}_3$, 0.450 gram; KH_2PO_4 , 0.072 gram; $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$, 0.060 gram; beer, 60 ml.; and distilled water to make 1 liter.

Medium B, for germination of spores: glucose 120 grams; $(\text{NH}_4)_2\text{HPO}_4$, 0.700 gram; KH_2PO_4 , 0.300 gram; $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$, 0.250 gram; beer, 67 ml.; peptone, 0.150 gram; and distilled water to make 1 liter.

Medium C, for fermentation: glucose 150.0 grams; $(\text{NH}_4)_2\text{-HPO}_4$, 0.388 gram; KH_2PO_4 , 0.188 gram; $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$, 0.156 gram; and distilled water to make 1 liter. CaCO_3 per drum variable, 100–150 grams.

Two types of apparatus were employed for submerged germination of the spores—namely, a glass bottle with mechanical shaker which was previously described (6) and a rotary aluminum drum which is identical with those used for the actual fermentation operation.

The method employed to grow the spore-bearing mycelia was to inoculate 50-ml. portions of medium A in 200-ml. Erlenmeyer flasks (area of mycelium, 40.7 sq. cm.) from potato-glucose-nutrient salt-agar slant stock cultures and then to incubate for 6 to 7 days. It is possible that slightly older cultures might be more effective, but this has not been definitely determined.

The spore-bearing mycelium was prepared for germination by placing it in a 4-liter bottle containing the proper amount of culture medium B, the concentration of ungerminated spores

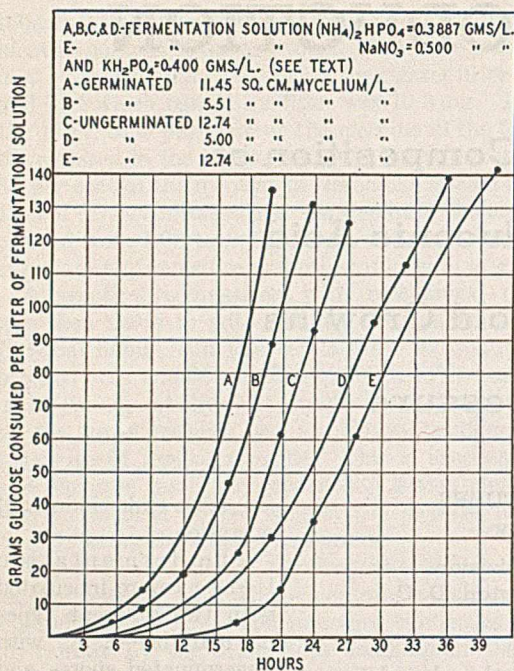


FIGURE 1. EFFECT OF GERMINATED AND UNGERMINATED SPORES AND NITROGEN SOURCES ON GLUCONIC ACID FERMENTATION

per unit volume of germination solution being kept constant.¹ Then, instead of shaking the bottle, a motor-driven stirring rod was introduced under aseptic conditions; in this way the mycelium was shredded and the spores were evenly dispersed throughout the medium. The contents of the bottle were then placed in the rotary drum set to rotate at 6.8 r. p. m., with an air flow of 1200 ml. per minute at normal air pressure. In later experiments the air pressure was increased to 30 pounds per square inch (2.11 kg. per sq. cm.) gage pressure. The course of the development of the spores and the rate of the fermentations were determined from samples withdrawn at intervals. Measured quantities of the solution containing the germinated spores were employed to inoculate the fermentation solution. The size of inoculum is expressed as the area of spore-bearing mycelium employed per liter of solution to be fermented.

The operation of the rotary drums (1, 6) and the analytical methods (3, 5) have been adequately described. The following standard conditions for operating the rotary drum for fermentation were: rotation, 13 r. p. m.; air-flow, 1200 ml. per minute; air pressure, 30 pounds on gage; calcium carbonate, 150 grams; culture solution, 3.2 liters. Under these conditions, harvests were made as soon as the calcium gluconate precipitate appeared. The hydrogen-ion determinations were made colorimetrically. All experiments were conducted at 30° C.

Studies on the Inoculum

FERMENTATIONS WITH SPORES. In previous studies with *Penicillium chrysogenum* some increase in the rate of fermentation was noted when germinated spores instead of ungerminated spores were used as inoculum. A more detailed study of this problem was undertaken with *Aspergillus niger*, strain 67, to effect economies in the size of the inoculum and the time necessary for fermentation. Nearly equal quantities of germinated and ungerminated spores were employed to inoculate the fermentation solutions in rotary drums. The results, based on the rate of glucose consumption, are shown in Figure 1. The use of spores subjected to the germination

¹ For example, 366.3 sq. cm. of spore-bearing mycelium were placed in 3 liters of medium B, or for 2 liters, 244.2 sq. cm. of spore-bearing mycelium were employed. In either case there would be 12.21 sq. cm. per 100 cc. By using 100 cc. of this preparation containing 12.21 sq. cm. to inoculate a drum containing 3.2 liters of medium C, $12.21 \div 3.2 = 3.81$ sq. cm. of original spore-bearing mycelium per liter of solution to be fermented (50-cc. portion = 1.9 sq. cm.; 200-cc. portion = 7.63 sq. cm.; 300-cc. portion = 11.45 sq. cm.), a means is provided for estimating the relative quantities of inoculum employed.

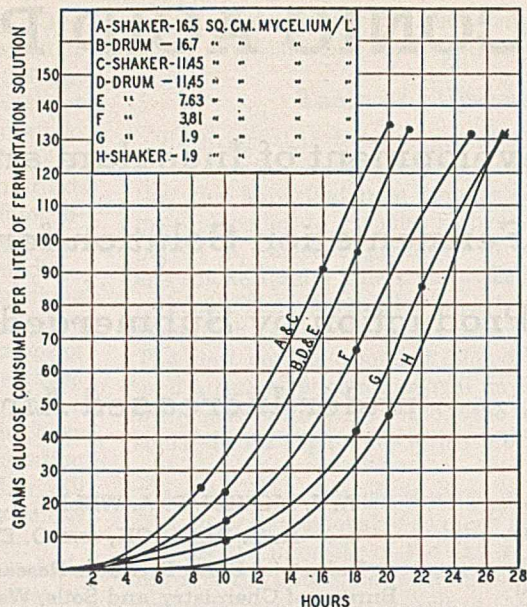


FIGURE 2. EFFECT OF QUANTITY OF SPORES GERMINATED IN DRUM AND SHAKER ON GLUCONIC ACID FERMENTATION

development of the spores has certain disadvantages, such as sterilization, agitation, and aeration in the preparation of large quantities of inoculum. Even with small quantities of inoculum it was believed that more uniform agitation and aeration could be obtained with the rotary drum, and that this would have some influence on the development of the inoculum. Therefore, an experiment was carried out to determine the comparative effect of the use of the rotary drum and the shaking bottle on the development of spores and on the capacity of the inoculum thus prepared to effect a rapid gluconic acid fermentation. Equal concentrations of spores were germinated in these two containers at atmospheric pressure. Samples were taken at 46 hours for determination of dry weight of the fungus growth, pH change in the medium, per cent germination, and titratable acidity. In the dry-weight determination all visible fragments of the original mycelium were removed; hence it is believed that these weights represent very closely the amount of growth made by the germinated spores. The data in Table I show that more growth had taken place per unit volume of culture medium in the drum than in the shaker. Microscopic examination showed that about 20 per cent more ungerminated spores were present in the shaker than in the drum. The hydrogen-ion concentration and titratable acidity showed that a slightly more rapid fermentation had occurred in the drum.

TABLE I. EFFECT OF METHOD OF PREPARATION ON PROPERTIES OF INOCULUM^a

Method of Preparation	Germination of Spores %	Dry Wt. of Fungus per 100 Ml. Gram	pH of Medium		0.1 N Free Acid per 100 Ml. Ml.
			Initial	Final	
Drum	90-95	0.572	5.6	3.4	28
Shaker	70-75	0.358	5.6	4.4	9

^a Culture medium, B; spore-bearing mycelium, 17.6 sq. cm. per 100 ml.; air flow, 1200 ml. per minute; rotation, 6.8 r. p. m.; air pressure, normal; age of inoculum, 46 hours.

Two different quantities of each inoculum thus prepared (11.45 and 1.9 sq. cm.) were employed to carry out standard fermentations of 15 per cent glucose in the rotary drums. The results (Figure 2) show that the fermentation proceeded

process for a period of 46 hours at normal air pressure leads to a more rapid initiation of the fermentation and a decrease of 8 to 12 hours in the time required for a complete fermentation. A comparison of curves B and C shows that, by using germinated spores, less than half the quantity of inoculum produces complete fermentation in approximately 4 hours less time.

PREPARATION OF INOCULUM. The use of the shaking bottle for the germination and de-

slightly faster with the larger quantities of inoculum prepared in the shaker. This difference becomes more striking when it is considered that there was 38 per cent less growth in the inoculum prepared in the shaker than in the drum. These results indicate that the condition of the inoculum exerts as much, if not more, influence than the actual quantity upon the duration of the fermentation, especially in shortening the lag period during the first 8 to 10 hours. The effect of the hydrogen-ion concentration upon the gluconic acid fermentation will be discussed later.

QUANTITY OF GERMINATED SPORES. In the studies conducted to obtain a comparison of ungerminated and germinated spores and in the studies on germination in rotary drum and shaking bottle, the variation in quantity of the inoculum employed had some influence on the length of the fermentation period. Studies were made of the effect of other quantities of inoculum (46 hours in rotary drum, normal air pressure, in the absence of calcium carbonate) upon time required for fermentation. The results of these studies are also presented in Figure 2. There was no pronounced difference between 16.5, 11.45, and 7.63 sq. cm. of spore-bearing mycelium per liter of solution to be fermented. The fermentations with the two lowest concentrations (3.81 and 1.9 sq. cm.) were only 4 to 7 hours slower than the much higher concentrations. In large-scale work the relation between the quantity of inoculum and the volume of the solution to be fermented may show some variation from the above results. The choice between the quantity of inoculum and the time required for the fermentation will be a matter of plant economics.

INFLUENCE OF AIR PRESSURE. Since an increase in the air pressure increased the rate of the fermentation with germinated spores (3, 6), it seemed likely that pressure might have some effect on the germination and subsequent growth of the spores. Spores were therefore subjected to the germination process for 46 hours at 0 and at 30 pounds per square inch gage pressure in the rotary drums. Samples consisting of 100 cc. (12.21 sq. cm.) from a drum containing 366.3 sq. cm. of spore-bearing mycelium in 3000 cc. were taken for dry-weight yields of the mycelial growth; these showed 0.525 and 0.522 gram, respectively, for 0 and 30 pounds gage pressure.

Determinations of the total acidity and of the hydrogen-ion concentration at 46 hours (pH 2.4 to 2.6 at 30 pounds and 3.8 to 4.0 at 0 pressure) showed that during the germination process a more rapid fermentation had occurred at 30 pounds than at 0 gage pressure. Standard fermentations of 15 per cent glucose solutions with samples of these lots of inoculum (3.81 sq. cm.) were carried out. There was a longer period before a rapid fer-

mentation began, thus increasing by about 20 hours the fermentation period with the inoculum developed under 30 pounds as compared with that developed under 0 gage pressure. This behavior indicated that the accumulation of a large quantity of free gluconic acid (pH 2.4 to 2.6) had a retarding effect on the subsequent fermenting capacity of the inoculum as compared with an inoculum developed at 0 gage pressure, where less free acid was formed.

An attempt, therefore, was made to prevent the development of a low pH by the addition of calcium carbonate to the germination solution and by a decrease in the glucose concentration. Different amounts of calcium carbonate were added to a germination solution containing 9.1 per cent glucose, but only by adding an amount of calcium carbonate in excess of that required to neutralize the acid formed could such an increase in the hydrogen-ion concentration be prevented. Some of the effects of an excess of calcium carbonate on the germination process are shown in Table II. More growth occurred in the absence of calcium carbonate. The presence or absence of calcium carbonate had no apparent effect upon the actual germination of the spores, which was about 90 per cent. After 21 hours the fermentation in the germination solution without calcium carbonate (pH 2.4) proceeded very slowly.

Standard fermentations of 15 per cent glucose were made with 24- and 46-hour portions of the inoculum thus prepared. The fermentation rates based on the glucose consumed are presented in Figure 3. The 46-hour inoculum developed in the presence of CaCO₃ gave the most rapid fermentation. A comparison of curves F (Figure 2) and A (Figure 3) shows only a slight decrease (1 hour) in the fermentation time when the spores are germinated at 30 pounds gage pressure in the presence of calcium carbonate, as compared with those germinated at atmospheric pressure in the absence of calcium carbonate. In later experiments (Figure 4, curve D) the calcium carbonate for 2 liters of germination solution was increased to 75.0 grams (pH change, 6.8 to 5.4), resulting in another slight decrease in the fermentation time. In the course of these investigations evidence has been accumulated which shows that throughout a series of experiments more uniform results can be obtained with the spores germinated under increased air pressure in the presence of calcium carbonate.

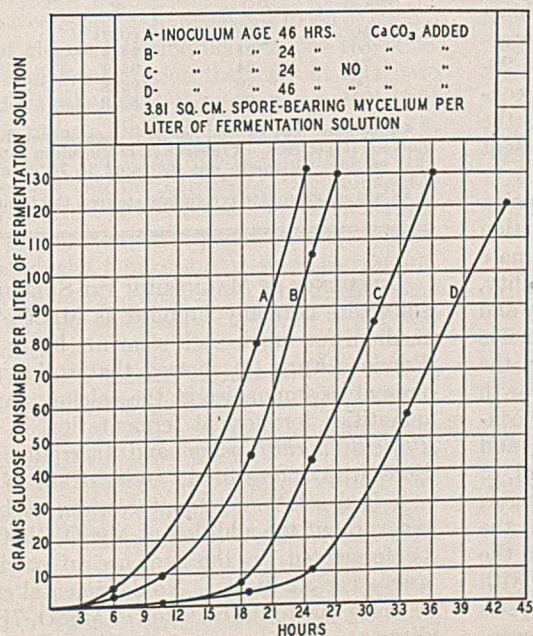


FIGURE 3. EFFECT OF CALCIUM CARBONATE AND AGE OF INOCULUM ON GLUCONIC ACID FERMENTATION AT 30 POUNDS PER SQUARE INCH GAGE PRESSURE

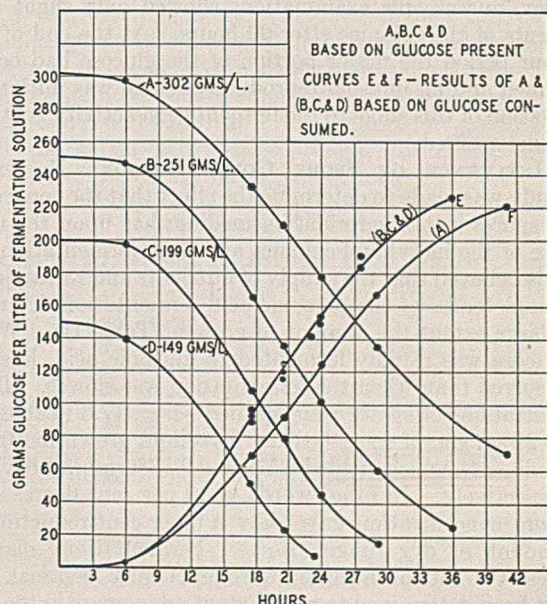


FIGURE 4. EFFECT OF GLUCOSE CONCENTRATION ON GLUCONIC ACID FERMENTATION
Inoculum age, 24 hours; 3.81 sq. cm. spore-bearing mycelium per liter of fermentation solution

TABLE II. EFFECT OF CALCIUM CARBONATE ON DEVELOPMENT OF INOCULUM IN ROTARY DRUM AT 30 POUNDS GAGE PRESSURE^a

CaCO ₃ per Drum Grams	Age of Inoculum Hours	pH of Medium		Dry Wt. of Fungus per 100 Ml. Gram	0.1 N Free Acid per Drum Ml.	Glucose Consumed per Drum Grams	Gluconic Acid Yield Based on:	
		Initial	Final				Glucose available %	Glucose consumed %
0	21	5.6	2.4	0.361	5840	120	57.9	87.8
56	21	6.8	4.4	0.304	1020	180	94.7	95.5
0	44	5.6	2.4	0.521	6450	146	63.9	79.7
56	44	6.8	4.6	0.426	180	182	95.0	95.0

^a Culture medium, B; spore-bearing mycelium, 12.21 sq. cm. per 100 ml.; glucose, 9.1 per cent; total volume in drum, 2000 ml.; other operations same as in Table I. Figure 3 gives fermentation results.

It is evident that a high concentration of hydrogen ion is detrimental to the fermenting capacity of the inoculum and that this effect is increased by prolonged exposure (Figure 3, curves C and D). This effect, at least under the conditions of these experiments, is not permanent. After the lag period of 19 to 25 hours a rapid oxidation of the glucose occurs, as shown in Figure 3, curves C and D. This lag period may be the time required for the development of sufficient new vegetative growth, or there may be, in the presence of a favorable hydrogen-ion concentration, a reactivation of the enzymes throughout the whole mycelium. The nature of the change affecting the fermenting capacity is not known. The low acidity (pH 2.4) of the culture medium when in small flasks, with the mycelium on the surface of the liquid medium, favors the accumulation of citric acid. No cases are known where a successful citric acid fermentation has been accomplished with submerged fungus growth. Likewise, the nature of the recovery is a matter of speculation.

INFLUENCE OF GERMINATION PERIOD. Experiments have been described (Table I and Figure 3) in which the spores were subjected for 24 and 46 hours to the germination treatment, and in which somewhat better results were obtained with the 46-hour than with the 24-hour process. Another series of fermentations has been made with 20-, 30-, and 44-hour lots of inoculum (3.81 sq. cm.) developed under the same conditions as shown in Table II. The best results (137 grams of glucose consumed per liter of fermentation solution in 19.5 hours with a yield of 96.8 per cent gluconic acid based on the glucose consumed) were obtained with the 30-hour lot. Accurate dry weights of the inoculum were not obtained; however, microscopic examinations showed only slight enlargements of the colonies after 20 hours. At the end of the 20-hour period the major portion of the glucose had been consumed and an unusual reproductive stage was initiated; the relation of this stage to the fermentation activity is at present undetermined.

INFLUENCE OF SPORE CONCENTRATION. No extensive study was made to determine the effect that the concentration of spores in the germination medium has upon the ultimate size of the individual colonies and their fermentation ability. It is believed that the supply of nutrients and the rapidity and completeness of the gluconic acid fermentation determine to a large extent the amount of growth (Table II). When the glucose was rapidly fermented to gluconic acid, less growth occurred than when the fermentation was slower. Two concentrations of spores were studied—i. e., 17.6 (Table II) and 12.21 sq. cm. of spore-bearing mycelium grown in 100 ml. of medium B, which yielded 0.572 and 0.538 gram of dry weight, respectively. In other words, a 30 per cent decrease in the spore concentration gave only a 6 per cent reduction in the amount of dry fungus tissue. Fermentations made with these two lots of inoculum were practically identical. It has not been determined to what extent an increase in the concentration of spores per unit volume of germination medium can be followed by a corresponding decrease in the volume of inoculum to effect a satisfactory fermentation.

Composition of Fermentation Solution

INFLUENCE OF NITROGEN SOURCES. In previous work of this division (4) it was shown that more rapid gluconic acid fermentation could be obtained with ammonium nitrogen than with nitrate nitrogen in surface cultures containing calcium carbonate. Similar results were obtained in the rotary drums under increased air pressure with the germinated spores of *Aspergillus ficuum*, strain 142. In these submerged fermentations the spores were germinated in the absence of calcium carbonate and with ammonium nitrate as the nitrogen source; that is, considerable growth had occurred before the inoculum was added to the solutions to be fermented which contained either nitrate or ammonium nitrogen. Further studies were made with *A. niger*, strain 67, in which ungerminated spores were employed to inoculate the solutions to be fermented which contained either ammonium or nitrate nitrogen with an excess of calcium carbonate (150 grams per 3.2 liters). Standard fermentations were carried out with both 0.388 gram per liter of diammonium phosphate and 0.500 gram per liter of sodium nitrate. To supply equal quantities of phosphate, 0.400 gram per liter of monopotassium phosphate was added to the fermentation solution containing sodium nitrate. The fermentations with these two nitrogen sources are shown in Figure 1 (curves C and E). With sodium nitrate a prolongation of the lag period occurred before a rapid fermentation began. The hydrogen-ion concentration did not drop below pH 5.0 during these fermentations in the presence of 150 grams of calcium carbonate per drum. The explanation of these results may be that ammonium nitrogen was absorbed faster than nitrate nitrogen in a slightly acid medium.

TABLE III. EFFECT OF CALCIUM CARBONATE ON GLUCONIC ACID FERMENTATION^a

CaCO ₃ per 3.2 Liters Grams	Age at Harvest Hours	Gluconic Acid Yield, Based on Glucose Available %	pH of Medium	
			Initial	Final
150	19	80.7 ^b	6.6	5.4
100	21	94.4	6.2	4.4
75	24	95.9	6.0	3.6
50	26	93.8	5.6	3.0
25	26	82.0	5.4	2.8

^a Inoculum, 3.81 sq. cm. per liter; age of inoculum, 24 hours; available glucose, 15 per cent. Preparation of inoculum same as in Table II, except that calcium carbonate was increased to 75 grams, giving a final pH of 5.4-5.6.

^b Calcium gluconate precipitate stopped the fermentation at this point.

INFLUENCE OF MAGNESIUM AND SULFUR. Magnesium and sulfur are normally supplied as MgSO₄·7H₂O to the culture medium for fungi, both elements being essential to growth. Previous work (4) showed that sulfur and magnesium are present as impurities in the calcium carbonate in sufficient quantities for normal fermentation in surface cultures of *Penicillium chrysogenum* and *Aspergillus ficuum*. Fermentations with spores of *A. niger*, strain 67, germinated in the standard solution without calcium carbonate, were carried out without the addition of MgSO₄·7H₂O to the solutions to be fermented, in the presence of calcium carbonate (100 grams per 3.2 liters). No detrimental effects were observed as being due to the omission of MgSO₄·7H₂O under these conditions. Studies were not made to determine the minimum magnesium and sulfur requirements for this fungus; hence these elements were supplied in quantities known to be satisfactory with or without calcium carbonate.

INFLUENCE OF AMOUNT OF CALCIUM CARBONATE. Mention has already been made (6) of the fact that calcium gluconate crystallizes out during the fermentation of a 15 per cent glucose solution containing 100 to 150 grams of calcium carbonate per drum. During the course of the fermentation, when the glucose concentration had fallen to about 2.5 per cent, these crystals appeared in sufficient quantity practically to stop further fermentation. Therefore, variations were made in the amount of calcium carbonate supplied per drum in an attempt to regulate or overcome the crystallization of calcium gluconate. The yields of gluconic acid and pH changes are shown in Table III. These data show that the fermentation can be completed without the appearance of calcium gluconate crystals if smaller amounts of calcium carbonate are employed. More free gluconic acid was obtained when the amount of calcium carbonate was decreased. The highest yield, based on glucose available, was obtained with 75 grams of calcium carbonate per drum. With varying amounts of calcium carbonate present, the fermentations were practically equal until a hydrogen-ion concentration greater than pH 4.0 appeared. The fermentation was somewhat retarded by a pH lower than 4.0 in those drums to which 25 and 50 grams of calcium carbonate were added. This result was apparently brought about both by the low pH and the period of time the fungus was subjected to this high acidity. Such a relation is indicated also by the data presented in Figure 3 and Table II.

EFFECT OF GLUCOSE CONCENTRATION. In surface cultures, where the movement of the glucose upward to the fungus mycelium and the movement of the excreted gluconic acid away from the mycelium depend upon diffusion, the rate of fermentation is increased by increasing the original glucose concentration. In other experiments (2) it was shown that mechanical agitation of the culture medium under the fungus mycelium increases the rate of fermentation. In these experiments with surface cultures the area of fungus in contact with the solution remained relatively constant throughout the course of the fermentation.

It has been shown that in the rotary drum the submerged fungus growth effects a nearly uniform rate of glucose consumption and accumulation of gluconic acid throughout the fermentation of a 15 per cent glucose solution. In other words, as the glucose concentration decreases to 10 or even 5 per cent, the rate of glucose consumption remains the same. During the progress of fermentation there are at least two quantitative variations other than the decreasing amount of glucose; namely, the minute fungus colonies are increasing in size and thus increasing the total absorption surface and, where there is no excess calcium carbonate, the amount of free acid and the hydrogen-ion concentration are increasing. In order to make a partial study of the effect of these quantitative variations, standard fermentations were carried out with four concentrations of glucose, to which the same amounts of inoculum and of calcium carbonate (75 grams per drum) were added.

The results based on the glucose present and the glucose consumed are shown in Figure 4. Curves A, B, C, and D show the changes in the glucose concentration at various intervals during the course of fermentation. The differences in the time required for a nearly complete fermentation were in almost direct ratio to the concentration of the original glucose solution. The actual quantities of glucose consumed per unit time in the 15, 20, and 25 per cent concentration (curves D, C, and B, respectively) were practically identical, as shown by curve E. There is some evidence of a retarding action on the rate of glucose consumption when an original concentration of 30 per cent glucose is employed (curve F). These results show that within a glucose concentration range of about 15 to 25 per cent there is little, if any, change in the

rate of glucose consumption. The yields of gluconic acid based on the glucose consumed were 96 to 98 per cent of theory. Satisfactory dry weight determinations of the fungus growth were not obtained, but microscopic examination of the growth at the end of the 24-hour period showed colonies of practically equal size in each solution. The changes in the hydrogen-ion concentration of the solutions were almost identical for each glucose concentration; i. e., all were pH 3.2 to 3.4 at the end of the 24-hour period and pH 3.0 to 3.2 for the 25 and 30 per cent solutions. It is believed that this high acidity was partially responsible for the slight decrease in the rate of fermentation noticeable in the later stages for each glucose concentration. Later fermentations were conducted with a 25 per cent glucose concentration and 100 grams of calcium carbonate per drum without materially affecting the course of the fermentation. Complete fermentation of a 25 per cent glucose solution is not possible when there is an excess of calcium carbonate because of the crystallization of calcium gluconate. These data show that there is some practical value in employing a glucose concentration higher than 15 per cent; i. e., 25 per cent more gluconic acid can be obtained per unit volume in a 20 per cent concentration for the additional cost of operating the drum for about 8 hours longer.

Summary

1. Fermentations of glucose to gluconic acid proceeded more rapidly when the inoculum consisted of germinated spores as compared with ungerminated spores.
2. Similar fermentations were obtained with the inoculum prepared in a rotating drum and in a shaking bottle at normal air pressure.
3. The time required for fermentation of a 15 per cent glucose solution varied to some extent with the quantity of inoculum employed.
4. Germination and growth of the spores in medium B for 30 hours in the rotary drum under increased pressure with an excess of calcium carbonate produced the most effective inoculum.
5. The fermentation capacity of the inoculum was inhibited by a high acidity, depending partially on the duration of exposure. The addition of suitable quantities of calcium carbonate controlled the acidity and the crystallization of calcium gluconate.
6. The fermentations were completed in less time with diammonium phosphate than with sodium nitrate as the source of nitrogen in the presence of an excess of calcium carbonate.
7. The calcium carbonate employed contained, as impurities, magnesium and sulfur in forms available to the fungus.
8. The concentration of glucose present, within wide limits, did not change the hourly fermentation rate.

Literature Cited

- (1) Herrick, H. T., Hellbach, R., and May, O. E., *IND. ENG. CHEM.*, **27**, 681 (1935).
- (2) May, O. E., Herrick, H. T., Moyer, A. J., and Hellbach, R., *Ibid.*, **21**, 1198 (1929).
- (3) May, O. E., Herrick, H. T., Moyer, A. J., and Wells, P. A., *Ibid.*, **26**, 575 (1934).
- (4) Moyer, A. J., and May, O. E., to be published.
- (5) Moyer, A. J., May, O. E., and Herrick, H. T., *Zentr. Bakt. Parasitenk.*, **II**, 95, 311-24 (1936).
- (6) Wells, P. A., Moyer, A. J., Stubbs, J. J., Herrick, H. T., and May, O. E., *IND. ENG. CHEM.*, **29**, 653 (1937).

RECEIVED April 9, 1937. Presented before the Division of Industrial and Engineering Chemistry at the 93rd Meeting of the American Chemical Society, Chapel Hill, N. C., April 12 to 15, 1937. This paper is Contribution 274 from the Industrial Farm Products Research Division.



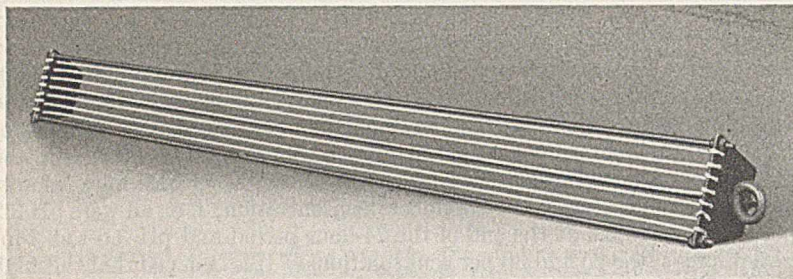


FIGURE 1. RACK WITH WIRES MOUNTED FOR USE IN THE VULCANIZER

High-Speed Vulcanization of Rubber

A. R. KEMP AND J. H. INGMANSON
Bell Telephone Laboratories, New York, N. Y.

PRIOR to about 1906 when organic accelerators were first employed in the tire industry, vulcanization practice for soft rubber generally involved the use of larger amounts of sulfur than is now customary. Acceleration of vulcanization was obtained by the use of liberal amounts of one or more of the oxides of zinc, calcium, magnesium, or lead. As the new and faster organic accelerators have been employed, the amount of sulfur used has been gradually decreased until it now ranges from about 0.5 to 5 per cent of the rubber; the general tendency is towards the use of the smaller quantity.

In the rubber-insulated-wire industry in this country, it is becoming general practice to employ the Western Electric Company's continuous vulcanizing process (1) whereby highly accelerated soft-rubber insulating compositions are completely vulcanized at 198° C. in a few seconds on the wire as it passes continuously at high speed from the insulating machine through a long pipe filled with steam under about 200 pounds per square inch (14.1 kg. per sq. cm.) pressure. This process is rapidly displacing the older one of coiling the insulated wires on drums or in pans filled with soapstone powder and vulcanizing in large autoclaves for periods of 1 to 5 hours under 20 to 40 pounds steam pressure (126° to 142° C.). The continuous process eliminates the objectionable soapstone dust and produces more uniformly vulcanized wire which is free from crossover defects and flattening of the insulation. The process also provides attractive economies in manufacture.

The literature reveals practically no information on the rate of vulcanization and quality of soft rubber vulcanized at temperatures ranging from 170° to 200° C. Many investigators, however, have studied the effect of temperature on rate

The continuous vulcanizing process now employed by the rubber-covered-wire industry involves the use of very active accelerators and vulcanizing temperatures considerably above those normally employed by the rubber industry.

Data are presented on the temperature coefficient of vulcanization velocity and quality of the product obtained at vulcanizing temperatures ranging from 170° to 198° C. In calculating vulcanization rates for high temperatures, a time correction should be applied in order to correct for the heating-up period. The average 10° C. temperature coefficient in this temperature range was found to be 2.16. Compounds vulcanized at 170° to 198° C. appear to be at least equal, in physical and aging properties, to the same rubber compositions vulcanized at 142° C.

of vulcanization and quality of the vulcanizate at temperatures below 170° C. Recently, for example, Shepard and Street (2) reviewed this subject and found that the optimum tensile properties of tire tread compounds did not vary when vulcanized at temperatures ranging from 127° to 160° C. They found that the aging quality tended to decrease as the temperature of vulcanization increased.

The purpose of the present paper is to present comparative data on the rate of vulcanization of soft rubber and on the quality of the product vulcanized in direct steam at temperatures ranging from 142° to 198° C.

Because of the difficulties involved in vulcanizing suitable test sheets of rubber in open steam, it was decided to prepare lengths of wire and use tubular insulation specimens for test purposes. These test specimens have the advantage of being directly comparable with insulated wire produced by the continuous vulcanizing process. The basic rubber compound selected for this investigation has suitable plastic properties for extrusion as a smooth covering on the conductor. When vulcanized, it has high tensile strength and cutting resistance. Using the base compound selected, three amounts of sulfur were added—namely, 1.0, 2.5, and 4.0 per cent of the rubber with suitable adjustments in accelerator and retarder content in order to obtain approximately equal curing rates. Cures were made for varying lengths of time at 142°, 170°, 185°, and 198° C. in open steam. The compounds used were as follows:

Ingredients	Compound		
	1	2	3
Pale crepe	100.00	100.00	100.00
Lithopone (standard 30% ZnS)	125.00	125.00	125.00
Zinc oxide (fast-curing type)	25.00	25.00	25.00
Stearic acid	1.00	1.00	1.00
Phenyl- α -naphthylamine	2.00	2.00	2.00
Sulfur	4.00	2.50	1.00
Litharge (sublimed)	1.00	1.00	1.00
Tetramethylthiuram monosulfide	0.50	0.75	2.00
Di- <i>o</i> -tolylguanidine	0.25	0.50
	258.50	257.50	257.50

The compounds were mixed in batches of about 1550 grams each in a size B Banbury mixer. The rubber was placed in the mixer and broken down for 1 minute. The zinc oxide, antioxidant, sulfur, and stearic acid were then added, and mixing was continued for 3 minutes. The lithopone was added, and mixing was continued for 7 minutes. The batch was then placed on a cool laboratory mill; after 2-minute mastication the accelerator and litharge were added, and the compound was finally refined four times through tight rolls, followed by 6 more minutes of milling.

Preparation of Samples

A seventeen-gage tinned bronze conductor was insulated to an outside diameter of approximately 0.28 cm. at an extrusion speed of about 14 meters per minute, using a No. 1/2 Royle machine. Lengths of insulated wire about 1 meter long were mounted on racks as shown in Figure 1 for vulcanizing. Vulcanization was carried out in the apparatus shown in Figures 2 and 3.

The vulcanizing chamber consists essentially of a 1.5-meter length of 5-inch extra heavy wrought-iron pipe located centrally within a somewhat shorter length of 8-inch extra heavy pipe which serves as a steam jacket. To one end of both pipes is welded a steel plate. The jacket pipe is welded to the inner pipe 6.25 cm. from the other end. Access to the inner pipe or vulcanizing chamber is obtained by means of a standard 5-inch Everlasting Model W straight-lever type of valve having an iron body with screw ends for a working steam pressure of 250 pounds per square inch (17.6 kg. per sq. cm.). Steam enters and is released from the vulcanizer by 1.5-inch Powell Giant lever throttle valves for 350 pounds (24.6 kg.) working steam pressure. Suitable pressure gages, auxiliary valves, and traps are shown in Figure 2. Steam at pressures up to 250 pounds per square inch pressure is supplied by a type S. A. Kane fire tube boiler operating at 7 horsepower. The vulcanizing tube is mounted on suitable iron supports and is well insulated with asbestos.

Before using the apparatus for vulcanizing, steam at a pressure equivalent to the desired temperature is allowed to enter the jacket and vulcanizing tube. After 30 minutes or a time sufficient to ensure that the apparatus is heated to the desired temperature, the steam is discharged from the inner vulcanizing tube. It is customary for two men to operate the apparatus. The end valve is opened, a rack on which wire samples are mounted is placed in the tube, and the valve is closed. The second operator

opens the quick-action steam valve and simultaneously sets a stop watch. The desired steam pressure is reached in the tube in a fraction of a second. When the time for vulcanization has elapsed, he closes the steam valve. The other operator opens the quick-action exhaust valve and then the end valve to the vulcanizing tube, and removes the rack by means of a hooked rod. It is estimated that the time involved in attaining temperature in the tube is less than 1 second, and for exhausting and opening the tube about 1 second.

Conductors were insulated with the three compounds and vulcanized in the manner described. Cures were made over the temperature ranges indicated and in the range near maximum tensile properties, for the most part at the following time intervals:

Steam Pressure Lb./sq. in.	Equivalent Temp. ° C.	Time Range	Time Interval
40	2.8	6-35 min.	2 min.
100	7.0	50-140 sec.	5 sec.
150	10.5	15-50 sec.	3 sec.
200	14.1	8-40 sec.	2 sec.

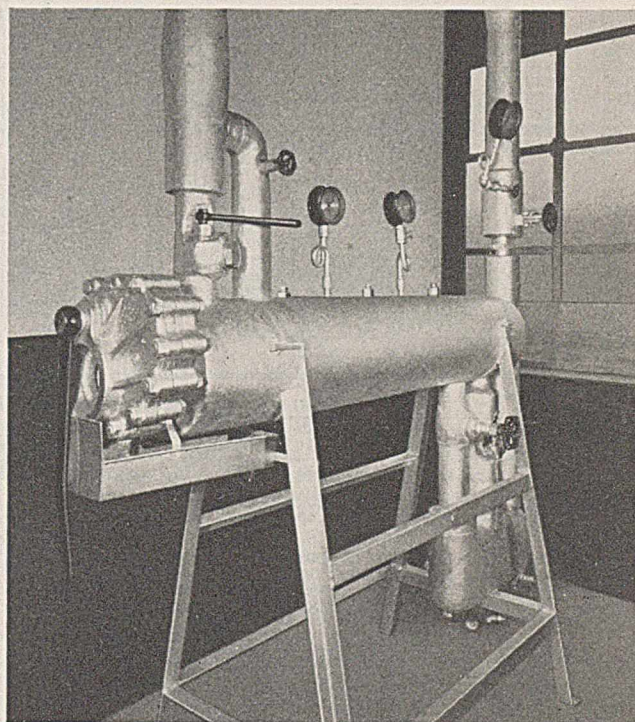


FIGURE 3. HIGH-PRESSURE VULCANIZING TUBE

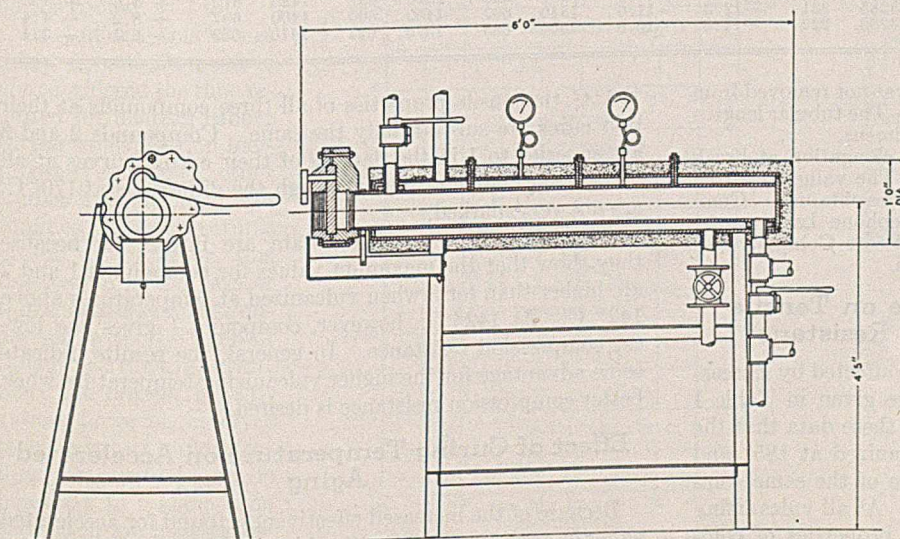


FIGURE 2. DIAGRAM OF VULCANIZING TUBE

After vulcanizing, the wires were allowed to rest at room conditions of temperature and humidity for at least 18 hours before specimens were selected for test. Five tensile-test specimens 15 cm. long were taken, representing original tests at each cure for each compound. Similarly, specimens representing cure to approximately maximum physical properties were selected for test after 48 and 96 hours of accelerated aging at 80° C. and 3.5 kg. per sq. cm. oxygen pressure. Three groups of four specimens each were selected for these original and aged compression tests. Compression tests were made in addition to tensile tests because the compression resistance or crushing load of rubber insulation on wire is frequently more important than tensile properties. In order to facilitate removal of the insulation from the tinned conductors for tensile test, the specimens were immersed in mercury to amalgamate the

TABLE I. EFFECT OF TIME OF CURE ON TENSILE STRENGTH, ELONGATION, MODULUS, AND COMPRESSION RESISTANCE

Compound 1						Compound 2						Compound 3					
Time of cure Sec.	Tensile strength Kg./sq. cm.	Elongation at break %	Modulus at elongation		Compression resistance Kg.	Time of cure Sec.	Tensile strength Kg./sq. cm.	Elongation at break %	Modulus at elongation		Compression resistance Kg.	Time of cure Sec.	Tensile strength Kg./sq. cm.	Elongation at break %	Modulus at elongation		Compression resistance Kg.
			Of 300%	Of 500%					Of 300%	Of 500%					Of 300%	Of 500%	
Cured at 142° C.																	
15 ^a	198.6	560	50.7	149.6	627	6 ^a	83.6	550	6.8	37.3	431.0	9 ^a	260	570	74.0	136.0	368
20 ^a	258.5	600	66.5	183.1	705	8 ^a	103.5	640	13.8	55.7	400.0	12 ^a	265	580	66.2	203.0	619
25 ^a	249.3	560	79.2	200.0	745	10 ^a	130.0	590	24.0	85.0	435.0	14 ^a	294	600	68.0	202.7	660
30 ^a	202.8	500	77.7	192.9	709	12 ^a	168.5	610	30.6	109.0	473.0	16 ^a	280	600	65.0	203.0	641
35 ^a	202.1	520	76.4	196.4	695	14 ^a	204.0	600	38.8	132.0	542.0	18 ^a	287	600	64.0	196.0	621
						16 ^a	239.0	590	54.3	168.0	578.0	22 ^a	290	620	68.5	186.0	628
						20 ^a	280.0	540	86.7	237.0	661.0	28 ^a	282	600	61.2	195.0	646
												35 ^a	267	600	59.5	183.5	608
Cured at 170° C.																	
60	198.9	630	37.7	122.9	564	60	234.0	600	48.6	160.0	565.0	50	61	460	26.6	...	377
80	296.5	590	77.8	211.2	636	70	284.0	560	78.2	228.0	790.0	60	112	430	...	162.3	417
100	282.4	600	70.4	200.0	750	75	290.0	570	76.6	224.0	809.0	65	111	450	41.2	...	422
120	168.3	480	72.1	...	700	80	283.0	550	85.0	236.0	720.0	70	263	540	78.1	217.0	468
140	172.2	460	72.5	...	723	90	298.0	570	80.0	231.0	687.0	75	270	540	80.5	228.0	600
						100	292.0	570	84.0	230.0	731.0	80	273	560	75.0	214.0	650
						120	281.0	540	92.0	238.0	710.0	90	296	600	69.4	207.0	676
												100	286	590	67.8	205.0	664
Cured at 185° C.																	
20	223.6	610	42.2	141.5	600	15	136.0	630	22.5	80.4	437.0	15	56	520	13.5	...	268
25	252.8	600	52.1	171.8	623	18	160.5	630	32.8	95.5	468.0	20	56	520	12.9	45.8	322
30	246.2	570	62.0	192.9	695	21	203.0	620	37.0	124.0	571.0	24	111	550	25.7	82.2	391
33	233.4	550	64.8	193.2	695	24	252.0	600	53.8	173.5	635.0	27	244	570	62.0	190.2	387
36	239.4	550	66.9	200.7	699	27	281.0	600	62.0	208.0	667.0	30	252	570	71.1	204.0	426
39	225.3	530	67.7	200.7	741	30	302.0	570	76.7	236.0	679.0	33	249	560	72.0	202.5	597
45	209.5	520	66.4	202.4	755	35	391.0	550	77.4	236.0	758.0	36	259	560	72.0	207.0	568
50	217.6	540	63.0	182.4	709							40	262	560	67.5	202.5	609
Cured at 198° C.																	
8	102.1	560	44.1	...	368	8	124.3	600	20.8	80.0	428.0	8	51	600	10.6	37.0	295
10	190.0	600	40.0	126.7	505	10	132.0	610	24.1	83.0	440.0	10	84	590	15.8	58.0	299
12	214.4	580	46.8	150.3	536	12	199.0	610	38.7	130.0	503.0	12	111	560	24.7	84.0	395
14	258.1	610	52.8	166.2	604	14	262.0	590	57.8	187.0	573.0	14	203	490	72.0	194.0	427
16	264.4	600	58.4	174.3	627	16	284.0	580	70.5	212.0	682.0	16	271	560	72.3	208.0	532
18	215.1	540	65.1	186.2	645	18	291.0	560	80.0	236.0	668.0	20	275	560	72.3	213.0	663
20	219.0	500	81.3	208.4	795	20	293.0	550	85.5	239.0	723.0	25	278	580	66.0	201.5	618
30	192.9	510	72.5	186.6	795	25	285.0	550	80.0	231.0	723.0	30	279	580	64.0	201.5	628
40	169.0	510	63.3	...	700												

^a Minutes.

TABLE II. EFFECT OF CURING TEMPERATURE ON ACCELERATED AGING

Time of Cure	Temp. of Cure ° C.	Tensile Strength At 80° C. and 3.5 Kg./Sq. Cm. O ₂						Change in Tensile Strength on Aging		Compression Resistance At 80° C. and 3.5 Kg./Sq. Cm. O ₂				Change in Compression on Aging			
		Original		48 hr.		96 hr.		48 hr.	96 hr.	Original		48 hr.		96 hr.			
		Lb./sq. in.	Kg./sq. cm.	Lb./sq. in.	Kg./sq. cm.	Lb./sq. in.	Kg./sq. cm.			Lb.	Kg.	Lb.	Kg.	Lb.	Kg.	%	%
		Compound 1															
20 min.	142	3715	262	3140	221	2735	192	-15.4	-26.3	1550	705	1450	660	1300	590	-6.4	-16.0
80 sec.	170	4215	298	3350	235	2680	188	-20.5	-36.4	1400	640	1300	590	1090	495	-7.1	-22.1
30 sec.	185	3500	246	3690	259	2950	208	+5.4	-16.0	1530	695	1350	614	1240	564	-11.7	-18.9
16 sec.	198	3750	264	3385	237	2670	187	-9.7	-28.8	1380	630	1410	610	1220	552	+2.1	-11.6
Compound 2																	
20 min.	142	3985	280	3335	235	2915	206	-16.3	-26.8	1460	663	1650	750	1420	645	+13.0	-2.7
90 sec.	170	4255	300	3230	228	2840	200	-24.0	-33.2	1510	687	1550	682	1360	618	-0.6	-15.0
30 sec.	185	4285	302	3510	247	3040	213	-18.0	-29.0	1490	676	1520	690	1300	591	+2.0	-12.7
20 sec.	198	4170	294	3245	229	2985	210	-22.1	-28.4	1590	722	1610	731	1410	641	+1.2	-11.3
Compound 3																	
14 min.	142	4175	294	3645	250	3260	230	-15.0	-21.9	1450	660	1450	660	1460	663	0.0	+0.7
80 sec.	170	3890	273	3310	234	3155	222	-14.9	-18.8	1430	650	1510	687	1480	672	+5.6	+3.5
40 sec.	185	3720	262	3265	230	3285	231	-12.2	-11.6	1340	607	1450	660	1400	637	+8.2	+4.4
20 sec.	198	3900	274	3360	237	3250	229	-13.8	-16.6	1460	663	1370	623	1410	639	-6.1	-3.4

tin coating previous to test. The insulation was not removed from the conductors until after accelerated aging. The tubular lengths of insulation were used as tensile test specimens.

Tensile strength, modulus, and per cent elongation at break were determined on a Scott tensile tester. The values reported are, for the most part, averages of the five values obtained. Compression tests were made on the Bell Telephone Laboratories machine manufactured by the Henry L. Scott Company (5). Values reported are the average of four tests.

Effect of Curing Temperature on Tensile Properties and Compression Resistance

Physical data on the three compounds as affected by increasing vulcanizing temperature and time are given in Table I and Figures 4 and 5. It is evident from these data that the tensile properties of the compounds vulcanized at 185° and 198° C. are practically equivalent to those of the same compounds vulcanized at 142° and 170° C. At all vulcanizing temperatures except 170° C., the tensile properties of compounds 2 and 3 are superior to those of compound 1. At

170° C. the tensile properties of all three compounds at their best cures are substantially the same. Compounds 2 and 3 are superior to 1 in the flatness of their curing curves at all vulcanizing temperatures, although the differences at 170° C. are not very marked.

The compression resistance data are interesting because they show that the maximum values for compounds 1 and 2 are higher than for 3 when vulcanized at temperatures above 142° C. At 142° C., however, compound 1 gives the lowest compression resistance. In general, the results indicate some advantage for the higher vulcanizing temperature when better compression resistance is desired.

Effect of Curing Temperature on Accelerated Aging

Because of the increased effectiveness found for accelerated aging in oxygen at 80° C. (6), this temperature was used for this series instead of 70° C. Oxygen pressure of 3.5 kg. per sq.

cm. was used because higher pressures do not appreciably increase the aging rate (6). The changes in tensile strength and in compression resistance which resulted from accelerated aging for each of the four curing temperatures investigated are shown in Table II and Figure 6. Evaluation by means of compression resistance indicated less deterioration on aging than did evaluation by tensile tests.

The compound containing 4.0 per cent sulfur showed better aging properties when cured at 185° and 198° C. than at 142° and 170° C. The other two compounds aged about the same, regardless of vulcanization temperature.

Temperature Coefficient of Vulcanization Velocity

For some time it has been recognized that the temperature of cure for soft rubber is proportional to the log of the time of equivalent cures at various temperatures. However, there has been considerable disagreement as to the precise relationship existing, probably because of variations in experimental conditions employed and in some cases to less precise measurements as indicated by Sheppard (14).

Investigations of the time-temperature relationship in the vulcanization of soft rubber have been confined to temperature ranges below 171° C. Investigations have also been previously confined to rubber compounds containing 2.5 or higher percentages of sulfur based on the rubber.

In studies of this nature other investigators have not considered the time required for heating rubber to the vulcanization temperature. Since other studies have usually been confined to temperatures of 160° C. or lower, this time period in the case of thin sheets is small in comparison with the over-all time of vulcanization. Since the present investigation, however, involves much higher vulcanization temperatures, it is necessary to make a time correction for heating because the time required to heat up to a tempera-

ture gradient of rapid cure is a considerable part of the total period required for cure.

In order to determine the time lag preceding active vulcanization of the insulated conductors, lengths of the wire were heated in the vulcanizer at 198° C. for periods from 2 to 12 seconds, increasing by 1-second increments. Finger tests and compression tests on these wires indicated that active cure commenced after a little more than 7 seconds of heating.

The rate of heat transfer through the insulation was determined experimentally on lengths of insulation into which a thermocouple had been inserted after removal of the conductor. The thermocouple fitted tightly in the space previously occupied by the conductor. Temperature readings were made with the aid of a potentiometer. For convenience a molten salt bath at 198° C. was used for heating. The time which elapsed from the moment of immersion until attainment of various temperatures was measured with a stop watch. The values as determined are plotted in the lower curve of Figure 7.

The upper curve in Figure 7 represents calculated temperatures at the center of the wire. These calculations were made according to the method of Williams (18) and to the data of

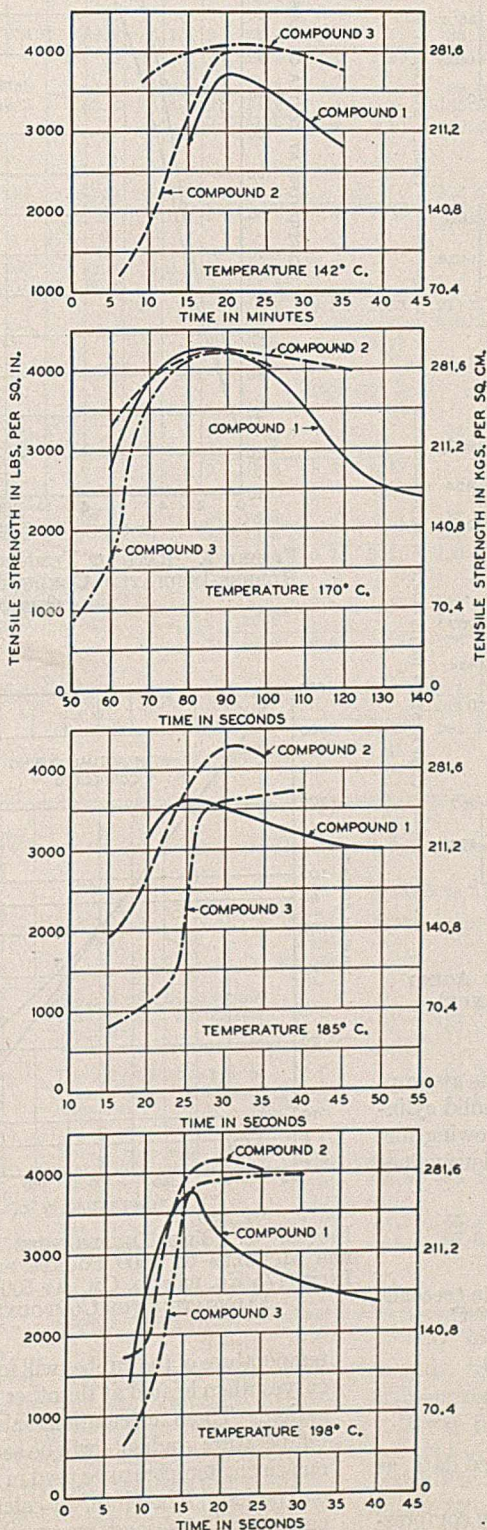


FIGURE 4. EFFECT OF CURING TIME ON TENSILE STRENGTH

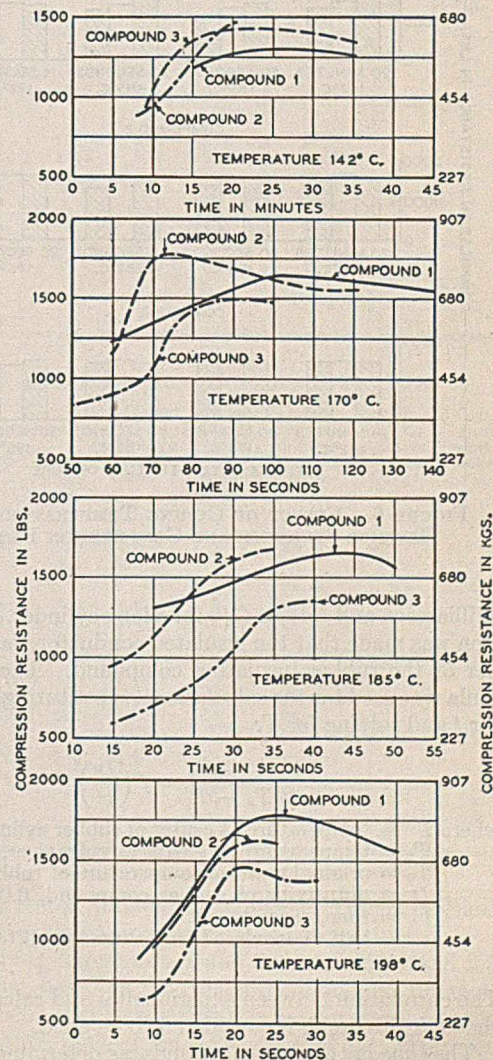


FIGURE 5. EFFECT OF CURING TIME ON COMPRESSION RESISTANCE

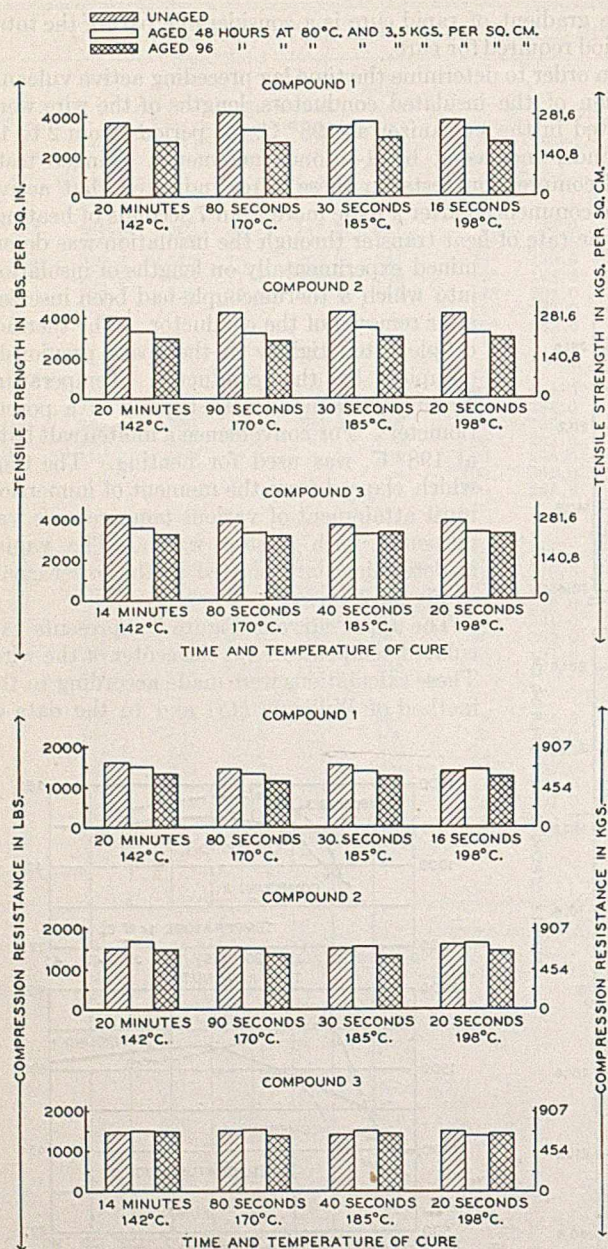


FIGURE 6. EFFECT OF CURING TEMPERATURE ON AGING (TENSILE STRENGTH AND COMPRESSION RESISTANCE)

Williamson and Adams (19) for a long cylinder. The assumption was made that the insulated conductor was a solid cylinder of the rubber insulating compound. The following formula was used for the calculations, substituting various values for t and solving for T :

$$\frac{T - T_1}{T_0 - T_1} = f\left(\frac{Dt}{r^2}\right)$$

where T = temperature at center of rubber cylinder in t seconds
 T_1 = temperature of steam in vulcanizer, 198° C.
 T_0 = original uniform temperature of rubber, 25° C.
 D = diffusivity of rubber compound, 0.00095
 t = time, seconds
 r = half of insulated-wire diameter, 0.14 cm.

The correlation between experimental and calculated data, as shown in Figure 7, is considered to be good.

The time lag of about 7 seconds, as determined by compression tests on the wire heated at 198° C., corresponds on the experimental heating curve to a temperature of about 140° C.

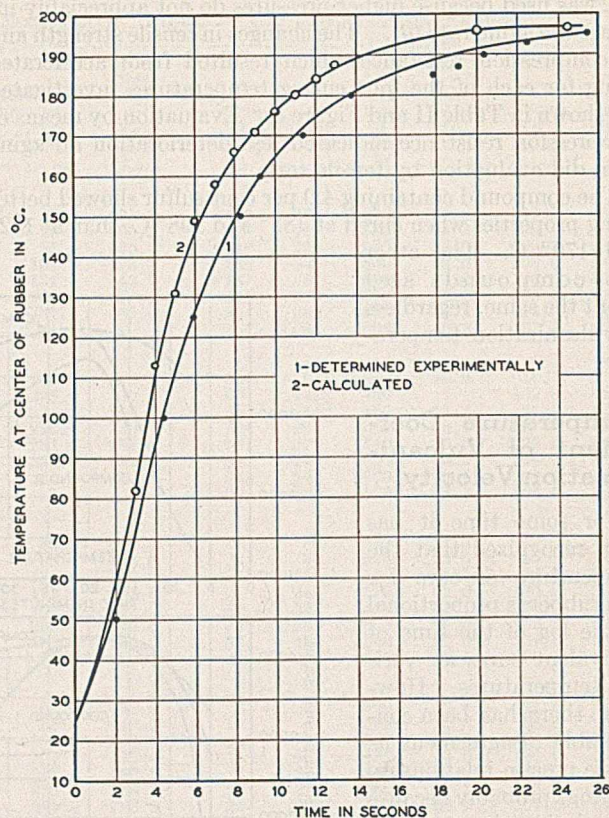


FIGURE 7. RATE OF TEMPERATURE RISE AT CENTER OF RUBBER-INSULATED CONDUCTOR WITH EXTERNAL TEMPERATURE OF 198° C.

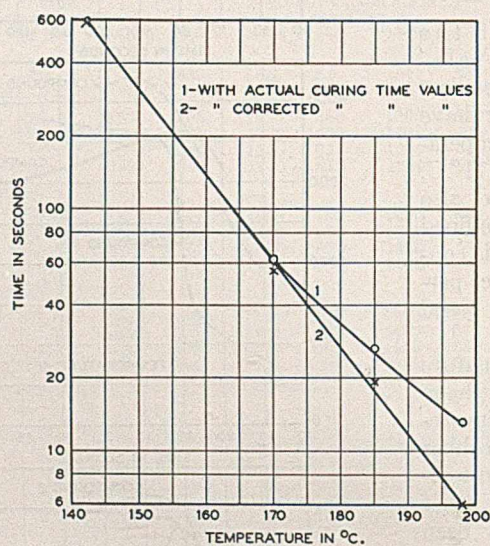


FIGURE 8. TIME-TEMPERATURE RELATION FOR MODULUS OF 2500 POUNDS PER SQUARE INCH (175 KG. PER SQ. CM.) AT 500 PER CENT ELONGATION FOR COMPOUND 3

for the rubber in the center whereas the total time required for optimum cures is only 20 seconds. It appears reasonable to assume that the rate of vulcanization when this temperature gradient is set up in the rubber is not appreciable as compared with the rate after a few more seconds of heating. Calculations indicate that the internal temperature of the rubber will follow similar time-temperature curves when heated at the other temperatures used for vulcanization. These calculations also indicate that comparable temperature gradients will be set up in the rubber at the various curing temperatures used in approximately the same 7-second period. Therefore, in calculating vulcanization rates, a correction of 7 seconds was made in the time of cure indicated for attaining each of the criteria used for each curing temperature. Data plotted in Figure 8 illustrate the justification for

TABLE III. TIME-TEMPERATURE RELATIONS FOR COMPOUNDS 1 AND 2

Value of Property, Kg./Sq. Cm.	Seconds to Attain Properties		° C. to Halve or Double Time of Cure		No. of Reliable Points on Curve	Product of Two Preceding Figures	Av. No. of ° C. to Halve or Double Cure	Temp. Coefficient	Value of Property, Kg./Sq. Cm.	Seconds to Attain Properties		° C. to Halve or Double Time of Cure		No. of Reliable Points on Curve	Product of Two Preceding Figures	Av. No. of ° C. to Halve or Double Cure	Temp. Coefficient
142° C. 170° C.								170° C. 185° C. 198° C.									
Time of cure when tensile at 300% elongation equals:	52.8	933.0	58.8	7.1	2	14.2			35.2	3	27.6		
					2	14.2	7.1	2.65	52.8	58.8	18.3	7.1	9.2	3	27.6	9.2	2.12
Time of cure when tensile at 400% elongation equals:	105.5	1043	60.8	6.8	2	13.6			88.0	56.5	14.4	5.3	8.3	3	24.9		
	123.2	1293	65.8	6.6	2	13.2			105.5	60.8	19.1	8.6	10.0	3	30.0		
					4	26.8	6.7	2.81	123.2	65.8	..	11.2	11.0	2	22.0		
Time of cure when tensile at 500% elongation equals:	176.0	1123	58.8	6.6	2	13.2			105.5	3	22.8		
					2	13.2	6.6	2.85	140.8	54.4	12.7	4.2	7.6	3	22.8		
					3	176.0	58.8	18.6	8.3	9.9	3	29.7		
					6	52.5	8.7	2.22						8	76.9	9.6	2.06
Time of cure when tensile at break equals:	211.3	899	53.6	6.9	2	13.8			211.3	53.6	..	4.5	7.9	2	15.8		
	246.2	1013	57.2	6.7	2	13.4			246.2	57.2	15.3	6.0	8.6	3	25.8		
					4	27.2	6.8	2.77						5	41.6	8.3	2.30
					Average		6.8	2.77						Average		8.95	2.17
Compound 2																	
Time of cure when tensile at 300% elongation equals:	35.2	760.8	2	13.6			35.2	..	12.0	4.4	9.0	2	18.0		
	52.8	928.8	53.6	6.8	2	13.6	6.8	2.77	52.8	53.6	16.6	6.2	9.0	3	27.0		
					5	45.0	9.0	2.16									
Time of cure when tensile at 400% elongation equals:	88.0	882.8	2	13.4			88.0	..	15.7	5.3	9.4	2	18.8		
	105.5	970.2	53.6	6.7	2	13.4			105.5	53.6	17.3	6.5	9.2	3	27.6		
	123.2	1052.8	57.1	6.7	4	26.8	6.7	2.81	123.2	57.1	19.3	8.1	9.9	3	29.7		
					8	76.1	9.5	2.07									
Time of cure when tensile at 500% elongation equals:	105.5	712.8	2	12.8			105.5	..	12.0	4.3	8.8	2	17.6		
	140.8	850.8	2	12.8			140.8	..	14.8	5.4	9.0	2	18.0		
	176.0	1089.8	53.2	6.4	2	12.8	6.4	2.95	176.0	53.2	17.2	6.8	9.5	3	28.5		
					7	64.1	9.16	2.13									
Time of cure when tensile at break equals:	246.2	982.8	53.8	6.7	2	13.4			211.3	..	14.3	5.0	8.6	2	17.2		
	281.7	61.5	..	2	13.4			246.2	53.8	16.3	6.1	9.0	3	27.0		
					2	13.4	6.7	2.81	281.7	61.5	19.5	8.6	9.9	3	29.7		
					Average		6.7	2.81						Average		9.2	2.12

TABLE IV. TIME-TEMPERATURE RELATIONS FOR COMPOUND 3

Value of Property Kg./Sq. Cm.	Seconds to Attain Properties		° C. to Halve or Double Time of Cure		No. of Reliable Points on Curve	Product of Two Preceding Figures	Av. No. of ° C. to Halve or Double Cure	Temp. Coefficient
	142° C.	170° C.	185° C.	198° C.				
Time of cure when tensile at 300% elongation equals:	35.2	..	52.8	18.1	5.6	8.6	3	25.8
	52.8	..	59.0	19.1	6.1	8.6	3	25.8
							6	51.6
							8.6	2.24
Time of cure when tensile at 400% elongation equals:	88.0	..	51.5	18.3	5.8	8.9	3	26.7
	105.5	..	54.5	18.8	6.0	8.8	3	26.4
	123.2	..	59.6	20.3	6.4	8.8	3	26.4
							9	79.5
							8.83	2.19
Time of cure when tensile at 500% elongation equals:	105.5	17.8	5.0	7.2	2	14.4
	140.8	537.8	..	18.3	5.5	8.5	3	25.5
	176.0	586.8	55.3	19.3	6.0	8.5	4	34.0
							9	73.9
							8.21	2.33
Time of cure when tensile at break equals:	211.3	..	59.3	18.9	7.2	9.3	3	27.9
	246.2	..	63.8	22.5	8.8	9.9	3	29.7
							6	57.6
							9.60	2.06
							Average	
							8.81	2.20

this procedure. The curved line represents uncorrected time values and the straight line, corrected time values.

Physical characteristics were taken rather than free sulfur content as criteria of cure for measuring curing rates. Shepard and Krall (12) and Eliel (4) indicated the advantages of physical tests for this purpose. The method of Sheppard (14) was used to determine the time required to double or halve the state of cure. The time required at various curing temperatures to attain the physical characteristics selected as criteria was taken from tensile and modulus curves. From each of these time values the time lag involved in heating up to an active temperature gradient—namely, 7 seconds—was deducted in each case. These corrected data for the compounds are recorded in Tables III and IV. In Figure 9 the time-temperature relation for constant values of modulus at 500 per cent elongation for compound 3 are plotted. From curves such as these which were plotted for the various physical criteria of the three com-

pounds, the corrected time required to attain given physical characteristics was determined at various temperatures.

It was found for compounds 1 and 2 containing 4 and 2.5 per cent of sulfur, based on the rubber content, that the temperature coefficient of vulcanization was not constant over the entire temperature range from 142° to 198° C. Over the range 142° to 170° C. a change in coefficient appears to take place in that a given temperature increment effects decreasing

acceleration of cure. However, over the range 170° to 198° C., the temperature coefficient was essentially constant. This may be accounted for on the basis that a slightly larger time correction for establishing a temperature gradient in the rubber should have been applied. For compound 3, containing 1 per cent of sulfur, the temperature coefficient of vulcanization was constant over the entire temperature range.

It appears significant that for the latter compound over the entire range of cures the coefficient is near 2, the value usually associated with organic reactions, and that approximately the same value is obtained for compounds containing larger amounts of sulfur only in the higher temperature range of cures. The apparent change in temperature coefficients found for compounds 1 and 2 in the lower temperature ranges and the absence of change for these compounds in the higher temperature range may be explained on the basis that only the sulfur in solution enters into reaction effecting cure,

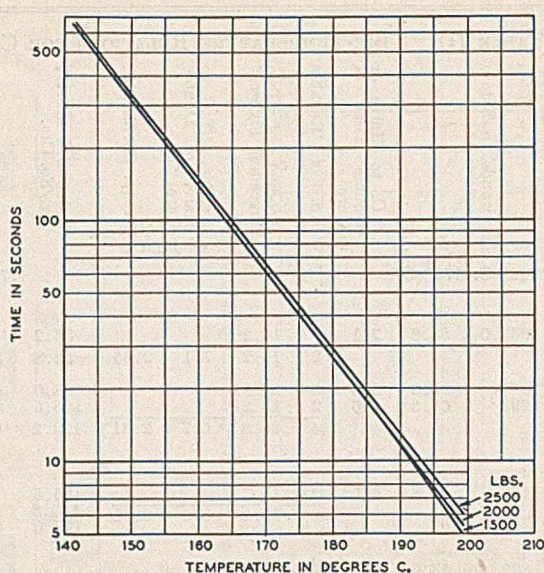


FIGURE 9. TIME-TEMPERATURE RELATION FOR CONSTANT VALUES OF MODULUS AT 500 PER CENT ELONGATION (COMPOUND 3)

TABLE V. TEMPERATURE COEFFICIENTS OF VULCANIZATION FOR 10° C. TEMPERATURE INCREASE

Literature Reference	Temp. Range, °C.	% Sulfur, Based on Rubber	Accelerator	Coefficient	Basis of Determination
(15)	50-75	10	None	2.84	Combined S
(15)	135-155	10	None	2.65	Combined S
(16)	128-168	10	None	2.3-2.6	Physical data
(16)	108-148	10	Organic	2.2-2.5	Physical data
(17)	140-148	10	None	2.4	Physical data
(10)	128-168	10	None	2.3	Combined S
(10)	128-168	10	None	2.3-2.4	Physical data
(10)	108-148	10	Aldehyde + NH ₃	2.4	Physical data and combined S
(10)	98-108	10	Aldehyde + NH ₃	5	Same
(14)	116.5-166.5	8	15% litharge	2.59	Same
(2)	135.5-162	6.25	None	2.5	Same
(2)	145-171	5	None	2.78-2.88	Physical data
(3)	125-150	4.5	10% litharge	2.45	Vulcanization coefficient of 3
(3)	125-150	4.5	10% litharge	2.2	Physical data
(7)	106-152	3.0	Various organic	1.81-2.00	Physical data
(7)	106-152	3.0	Various organic	1.87-2.11	Vulcanization coefficient
(11)	104.4-154.4	3.0	Two organic	1.92-2.52	Physical data
(11)	104.4-154.4	3.0	Two organic	2.20-2.40	Vulcanization coefficient
(9)	104.4-154.4	3.0	Two organic	1.91-2.32	Physical data
(9)	104.4-154.4	3.0	Two organic	2.30-2.67	Vulcanization coefficient
(4)	110-150	2.5	Various organic	2.0	Physical data
Kemp and	142-170	4	Organic	2.65-3.07	Physical data
Ingman-	170-198	4	Organic	2.13-2.19	Physical data
son	142-170	2.5	Organic	2.65-2.85	Physical data
	170-198	2.5	Organic	2.06-2.24	Physical data
	142-198	1.0	Organic	2.17-2.28	Physical data

and that at the higher temperatures of vulcanization there is not sufficient time for the sulfur in excess of the amount in solution to diffuse. As a result, vulcanization is localized. At the lower vulcanization temperatures, however, the time of vulcanization is sufficiently long to allow the sulfur present in excess of saturation to diffuse and accelerate the vulcanization reaction. This would also explain the constant rate of vulcanization found for compound 3 containing 1 per cent of

sulfur (based on the rubber) which approximates the solubility of sulfur in rubber at normal temperatures.

The coefficients of vulcanization determined here are given in Table V, together with coefficients found by other investigators and information on the procedures followed.

Although tetramethylthiuram monosulfide alone and in combination with di-*o*-tolylguanidine were used as accelerators in this investigation, several other accelerators and combinations of accelerators have also been found effective for vulcanizing insulation on wires at 198° C.

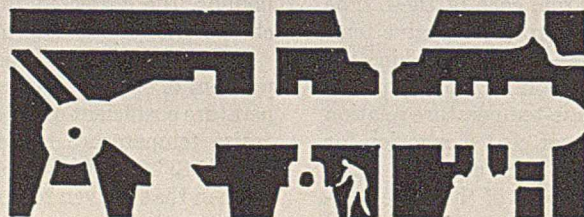
Acknowledgment

Acknowledgment is made to G. N. Vacca and G. S. Mueller for carrying out much of the experimental work involved in this investigation.

Literature Cited

- Brillhart, S. E., *Mech. Eng.*, 54, 405 (1932).
- Dawson, T. R., Research Assoc. Brit. Rubber Mfrs. Handbook, p. 154 (1935).
- Dawson, T. R., and Porritt, B. D., Research Assoc. Brit. Rubber Mfrs., *Lab. Circ.* 53 (1929).
- Eliel, K. W., *Trans. Inst. Rubber Ind.*, 12, 161 (1936).
- Hippensteel, C. L., *IND. ENG. CHEM.*, 18, 409 (1926); *Bell. Lab. Record*, 5, 153 (1928).
- Ingmanson, J. H., and Kemp, A. R., *IND. ENG. CHEM.*, 28, 889 (1936).
- Morris, R. E., *Ibid.*, 25, 1400 (1933).
- Park, C. R., *Ibid.*, 22, 1004 (1930).
- Park, C. R., and Maxwell, R. B., *Ibid.*, 24, 148 (1932).
- Rossem, A. van, *Com. Netherlands Govt. Inst. for Advising Rubber Trade and Rubber Ind. Int. Assoc. Rubber Cultivation in Netherlands Indies*, VI, 179 (1918).
- Sandstrom, R. V., *IND. ENG. CHEM.*, 25, 684 (1933).
- Shepard, N. A., and Krall, S., *Ibid.*, 14, 951 (1922).
- Shepard, N. A., and Street, J. N., *Ibid.*, 24, 574 (1932).
- Sheppard, J. R., *India Rubber World*, 80, 56 (1929).
- Spence, D., and Young, J., *Kolloid-Z.*, 11, 28 (1912).
- Twiss, D. F., and Brazier, S. A., *J. Soc. Chem. Ind.*, 39, 125T (1920).
- Vries, O. de, *Mededeel. Centraal Rubbersta.*, No. 1, 14, 31 (1916).
- Williams, I., *IND. ENG. CHEM.*, 15, 154 (1923).
- Williamson, E. D., and Adams, L. H., *Phys. Rev.*, 14, 99 (1919).

RECEIVED April 17, 1937. Presented before the Division of Rubber Chemistry at the 93rd Meeting of the American Chemical Society, Chapel Hill, N. C., April 12 to 15, 1937.



Litharge as Accelerator for Chloroprene Plastic Polymer

W. J. CLAPSON

The Eagle-Picher Lead Company,
Joplin, Mo.

Litharge is compared with basic-carbonate white lead, zinc oxide, and magnesia as accelerators for the chloroprene plastic polymer Neoprene Type E in stocks loaded with 100 parts of soft carbon black. Basic-carbonate white lead behaves similarly to litharge but is slower in setup. The effect of sulfur, wood rosin, stearic acid, pine tar, and lead oleate on cure, and of certain of these on water, gasoline, and kerosene absorption with litharge and with magnesia is discussed. Litharge gives good resistance to gasoline and kerosene; it is particularly effective in conferring low water absorption.

THE desirability of using certain metallic oxides to accelerate the vulcanization of the chloroprene plastic polymer known as DuPrene Type F was shown by Bridgwater and Krismann.¹ However, the tendency of that polymer to scorch in the presence of zinc oxide or litharge greatly restricted the use of these materials and substantially prohibited the use of zinc oxide alone. This difficulty does not appear to be as pronounced in the case of the polymer now known commercially as Neoprene Type E. The present paper discusses certain properties obtained with the latter material (referred to as polymer) with special reference to litharge as accelerator for it.

Stocks were compounded on a 15 × 30 cm. laboratory rubber mill, with roll temperatures maintained at about 40° C. The mixed stocks were sheeted off at about 0.23 cm. (0.090 inch);

the cured slabs were 0.20 cm. (0.080 inch) thick. All cures were made at 148.9° C. (300° F.) in the steam cavities of the press, corresponding to an equilibrium temperature in the stock of about 147.5° C. (297.5° F.). The water absorption tests at 100° and 110° C. were made by immersing the specimens in water and placing them in an autoclave in saturated steam maintained at the temperature indicated. Weight changes were determined by weighing on an analytical balance; volume changes were measured by the Navy method, which consists in determining the water displacement of the sample by weighing it on a Jolly balance. In the case of the gasoline and kerosene absorption tests, the volume increases reported were obtained immediately on removing the sample from the liquid; the stress-strain data were obtained after the sample had been allowed to dry 4 hours in air. The gasoline used was lead-free motor gasoline of 60° to 62° Bé. (Sinclair Refining Company). All members of a series were prepared by the master batch method, the variable ingredient being added to an appropriate portion of the master batch, and were cured simultaneously.

Systematic Variation of Litharge

To demonstrate the effect of adding litharge to polymer, the stocks formulated as in Table I were mixed. Results are shown in Figure 1.

That the litharge markedly improved the stiffness is evident. It is also evident that increasing the litharge content above 10 parts had only a slight additional accelerating effect. Similar results with respect to the effect of litharge were obtained in a series parallel with the above but containing no sulfur.

TABLE I. SYSTEMATIC VARIATION OF LITHARGE

Polymer	D2	D3	D4	D5	D6	D7
Thermax ^a	100	100	100	100	100	100
Cottonseed oil	3	3	3	3	3	3
FF wood rosin ^b	5	5	5	5	5	5
Sulfur	1	1	1	1	1	1
Litharge ^c	...	10	20	30	50	100

^a Trade name for a soft variety of carbon black.

^b FF No. 20 wood rosin (Hercules Powder Company).

^c Sublimed litharge was used throughout.

Effect of Sulfur

Bridgwater and Krismann showed that sulfur affects the rate of cure of Type F polymer; the effect of sulfur on unaccelerated Type E polymer is shown in the left half of Figure 2.

Obviously the addition of 1 part of sulfur improved the stress-strain properties. Contrasted with the foregoing result is the effect of adding sulfur to a litharge-accelerated base. The formulas and data are shown in the right half of Figure 2. Wood rosin and cottonseed oil were added as 10 parts of Prenol A (National Rosin Oil and Size Company).

Sulfur exerts a slight, though noticeable, retarding effect in this type of litharge-accelerated stock. When selenium, as Vandex (R. T. Vanderbilt Company), is substituted for sulfur in the formulas of Figure 2, the retarding effect is slightly greater than for sulfur. The effect of sulfur on water absorption is discussed below under water absorption.

Softeners

WOOD ROSIN. In the preceding formulas, FF wood rosin has consistently appeared as one of the ingredients. Bridgwater and Krismann show that, in the Type F polymer which they were using, wood rosin or similar softener was necessary for the development of optimum properties. However, in the present type of polymer and of formulation there is a general tendency for it to reduce moduli of elasticity and tensile strengths, as shown in the data of Figure 3. Nevertheless, practical processing is claimed to be benefited by the presence of some wood rosin.

COMPARISON WITH OTHER SOFTENERS. In view of these stress-strain results, it is of interest to compare wood rosin

¹ IND. ENG. CHEM., 25, 280 (1933).

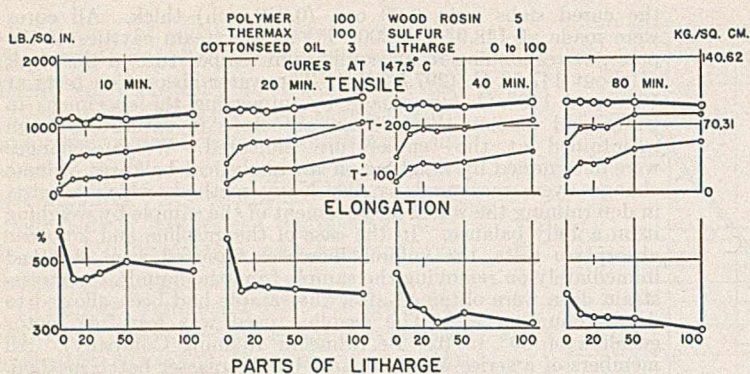


FIGURE 1. EFFECT OF LITHARGE ON CURE

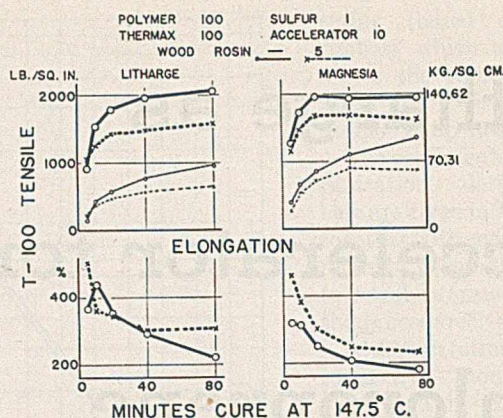


FIGURE 3. EFFECT OF WOOD ROSIN ON CURE OF LITHARGE AND MAGNESIA

Extra light calcined magnesia (General Magnesite and Magnesia Company) was used throughout.

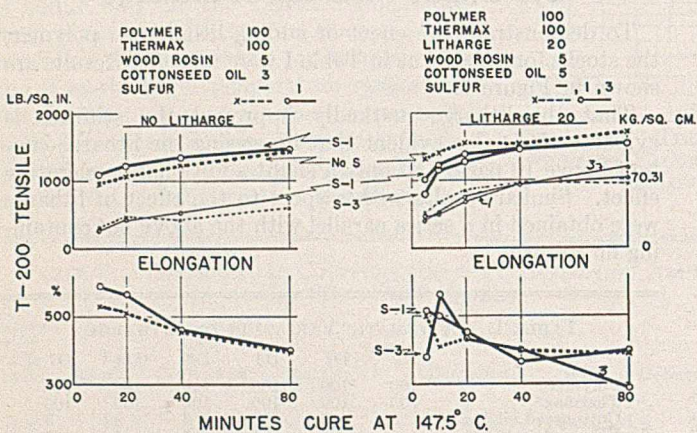


FIGURE 2. EFFECT OF SULFUR ON CURE, WITH AND WITHOUT LITHARGE

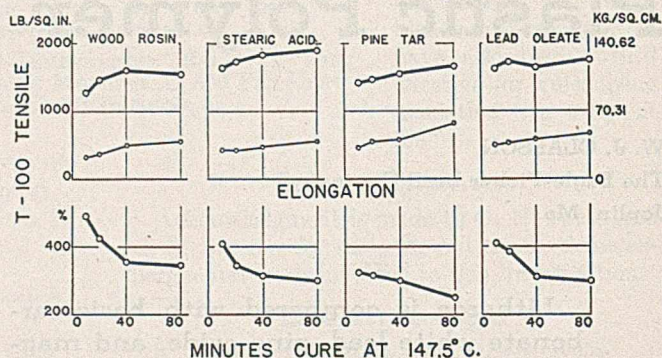


FIGURE 4. EFFECT OF SOFTENERS ON CURE OF LITHARGE STOCK

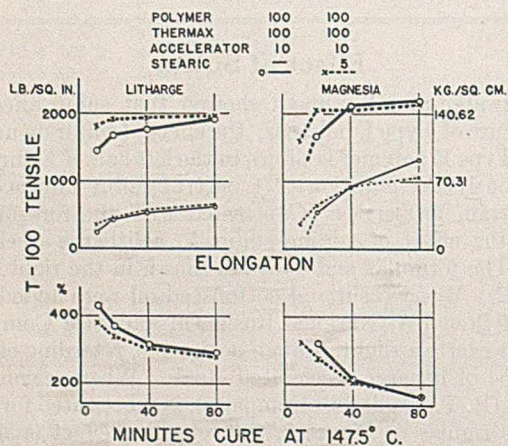


FIGURE 5. EFFECT OF STEARIC ACID ON CURE OF LITHARGE AND MAGNESIA

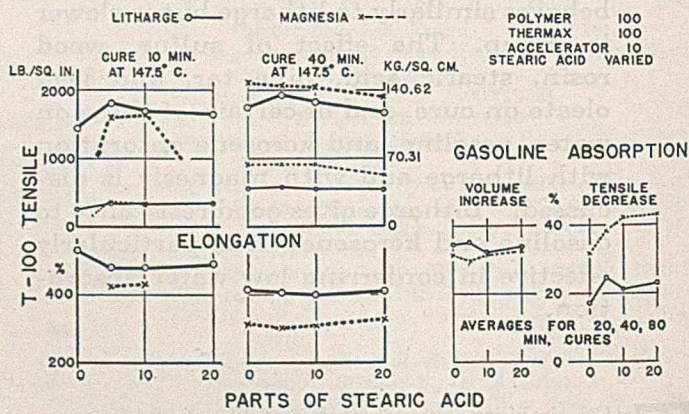


FIGURE 6. SYSTEMATIC VARIATION OF STEARIC ACID WITH LITHARGE AND MAGNESIA

TABLE II. RELATIVE WATER ABSORPTIONS AT DIFFERENT TEMPERATURES

Immersion Period	C1, Base ^a	C2, Base + 2 ZnO	C3, Base + 10 MgO	C4, Base + 2 ZnO + 10 MgO	C5, Base + 20 PbO	C6, Base + 20 PbO + 10 MgO	C7, Base + 20 PbO + 2 ZnO	C8, Base + 20 PbO + 10 MgO + 2 ZnO	Per Cent Gain in Weight	
									Time	
209 days at 27° C.	8.7	10.4	27.3	23.1	4.9	12.3	4.7	12.5		
210 hours at 110° C.	50.5	55.3	80.6	61.0	15.6	40.4	15.5	32.8		
Hours ^b at 110°, approx. equal to 209 days at 27° C.	22	28	50	65	32	48	32	60		
Days ^c at 27°, approx. equal to 1 hour at 110° C.	9.5	7.5	4.2	3.2	6.5	4.4	6.5	3.5		

^a Same formula as D2, Table I.

^b Obtained by interpolation from time-weight data.

^c Derived from the data in preceding line.

with some other common softeners. Data comparing wood rosin, stearic acid, pine tar, and lead oleate in a litharge-accelerated base appear in Figure 4.

Both stearic acid and lead oleate gave stocks which were easily handled on the mill; on the other hand, the pine tar and wood rosin stocks tended to stick to the rolls.

Stearic acid gave stiffer vulcanizates with higher tensile strengths than did wood rosin; lead oleate behaved similarly to stearic acid but tensile strengths were a little lower; pine tar gave stiffer, shorter stocks than wood rosin but lower moduli and tensile strengths than the stearic acid stocks.

The excellence of these results with stearic acid prompted a further study. Bridgwater and Krismann stated that stearic and other fatty acids have little or no stiffening and activating effect on chloroprene polymers (presumably in the presence of magnesia or magnesia plus zinc oxide as accelerators). However, it appears that in Type E polymer stearic acid has appreciable effect, as shown by the data in Figure 5.

It is evident that 5 parts of stearic acid improved the cure and modulus appreciably; however, as shown in Figure 6, 10 parts or more gave no additional improvement. With 10 to 20 parts, moduli and tensile strengths are lowered, doubtless because of excess softener. The retarding effect of 20 parts stearic acid on the magnesia stock is noteworthy. Stearic acid did not improve resistance to gasoline. Other data at hand show similar results as regards resistance to kerosene. (The dotted lines leading to some indefinite point near the axis indicate a porous cure; e. g., the magnesia stock with no stearic acid did not cure at 10 minutes.)

Water Absorption

Polymer, like rubber, absorbs water slowly over long periods. Specimens containing zinc oxide, litharge, and magnesia, singly and in combination, were still gaining in weight after 209-day immersion in water at about 27° C. A duplicate set was also still gaining after 210-hour immersion in water at 110° C. Absorption is enormously faster at 100° than at 27°, and still faster at 110° C. However, the relative rate for the three temperatures apparently changes with formulation; therefore, the relative rating of a given pair of stocks depends on the temperature of the test. This point is illustrated by the data in Table II. At 27° C. stocks C6 and C8 had higher water absorption than the base but at 110° they had lower water absorption than the base. Table II also demonstrates the low water absorption conferred by litharge, the high water absorption conferred by magnesia, and the effect of various combinations. The effect of zinc oxide in increasing the water absorption of the base as contrasted with its effect in decreasing water absorption in combination with magnesia or litharge is interesting.

In another experiment specimens of stocks C1 to C8 (Table II) and D2 to D7 (Table I) were soaked in water at 27° C. for a month and then allowed to dry in air under room conditions. After drying for 2 months, the specimens had reached substantially constant weight which was lower than the original weight in the case of the stocks containing no magnesia (indicating leaching) and higher than the original weight in the case of magnesia-containing stocks. Further loss in weight of the latter stocks occurred slowly under reduced pressure (6 mm. or less) at 70° C., under which conditions magnesium hydroxide decomposes. The evidence, while not unimpeachable, indicates the possible formation of magnesium hydroxide when magnesia stocks are subjected to water. However, the total amount of water absorbed is much in excess of that which can be accounted for by the conversion of magnesia to magnesium hydroxide.

There are indications that water absorption of the non-accelerated polymer is increased by sulfur (Table III) and

TABLE III. EFFECT OF SULFUR ON WATER ABSORPTION OF NONACCELERATED STOCK

	D1	D2
Polymer	100	100
Thermax	100	100
FF No. 20 wood rosin	5	5
Cottonseed oil	3	3
Sulfur	...	1
Cured 60 min. at 147.5° C.		
Per Cent Gain in Weight after Immersion in Water		
28 days at 27° C.	2.8	3.1
12 hours at 100° C.	4.8	5.5
12 hours at 110° C.	6.6	7.8

TABLE IV. EFFECT OF SULFUR ON WATER ABSORPTION OF LITHARGE-ACCELERATED STOCK

	D12	D14
Polymer	100	100
Thermax	100	100
FF wood rosin	10	10
Cottonseed oil	3	3
Litharge	20	20
Sulfur	...	1
Cure at 147.5° C.,		
Min.	Per Cent Gain in Weight after Immersion for	
	24 Hours in Water at 110° C.	
40	6.3	5.6
80	6.7	6.2

TABLE V. EFFECT OF SOFTENERS ON WATER ABSORPTION^a

Compound	Softeners	Increase after Immersion in Water at 110° C. for 24 Hours ^a % by vol.
J1	Wood rosin	10.4
J2	Stearic Acid	9.9
J3	Pine tar	7.8
J4	Lead oleate	9.2

^a Average of 20- and 40-minute cures at 147.5° C.

that, on the other hand, water absorption of a litharge-accelerated base is decreased slightly by sulfur (Table IV).

Litharge, as just shown, confers low water resistance on polymer. Water absorption data on the compounds of Table I, cured 60 minutes at 147.5° C., are shown in Figure 7. Water absorption decreased sharply with 10 to 20 parts of litharge and less sharply, though continuously, with litharge up to 100 parts.

The effect of the softeners in stocks J1 to J4 is shown in Table V. It is evident that the variation in softener affected water absorption but little; the slight effect was in favor of pine tar.

Comparison of Accelerators

Of the lead-containing accelerators tested—litharge, basic-carbonate white lead, sublimed white lead, and sublimed lead—litharge and basic-carbonate white lead (B. C. W. L.) show most promise. A comparison of litharge, B. C. W. L., zinc oxide, and magnesia in a loaded stock containing sulfur but no softener or acidic activator is shown in Figure 8.

Analogous to its action in rubber, B. C. W. L. is slower in rate of setup than litharge, but otherwise they give stocks of similar rate of cure and stress-strain properties. Zinc oxide gave fast setup and moderate stress-strain properties. Magnesia gave faster setup than litharge, but not as fast as zinc oxide, and short stiff stocks.

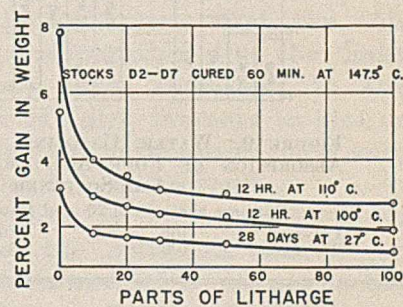


FIGURE 7. EFFECT OF LITHARGE ON WATER ABSORPTION

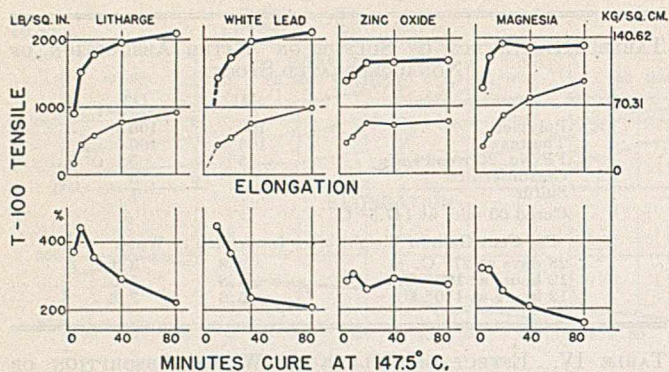


FIGURE 8. COMPARISON OF CURE OF FOUR ACCELERATORS WITHOUT ACID SOFTENER

Polymer	100	Sulfur	1
Thermax	100	Accelerator	10

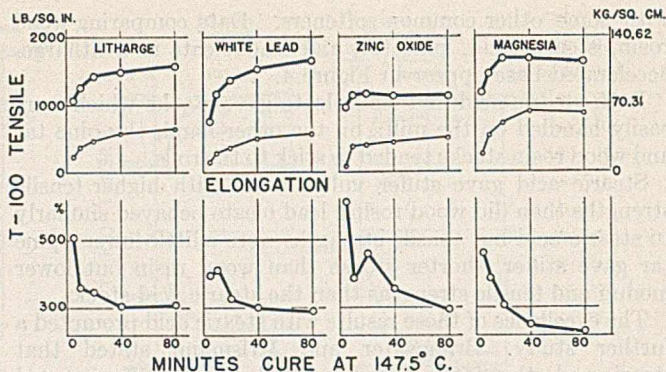


FIGURE 10. COMPARISON OF CURE OF FOUR ACCELERATORS WITH WOOD ROSIN

Polymer	100	Wood rosin	5
Thermax	100	Accelerator	10
Sulfur	1		

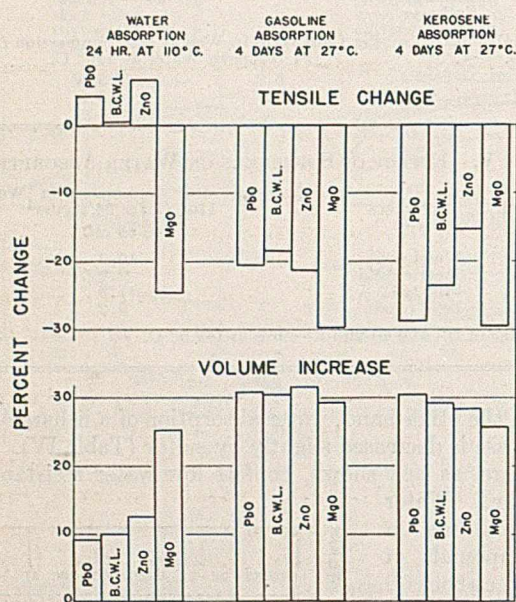


FIGURE 9. WATER, GASOLINE, AND KEROSENE ABSORPTION OF FOUR ACCELERATORS WITHOUT ACID SOFTENER

Data are averages of 20- and 40-minute cures.

Polymer	100	Sulfur	1
Thermax	100	Accelerator	10

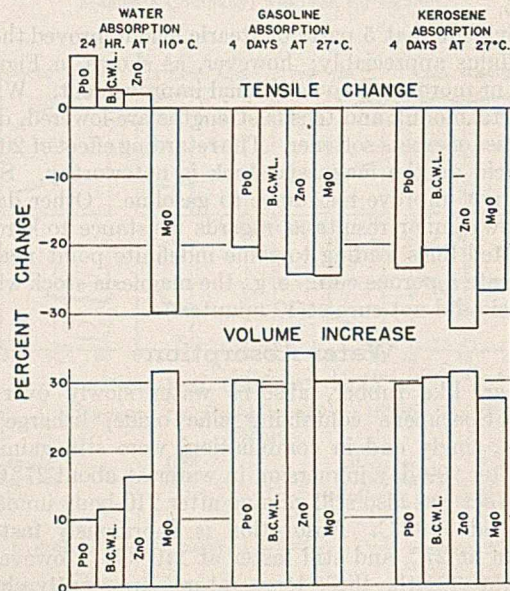


FIGURE 11. WATER, GASOLINE, AND KEROSENE ABSORPTION OF FOUR ACCELERATORS WITH WOOD ROSIN

Data are averages of 20- and 40-minute cures.

Polymer	100	Accelerator	10
Thermax	100	Wood rosin	5
Sulfur	1		

All of the foregoing stocks were difficult to sheet out smoothly in the uncured state, especially the magnesia stock, because of lack of plasticizer as shown by their ready conversion to smooth stocks on addition of wood rosin.

Their relative resistances to water, gasoline, and kerosene are shown in Figure 9. Of the four, litharge gave lowest and magnesia highest water absorption. Differences in resistance to gasoline and to kerosene are not indisputably established.

When 5 parts of wood rosin are added to the compounds of Figures 8 and 9, the resulting stocks compare as to curing properties as in Figure 10.

As in the preceding series, B. C. W. L. was slower in setup and magnesia faster in setup than litharge. Zinc oxide was about equal to litharge in setup but gave lower tensile strengths and generally lower moduli.

The relative resistances of these stocks to water, gasoline, and kerosene are shown in Figure 11. Litharge and B. C. W. L. behaved similarly; both gave lower water absorption than zinc oxide and than magnesia, especially the latter. Smaller differences are shown as regards resistance to gasoline and to kerosene.

If stearic acid is substituted for the wood rosin in the stocks of Figures 10 and 11, the relative curing results for the four accelerators remain substantially as described.

Summary

The chloroprene plastic polymer known commercially as Neoprene Type E is discussed with special reference to litharge as an accelerator of vulcanization. All data pertain to stocks loaded with 100 parts of soft carbon black.

Substantially maximum stress-strain properties and rate of vulcanization are obtained with 10 to 20 parts of litharge, although water absorption decreases with the litharge content (at least up to 100 parts of the latter). Rate of cure, stress-strain properties, and water absorption appear to be increased by sulfur in the absence of accelerator but decreased by sulfur in the presence of litharge. Litharge sets up faster than magnesia in the absence of one per cent of sulfur but slower than magnesia in the presence of one per cent of sulfur.

Stearic acid activates both litharge and magnesia, but the former is the less sensitive to the quantity of stearic acid. Wood rosin may have a mild activating effect on litharge and

on white lead but tends to reduce moduli and tensile strengths. Pine tar gives short stiff stocks; lead oleate behaves similarly to stearic acid. Stearic acid does not improve gasoline and kerosene absorption. Stearic acid and lead oleate stocks do not adhere to the rolls as do wood rosin and pine tar stocks.

Basic-carbonate white lead is slower in setup but otherwise behaves similarly to litharge. Zinc oxide gives fast setup and moderate physical properties; it is retarded by wood rosin.

Litharge confers low water absorption, magnesia gives high water absorption. Water absorption increases with the temperature, the rate of increase being dependent on the

formulation. Water absorption is not appreciably influenced by the softeners used.

Acknowledgment

Thanks are due to John H. Baldwin and Francis E. Moseley of the Research Department for their assistance in obtaining the data published herein and to E. W. McMullen, director of research, and J. R. MacGregor, vice president, for permission to publish the paper.

RECEIVED April 17, 1937. Presented before the Division of Rubber Chemistry at the 93rd Meeting of the American Chemical Society, Chapel Hill, N. C., April 12 to 15, 1937.

Colloidal Structure of Rubber in Solution

S. D. GEHMAN AND J. E. FIELD

The Goodyear Tire & Rubber Company, Akron, Ohio

THE type of colloidal behavior exhibited by rubber solutions presents the nature of the colloidal structure in solution as a complicated problem with nearly as many aspects as there have been fields of experimentation. Most of the methods of colloidal research have been applied, at least to some extent, to rubber solutions. A satisfactory scientific understanding of the structure will eventually require a convergence of the points of view arrived at by these different methods. Each source of independent information about the structure imposes its limitations upon the possibilities. In this work the writers have relied principally upon what is essentially a new and untried method of colloidal research as applied to rubber solutions—a study of the intensity and depolarization of the transversely scattered light. In addition to securing this new information, they have attempted to show how the results are related to those obtained from the method which has been of greatest general use in the past—namely, viscosity measurements.

Light-scattering measurements have been used for many years in the study of suspensions and colloidal systems such as gelatin solutions (13, 14), agar-agar sol-gel transitions (5), gum mastic (18), and numerous other colloidal suspensions. No systematic study of the light scattered by rubber solutions seems to have been made.

Optical Apparatus and Method

The optical system for making measurements of the relative intensity and depolarization of the transversely scattered light is illustrated in Figure 1:

The system is mounted in a darkroom. The source of light, *S*, is a 1000-candle-power Pointolite tungsten arc. The lens

Measurements are reported of the intensity and depolarization of the light scattered transversely by solutions of purified rubber in various solvents. Viscosity measurements on the same solutions are included. The viscosity is shown to be a function of the dielectric polarization of the solvent.

Experimental results are compared with the expectations on the basis of various theories of light scattering. Intensity and depolarization measurements are consistent in indicating that the colloidal units responsible for the light scattering are large compared to the wave length of light, increase in size as the concentration is increased, and vary in size for the different solvents.

The scattering is best explained by assuming in the solutions anisotropic scattering units similar in nature to the cybotactic groups of a liquid which may interlock sufficiently to give a continuous structure throughout the solution.

system, *L*, *L'*, is focused to give a beam of approximately parallel light, the angular divergence from the axis being 2.5°. The source and lenses are mounted on an optical bench in a light-tight housing, cooled by a fan. The beam is limited by diaphragms with rectangular openings, so that it has a cross section of 0.5 × 2 cm. at the light-scattering cell. *F* is a yellow filter (Corning No. 351) which makes the light more homogeneous and removes any blue light that might cause fluorescence. It also protects the solutions. The right-angle prism, *G*, reflects part of the light beam into one entrance of a Martens polarizing photometer, *T*. This reflected beam is reduced in intensity by a neutral glass filter, *F'*, and then serves as a standard of comparison. This arrangement eliminates errors due to variations in the brightness of the source. *P* is a Polaroid disk which can be introduced in such a way as to polarize the incident beam with the direction of vibration either vertically or horizontally, as

may be desired. *B* is a small steel box provided with appropriate windows. It is filled with water in order to minimize light reflections from the glass cell containing the rubber solution. When the cell is placed in the box in position *R*, the scattered light enters the right-hand entrance of photometer *T*. This polarizing photometer consists of a double-image prism arranged so that half of the field is illuminated by the vertically polarized component from the right-hand entrance, whereas the other half of the field is illuminated by the horizontal component from the left-hand entrance, as it is mounted. The field is then matched by rotation of a Nicol prism. The ratio of the intensities of the two beams is given by the square of the tangent of the angle of rotation from the zero position. In practice, two

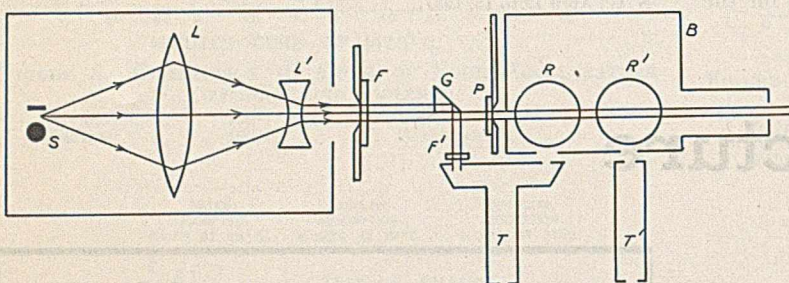


FIGURE 1. DIAGRAM OF OPTICAL SYSTEM FOR MEASURING RELATIVE INTENSITY AND DEPOLARIZATION OF TRANSVERSELY SCATTERED LIGHT

match points are read on either side of the zero position and the angle taken as half of the difference of the readings.

The description of the photometer shows that it is designed for use with unpolarized light. Since the scattered light is polarized, photometer *T* gives the relative intensity of only the vertical component, as it is mounted. *T'*, however, is a single-entrance polarizing photometer so that the tangent squared of the angle of the Nicol, in this case, gives the ratio of the intensities of the horizontal and vertical components, the cell being placed at *R'* to secure the reading. Knowing the ratio of the horizontal and vertical components, and the relative intensity of the vertical component, the relative total intensity can be calculated. The equipment thus makes possible a complete analysis of the scattered light for any state of polarization of the incident beam.

The intensity of the light scattered by solutions of purified rubber is so low that great care is required in matching the fields, and the eye must be completely dark-adapted. The sensitivity of the eye decreases for low intensities (12). Sufficient readings were taken so that the average could be duplicated to within a few tenths of a degree of arc of the photometer dial.

Light-Scattering Cell and Solutions

To make the light-scattering and viscosity measurements desired, a technic was required that would fulfill the following requirements:

1. Eliminate motes and dust from the solvent.
2. Protect the solutions from air.
3. Permit the concentration of a solution to be changed by the addition of dust-free solvent without exposure to air.
4. Provide for viscosity measurements on the identical solutions used for light-scattering measurements.

These needs were met by the use of the combined viscometer and light-scattering cell shown in Figure 2:

It consisted of a spherical and a tubular unit joined by a connecting tube. The bulb of the spherical unit has a volume of about 35 cc. The tubular unit is graduated and has a volume of about 60 cc. Light-scattering measurements were made on the solution when in the spherical bulb, the bulb being immersed in the water bath previously described. To make viscosity measurements, an Ostwald type viscometer is attached as shown. The capillary diameter was 0.4 mm. The viscometer may be filled from the top, without any interchange of fluid between the sphere and tube, by tilting the entire unit. The whole cell was immersed in a water thermostat at 30° C. for the viscosity measurements.

When making up a solution, a weighed amount of rubber was introduced into the bulb and the solvent poured into the tube.

The system was evacuated with a water pump, and some of the solvent was boiled off and sealed. The bulb containing the rubber was placed in an acetone-solid carbon dioxide mixture, and the solvent was allowed to distill over from the tube without boiling. This procedure eliminates all motes and dust from the solvent (1, 21). At such low temperatures the rubber does not readily go into solution, so that it and the bulb and viscometer could be washed several times with dust-free solvent before the final distillation which filled the bulb. Several days were sometimes required for the rubber to go into solution, during which time the cell was kept in a refrigerator. After light-scattering and viscosity measurements were made at one concentration, the solution could be diluted by pouring a measured volume of solution into the tube and distilling back the same volume of solvent. In this way light-scattering and viscosity curves could be obtained as a function of the concentration without exposure of the solutions to air and dust. At the end of the process, values are obtained for the pure solvent.

The rubber used throughout this work was petroleum ether diffusion rubber obtained from acetone-extracted pale crepe rubber by a continuous extraction process such as described by Pummerer (27). Petroleum ether was selected as the extracting fluid rather than ethyl ether because it seemed to preserve the gel structure of the crepe rubber better. The apparatus used for the extraction is shown in Figure 3, which is self-explanatory. Rubber stoppers, protected by aluminum foil, were used for the connections. The extracted rubber was precipitated with acetone and dried *in vacuo*.

It was always handled with the greatest care to avoid contamination with dust.

Theory

Before presenting the results, it will be advantageous to give a brief résumé of the theoretical background of the method of light-scattering measurements as applied to the investigation of colloids. This will greatly facilitate the discussion of the results and is necessary in order to understand them.

Four types of light scattering should be considered in the case of light scattering by rubber solutions:

1. Scattering by colloidal particles.
2. Scattering due to local density fluctuations (6, 31).
3. Scattering due to composition fluctuations (6).
4. Scattering due to the random orientation of anisotropic molecules (29).

By fluctuations are meant statistical varia-

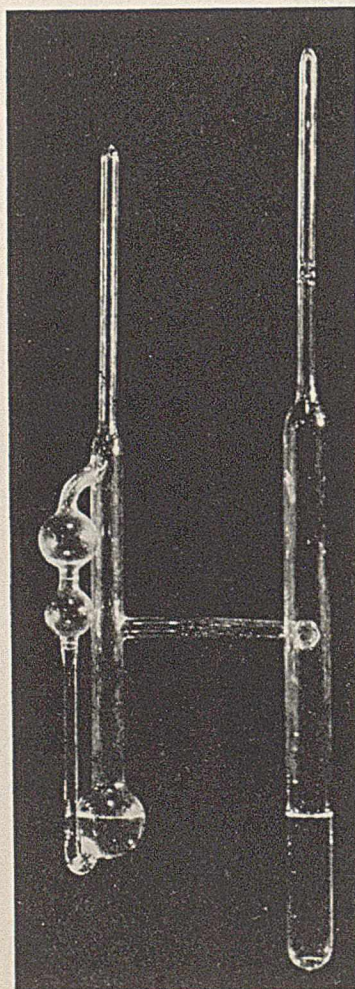


FIGURE 2. VISCOMETER AND LIGHT-SCATTERING CELL

tions from the average values due to the thermal agitation of the molecules.

Rayleigh worked out the procedure for calculating the light scattered by small, spherical particles in suspension. His fundamental equation is well known and has frequently been

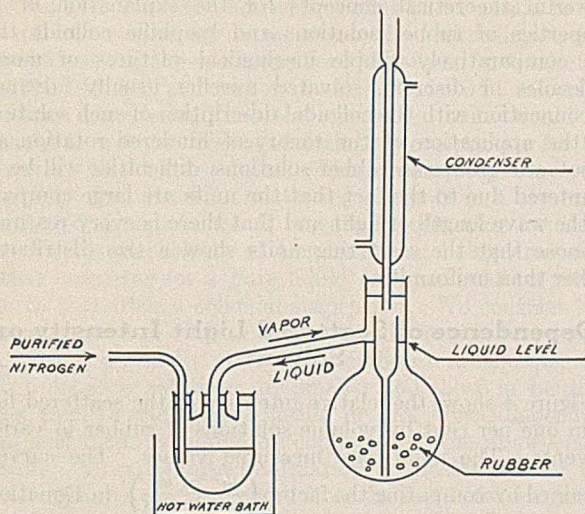


FIGURE 3. RUBBER EXTRACTION APPARATUS

the basis for light-scattering studies of colloids. A modification of this equation by Putzeys and Brosteaux (28) is given here:

$$\frac{Ir^2}{E} = \frac{9\pi^2}{2\lambda^4 N} \left(\frac{\mu_1^2 - \mu_2^2}{\mu_1^2 + 2\mu_2^2} \right)^2 \frac{6(1 + \rho)}{6 - 7\rho} \phi^2 g M \quad (1)$$

- where I = intensity of transversely scattered light
- E = intensity of incident beam
- r = distance at which I is observed
- λ = wave length of light
- N = Avogadro's number
- μ_1 = refractive index of the protein
- μ_2 = refractive index of the medium
- ϕ = specific volume of the protein
- g = concentration, grams per cc.
- M = mol. weight of large molecules assumed responsible for scattering
- ρ = ratio of horizontal to vertical component in scattered light

Equation 1 was used by Putzeys and Brosteaux for the determination of the relative molecular weights of proteins from measurements of the intensity of the light scattered by water suspensions of the proteins. The factor $6(1 + \rho)/(6 - 7\rho)$ is a correction factor introduced by Cabannes to take care of the observed depolarization due to imperfect spherical symmetry.

Putzeys and Brosteaux compared the intensity of the light scattering from a series of proteins in water solution, the molecular weights of which were available from the ultracentrifuge; they concluded that the intensity of the scattered light was directly proportional to the molecular weights and was not influenced by solvation, ion concentration, or aggregation.

Rayleigh's equation is limited to small, spherical particles in random arrangement. Calculations have also been made for the scattering from larger spherical particles (2, 3, 32). Gans (8) elaborated the theory to apply to differently shaped particles. He adopts the more general assumption that the particles are ellipsoids of the revolution. Depending upon the ratio of the axes, these particles in the limiting cases can be rods, spheres, or plates.

The assumptions for Gans' theory are:

1. All the scattering is due to particles having a different refractive index from the medium.
2. The particles are small compared to the wave length of light but large enough to be assigned a definite index of refraction and geometrical form.
3. The distance between the particles is large compared to the wave length of light.
4. The particles are in random orientation and distribution.

Under these limitations there can be practically no question of the validity of the theoretical work, but there is considerable question as to how closely a rubber solution fulfills these conditions.

Gans defines the depolarization of the scattered light, incident light unpolarized, as

$$\theta' = \frac{J_2}{J_1 - J_2} \quad (2)$$

where J_2 = intensity of horizontally vibrating component in scattered light
 J_1 = intensity of vertical component

The quantity ρ in Equation 1 is J_2/J_1 , so that

$$\theta' = \frac{\rho}{1 - \rho} \quad (3)$$

Gans showed that the depolarization is a function of the concentration and used θ'_0 to indicate the depolarization, extrapolated to zero concentration—i. e., the depolarization for a single particle. θ'_0 is dependent on the particle shape. From Gans' equations, the following values have been derived for θ'_0 :

Particle Form	θ'_0
Rods	$\frac{(m^2 - 1)^2}{m^4 + 8m^2 + 21}$
Spheres	0
Plates	$\frac{2(1 - m^2)^2}{7m^4 + 6m^2 + 2}$

where $m = \frac{\mu_1}{\mu_2}$ = refractive index of particle / refractive index of medium

According to these equations it should be possible to determine the general shape of the colloidal unit from the depolarization of the scattered light. Thus, for a solution of rubber in ether, $m = 1.13$ and we compute the following values for θ'_0 :

Particle Form	θ'_0
Rods	0.00236
Spheres	0
Plates	0.00734

It is apparent from the expressions for θ'_0 that, the depolarization increases as m deviates from unity.

If θ is the depolarization of the scattered light for vertically polarized incident light, Gans has shown that:

$$\theta' = 2\theta \quad (4)$$

If ρ_u is the depolarization ratio for unpolarized incident light, ρ_v for vertically polarized incident light, then from Equations 3 and 4,

$$\rho_u = \frac{2\rho_v}{1 + \rho_v} \quad (5)$$

Furthermore, it follows from Gans' theory that if the incident light is horizontally polarized, the scattered light will be unpolarized; i. e., $\rho_h = 1$.

Gans' equations show that the intensity of the scattered light is proportional to V^2 , if V is the volume of the particle, and is rather insensitive to particle shape.

For $m = 1.13$ as before, we calculate the following relative intensities of the light scattered by single particles of equal volume, the incident light being unpolarized:

Particle Shape	Relative Intensity
Rods	1.02
Spheres	1.00
Plates	1.03

When the particles are large compared to the wave length of light, Gans' theory does not apply and the intensity of scattered light decreases as the particle size increases for the same concentration (10).

Krishnan (15, 16, 17) developed a new method for investigating structure in liquids, glasses, etc., by means of light-scattering measurements. It surmounts to some extent the limitation of previous theory to particles small compared to the wave length of light. The method utilizes measurements of ρ_u and ρ_v which have already been defined. In contrast, ρ_h is the ratio of the vertical to the horizontal components in the scattered light for horizontally polarized incident light. Gans' theory shows that $\rho_h = 1$ and this value is actually observed for ordinary liquids and for suspensions of particles which are small compared to the wave length of light. Krishnan discovered, however, that for some systems ρ_h is definitely less than one, since the scattering units, which he regards as molecular clusters, are large. He derived the relation

$$\rho_u = \frac{1 + \frac{1}{\rho_h}}{1 + \frac{1}{\rho_v}} \quad (6)$$

Equation 6 reduces to Equation 5 when $\rho_h = 1$. Hence the deviation of ρ_h from unity is an indication of the size of the scattering units. To a first approximation, $2\rho_v/(1 + \rho_v)$ represents the portion of ρ_u due to the anisotropy of the scattering units. The portion due to the finite size of the units is, then, $\rho_u - (2\rho_v)/(1 + \rho_v)$ which Krishnan calls $\Delta\rho_u$.

The theory of the Krishnan effect, the deviation of ρ_h from unity, was further developed by Gans (9) and Vrkljan and Katalinić (33). Their analysis shows that the effect also depends upon the geometrical form of the scattering units. A large unit with spherical symmetry still gives $\rho_h = 1$. For rod-shaped scattering units with appropriate assumptions about the optical anisotropy, Vrkljan and Katalinić give for the length of the unit:

$$l^2 = \left(\frac{1}{\rho_h} - 1\right) \frac{84}{k^2} \quad (7)$$

where $k = \frac{2\pi}{\lambda'}$

λ' = wave length of light in the system

Theory is still inadequate to explain completely the optical properties of liquids, but the causes of the discrepancies with classical theory are beginning to be recognized and dealt with (23). The modern view of the structure of a liquid must be taken into account. It can no longer be considered that the positions and orientations of the molecules are random. On the contrary, the molecules of a liquid form quasi-crystalline or cybotactic groups, small compared to the wave length of light, which are anisotropic for anisotropic molecules. The hindered rotation of the molecules and the anisotropy of the electric forces must be introduced into the calculations to explain the depolarization of the scattered light and the optical properties of pure liquids. Evidence for the existence of cybotactic groups is also available from other fields (4, 20, 34).

For rubber solutions these factors must be very important in their influence upon the light scattering, and it seems probable that the ultimate explanation of the results will be in these terms rather than in the terms generally applicable to a colloidal suspension. Light-scattering measurements afford the possibility of the introduction of newer and more powerful theoretical concepts for the explanation of the properties of rubber solutions and lyophilic colloids than the comparatively simple mechanical pictures of macromolecules or discrete, solvated micelles usually advanced in connection with the colloidal description of such solutions. In the application of the theory of hindered rotation and cybotactic groups to rubber solutions, difficulties will be encountered due to the fact that the units are large compared to the wave length of light and that there is every reason to suppose that the scattering units show a size distribution rather than uniformity.

Dependence of Scattered Light Intensity on Solvent

Figure 4 shows the relative intensity of the scattered light from one per cent by volume solutions of rubber in various solvents. The points are measured values. The curve is obtained by computing the factor $\left(\frac{\mu_1^2 - \mu_2^2}{\mu_1^2 + 2\mu_2^2}\right)^2$ in Equation 1 for each solution and dividing by the value of the factor for the ethyl ether solution. This gives computed values rela-

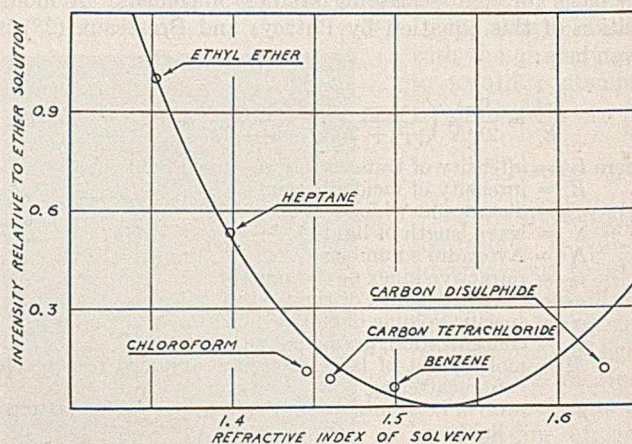


FIGURE 4. RELATIVE INTENSITY OF SCATTERED LIGHT FROM ONE PER CENT BY VOLUME SOLUTIONS OF RUBBER IN VARIOUS SOLVENTS

tive to the ethyl ether solution. As previously pointed out, this intensity factor is practically independent of the particle shape, so that if the scattering units were of the same size in the different solvents and the type of scattering conformed to Gans' assumptions, the curve should coincide with the experimentally observed values.

Although the intensity for the heptane solution is on the curve, the other solvents show marked departures. The scattering for the carbon disulfide, carbon tetrachloride, and chloroform solutions falls below the curve, whereas that from the benzene solution is greater than expected relative to the ether solution. The same facts are indicated even more strikingly by the following relative intensities observed for 10 per cent by volume solutions of petroleum-ether diffusion rubber:

Solvent	Relative Intensity of Scattered Light Calculated	Observed
Ethyl ether	1.000	1.000
Heptane	0.507	0.643
Benzene	0.016	0.139

Thus the relative intensity of the scattering of ether and heptane solutions might indicate a reasonable conformance to the conditions for the application of Gans' theory of the scattering by colloids and a reasonably identical scattering unit. For the other solvents used, either the scattering units or the mechanism of the scattering process appears to be different and the difference in the index of refraction of the solvent and the rubber is no longer the controlling factor. The intensity of the scattering for chloroform, carbon tetrachloride, benzene, and carbon disulfide tends to be the same. It seems improbable that the scattering units would be different in just the degree necessary to compensate for the differences in refractive index. Much more probable is the possibility that the light scattering arises from a structure of oriented groups which is essentially the same for these solvents, the mechanism of the scattering being analogous to that occurring for a pure liquid or liquid solution rather than to that from a colloidal suspension. We consider this a sounder point of view than to conclude from Figure 4 that the scattering units in chloroform, carbon tetrachloride, and carbon disulfide solutions are smaller and those in benzene larger than in the ether solution or vice versa, depending upon how large the units are compared to the wave length of light. More definite information about the size of the scattering units can be secured from the depolarization measurements which will be discussed later.

Dependence of Scattered-Light Intensity and Viscosity on Concentration

Curves showing the relative intensity of the scattered light for various solvents used are given in Figures 5 and 6. Petroleum-ether diffusion rubber was used in both cases but was extracted from different batches of acetone-extracted crepe rubber and showed a large variation in the solution viscosity.

The specific viscosity of a 0.25 per cent solution in ethyl ether of the rubber used for the data of Figure 5 was 1.12 and that for the rubber in the case of Figure 6 was 2.02, nearly twice as great.

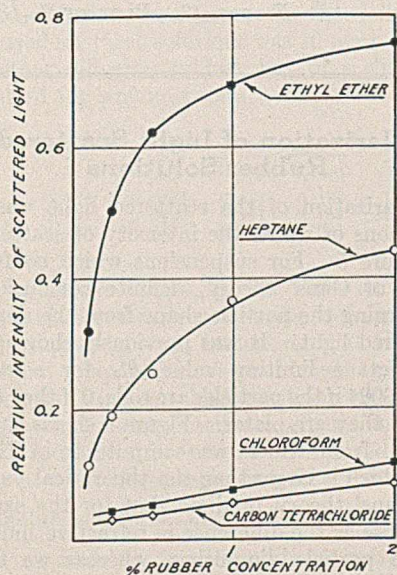


FIGURE 5. RELATIVE INTENSITY OF SCATTERED LIGHT FOR VARIOUS SOLVENTS

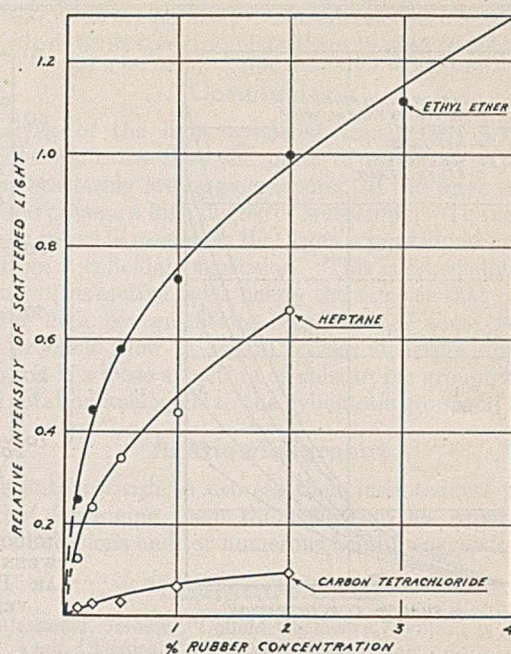


FIGURE 6. RELATIVE INTENSITY OF SCATTERED LIGHT FOR VARIOUS SOLVENTS

pensions. The intensity of the light scattering for the rubber solutions is not, in general, proportional to the concentration. The writers do not believe that the flattening of the curves at the higher concentrations in Figure 5 was influenced to any measurable extent by light absorption and secondary scattering which serve to flatten this type of curve for more opaque suspensions. The writers failed to measure any light absorption by means of a Weston photoelectric cell mounted to receive the incident beam after passage through the solutions.

The curves in both Figures 5 and 6 for ethyl ether and heptane solutions show a distinct change in slope at about 0.4 per cent by volume concentration which may be indicative of a change in structure at this concentration, somewhat corroborating the views of Staudinger. Unfortunately, the intensity of the light scattered from carbon tetrachloride and chloroform solutions is so low that for these solvents we cannot say much about the form of the curve at low concentrations. The flattening of the intensity curves shows that the tendency of the rubber solutions to scatter light like a pure liquid is most pronounced at the higher concentrations. Another possible interpretation is that the size of the scattering unit changes with the concentration. As the concentration is increased, the structure should approximate that of solid rubber and it is conceivable that the intensity of the scattered light would actually decrease if the curves were extended far enough.

The viscosity curves in Figure 7 show an entirely different character from the light-scattering intensity curves. The viscosity measurements were made on the identical solutions used for the light-scattering measurements shown in Figures 4 and 5. The viscosity curves are convex towards the concentration axis, whereas the intensity curves are concave.

There is some disagreement in the literature upon the relative viscosities of benzene and carbon tetrachloride solutions of rubber, and the meagerness of the data has been pointed out by Philippoff (26). Philippoff also summarized the mathematical treatment of the viscosity-concentration curve. The explanations of McBain (19) for the viscosity

The curves of Figure 5 illustrate the point previously made that the light-scattering properties of rubber solutions show marked differences from ordinary lyophobic colloidal sus-

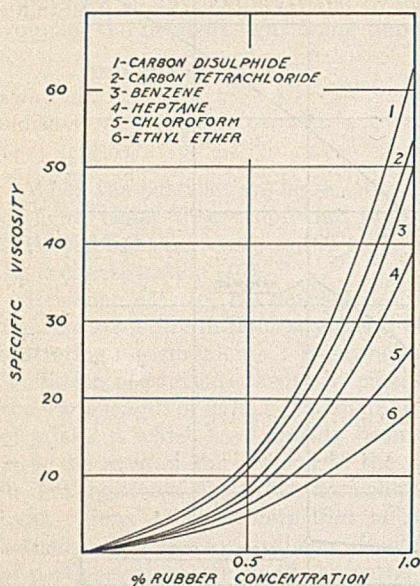


FIGURE 7. VISCOSITY CURVES

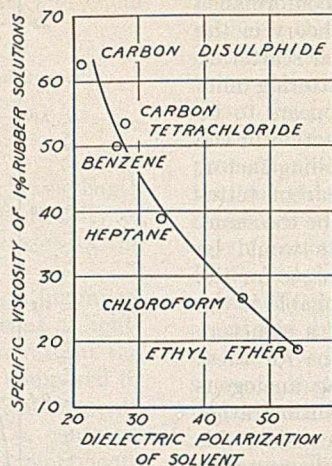
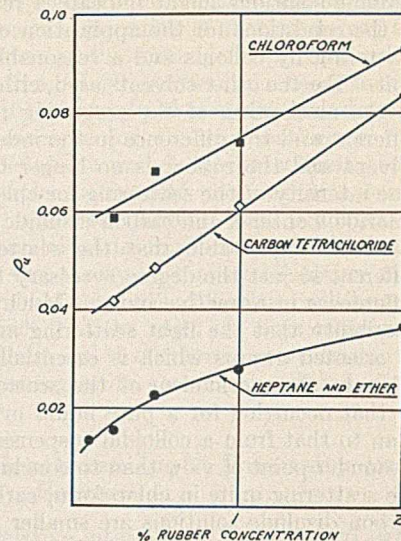
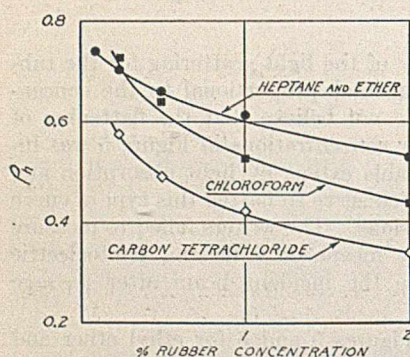
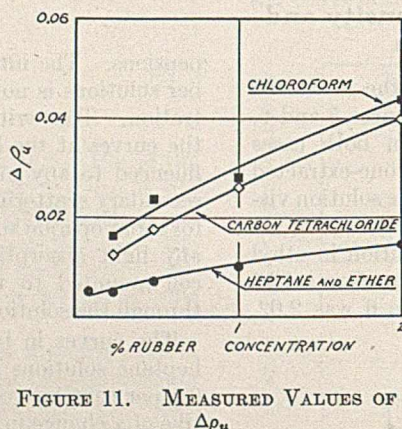
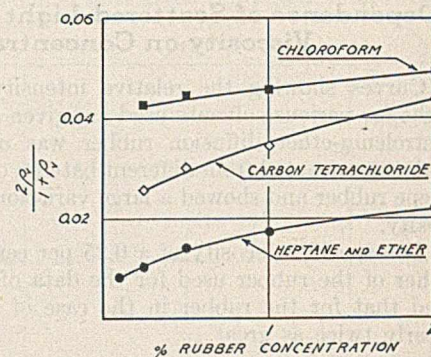


FIGURE 8. RELATION BETWEEN DIELECTRIC MOLECULAR POLARIZATION OF SOLVENTS AND VISCOSITY

FIGURE 9. MEASURED VALUES OF ρ_u FIGURE 10. MEASURED VALUES OF ρ_h FIGURE 11. MEASURED VALUES OF $\Delta\rho_u$ FIGURE 12. PLOT OF $2\rho_v/(1 + \rho_v)$

of colloidal solutions are closely related to some of the ideas arrived at from our work.

Figure 8 shows the interesting relation found to exist between the dielectric molecular polarization of the solvents and the viscosity. The dielectric molecular polarization is given by

$$P_{e,m} = \frac{K - 1}{K + 2} \frac{M}{d} \quad (8)$$

where K = dielectric constant
 M = molecular weight
 d = density of solvent

Ostwald previously pointed out the connection of the dielectric polarization with various colloidal phenomena (24, 25), and it has been used in studies of the swelling of rubber (7), but the writers believe this to be the first time that such a direct relation to the viscosity of rubber solutions has been shown. The direct implication is that electrical forces are concerned in the viscosities of the solutions. An older interpretation of this same function of the dielectric constant was that it represented the actual volume occupied by the atomic nuclei of the liquid (11).

Depolarization of Light Scattered by Rubber Solutions

The depolarization of the scattered light was measured for the solutions of which the intensity of scattered light is given in Figure 5. For suspensions which conform to the assumptions of Gans' theory, definite conclusions can be drawn concerning the particle shape from the depolarization of the scattered light. It was previously shown that Gans' theory predicts a limiting value, θ'_0 , for a rubber-ether solution of 0.0024 if the particles are rods, 0 if they are spheres, and 0.0073 if they are plates. Figure 9 shows the measured values of ρ_u , from which we compute from Equation 3, $\theta'_0 = 0.01$, which is larger than the theoretical values. Furthermore, Gans' theory predicts that for the same particle θ'_0 will decrease as the difference in refractive index between medium and particle diminishes, whereas we find that a carbon tetrachloride solution of rubber shows a larger depolarization than the ether solution. This is definite proof that the rubber solutions do not conform to the assumptions of Gans' theory. To secure information about the structure from the depolarization of the scattered light, it is therefore necessary to adopt the analysis of Krishnan and measure, in addition to ρ_u , ρ_v and ρ_h . Measurements of ρ_h are shown

in Figure 10. The fact that ρ_h is less than unity is evidence that the scattering units are large compared to the wave length of light and helps to explain the discrepancies with Gans' theory. For any one solvent, the smaller the values of ρ_h , the larger are the scattering units; hence Figure 10 shows that the scattering units become smaller at lower concentrations. This can be correlated with the form of the intensity curves (Figure 5) when it is realized that particles large compared to the wave length of light scatter less light as they become large. Depolarization factors for the benzene solutions are not given because the intensity for the solution was so low compared to that from the solvent that the values were influenced by the scattering from the pure solvent. A correction is difficult to apply because of the nonadditive character of the scattering (22).

In Krishnan's analysis, the size of the scattering unit is also indicated by $\Delta\rho_u = \rho_u - \frac{2\rho_v}{1 + \rho_v}$. These values are plotted in Figure 11, and the data again show an increase in the size of the scattering unit with the concentration. The factor $2\rho_v/(1 + \rho_v)$, which is the part of ρ_u because of the anisotropy of the scattering units, is plotted in Figure 12 and also increases with concentration. At zero concentration, the value agrees fairly well, for the ether solution, with the depolarization predicted by Gans' theory for plate-shaped particles. The anisotropy factor is a large part of ρ_u , showing that the scattering units have a large anisotropy. Gans' theory predicts an increase of the depolarization with the concentration but, for these comparatively dilute solutions, the writers do not consider that the increases observed are due to this cause. The principal reasons for this view are the decrease of ρ_h with concentration and the fact that the depolarizations do not correspond to those provided for by the theory. As a check on the accuracy of the depolarization measurements, the measured values of ρ_v and ρ_h can be inserted in Equation 6 and values of ρ_u can be calculated to compare with the measured values. In general, a fair agreement is obtained. The equipment was also checked by comparing depolarizations measured for the pure solvents with those given in the International Critical Tables.

Some observations on the depolarization factors for more concentrated solutions are given in the following table; the rubber used for these solutions was 10 per cent by volume petroleum-ether diffusion rubber, but of a different batch from that used for previous data:

Solvent	ρ_h	ρ_v	ρ_u		$\frac{2\rho_v}{1 + \rho_v}$	$\Delta\rho_u$
			Obsvd.	Calcd.		
Ethyl ether	0.418	0.0428	0.137	0.139	0.0821	0.0549
Heptane	0.353	0.0440	0.147	0.161	0.0844	0.0626
Benzene	0.445	0.0949	0.305	0.281	0.1731	0.1319

The depolarization factors, ρ_u , for these solutions are as large as those observed for pure liquids such as the solvents; but for these liquids $\rho_h = 1$, indicating that the cybotactic groups are small compared to the wave length of light, whereas the scattering units in the rubber solutions are large.

Use of Equation 7 makes possible a calculation of the length of the scattering unit, if the assumptions involved are accepted. Substituting $\rho_h = 0.535$ corresponding to the measurement of a 2 per cent solution in ether, and $N = 5800 \text{ \AA.} \times \frac{1}{1.35} l$ comes out as 5900 \AA. , in somewhat better than qualitative agreement with values given by Schulz (30) for the size of the colloidal unit from viscosity and osmosis measurements. For the ether solution at 0.1 per cent concentration, l is, by the same calculation, 3600 \AA. Assuming the usual spacings and angles for the rubber hydrocarbon chain molecule, this would correspond to a molecular weight of 53,000. For the carbon tetrachloride solutions l is 7400 \AA. at 2 per cent

and 3400 \AA. at 0.1 per cent. The curves decrease so rapidly that it is difficult to extrapolate them to zero concentration.

Conclusions

Analysis of the light scattered transversely by rubber solutions indicates that the units of structure responsible for the scattering are large compared to the wave length of light and possess a high degree of anisotropy. The scattering in many respects resembles that from a pure liquid more than that from a colloidal suspension. This is especially true for solvents of refractive index nearly the same as that of rubber and for high concentrations. In view of these facts the most probable view in regard to the structure appears to be that it is a loose structure of anisotropic groups with hindered rotation analogous to the cybotactic groups in a liquid.

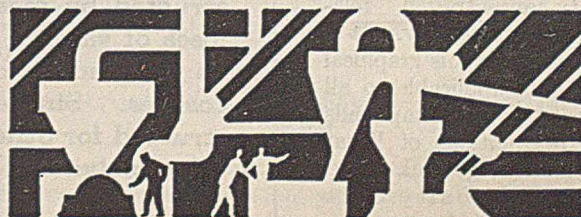
Acknowledgment

The authors wish to express their indebtedness to H. J. Osterhof for giving them the benefit of his experience in many discussions and for numerous helpful suggestions.

Literature Cited

- (1) Alexander, Jerome, "Colloid Chemistry," Vol. 1, p. 340, New York, Chemical Catalog Co., 1926.
- (2) Blumer, H., *Z. Physik*, **32**, 119 (1925).
- (3) *Ibid.*, **38**, 304 (1926).
- (4) Cartwright, C. H., *Phys. Rev.*, **49**, 470 (1936).
- (5) Donnan, F. G., and Krishnamurti, K., *Colloid Symposium Annual*, **7**, 1 (1930).
- (6) Einstein, A., *Ann. Physik*, **33**, 1275 (1910).
- (7) Ermolenko, N., and Levina, S., *Kolloid-Z.*, **75**, 59 (1936).
- (8) Gans, R., *Ann. Physik*, **62**, 330 (1920).
- (9) Gans, R., *Physik. Z.*, **37**, 19 (1936).
- (10) Gehman, S. D., and Morris, T. C., *IND. ENG. CHEM., Anal. Ed.*, **4**, 157 (1932).
- (11) Getman, F. H., "Theoretical Chemistry," p. 113, New York, John Wiley & Sons, 1922.
- (12) Holway, A. H., *J. Optical Soc. Am.*, **27**, 120 (1937).
- (13) Kraemer, E. O., and Dexter, S. T., *J. Phys. Chem.*, **31**, 764 (1927).
- (14) Krishnamurti, K., *Proc. Roy. Soc. (London)*, **A129**, 490 (1930).
- (15) Krishnan, K. S., *Proc. Indian Acad. Sci.*, **1A**, 717 (1935).
- (16) *Ibid.*, **1A**, 915 (1935).
- (17) *Ibid.*, **3A**, 211 (1936).
- (18) Lange, B., *Z. physik. Chem.*, **132**, 1 (1928).
- (19) McBain, J. W., *J. Phys. Chem.*, **30**, 239 (1926).
- (20) Madge, E. W., *Physics*, **5**, 39 (1934).
- (21) Martin, W. H., *J. Phys. Chem.*, **24**, 478 (1920).
- (22) *Ibid.*, **26**, 75 (1922).
- (23) Mueller, H., *Phys. Rev.*, **50**, 547 (1936).
- (24) Ostwald, Wo., *Kolloid-Z.*, **45**, 56 (1928).
- (25) *Ibid.*, **70**, 96 (1935).
- (26) Philippoff, W., *Rubber Chem. Tech.*, **10**, 76 (1937).
- (27) Pummerer, R., *Ibid.*, **2**, 367 (1929).
- (28) Putzeys, P., and Brosteaux, J., *Trans. Faraday Soc.*, **31**, 1314 (1935).
- (29) Raman, C. V., and Krishnan, K. S., *Phil. Mag.*, **5**, 498 (1928).
- (30) Schulz, G. V., *Rubber Chem. Tech.*, **6**, 101 (1933).
- (31) Smoluchowski, M. V., *Ann. Physik*, **25**, 205 (1908).
- (32) Stutz, F. G. A., *J. Franklin Inst.*, **210**, 67 (1930).
- (33) Vrkljan, V. S., and Katalinić, M., *Physik. Z.*, **37**, 482 (1936).
- (34) Warren, B. E., *Phys. Rev.*, **44**, 969 (1933).

RECEIVED April 17, 1937. Presented before the Division of Rubber Chemistry at the 93rd Meeting of the American Chemical Society, Chapel Hill, N. C., April 12 to 15, 1937.



Viscosity-Concentration Relations in Ethylcellulose Solutions

TOIVO A. KAUPPI AND SHAILER L. BASS

The Dow Chemical Company, Midland, Mich.

IN THE industrial utilization of cellulose derivatives the viscosity of their solutions and its dependence on concentration are of great practical importance. This subject has been studied intensively by many investigators, and several valuable theoretical conclusions have been drawn as to the structure and behavior of cellulosic compounds in solution. Philippoff (3) recently presented a thorough review of the field. However, these investigations have not served to give the industrial user of cellulose derivatives a simple method of expressing viscosity-concentration behavior. This is due in part to the necessarily complex form of the viscosity-concentration equations proposed, and in part to the fact that practically all of the equations apply to relative viscosity and not to actual solution viscosity. It is desirable in scientific investigation to use relative viscosity (viscosity of the solution divided by that of the solvent) in order to eliminate as far as possible the specific effect of the solvent; but in lacquer technology the viscosity of the solution itself is of more practical interest.

The purpose of this paper is to present a method of expressing the viscosity-concentration relation of ethylcellulose in simplified graphical form. The availability of a standardized domestic ethylcellulose in a range of viscosity grades and the scarcity of viscosity data on ethylcellulose made a study of its viscosity-concentration relations seem necessary. It is believed that this graphical method is applicable to all other cellulose compounds and to solutions of linear polymers in general.

From viscosity data on solutions of nitrocellu-

lose and of other polymers, Philippoff (3) concluded that the dependence of viscosity upon concentration of the solution involved only one arbitrary constant, as shown in Equation 1.

$$\eta_{rel.} = \left(1 + \frac{[\eta]c}{8}\right)^8 \quad (1)$$

where c = concentration, weight per cent
 $\eta_{rel.}$ = viscosity of solution relative to that of solvent
 $[\eta]$ = a constant

In Equation 1, $\eta_{rel.}$ is defined as follows: The viscosity of a solution of a cellulose derivative is dependent on the pressure differential which causes the solution to flow through the viscometer used for measurement. As the pressure differential is increased, the viscosity gradually decreases, reaching a limiting minimum value at very high pressures. At the other extreme, when the pressure differential is low, another limiting viscosity is reached which is a much higher viscosity than that obtained at high pressures, according to Philippoff's Figure 1 (3). The maximum relative viscosity measured at low pressures is the one used in Equation 1.

The arbitrary constant $[\eta]$ represents the "intrinsic viscosity" of the polymeric material used. Philippoff found that a change in the solvent or the temperature of measurement did not influence the validity of the equation but only altered the values of the constant.

In order to obtain a linear graphical relation between the absolute viscosity measured and the concentration, Equation 1 was transformed to the expression:

$$\eta_{abs.} = k \left(1 + \frac{[\eta]c}{8}\right)^8 \quad (2)$$

where $\eta_{abs.}$ = absolute viscosity of solution, centipoises
 k = absolute viscosity of solvent

By further transformation and combining the constants, the expression

$$\sqrt[8]{\eta_{abs.}} = k' + Kc \quad (3)$$

was obtained.

Equation 3 shows that a straight line should result when concentration is plotted against the eighth root of the absolute viscosity. It implies that the

The equation proposed by Philippoff relating the viscosity of a polymer to its concentration is applied to ethylcellulose solutions. The eighth root of the absolute viscosity is shown to be a linear function of the concentration under conditions of viscosity measurement obtaining in an Ostwald viscometer at concentrations above 5 per cent of ethylcellulose. The effect of solvents is to displace the straight line obtained above 5 per cent concentrations for a given intrinsic viscosity ethylcellulose without altering the shape of the curve.

A viscosity-concentration chart has been constructed which expresses the viscosity of commercially available ethylcellulose at concentrations from 5 to 20 per cent by weight as straight-line relations. A blending chart has been constructed by means of which ethylcelluloses of varying intrinsic viscosities may be blended to obtain intermediate viscosities. Similar charts may be constructed for other cellulose derivatives or other polymers.

viscosity should be determined either at low concentration or at pressure heads in the viscometer below which structural viscosity does not affect the measurement, according to Philippoff's Figure 17 (3).

Viscosity-Concentration Curves

The viscosities of solutions of four ethylcellulose samples with differing intrinsic viscosities were determined. A series of modified Ostwald viscometers with different capillary sizes was used, covering a viscosity range up to 5000 centipoises. The viscometers were calibrated against standard glycerol solutions at 25° C. The ethylcellulose used had an ethoxyl content in the range now recognized as standard for the commercially available material (1).

The curves of Figure 1 show the viscosity of solutions of ethylcellulose at concentrations from 1 to 15 per cent. The solvent was composed of 80 parts toluene and 20 parts absolute ethanol by volume. The curves were obtained by plotting the eighth root of the absolute viscosity in centipoises at 25° C. against the concentration in weight per cent. It is apparent from the curves that, in the range of concentrations above 5 per cent, the viscosity values lie on straight lines. At approximately 5 per cent there is a break in the line and the slope increases for the lower concentrations. It was found that these lines become curved as the concentration approaches zero.

Viscosity measurements on the low-viscosity ethylcellulose shown in curve IV of Figure 1 were carried out up to 25 per cent concentration. The values continued to lie on the straight line of this curve, indicating that extrapolation of the lines to higher concentrations was justifiable.

When the relative viscosity was plotted instead of the absolute viscosity in constructing the graph of Figure 1, curves of the same shape were obtained which showed breaks at the same concentration.

Effect of Solvent

The viscosity-concentration relations of the 30-centipoise ethylcellulose in 80-20 toluene-ethanol solution were determined in other solvents. The curves of Figure 2 show the behavior of the 30-centipoise ethylcellulose in a number of mixed solvents. The viscosity in toluene is shown for comparison, since ethylcellulose exhibits unusually high viscosity in the aromatic hydrocarbons. Figure 2 shows that a change in the solvent simply displaces the curves in a manner which is similar to a change in the intrinsic viscosity of the ethylcellulose shown in Figure 1.

Effect of Temperature

Philippoff (3) showed that changing the solvent or the temperature of measurement does not alter the form of the viscosity-concentration curves but simply changes the viscosity constant $[\eta]$. It can be expected, therefore, that the effect of temperature change on the viscosity-concentration lines as plotted will be only to displace the lines in the same manner in which they are displaced by varying the solvent.

Effect of Ethoxyl Content

The viscosity-concentration curves of ethylcelluloses having ethoxyl contents from 45 to 50 per cent were also determined and found not to differ in character from the curves shown. This would be expected from the effect of solvent changes, since ethoxyl content is closely related to solubility behavior. It is further proof that any means of influencing the viscosity, whether by changing the solute, the solvent, or the temperature, does not alter the straight-line relation above

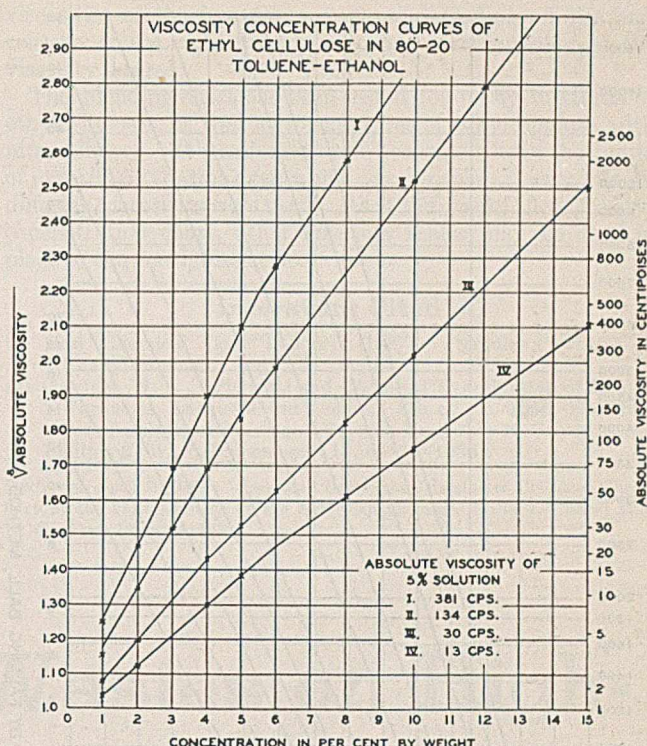


FIGURE 1

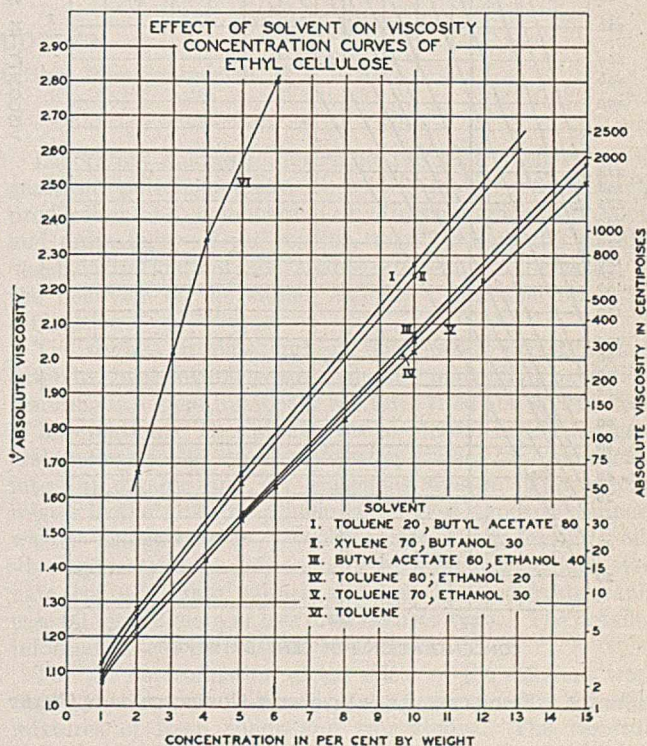


FIGURE 2

5 per cent concentration but only changes the position of the line.

Construction of Viscosity-Concentration Chart

The viscosity-concentration curves of a number of ethylcelluloses of varying viscosities were determined and plotted as in Figures 1 and 2. By interpolating graphically between

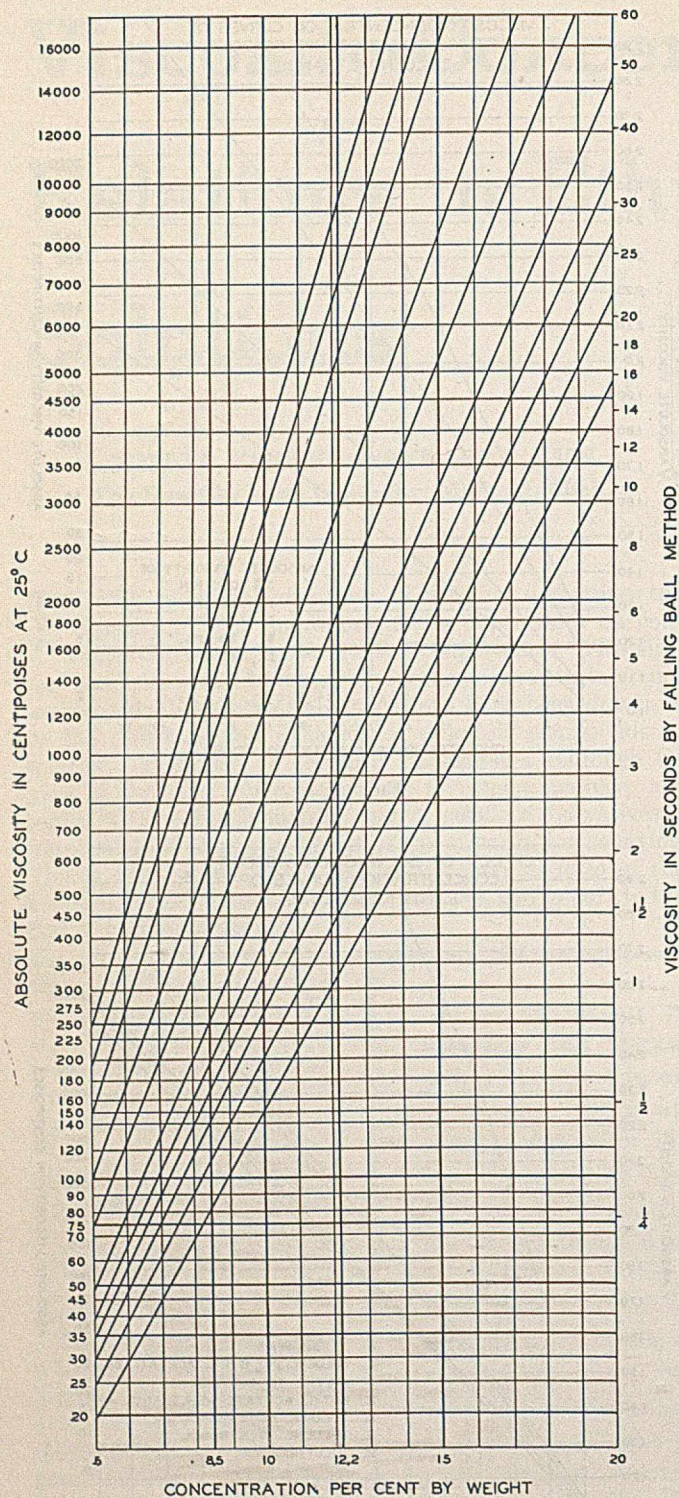


FIGURE 3. ETHYLCELLULOSE VISCOSITY-CONCENTRATION CHART

these curves and by omitting the concentrations below 5 per cent, the viscosity-concentration curves of ethylcelluloses of different intrinsic viscosities may be represented by a series of straight lines of varying slope. The resulting chart is shown in Figure 3. Thus, if the viscosity of an ethylcellulose at one concentration is known, the viscosity at any other concentration may be found by following the proper viscosity-concentration line, interpolating between the lines where necessary. If the viscosity variations caused by a change of solvent or of temperature are known at any one concentra-

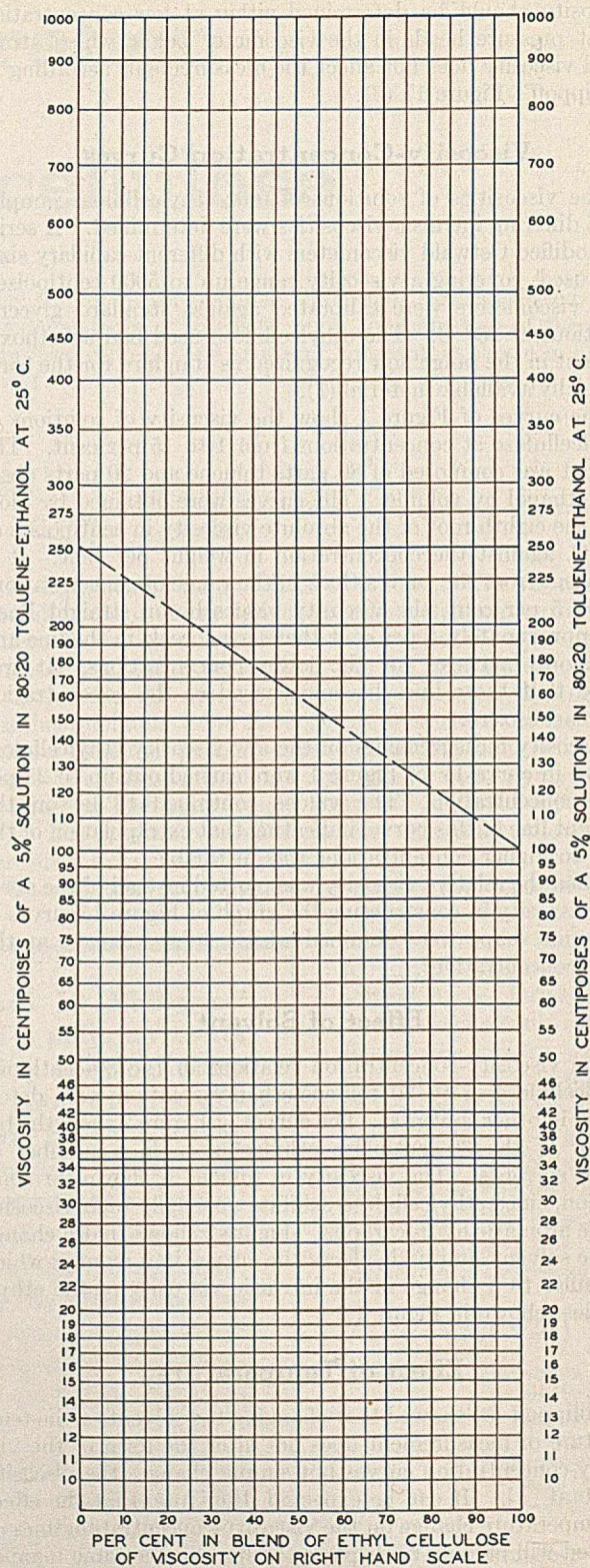


FIGURE 4. ETHYLCELLULOSE BLENDING CHART

tion, then the variations caused by the same change at another concentration can be found.

For measuring the viscosities of very viscous solutions, the falling-sphere method (A. S. T. M. D-301-33) is preferred. The conversion factor from centipoises measured by the Ostwald viscometer to seconds by the falling-sphere method was found to be 310. The right-hand scale of Figure 3 indicates the falling-ball viscosities in seconds equivalent to the centipoise viscosities shown on the left-hand scale.

Construction of Blending Chart

It is often necessary to mix two samples of a cellulose derivative to obtain a desired viscosity. Philippoff (3) presented a blending formula as follows:

$$C_o[\eta]_o = \sum C_i[\eta]_i \quad (4)$$

where C_o = total concentration in mixture

C_i = concentration of individual constituents

$[\eta]$ = viscosity constant of viscosity-concentration from Equation 1

As shown above, $[\eta]$ is constant when the viscosity is determined under conditions such that structural viscosity does not influence the values obtained. Therefore it was not known whether the formula would apply when ordinary conditions of viscosity measurement were used.

Figure 4 shows a blending chart similar to the logarithmic chart used for nitrocellulose (2). It was constructed by plotting the percentage of one component in the mixture against the eighth root of absolute viscosity in 5 per cent solution. The chart is used by drawing a line between the

viscosities of the two components and reading off the percentage of the right-hand component corresponding to the viscosity desired.

This blending chart has been tested for many mixtures of ethylcelluloses, as well as for mixtures of ethylcellulose with nitrocellulose. It was found to be accurate within the limits of experimental error even when components of very widely differing viscosities were used. As in the case of the viscosity-concentration chart, other viscosity scales may be used in place of the centipoise scale.

Literature Cited

- (1) Dow Chemical Co., "Ethocel" (1937); Hercules Powder Co., "Ethylcellulose," 1937.
- (2) Gardner, H. A., "Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors," 8th ed., p. 1056, Washington, Institute of Paint and Varnish Research, 1937.
- (3) Philippoff, W., *Cellulosechem.*, 17, 55-77 (1936).

RECEIVED April 19, 1937. Presented before the Division of Cellulose Chemistry at the 93rd Meeting of the American Chemical Society, Chapel Hill, N. C., April 12 to 15, 1937.

Effect of Trade Wastes on High- and Low-Temperature Digestion

WILLEM RUDOLFS

N. J. Agricultural Experiment Station, New Brunswick, N. J.

Certain organic wastes may cause a delay in digestion time and gas production; others have less effect. With acclimatization, a nonodorous well-draining ripe sludge may be produced when from 10 to 20 per cent organic wastes are added intermittently on the basis of the volatile matter in the fresh solids, and as much as 20 to 40 per cent when added continuously either under mesophilic or thermophilic conditions.

Odors tend to increase with organic and poisonous wastes. Thermophilic sludge is less sensitive to organic trade wastes than sludge digested under mesophilic conditions. Drainability of sludge produced from waste-sewage sludge mixtures is poorer. The composition of the gases produced is but slightly affected.

THE transformation of putrefactive organic solids by bacterial action to gases and an inodorous, well-draining residue is affected by several factors. The studies of several factors, such as temperature, inoculation, and reaction control, have yielded considerable practical information. The information available on the effects of certain trade wastes upon sludge digestion under mesophilic conditions is not great, and still less is known about the effects of such wastes under thermophilic conditions.

Laboratory studies to determine the relative effects of organic and poisonous wastes on volatile matter reduction, gas production and composition, hydrogen sulfide formation, and drainability of the residue, together with the possible "acclimatization" of the sludge, present an indication of the behavior of the sludge and show probable operation difficulties.

The studies on high- and low-temperature digestion have extended over several years, including pilot plant operation, resulting in a great number of mixtures tried and a large mass of information. The intention is to present briefly the general findings on two groups of wastes, divided for convenience into (a) organic and (b) poisonous wastes. The specific wastes in the first group include different types of tannery waste, slaughterhouse, wool-scouring, rug-cleaning and -dyeing wastes; the poisonous wastes include sodium arsenate, copper sulfate, sulfuric acid; gasoline and waste crankcase oil form a more or less intermediate type. The detailed information will be presented elsewhere.

For the determination of the effect of the different trade wastes, varying quantities of wastes were added to digesting mixtures of fresh solids and ripe sludge. The resulting sludges were then used for the same and increased additions of waste to determine the limits of toleration and the degree of acclimatization, if any. The organic trade waste additions varied from 10 to 60 per cent on the basis of fresh solids added, the mineral oils from 1 to 25 per cent, and the poisonous from 0.01 to 5 per cent. The individual series of experiments lasted until practically all gas that could be expected had been produced, and results were compared on the basis of a number of control mixtures. Gas formation was recorded daily, and gas composition, hydrogen sulfide production, and volatile matter reduction at intervals.

Mesophilic Digestion

In general, the quantities of gas produced per gram of volatile matter added decreased in all cases with increasing quantities of waste added. In several instances the addition of small quantities of organic wastes caused the production of more gas than the controls. For convenience a number of statements are given for the different types of waste.

TANNERY WASTE. The general relation between percentage volatile matter reduction and gas production held for all mixtures receiving tannery composites, tannery vat and tannery lime wastes. Additions of tannery composite waste up to 14 per cent by volume produced as much or more gas than the control, even though the volatile matter had not been reduced to the same extent. Hydrogen sulfide production was comparatively low.

BLOOD WASTE. These wastes produced violent foaming, high production of hydrogen sulfide, and low gas per gram of volatile matter and an odorous sludge.

WOOL-SCOURING WASTE. Addition of about 10 per cent by volume had only a slight effect although some retardation was apparent. With 20 per cent addition the digestion time was increased about 25 per cent.

RUG DYE WASTE. At the peak of daily gas production for the control mixtures, gas production from 10 per cent dye waste mixture was about 35 per cent less, and with increasing quantities retardation was greater.

GASOLINE. Addition of 0.1 per cent gasoline caused retardation, and additions of 0.5 per cent by volume affected digestion to such an extent that after 150-day digestion the mixture had not progressed as far as the control in 30 days.

SODIUM ARSENATE. With the addition of 4 p. p. m. the digestion had, for example, progressed after 60 days as far as the controls in 12 days.

COPPER SULFATE. Gas production was but slightly affected by copper sulfate in concentration up to 0.025 per cent of the total mixture. Gas production was more affected than liquefaction.

Acclimatization

Repeated additions of the same waste to sludge produced previously under mesophilic conditions when similar quantities of waste have been added showed that the observed retardation was reduced or overcome. This process of acclimating was further tested by adding increasing quantities of the same type of waste. It was possible in this way to increase the quantities of organic waste from 15 to 20 per cent on the basis of volatile matter in the fresh solids to 20 to 40 per cent.

In other words, when waste is received intermittently, the digesting sludge tolerates considerably less than when received continuously. In the case of gasoline the sludge could be only slightly acclimated to a maximum of about 1 per cent addition. It was even more difficult to acclimate sludge to copper sulfate and nearly impossible to sodium arsenate.

Of considerable interest is that, in nearly all cases when trade wastes are added, gasification is retarded, reduced, or inhibited, whereas volatile matter reduction, or so-called liquefaction, is affected to only a slight extent.

It is natural to expect that with increased liquefaction hydrogen sulfide production increases. The quantities of hydrogen sulfide found in the gas varied from 0.1 to 4 per cent. With from 1 to 2 per cent hydrogen sulfide in the gas, corrosion problems in flues, condenser pipes, and boilers increase. Upon acclimatization the hydrogen sulfide production decreased.

Thermophilic Digestion

Experiments conducted under thermophilic conditions were similar to those with mesophilic sludge. On the basis of volatile matter reduction, quantities of organic trade wastes up to 10 per cent had no effect and a slight retardation was noticed with quantities of 20 per cent. It was found that acclimating thermophilic sludge was easier than acclimating mesophilic sludge. The quantities of organic trade waste could be increased without difficulty. Gasoline appeared again to be toxic, but the quantities could eventually be increased to as much as 5 per cent on a volume basis of sludge. This would be equivalent to about 15 p. p. m. gasoline present in an average sewage of about 200 p. p. m. suspended solids, provided all the gasoline settled with the sludge and no gasoline was present in the seed material. Thermophilic sludge appeared to be somewhat more sensitive to poisons. The results seem to indicate clearly that thermophilic sludge is not only capable of handling moderate quantities of waste but will produce as much gas as from mixtures without waste, digested under mesophilic conditions, in a shorter time, without requiring acclimation to the same extent.

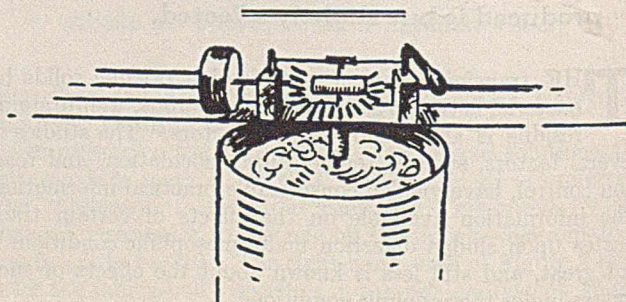
Dewatering

Experiments on vacuum filtration on filters standardized against an Oliver filter showed that in all cases (except when larger quantities of poisons were added) dewatering of the digested sludge-waste mixtures was poorer than of the controls. In general, it appears that with the increase in the quantity of trade waste added, the dewatering and drying of the digested sludges would be adversely affected. This does not hold when certain inert or mineral wastes are present.

Odors

Odor production as measured by the quantities of hydrogen sulfide in the gas varied under thermophilic conditions from 0.01 to 0.4 per cent. This compares with 0.06 to 2.7 per cent found in the gas formed under mesophilic conditions. The fact, that less hydrogen sulfide was present in the gas when thermophilic digestion was employed, does not indicate the total odor produced. In addition to the volatile sulfur, certain ammoniacal odors are produced which in combination with the hydrogen sulfide become very offensive. In the case of thermophilic digestion the odors from the sludge were more pronounced, chiefly due to the fact that ammonia compounds cause the sludge to smell like warm barnyard manure. The poisons, with less effect on thermophilic mixtures, caused relatively greater odor production than similar mixtures digested under thermophilic conditions. Mercaptan (pig pen and onion) odors together with the warm ammoniacal odors were very offensive with poisons.

RECEIVED April 20, 1937. Presented before the Division of Water, Sewage, and Sanitation Chemistry at the 93rd Meeting of the American Chemical Society, Chapel Hill, N. C., April 12 to 15, 1937. Journal Series Paper, Division of Water and Sewage Research, N. J. Agricultural Experiment Station.



DRYING GRANULAR SOLIDS

NORMAN H. CEAGLSKE¹ AND O. A. HOUGEN²

University of Wisconsin, Madison, Wis.

The drying rate of a granular substance is determined not by diffusion but by capillary forces. The moisture distribution cannot be calculated correctly from diffusion equations but depends upon the complex suction-water concentration relation of the substance. This relation is dependent upon particle size, degree of packing, and distribution of pore spaces and hence must be determined by experimental methods.

In the drying of a granular solid the rate of water flow is determined by capillary forces and not by moisture concentration gradients; the flow may be in the direction of increasing concentration. These two facts are contrary to the requirements of the diffusion law.

A simple method was described by Haines

THIS investigation of the drying of granular solids was nearing its termination when an unexpected discovery suddenly altered the authors' insight into the problem. With the departure of both authors from the University of Wisconsin, further work on this new approach to the problem of drying granular solids was postponed. To encourage others to follow this lead to an earlier and more fruitful conclusion, this paper is presented at the risk of many imperfections.

In the drying of relatively thick solids where large moisture concentration gradients are established within the solid, it is usually though incorrectly stated that moisture moves up to the drying surface by diffusion. The term "diffusion" in this connection is unfortunate and misleading. Diffusion refers to the spontaneous changes induced by molecular motion, as in the intermingling of two different gases without the aid of mechanical action or as in the equalization of temperature within a solid. Moisture flow in the solid during drying does not conform to this definition of diffusion. The flow of moisture is induced by gravitational and interfacial forces. Despite its invalidity, it has become common practice to employ the diffusion law in calculating the rate of movement of moisture and its distribution within a solid during drying.

Newman (9, 10) did exceptionally good work in applying the diffusion equations to the drying of solids of various shapes and for the difficult situations where different surface evaporation rates must be considered, as well as fluid flow within the solid. The resultant tables and graphs, prepared after the most tedious computations, have proved of particular utility in problems dealing with heat flow and apply well in the drying of certain solids. For instance, these methods have been used successfully in calculating the drying schedules for timbers and lumber where different sizes and shapes are dried under many different surface drying conditions. K. W. Loughborough, of the United States Forest Products Labora-

for obtaining the suction-water content and was used here.

Methods are described for calculating the moisture distribution and average moisture content of a granular solid for any thickness and for calculating the drying-rate curves during the first and second falling periods, provided the value at the constant-rate period is known.

The present treatment is still in a rough state but indicates the possibility of readily determining such properties as moisture distribution, drying rate, and time of drying in a wide variety of materials. The investigation should be extended to include the effect of position and of vertical and horizontal surfaces, and also substances of high capillarity where equilibrium moisture content is appreciable.

tories, reported that Newman's tables and curves based upon the integrated diffusion equation have so far been the only adequate means of calculating mathematically the drying schedules of lumber. Sherwood (12, 13) also recommended this procedure but stated its limitations—namely, that water movement is produced by capillary and not by diffusional forces, and that the apparent success of the diffusion equations for calculating the drying time of substances such as wood and clay lies in the fact that these calculations are made by integration methods which compensate for the errors due to the assumption of wrong distribution. Even though erroneous concentration gradients are obtained by diffusion equations, the integrated results for the time of drying emerge as a satisfactory approximation for many substances. Serious error is involved in assuming the validity of the diffusion equations, as demonstrated in this paper.

Limitations of Diffusion Equations

The diffusion equations applicable to flow in one direction are as follows:

$$\frac{dW}{Ad\theta} = -\alpha \frac{dc}{dx} \quad (1)$$

$$\frac{\partial c}{\partial \theta} = \alpha \frac{\partial^2 c}{\partial x^2} \quad (2)$$

The advantages of the application of these equations to drying are the convenience in being able to employ the analogy of heat flow and the availability of the mathematical solutions of these equations. The diffusion equations neglect the effect of gravity and of capillary forces and assume that the rate of flow is directly proportional to the concentration gradient. If the analogy to heat flow is applied, it must follow that at equilibrium the moisture concentration is uniform throughout the solid, whereas this is never true when the influence of gravity is appreciable. Furthermore, water may flow from a low-concentration region to one of high concentration when the right differences in pore spaces exist.

¹ Present address, University of Iowa, Iowa City, Iowa.

² Present address, Armour Institute of Technology, Chicago, Ill.

Water will flow to regions of highest capillarity, regardless of concentration. These conditions are all contrary to the situation with heat. The diffusion equations apply only if the capillary tension producing flow varies directly with the unsaturation of the solid, where the body is uniform in composition and where the gravitational effect is negligible. Possibly such a situation is approximated in fine fibrous structures or even in fine clays.

Buckingham (1), Gardner (2-5), and Wilsdon (15) attempted the difficult problem of applying variable diffusivities to the diffusion equation, employing a capillary potential instead of a concentration potential, thus:

$$\frac{dW}{d\theta} = -\alpha \frac{d\psi}{dx}$$

The evaluations of α and ψ in terms of concentration proved extremely difficult, and the application of the resultant equations to decreasing drying rates was not satisfactory. Further, it seems illogical to patch up equations which are based upon false premises, especially when such equations are extremely difficult to solve.

Work of Haines

The flow and distribution of water in a granular solid resulting from absorption, drainage, or evaporation were demonstrated by the extensive work of Haines (6, 7, 8) of the Rothamsted Experiment Station, England. Haines started with the behavior of small spherical particles of uniform diameter and in closest packing. The intricate geometry of this situation was first completely solved by the classical work of Slichter (14) in 1898.

Haines stated that the moisture distribution in an unsaturated granular solid is determined by the suction produced by interfacial tension. Haines presented the situation for both increasing and decreasing water contents and explained why for a given suction the water content is much higher during decreasing than during increasing stages. Since in drying we are interested in starting with a saturated solid and decreasing its water content, discussion will be confined to this case. Under any other condition of drying, the initial water distribution will depend upon the previous history of the solid; that is, for a given average moisture content the moisture distribution will depend upon whether the initial water content had been reached by wetting, by drainage, or by evaporation.

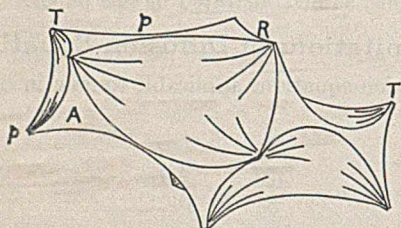


FIGURE 1. SHAPE OF PORE SPACE IN UNIT ELEMENT OF SPHERES IN CLOSEST PACKING (14)

The geometrical configuration of the void space in closest packing of uniform spheres as developed by Slichter is shown in Figure 1. The pore spaces between closely packed spheres are of two types, tetrahedral *T*, and rhomboidal *R*. The *T* spaces correspond to the voids between four spheres in closest packing with one sphere nested in the socket formed by the other three; all four are in mutual contact. In this space there are six points of contact between spheres such as *p* and four branches such as *A* of triangular cross section with curved

lines following the contours of the spheres. These branches connect one cell with another. The radius of the largest sphere which can be inscribed in a branch opening at its narrowest restriction is $0.155r$ where r is the radius of the large sphere.

A rhomboidal cell *R* is confined between six spheres in closest packing, a layer of three superimposed upon a layer of three with three spheres in mutual contact at the point of depression. In this configuration there are twelve points of contact *p* and eight branches *A* of curved triangular cross sections. The largest sphere that can be enclosed within a rhomboidal cell has a radius of $0.288r$. The eight branches of each rhomboidal cell are connected with tetrahedral cells, and the four branches of each tetrahedral cell are connected with rhomboidal cells. Thus there are two tetrahedral cells for each rhomboidal cell. The relative space occupied

by the cells is 25.95 per cent of the total volume.

The capillary forces, also called suction or pressure deficiency, developed by the limiting curvatures in this ideal configuration can be easily calculated. A bubble of air entering a tetrahedral cell has a suction of

$$\frac{T}{r} \left(\frac{1}{0.155} + \frac{1}{0.155} \right) = 12.9 \frac{T}{r}$$

The suction of an air bubble in a rhomboidal pore space is likewise

$$\frac{T}{r} \left(\frac{1}{0.288} + \frac{1}{0.288} \right) = 6.1 \frac{T}{r}$$

When just enough water is held between the points of contact of the spheres to form a continuous film from one particle to the next, the geometry of the situation is shown in Figure 2. A nodoid of revolution is produced at the point of contact with a surface of double curvature, concave with respect to radius *c* and convex with respect to radius *b*. For continuous films, $\theta = 30^\circ$. At this angle $c = 0.155r$ and $b = -0.423r$. Under these conditions the pressure deficiency is

$$\frac{T}{r} \left(\frac{1}{0.155} - \frac{1}{0.423} \right) = 4.1 \frac{T}{r}$$

Haines refers to the state where water is held at points of contact and where the nodoids do not make contact—that is, with θ less than 30° , as the pendular state. As more water is added causing coalescence and a continuous water film, the state is called funicular. When all cells have been completely filled with water, the capillary state is reached.

Drying a Granular Solid

With a granular solid such as sand a more complicated situation exists, since the sand particles are neither spherical nor uniform in size. Very high curvatures exist at sharp corners and edges. Consider the drying of a horizontal layer of sand of uniform thickness supported in a metal pan and exposed to drying in an air stream passing over the top surface only; the sand is originally saturated with water, and no air spaces exist. Assume also that the air passes over at a constant average temperature, humidity, and direction and that the sand and water are originally at the wet-bulb temperature of the air. As evaporation proceeds, the water surface is depressed into the branched openings between sand grains on the surface. The curvatures which develop produce a slight suction. However, the suction produced cannot

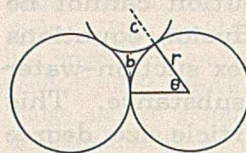


FIGURE 2. WATER RING BETWEEN TWO SPHERES

draw water to the surface without permitting its replacement with air. Any attempt to lift the entire column of water bodily through the sand is resisted by the weight of the water column and by the suction produced at the bottom surface when a curvature is formed there. In order to blow air into the first layer of pore spaces, a suction must be produced, which in the case of uniform spheres in closest packing, is $12.9 T/r$ dynes per sq. cm. This value is called the entry suction. For sand of irregular size and shape the entry suction is much less than $12.9 T/r$, where r is taken as the average particle radius. For the case of spheres the same entry suction will be required to open each pore space, the entry suction remaining constant at $12.9 T/r$. For sand the entry suction, expressed in centimeters of water, will increase as successively smaller pore spaces are opened. With uniform spheres the suction at the surface remains constant until all cells have been opened. With evaporation beyond this point the funicular distribution of water ceases and the pendular state begins with progressively increasing suctions as the curvatures of nodoids become greater and greater. For the ideal packed spheres the funicular state ends in drying when the moisture content is equal to 0.8 per cent by volume or 6 per cent saturation. With sand the entry suction and the percentage saturation at the end of the funicular state will depend upon the size and distribution of particles and cells.

When drying a horizontal layer of granular solid, a higher suction must be established at the top surface when air enters pores below the surface. The suction at the surface must equal the entry suction plus the height of the column of water sustained:

$$P_s = P_e + l$$

where P_s = suction at surface, cm. water
 P_e = entry suction, cm. Hg
 l = distance from top surface to saturated water surface, cm.

When water appears in the pendular state, the suction is uniform since a continuous film producing a column pressure no longer exists.

The purposes of this investigation were to ascertain the actual conditions of moisture concentration gradients in a drying solid, to point out the limitations of the diffusion equation, and to propose a new method of calculating moisture distribution.

Measuring Suctions

Haines (6) describes a simple method of measuring suction in a porous solid. A thin layer of the granular solid is placed on a sealed filter paper in a Büchner funnel 9 cm. in diameter and connected with a buret manometer. The apparatus is filled with water, and, by adjusting the height in the buret in small steps, a given series of suction values is obtained. The corresponding decrement of moisture when equilibrium is reached after each step is given by the buret readings, enabling the moisture content to be followed under changes of suction at will. The reference level for pressure is taken as the surface of the material. The suction can be measured for both rising and falling moisture contents; the latter are of interest in drying.

Water Distribution

The water content in sand corresponding to a given suction was measured experimentally by the method just described. The results are shown graphically in Figure 3 where the suction is expressed in centimeters of water. These values were obtained by using a layer of sand, 0.5 cm. thick but suffi-

ciently thin to neglect the height of water column within the sand itself. Initial values of water content up to the entry suction could not be obtained correctly by using a thin layer. These values were obtained on a layer 2.54 cm. thick. The large thickness of sand introduces no error in measuring entry suction since saturation exists below the surface, and hence practically no suction exists below the surface. Much work still needs to be done in perfecting experimental methods in obtaining these suction-water relations. Results are given here to illustrate the physical basis in establishing water distribution in a granular solid.

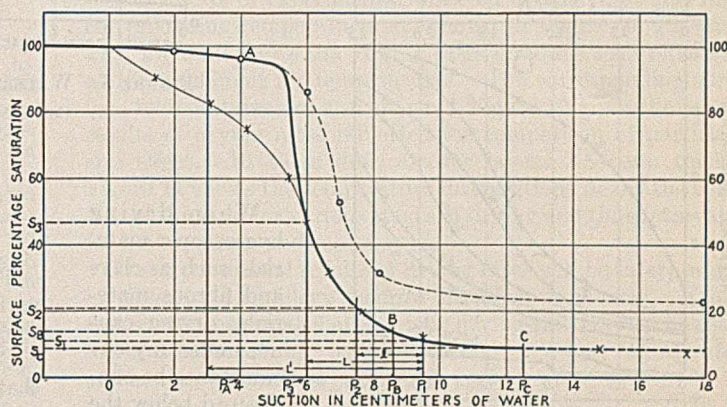


FIGURE 3. SUCTION-WATER CONTENT OF SAND

The sand used for these experiments had an average radius of 0.064 cm.; the screen analysis is given later. For uniform spheres of radius r in closest packing, the entry suction is $12.9 T/r$ or 15 cm. of water. The entry suction P_A , given by point A in Figure 3, is 4 cm. of water. A low value is to be expected because of the nonuniformity of sand and its method of packing.

From Figure 3 the water distribution in the sand can be calculated for any thickness and for any average water content. For positions in the sand below values of the entry suction P_A , saturation should be assumed. For values above 12.5 cm. (point C) increased suction does not withdraw further liquid water. At this stage the pendular state of water distribution exists corresponding to a saturation of 9 per cent.

Suppose it is desired to calculate the moisture distribution in a horizontal layer of sand. For a suction of P_1 cm. at the surface the percentage moisture at the surface is S_1 . For a distance l cm. below the surface the percentage saturation can be obtained by measuring the value S_2 from the graph at $P_1 - l$ cm. For a total thickness of sand of L cm., the percentage saturation at the bottom is S_3 cm. For positions extending below the entry suction A, 100 per cent saturation should be assumed rather than the values on the graph. For example, with a layer L' cm. thick the bottom of the sand is fully saturated. After plotting the moisture distribution over the entire thickness of the sand layer, the average moisture content can be obtained by graphical integration. By this method the moisture distribution for various average water contents was obtained for thicknesses of 2.54, 5.08, and 7.60 cm., respectively, and is shown in Figures 4A, 5A, and 7A.

This scheme cannot be used after the surface reaches the pendular state—that is, beyond point C. In drying beyond this point the water film starts to break at the top surface where the concentration is least. The broken nodoids of water will then dry by evaporation *in situ*, producing a layer of complete dryness at the surface. The thickness of complete dryness increases as drying continues.

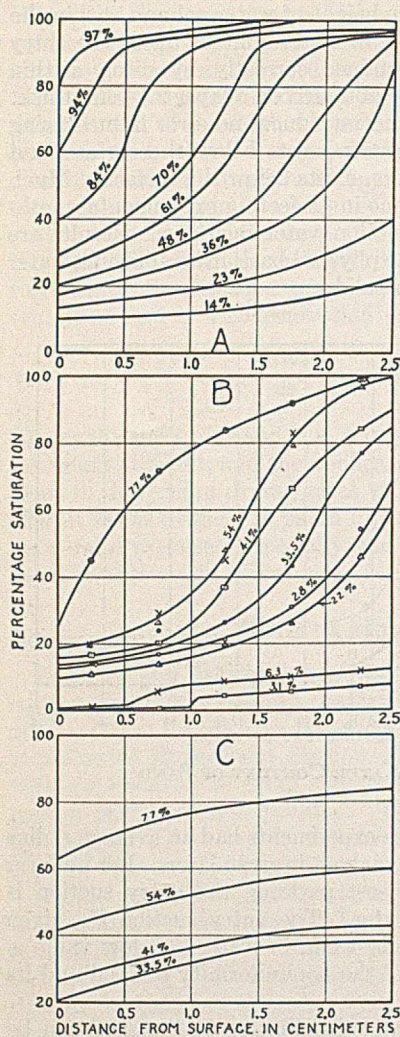


FIGURE 4. WATER DISTRIBUTION IN SAND LAYER 2.54 CM. THICK

A. Calculated B. Experimental
C. Calculated by diffusion equation

removal of free moisture exceeding the pendular state. The sand used in these tests had a negligible equilibrium moisture content. A curvature 1 micron in radius will reduce the vapor pressure of water only 0.11 per cent, whereas at 1 millimicron the reduction is 50 per cent. In relatively coarse sand the amount of water present with these fine curvatures is negligible.

Measurement of Moisture Distribution

Moisture concentration gradients were measured experimentally in sands subjected to various times of drying. The same sand was used as in the suction experiments.

The sand was placed in a container consisting of five superimposed hard rubber rings with the bottom ring closed. Inside dimensions of each ring were 2.8 cm. in diameter and 0.51 cm. in height; the total inside height of all five rings was 2.54 cm. The rubber rings were sanded smooth on the flat surfaces and cemented together with a thin film of petrolatum or paraffin. Several samples of sand were saturated with water and placed in a desiccator at room temperature. After a definite time one sample was removed. The rings were separated by a shearing motion, and the layers were placed in separate weighing bottles and weighed. The samples were then dried at 105° C. and weighed again. The dry sand was removed, and the empty ring and weighing bottle were weighed. The moisture content of each ring was then obtained, and the average moisture content of the entire sample calculated. This procedure worked satisfactorily for the coarse sand.

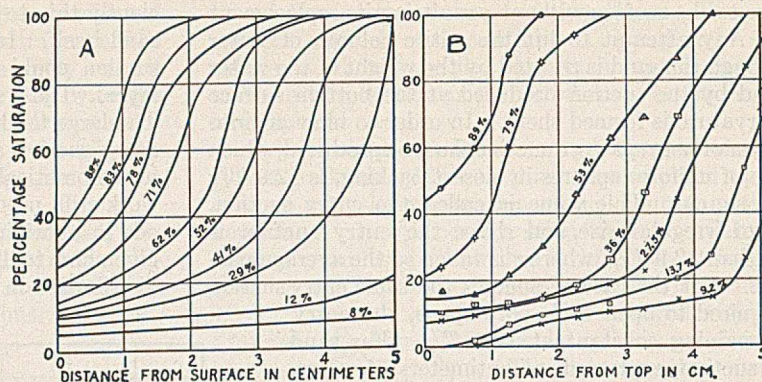


FIGURE 5. WATER DISTRIBUTION IN SAND LAYER 5.08 CM. THICK

A. Calculated

B. Experimental values

When drying hygroscopic materials such as clays and fibrous materials, drying cannot under any circumstance be continued below the moisture content in equilibrium with the air of given temperature and relative humidity. In such materials, because of extreme fineness of capillary openings, the vapor pressure of the retained water is reduced far below normal. The above procedure applies only to the

Results of Moisture Concentration Experiments

The moisture concentration gradients of the sand at various stages of drying are shown in Figures 4B, 5B, 7A for thicknesses of 2.54, 5.08, and 7.6 cm.

Comparison of Figures 4A with 4B, 5A with 5B shows that the experimental values of water distribution correspond with the values calculated from capillary suction. The actual numerical values deviate somewhat because of the present crude method of measuring suction values; but the extremely complex shape of the gradients beginning with convex curves, changing to curves with double inflection, continuing to concave shapes, and ending with straight lines, are reproduced exactly by calculation. The moisture concentration curves correspond to portions of the complex suction-water content curve.

In Figure 4C the moisture distribution was calculated from the diffusion equation for the constant rate period, assuming as boundary conditions that the rate of evaporation is constant. Sherwood (11) calculated the water distribution in clay and wood by this method (Figures 6A and B). It is evident that the water distribution as calculated from the diffusion equation during the constant-rate period gives a parabolic curve (Figures 4C, 6A, and 6B), whereas actually the curves are initially convex, change to curves with double inflection, and then become concave, altering steadily in shape and inflection. This remarkable change is in agreement with the behavior of capillary tension but entirely inconsistent with the behavior of diffusion. Sherwood assumes that the slope of the water concentration gradient at the surface is constant during the constant-rate period of drying whereas with sand it is evident that the gradient changes from an extremely high value to an extremely low value as drying proceeds, even though the rate of drying remains constant. The rate of drying during this period is independent of conditions below the surface, which is contrary to the law of diffusion. During this period the actual fraction of wetted area at the surface remains constant even though the percentage moisture content is decreasing. These facts indicate that there is no physical basis for the use of the diffusion equations. The only excuse for their use is that they permit an analogy with heat flow and the use of all the convenient graphical solutions existing, which fortunately seem to hold well on materials such as wood and clay for obtaining the integrated results of drying rates but not for moisture distribution.

A further refutation of the diffusion equations is that, in drying, the water may actually move in the sand towards a region of higher concentration, provided a difference in pore structure exists. This behavior is entirely inconsistent with

the principle of heat flow but can easily be explained by the behavior of capillary forces. For example, when a layer of fine sand is placed upon a layer of coarse sand and drying takes place from the surface of the fine sand, the coarse sand dries out more rapidly. The water concentration in the fine sand becomes higher than in the coarse sand, and the water actually flows in the direction of higher concentration (Figure 7B). For the same water content the capillary force in the fine sand is much greater than in the coarse sand.

Drying Rates

A Sturtevant compartment dryer was used as shown in Figure 8:

The rack inside which supports the sand was connected by levers to a balance on top of the dryer. This scheme permitted direct weighing of sand while it was in the dryer without interruption of drying. The balance read direct to 5-gram intervals, but a greater sensitivity was obtained when evaporating to a definite loss. The sand was placed in Bakelite pans, 800 sq. cm. in area. Heat flow into the bottom and sides was minimized by 1.3-cm. balsam wool insulation. Temperatures in the sand

were measured at five levels with copper-constantan thermocouples evenly spaced and with leads placed in isothermal planes. The temperature of the air stream entering and leaving the sand surface was similarly measured. The entering air was maintained at constant temperature and humidity. In drying, the time required for a predetermined loss of water was accurately measured. This scheme gave values of the drying rate, $dW/d\theta$, and is more nearly accurate than measuring the slope of the time-concentration diagram. Dry sand of the desired size was weighed and placed in the pan and transferred to the dryer. The sand was initially saturated with distilled water at room temperature. Three sizes of sand of fairly close gradation were tested.

Coarse Sand No. 3.5		Medium Sand No. 2		Fine Sand No. 1/0	
Mesh	%	Mesh	%	Mesh	%
8-12	6	30-40	32	70-100	39
12-14	65	40-50	52	100-140	38
16-20	27	50-70	15	140-200	18
20-30	1	<70	1	<200	5
<30	1		100		100
	100				

Air space, %	41	46.6	42.0
Water satn., wt. %	35	36.1	33.1
Av. radius, cm.	0.064	0.016	0.005
Av. density of dry sand	1.38	1.29	1.27

The results of experimental work on drying rates and the corresponding temperatures are shown in Figures 9, 10, and 11. Figure 9 shows the drying rates for three sizes of sand, at three different air temperatures. The corresponding surface temperatures are also shown. Figure 10 gives the same results of drying rates replotted for comparison of particle-size effect. All these data are for layers 2.54 cm. thick. Figure 11 shows the temperature distributions below the surface of the sand for various stages of drying and time intervals for both medium and coarse sands.

The experimental results of drying rates will be interpreted in view of the capillary theories discussed previously. Each test shows the usual characteristic drying-rate curves consisting of a constant-rate period, followed by a first falling-rate and ending with a final falling-rate curve.

Constant-Rate Period

In the constant-rate period the rate of drying is constant because surface conditions remain unchanged. The sand assumes nearly the wet-bulb temperature of the air, and the temperature, humidity, and velocity of the air remain constant. In order to explain further the constancy of the drying rate, it is assumed that the fraction of wetted surface of the sand remains constant even though the pore spaces are gradually opened and depleted of their water content. The flow of water by capillarity is sufficient to maintain a uniformly wetted surface during this period. The suction required to open the surface cells is much greater than that necessary to maintain them open. For example, with uniform spheres in close packing the entry suction is $12.9 T/r$; the difference between this and the actual suction represents the maximum potential producing flow. With sand the values are much lower; the entry suction for sand of 0.064-cm. radius is actually $4'$ cm. of water (point A, Figure 3). With the surface cells open, water begins to flow towards the surface and the cells below the surface begin to open when their entry suction is attained. The suction at the surface steadily increases by an amount equal to the gravity head from surface to saturation level. A stream of water reaches the sur-

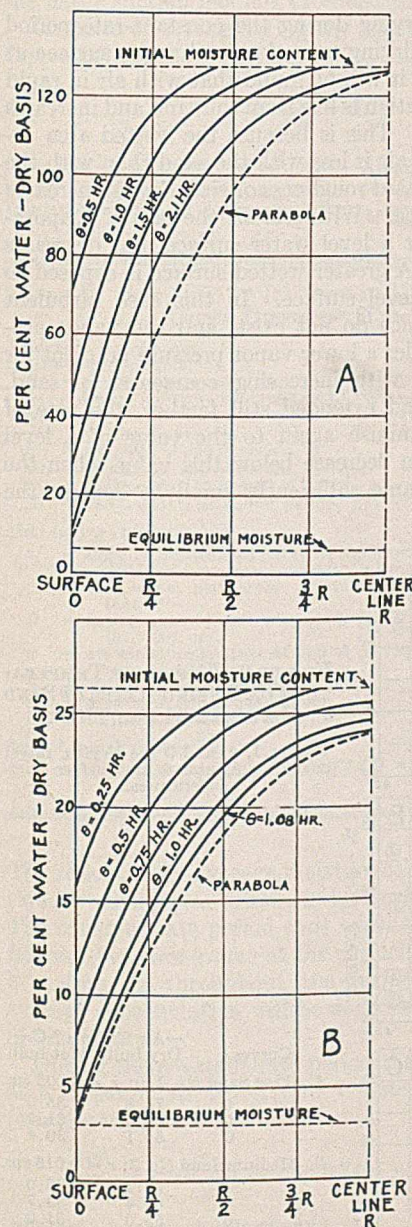
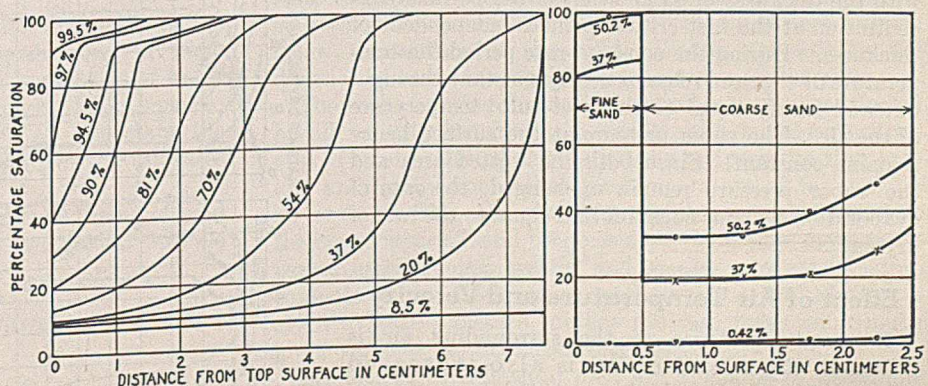


FIGURE 6. WATER DISTRIBUTION IN SAND LAYER CALCULATED BY DIFFUSION EQUATION (13). (A, CLAY; B, WOOD)



A. Calculated (7.6 cm. thick) B. (Experimental) with fine layer on top
FIGURE 7. WATER DISTRIBUTION IN SAND LAYER

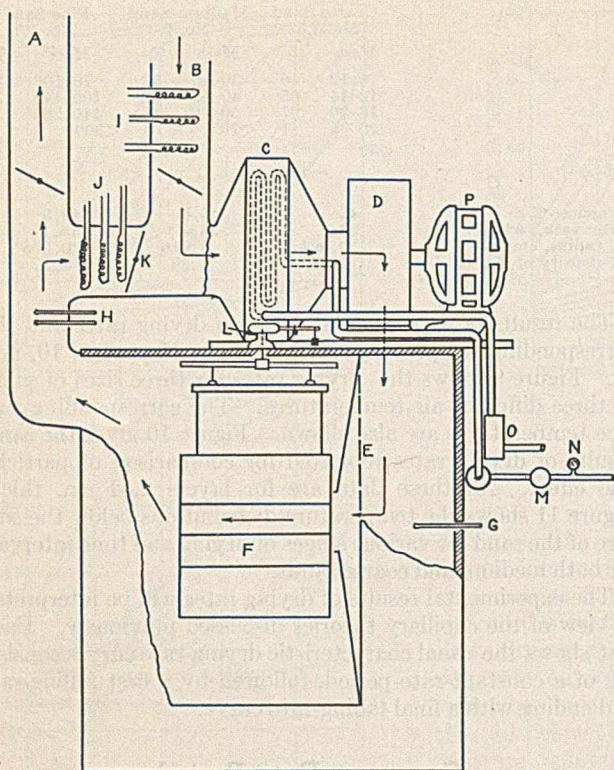


FIGURE 8. EXPERIMENTAL DRYER

- | | |
|---|-------------------------------------|
| A. Air outlet | I, J. Thomas meters |
| B. Air inlet | K. By-pass damper for recirculation |
| C. Heater | L. Scale |
| D. Fan | M. Temperature regulator |
| E. Air regulation shutters | N. Steam gage |
| F. Pan | O. Trap |
| G. Inlet wet- and dry-bulb thermometers | P. Motor |
| H. Outlet thermometers | |

face sufficient to maintain a constant wetted area and a constant evaporation rate. When the curvature of water at the surface reaches a value corresponding to the suction P_B , the end of the constant-rate period is reached. The water at the surface begins to recede to higher and higher curvatures, and the wetted area begins to diminish as the water is pulled in between the grains; the first falling-rate period then begins.

The end of the constant-rate period occurs for this sand when the suction is 8.6 cm. of water at the surface, corresponding to a moisture content at the surface of 14 per cent. This point may be called the first critical point (B, Figure 3). The average concentration at the first critical point as customarily used has no significance, since this value increases with the thickness of sand whereas the surface concentration at the first critical point is independent of thickness. During the constant-rate period the temperature of the sand remains nearly constant throughout and nearly equal to the wet-bulb temperature of the air. The vapor pressure at the surface hence remains constant. Since both the wetted area and the vapor pressure remain unchanged, the rate of evaporation remains constant and equal to the rate of drying.

Effect of Air Temperature and Velocity

If the temperature of the surrounding air is increased, the rate of drying is also increased (Figure 9). This would be expected from the increase in vapor pressure with temperature. When the drying rate is divided by the vapor pressure

difference from surface to air, the quotient is nearly constant, consistent with the theory that the rate of evaporation is proportional to the vapor pressure difference at the surface; that is,

$$\frac{dW}{Ad\theta(p_s - p_a)} = k$$

where k = a drying coefficient dependent upon air velocity

With increased air velocity the drying rate increases during the constant rate period because of greater agitation of the air film at the surface.

Effect of Sand Size

With increasing size of sand, the rate of drying increases because of an increased wetted area at surface, and a less entry suction is required for air to enter the coarse sand than the fine sand.

Comparison with Evaporation from Level Water Surface

When the rate of drying during the constant-rate period is compared with the drying rate of a level water surface at the same temperature, it will be found that with air in rapid flow the rate of evaporation is less from the sand and increases with the size of sand. This is because the wetted area exposed to the turbulent air is less with the sand than with the level surface; an increased roughness or size of sand increases the degree of turbulence. With still air the rate of evaporation is greater than for a level water surface and decreases with increasing size. A greater wetted surface is exposed to the air than with a level surface. In this case turbulent conditions at the surface do not exist, and the vapor produced must diffuse under a lower vapor pressure gradient for increasing thicknesses with increasing coarseness of sand.

With fineness of sand extended still farther, the rate of evaporation would diminish again to the value of a level water surface and then decrease below this value when the surface curvature became sufficiently small to depress the

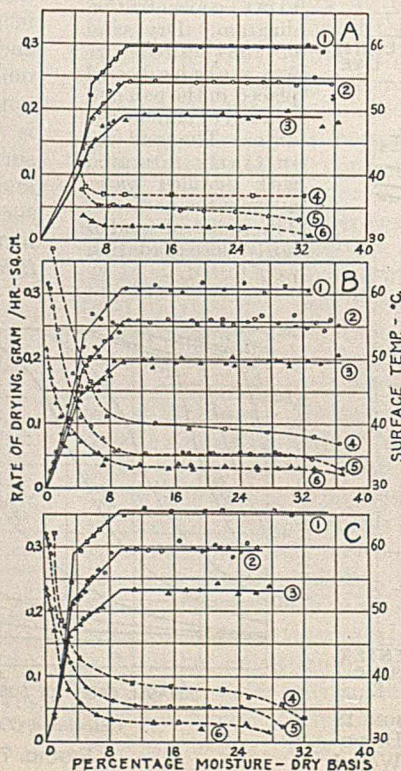


FIGURE 9. EFFECT OF TEMPERATURE ON DRYING RATES OF SAND LAYERS 2.54 CM. THICK

Curves 1, 2, and 3 are drying rates; curves 4, 5, and 6 are surface temperatures.

Curves	—Air Temp., ° C.—	
	Dry bulb	Wet bulb
A. Fine Sand No. 1/0; $r = 0.005$ cm.		
1	4	75.8
2	5	65.4
3	6	55.1
B. Medium Sand No. 2; $r = 0.016$ cm.		
1	4	76.1
2	5	65.4
3	6	55.0
C. Coarse Sand No. 3 1/2; $r = 0.064$ cm.		
1	4	77.8
2	5	64.0
3	6	55.0

normal vapor pressure. These effects are relatively as follows:

Air Condition	Air Temp. ° C.	Water	Coarse Sand	Medium Sand	Fine Sand
Still	22	1.00	1.02	1.08	1.12
Turbulent	55	1.00	0.78	0.68	0.66
Turbulent	65	1.00	0.78	0.70	0.64
Turbulent	75	1.00	0.76	0.66	0.68

Effect of Sand Thickness

The rate of drying in the constant-rate period is not influenced by the thickness of sand (Figure 12) since the wetted area is not influenced by thickness. The fraction of water removed during the constant-rate period decreases more than directly with the thickness. For example, with thin layers (2.54 cm.), 74 per cent of the water has been removed, unsaturation exists throughout the entire layer, and the entry suction has been exceeded throughout the sand. With a thick layer (7.6 cm.), only 23 per cent of the water has been removed, much of the sand still remains fully saturated, and the entry suction has not extended to the bottom.

The rate of drying during the constant rate period can be expressed by the equation,

$$\frac{dW}{A d\theta} = k \Delta p$$

where k = a drying coefficient which increases with air velocity and slightly with increasing particle size when air is in turbulent motion and decreasing with size of sand when air is still.

TABLE I. SUMMARY OF RESULTS IN DRYING SAND LAYERS OF THREE DIFFERENT THICKNESSES

Thickness of sand, cm.	2.54	5.08	7.62
Constant-rate period:			
R_1 = drying rate, grams/(hr.) (sq. cm.)	0.325	0.325	0.325
w_s = initial moisture content (satd.), %	35.0	35.0	35.0
w_B = av. moisture content at end of period (dry basis), %	9.2	20.0	27.0
S_B = av. satn. at end of period, %	26.3	57.0	77.0
ΔS = unsatn. at end of period, %	73.7	43.0	23.0
P_B = surface suction at end of period, cm.	8.6	8.6	8.6
S_s = surface satn. at end of period, %	14	14	14
First falling-rate period:			
a = slope of drying rate curve in equation $dW/A d\theta = aw$ = constant where w = av. percentage moisture content	0.0135	0.0157	0.0210
R = drying rate at end of period, gram/(hr.) (sq. cm.)	0.250	0.090	0.072
w = av. moisture content at end of period (dry basis), %	4.0	5.0	15.0
S = av. satn. at end of period, %	11.5	14.3	43.0
P = suction at end of period, cm.	12.5	12.5	12.5
S = surface satn. at end of period, %	8.1	8.1	8.1
Second falling-rate period:			
b = slope of curve in equation $dW/A d\theta = bw + \text{constant}$	0.062	0.0175	0.0048

The reduction in average moisture content during this period rapidly diminishes with an increasing thickness of sand. The constant-rate period ends when the curvatures of water nodoids between grains at the surface reach a value equal to a suction P_B throughout the surface. At this state the average concentration will be dependent upon the thickness of the layer.

During the constant-rate period the rate of drying of sand at a constant air velocity of 7 meters per second may be formulated thus:

$$\frac{dW}{A d\theta} = cr^{0.11} \Delta p = c \Delta p (0.740) = (0.0207) \Delta p \quad (3)$$

where r = av. radius of sand, cm.
 Δp = $p_s - p_a$, pressure difference, mm. Hg
 c = a coefficient depending primarily upon air velocity = 0.028 when velocity of air is 7 meters/sec.

Others have found that the drying rate varies as the 0.8 power of the air velocity. The equation then becomes:

$$\frac{dW}{A d\theta} = 0.0059 r^{0.11} V^{0.8} \Delta P \quad (4)$$

This equation is applicable until the suction at the surface is equal to 8.6 cm., P_B (Figure 3). The time interval or fraction of water removed during this period will depend upon the thickness of the sand layer and diminishes rapidly with thickness. The average moisture content can be estimated from the unsaturation curve by integrating the average unsaturation over a distance measured from the left of point P_B equal to the thickness of the sand layer and extending to the left of the origin where thickness of sand exceeds the distance P ; thus for a thickness of

$$\begin{aligned} 2.54 \text{ cm., } w_B &= 9.2\% \text{ or } 26.3\% \text{ saturation} \\ 5.08 \text{ cm., } w_B &= 20\% \text{ or } 57\% \text{ saturation} \\ 7.6 \text{ cm., } w_B &= 27\% \text{ or } 77\% \text{ saturation} \end{aligned}$$

First Falling-Rate Period

When the suction at the surface exceeds 8.6 cm. of water, the rate of drying begins to fall off linearly with the moisture content of the sand. When the suction exceeds this value, the water is drawn into nodoids of higher curvature and the actual wetted area at the surface diminishes. The concentration gradient when the surface is at the critical value does not follow a parabolic distribution as assumed by Sherwood for clay but can be obtained from Figure 3 by the method previously described. The slope of the drying-rate curve during this period increases with increasing thickness of sand or may be directly related to the unsaturation of the sand when this period begins. Insufficient data are available to establish an exact relation for this slope, but the following empirical equation satisfies the results:

$$R_2 = \left(\frac{0.25}{\Delta S} + 0.01 \right) (w - w_B) + R_1 \quad (5)$$

where R_1 = constant rate = 0.325
 R_2 = variable rate during first falling-rate period

$$\text{hence } R_C = \left(\frac{0.25}{\Delta S} + 0.01 \right) (w_C - w_B) + R_1 \quad (6)$$

Second Falling-Rate Period

The first falling-rate period ceases when the curvatures at the surface become so great as to break the continuity of the water film, the surface becomes dry, and the dry region extends progressively below the surface of the sand.

The second falling-rate period now begins. The pendular state exists near the surface. Evaporation takes place from isolated nodoids, and hence the evaporating surface retreats below the surface of the solid. Drying proceeds by the diffusion of vapor through the dried portion of the solid.

The rate of drying during this period is no longer affected by air velocity but increases rapidly with increased coarseness of sand. During this period the temperature rises rapidly and finally approaches the temperature of the moving air stream. The rate of drying rapidly approaches zero as the entire layer of sand becomes dry. This slow drying-rate period extends over greater and greater average moisture contents as the thickness of sand increases, and also for a given average moisture content the rate takes on a much lower value as the thickness increases.

Insufficient experimental data are available to determine exactly the variation in drying rate during this period. The slope in each experiment was practically linear. An empiri-

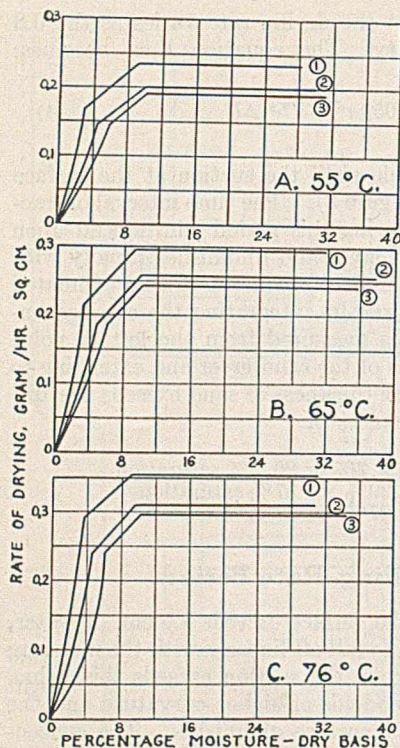


FIGURE 10. EFFECT OF SAND SIZE ON DRYING RATES

Thickness of sand layer, 2.54 cm.; curve 1, coarse sand No. 3 $\frac{1}{2}$; curve 2, medium sand No. 2; curve 3, fine sand No. 1/0

L = thickness of sand layer, cm.

Application of Results to Drying Problems

Upon the basis of the theory given here, the time of drying and the moisture distribution during drying of a granular solid can be readily obtained. First a suction-moisture content relation should be established for the material involved. Then a drying-rate curve should be experimentally established for material of one given thickness under constant drying conditions of air temperature, humidity, and velocity. From this curve the average moisture content can be obtained at the first and second critical point for the given thickness. From the suction-moisture content diagram the moisture distribution for any surface concentration can be constructed as previously described. The corresponding surface concentration corresponding to the experimentally determined average water concentration at the first critical point can then be obtained. From this the corresponding suction is obtained from the suction-concentration curve. Similarly the suction is obtained for the second critical point. Having established the values of the critical suctions, the corresponding average percentage saturations for any given thickness can be obtained. R_1 , w_B , and w_C (Figure 13) are obtained experimentally. The value of R_C can be obtained from either Equation 6 or 7; which is the better cannot be stated at this time.

Problem

Calculate the time required to dry completely a 6-cm. layer of coarse sand such as was used in this investigation. The sand is to be dried from the top surface only and is initially at the wet-bulb temperature. Air is circulated over the surface at 60° C. and 10 per cent humidity at a velocity of 10 meters per second. The sand is initially saturated with water containing 35 per cent by weight of dry sand. The dry sand has a density 1.38 grams per cc.

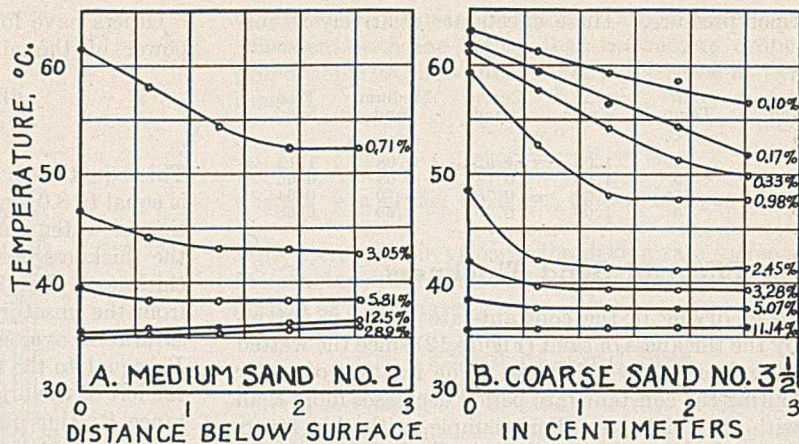


FIGURE 11. TEMPERATURE DISTRIBUTION DURING DRYING

Air temperature constant at 65° C.; sand layer, 2.54 cm. thick; percentages refer to average moisture contents

cal equation satisfying the drying rates during this period is as follows:

$$\frac{dW}{Ad\theta} = aw \quad (7)$$

where $a =$

$$\frac{1}{10^{0.216L + 0.67}}$$

The initial drying rate during the constant-rate period from Equation 4 is:

$$R_1 = 0.00433 V^{0.8} \Delta p \quad (8)$$

At 60° C. and 10 per cent humidity, the wet-bulb temperature of air is 30.6° C. and the dew point is 20.6° C.

Vapor pressure at 30.6° C. = 32.6 mm. Hg

Vapor pressure at 20.6° C. = 18.0 mm. Hg

$\Delta p = 14.6$ mm. Hg

$R_1 = 0.00433 (10)^{0.8} (14.6) = 0.40$ gram/(hr.) (sq. cm.)

The suction at the surface at the end of the constant-rate period for this sand is 8.6 cm. and at the end of the first falling-rate period is 12.5 cm., with corresponding percentage saturation at the surface of 14.0 and 8.1 per cent, respectively. The average percentage saturation of the sand corresponding to these suctions at the surface can be obtained by integrating under the curve (Figure 3) over a distance of 6 cm. measured to the left of the value 8.6 and 12.5 cm., respectively, where the thickness of sand is 6 cm. These values are 61 and 13.6 per cent, respectively. The corresponding values of the average moisture contents, w_B and w_C are:

$$w_B = 0.61 \times 35 = 21.4\%$$

$$w_C = 0.136 \times 35 = 4.75\%$$

where 35% = saturation value

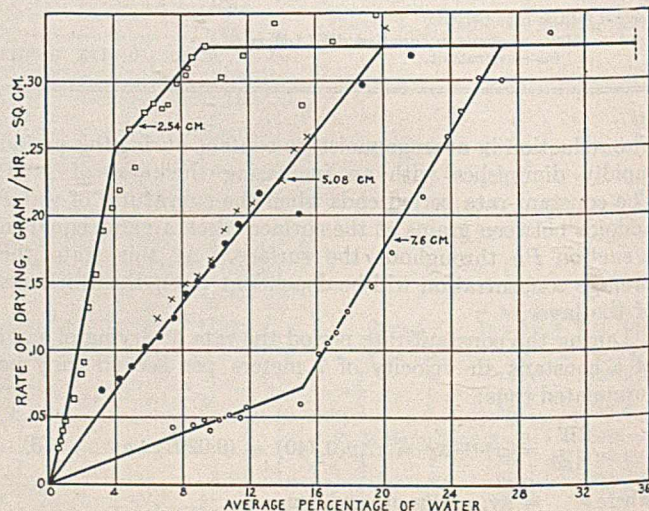


FIGURE 12. DRYING RATES FOR SAND LAYERS OF THREE DIFFERENT THICKNESSES

The unsaturation, Δs , at the end of the constant-rate period is $100 - 61 = 39$ per cent. The value of the drying rate at the end of the first falling-rate period is:

$$R_c = \left(\frac{0.25}{39} + 0.01 \right) (4.75 - 21.4) + 0.40 = -0.274 + 0.40 = 0.126$$

Weight of dry sand/sq. cm. of area = $1.38 \times 6 = 8.28$ grams
 Weight of water initially present = $0.35 \times 8.28 = 2.90$ grams
 Weight of water at end of constant-rate period = $0.214 \times 8.28 = 1.77$ grams
 Weight of water at end of first falling-rate period = $0.0475 \times 8.28 = 0.394$ gram
 Weight of water at end of final period = 0

Weight of water removed during constant-rate period = 1.13 grams
 Weight of water removed during first falling-rate period = 1.38 grams
 Weight of water removed during final falling-rate period = 0.39 gram
 2.90 grams

Av. drying rate during first period = 0.40 gram/(hr.) (sq. cm.)
 Av. drying rate during second period = $\frac{0.40 + 0.126}{2} = 0.263$ gram/(hr.) (sq. cm.)

Av. rate of drying during the final period = $\frac{0.126}{2} = 0.063$ gram/(hr.) (sq. cm.)

Time of first period = $\frac{1.13}{0.40} = 2.82$ hr.

Time of second period = $\frac{1.38}{0.263} = 5.25$ hr.

Time of third period = $\frac{0.39}{0.063} = 6.20$ hr.

Total time = 14.27 hr.

Effect of Arrangement of Sand Layers on Drying

When a layer of coarse sand is placed upon a layer of fine sand, or vice versa, some startling results occur which are consistent with the theories of capillary flow. Experiments were performed with 2.54-cm. layers of sand containing 25, 50, 75, and 100 per cent of coarse sand as a top layer and then reversing with the same percentages of fine sand as the top layer. As expected, the rate of drying was determined by the capillary forces of the top layer only. During the constant-rate period the rate of drying was greater with the coarse sand on top than with the fine sand on top. In either situation the rate of drying was independent of the sand below the top layer. With the coarse sand on top the constant-rate period was extended over a period proportional to the thickness of the top layer. The water in this top coarse layer was nearly all removed before drying began on the bottom layer. The suction produced in the coarse layer necessary to remove nearly all the moisture was always less than the entry suction required to blow air into the fine layer. When the bottom layer began drying at its constant-rate period, the value was greatly reduced because of the great distance through which its vapor had to travel by diffusion. The time of the constant-rate period was proportional to the thickness of the fine layer (Figure 14).

With fine sand on top, the constant rate of drying was again independent of the coarse sand below, but the time over which the constant-rate period extended increased as the thickness of the fine sand layer decreased. The drying curves followed the three characteristic stages

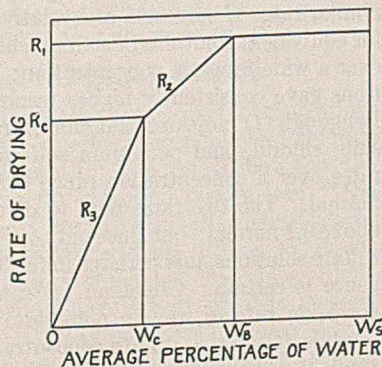
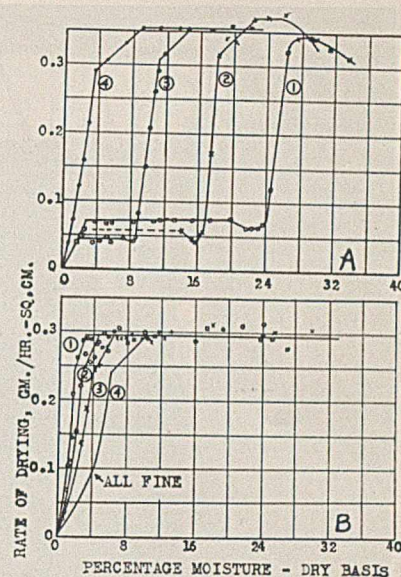


FIGURE 13. DIAGRAM FOR CALCULATING TIME OF DRYING

FIGURE 14. EFFECT OF ARRANGEMENT OF LAYERS OF FINE AND COARSE SAND UPON DRYING RATES

A. Coarse Sand on Top	
Curve	% coarse
1	25
2	50
3	75
4	100

B. Fine Sand on Top	
Curve	% fine
1	25
2	50
3	75
4	100



whereas with the coarse sand on top six stages of drying took place. The suction in the fine sand was always sufficient to pull the water out of the coarse sand. As soon as air penetrated through the layer of fine sand, it passed with trigger action into the layer of coarse sand. The significance of this is great. To retard rate of drying, sprinkle coarse sand on top; to hasten drying, sprinkle a layer of fine wet sand on top.

Nomenclature

- c = concentration, grams/cc.
 - d = differential operator
 - k = drying coefficient, grams/(hr.) (sq. cm.)/mm. of Hg difference in vapor pressure
 - l = distance from top of drying surface, cm.
 - p = vapor pressure, mm. Hg
 - r = radius of sphere or particle, cm.
 - w = moisture concentration, grams/gram dry sand
 - x = distance, cm.
 - A = area, sq. cm.
 - P = suction, cm. of water
 - R = drying rate, grams/(hr.) (sq. cm.)
 - ΔS = unsaturation, %
 - S = saturation, %
 - T = surface tension, dynes/cm.
 - W = weight of water, grams
 - V = velocity of air, meters/sec.
 - α = diffusivity, sq. cm./hr.
 - θ = time, hr.
 - ψ = capillary potential
- Subscript s = sand surface
 Subscript a = air stream
 Subscripts A, B, C = conditions at entry suction, and first and second critical points, respectively

Literature Cited

- (1) Buckingham, E., U. S. Dept. Agr., Bur. Soils, *Bull.* 38 (1907).
- (2) Gardner, W., *Phys. Rev.*, [21] 18, 206-9 (1921).
- (3) Gardner, W., *Soil Sci.*, 7, 313-17 (1919).
- (4) *Ibid.*, 10, 103-26 (1920).
- (5) Gardner, W., and Widstoe, J. A., *Ibid.*, 11, 215-32 (1921).
- (6) Haines, W. B., *J. Agr. Sci.*, 17, 264-90 (1927).
- (7) *Ibid.*, 20, 97-116 (1930).
- (8) Keen, B. A., "Physical Properties of the Soil," Chap. III, London and New York, Longmans, Green and Co., 1931.
- (9) Newman, A. B., *Trans. Am. Inst. Chem. Engrs.*, 27, 203 (1931).
- (10) *Ibid.*, 27, 310 (1931).
- (11) Sherwood, T. K., *IND. ENG. CHEM.*, 25, 1134 (1933).
- (12) *Ibid.*, 26, 1096 (1934).
- (13) Sherwood, T. K., *Trans. Am. Inst. Chem. Engrs.*, 32, 150-68 (1936).
- (14) Slichter, C. S., U. S. Geol. Survey, 19th Ann. Rept., Part 2, pp. 301-84 (1898).
- (15) Wildon, B. H., *Mem. Dept. Agr. India, Chem. Series*, 6, 154-86 (1921).

RECEIVED April 29, 1937. Presented before the meeting of the American Institute of Chemical Engineers, Toronto, Canada, May 26 to 28, 1937.



SEVEN-INCH O. D. SEAMLESS PIERCER OUTLET

Initial Corrosion Rate of Mild Steel

INFLUENCE OF THE CATION

C. W. BORGMANN

National Tube Company (Subsidiary of U. S.
Steel Corporation), Pittsburgh, Pa.

THE electrochemical nature of the corrosion of iron in solutions of sodium and potassium chlorides has been thoroughly confirmed by Evans and Hoar (5) and others (3). Evans and Hoar were able to calculate the corrosion rate from strictly electrochemical measurements, and the results thus calculated agreed closely with direct determinations. Further, a study of the initial corrosion rates of iron in potassium chloride solutions (between 0.001 and 3.0 *N*) indicated that the variation in rate with concentration was due chiefly to changes in the properties of the solutions. In dilute solutions the conductivity largely determines the rate of attack, whereas in more concentrated solutions the solubility of oxygen limits the corrosion rate. It was shown experimentally that the cathode of the differential aeration cell (under the half-immersed conditions employed) was markedly polarized, whereas the anode potential was little influenced by the corrosion current. Resistance measurements indicated that the active cathodic area is confined to the neighborhood of the water line on the specimen. Also the variations in corrosion rate, often noted between seemingly identical specimens, have been explained by Borgmann and Evans (2) on the basis of the existence of discrete "active" cathode areas which vary from specimen to specimen.

The importance of the cathodic reaction (depolarization by oxygen) is apparent, and further studies of factors influencing this reaction are desirable. The influence of the cation on the corrosion rate appeared to be one of the first points requiring a thorough investigation.

Heyn and Bauer (11), in one of the earliest studies relevant

to the question, determined the corrosion rate of a high-carbon steel under totally immersed conditions in a variety of salt solutions. These results indicate that the cation is not nearly as effective in determining the rate of corrosion as is the anion. Friend and Brown (10) and Friend (9) determined the corrosion of iron (Kahlbaum's pure iron foil) in a large number of solutions and qualitatively checked the results of Heyn and Bauer. However, these tests were conducted at room temperature, and evaporation losses were made up with distilled water from time to time, thus throwing some doubt on the validity of the results and their quantitative interpretation. The more carefully controlled work of Evans and Hoar (7), on the other hand, indicated that the cation may be quite influential, at least during the initial period of attack. Similar rates of corrosion of a relatively pure iron were found for equivalent solutions of sodium chloride and sodium sulfate over a wide range of concentration; potassium chloride solutions gave consistently higher results. The precise work of Bengough (1) indicates that zinc corrodes in equivalent potassium chloride and potassium sulfate solutions at equivalent rates over a concentration range from 0.0002 to at least 0.1 normal. The two rates tend to diverge with concentrations above 0.1 normal; but since only one point is reported for the sulfate solutions, it is perhaps unfair to assume that the divergence is certain. Chapman (4) made a comparison of the corrosion rate of iron in potassium chloride and potassium fluoride, found that up to a concentration of 0.8 *N* the rate was similar. Above this concentration a fluoride film partially inhibited further attack. In view of the conflicting results,

it seemed profitable to study, under closely controlled experimental conditions, the initial corrosion rates of a mild steel in solutions of a large number of salts having a common anion.

Experimental Procedure

The material used in the test was cold-rolled strip steel (carbon 0.06 per cent, manganese 0.32, sulfur 0.030, and phosphorus 0.016). A few experiments were made on zinc sheet of the following approximate analysis: lead 0.08 per cent, cadmium 0.003, and iron 0.006.

Specimens (2.5 × 6.5 cm.) were cut from the sheet. The surface was emiered with No. 1 (Behr-Manning) paper followed by No. 0 and finally by No. 00 paper. The direction of abrasion was always at right angles to that of the previous size emery, and the final direction was parallel to the rolling direction (lengthwise of the specimen). The steel was carefully degreased with carbon tetrachloride on absorbent cotton. The specimens were weighed to the nearest 0.1 mg. and placed in a vertical position in 100-ml. Berzelius (Pyrex glass) beakers. The "loaded" beakers were then placed in desiccators over anhydrous calcium chloride located in a large, constant-temperature air bath maintained at 35° C. ± 0.1° and allowed to remain for 24 hours. The test solution was prepared in advance (from Merck's c. p. chemicals and distilled water of low conductivity) and thoroughly aerated with carbon-dioxide-free air at room temperature. The solution was then placed in the air bath for 24 hours. At this time the solution was added to the beakers containing the specimen until 3.5 cm. of the specimen were immersed (approximately 80 ml.). The beakers were then placed in a second desiccator (over 3 N sodium hydroxide) for the duration of the test (48 hours unless otherwise stated). The chloride content, oxygen content, and hydrogen-ion concentration of the solutions were then measured. At the end of the test period, the specimens were removed from the beakers and washed under running water, and the loosely adherent corrosion products were rubbed off with the fingers. The last traces of corrosion products were removed by a cathodic treatment in citric acid. All results given in the tables are the average of four determinations. The procedure was essentially that employed by Evans and his co-workers, modified slightly to assure accurate work at the somewhat higher temperature necessarily employed during a North Carolina summer.

Chlorides of the Alkali Metals

The results of the tests in solutions of various concentrations of lithium chloride, sodium chloride, and potassium chloride are given in Table I and Figure 1. The results show that the cation markedly influences the corrosion rate of iron. The potassium salt is the most corrosive in all concentrations tested, with the sodium salt next and the lithium salt least. The rate of corrosion of iron in potassium chloride solutions was measured by Evans and Hoar (6) and found to be constant up to at least 96 hours. The same was found to be true with 0.306 and 2.42 N solutions of lithium chloride as shown in Figure 2. It seemed reasonable to assume that the rate of corrosion of iron in sodium chloride solutions is likewise con-

A study has been made of the specific influence of the cation on the initial corrosion of mild steel in aqueous solutions. In many solutions the corrosion rate is controlled by the cathodic reaction. It has been shown experimentally that in such solutions the cation markedly influences the corrosion process. If the anion in neutral solutions is nonoxidizing and nonreducing and forms soluble primary products with the metal, the corrosion rate depends on the nature of the cation. The cation was also found to exert considerable influence on the rate of corrosion in salts which hydrolyze to give acidic reactions. The influence of additions of one salt to another, maintaining the anion concentration constant, was studied for solutions of potassium chloride, calcium chloride, and ammonium chloride. A few tests indicated that the initial corrosion of zinc is also influenced by the nature of the cation present.

stant, and hence no tests were made.

The "ideal" distribution of attack, as found in potassium chloride solutions, was described by Evans. This distribution (Figure 3A) was found in the present test with all concentrations of potassium and sodium chlorides. The only influence of concentration was to decrease the height of the attack along the edges and to increase the width of the attacked band at the bottom of the specimen. For example, in 2 N sodium chloride the attacked area was a 1.5-cm. band at the bottom with little or no tendency for attack along the edges above this area. Dilute (up to 0.36 N) lithium chloride solutions give essentially this same distribution. There was, however, a band of adherent oxide (the interference colors were often brilliant) between the attacked and protected areas. This band was narrowest in the most dilute solution and increased in width with concentration. With 0.72 N lithium chloride and more concentrated solutions the attacked area had spread over nearly the entire submerged surface; a strip of only 2 to 3 mm. near the surface of the solution remained bright. With the two higher concentrations a noticeable etching had taken place just above the apparent water line.

The layer of corrosion products clinging next to the metal in sodium and potassium chloride solutions was in every case

a black granular compound (undoubtedly ferrosferric oxide, Fe₃O₄) which was easily removed by gentle rubbing with the fingers. This layer in turn was covered with an orange-brown layer of Fe₂O₃·xH₂O in the more dilute solutions and a dark green layer of a partly oxidized hydrated ferrous hydroxide in the concentrated solutions. The low solubility of oxygen in the more concentrated solutions is ample cause for the difference. There was always present a certain amount of orange-brown ferric hydroxide in the lithium chloride solutions. The layer of ferrosferric oxide on the surface, noted in sodium and potassium chlorides, was not present in the higher concentrations, the attacked area being covered with a dark-green slime which was removed only in the citric acid treatment. In the intermediate concentrations there was a tendency for the attack to be more pronounced in small isolated areas. In general, there is a definite difference in the character of the attack by the lithium salt, a fact that agrees well with the usual differences in properties found between the first and the other members of a periodic group.

Chlorides of Alkaline Earth Metals and Magnesium

The results of the tests on calcium, barium, strontium, and magnesium chloride solutions are given in Table II and Figure 4. The amount of corrosion is less in every case than that

TABLE I. INITIAL CORROSION OF IRON IN SOLUTIONS OF ALKALI CHLORIDES

Salt	Normality of Soln.	Av. Weight Loss in 48 Hr.,	Standard Deviation,
		\bar{X} Mg.	σ^a Mg.
LiCl	0.0035	7.9	0.09
	0.035	9.9	0.55
	0.360	9.8	1.33
	0.721	7.3	0.42
	1.439	6.6	0.31
NaCl	1.869	5.8	0.17
	0.005	9.7	1.00
	0.049	11.9	1.00
	0.250	12.9	0.90
	0.497	14.2	0.54
KCl	1.248	9.7	0.24
	1.964	8.1	0.83
	0.005	9.8	0.33
	0.049	12.7	0.59
	0.252	14.5	0.50
	0.492	16.1	0.57
	1.239	12.7	0.33
	2.019	10.0	1.00

$$a \sigma = \sqrt{\frac{\sum(X - \bar{X})^2}{n - 1}}$$

TABLE II. INITIAL CORROSION OF IRON IN SOLUTIONS OF ALKALINE EARTH AND MAGNESIUM CHLORIDES

Salt	Normality of Soln.	\bar{X}	σ
		Mg.	Mg.
CaCl ₂	0.0054	8.1	0.62
	0.050	8.3	0.68
	0.250	6.6	0.19
	0.490	6.9	0.43
	1.202	5.1	0.23
SrCl ₂	1.883	4.6	0.29
	0.0054	7.6	0.31
	0.051	7.5	0.26
	0.257	8.0	0.69
	0.503	8.2	0.29
BaCl ₂	1.255	5.0	0.12
	1.978	4.5	0.19
	0.0052	8.0	0.50
	0.0495	9.2	0.29
	0.254	8.5	0.75
MgCl ₂	0.506	8.1	0.43
	1.980	3.6	0.14
	0.005	3.7	0.12
	0.050	3.7	0.23
	0.270	4.7	0.29
	0.493	5.4	0.23
	1.420	3.1	0.16
	1.986	3.1	0.21

for equivalent solutions of the alkali chlorides. There is but little difference in the corrosion rate in the alkaline earth salts. The tendency is, however, for the metal of greatest atomic weight to be the most corrosive, which is also true of the alkali chlorides. Magnesium chloride is the least corrosive of any at the temperature of the test. At higher temperatures such solutions may, however, be very corrosive (as often reported in the literature of boiler water practice).

The variation of corrosion rate with time was measured for two typical salts, calcium and magnesium chlorides, up to 96 hours and no change was found (Figure 5).

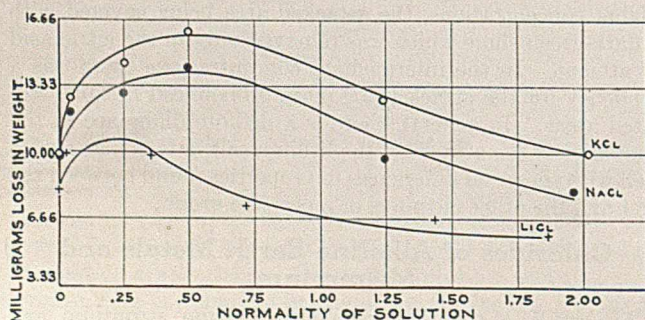


FIGURE 1. CORROSION-CONCENTRATION CURVES FOR ALKALI CHLORIDES

The distribution of attack in the alkaline earth chloride solutions was similar to that noted for the alkali chlorides. However, the attacked area was always larger (Figure 3B) than for equivalent concentrations of the alkali chlorides. The size of the attacked area (particularly the width of the horizontal band at the bottom) may be taken as an indication of the "probability of breakdown" (15). The hydroxide formed at the cathode in alkaline earth electrolytes is not strong enough to give protection to as large an area of the iron as it is, for example, in potassium chloride solutions. The higher the concentration, the larger was the attacked area, covering 80 to 90 per cent of the surface in the 2N solutions. An etching of the surface above the apparent water line was also noted at the higher concentrations. This attack was similar to that already mentioned with lithium chloride. The magnesium chloride solutions gave a somewhat different distribution of attack. The attacked area was always a horizontal band across the lower portion of the specimen, with little or no tendency to edge attack. The width of the band in 0.005N solution was 1.0 to 1.5 cm. and increased with con-

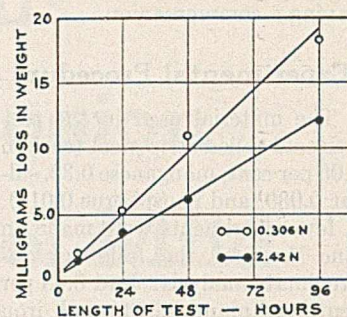


FIGURE 2. INITIAL CORROSION OF IRON IN LITHIUM CHLORIDE

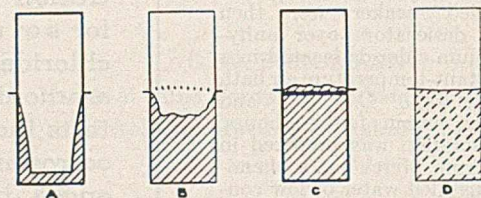


FIGURE 3. TYPICAL DISTRIBUTIONS OF ATTACK

- Usual U-type attack found in dilute solutions of alkali and alkaline earth chlorides.
- Distribution of attack in concentrated solutions of alkaline earth chlorides; note etching above water line.
- Distribution of attack in ammonium chloride solutions; the heavy band near the water line is area of intense attack.
- Typical attack in manganese or cadmium chloride; light etching over entire surface.

centration until at 2.0N there were only 2 to 3 mm. of unattacked metal. The interference colors of a thin film were visible over nearly all of the protected area.

In general, the corrosion products in the alkaline earth chlorides were similar to those already reported for sodium and potassium chloride. There was a tendency, however, toward the formation of more ferric hydroxide than with the alkali salts. With dilute magnesium chloride solutions there were both green and orange hydroxides on the surface, but at higher concentrations the products range from bright yellow to orange, in distinction to the very dark green in 2N potassium chloride, for example.

Ammonium Chloride

The results of tests in ammonium chloride solutions are given in Table III and Figure 6. In these solutions the attack increased with concentration to at least 2 normal. The amount of attack was similar to the other chlorides at low concentration but became markedly greater above 0.05 nor-

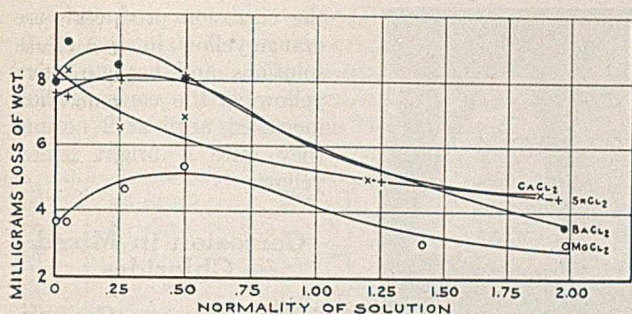


FIGURE 4. CORROSION-CONCENTRATION CURVES FOR ALKALINE EARTH AND MAGNESIUM CHLORIDES

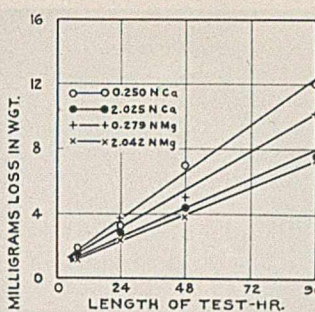


FIGURE 5. INITIAL CORROSION OF IRON IN SOLUTIONS OF CALCIUM AND MAGNESIUM CHLORIDES

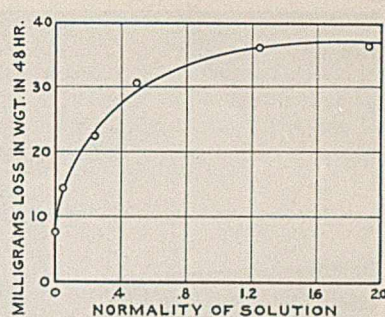


FIGURE 6. CORROSION-CONCENTRATION CURVES FOR AMMONIUM CHLORIDE

mal. The variation of rate with time was investigated for two concentrations. The corrosion rate was constant for the 0.258 *N* solution up to 96 hours, but there was a slight decrease of rate with time in the 2.09 *N* solution. The results of the time tests are shown in Figure 7.

The nature of the attack by ammonium chloride solutions was markedly different from that by the chloride solutions previously described. The entire submerged area was etched, but the major portion of the attack was just below the water line (Figure 3C). In the higher concentrations there was a heavy attack on the metal above the solution level. Gas bubbles, probably hydrogen, were seen clinging to the metal surface in all solutions. Undoubtedly the major portion of the attack was of the hydrogen evolution type.

The corrosion product next to the metal surface was ferrous-ferric oxide but this was covered in every case with a bright yellow-orange ferric hydroxide.

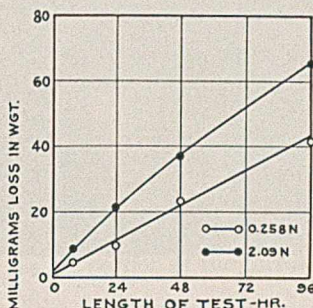


FIGURE 7. INITIAL CORROSION OF IRON IN AMMONIUM CHLORIDE SOLUTIONS

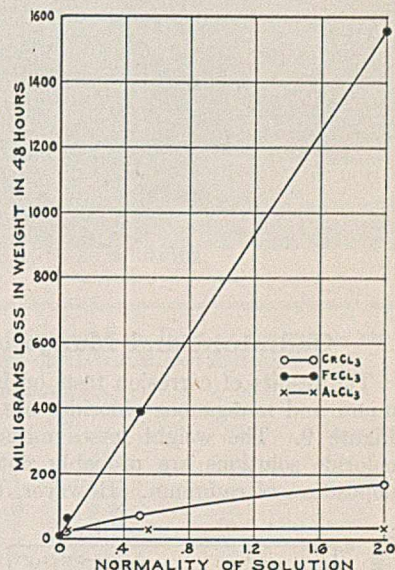


FIGURE 8. CORROSION-CONCENTRATION CURVES FOR FERRIC, CHROMIC, AND ALUMINUM CHLORIDES

TABLE III. INITIAL CORROSION OF IRON IN AMMONIUM CHLORIDE SOLUTIONS

Normality of Soln.	\bar{X} Mg.	σ Mg.
0.005	7.7	0.29
0.050	14.4	0.43
0.257	22.5	1.14
0.499	30.7	1.35
1.250	36.2	2.89
1.920	36.4	1.49

Chlorides of Trivalent Iron, Chromium, and Aluminum

The results of the tests in solutions of ferric chloride, chromic chloride (green), and aluminum chloride are given in Table IV and Figure 8. These salts of trivalent cations hydrolyze to give acidic reactions in solution. Two of the salts are capable of acting as oxidizing agents but the third is not. The results were interesting in that in every case the corrosion rate increased with concentration (up to 2 normal), and the oxidizing salts corroded iron more rapidly than the nonoxidizing one. The most outstanding result was the extremely rapid (linear with concentration) attack of iron by ferric chloride. It is well known that ferric salts are very corrosive to iron, but we would hardly expect the great difference between the ferric and chromic salts. It appears that the ferric salt can act far more readily as a depolarizer than the chromic. That these salts did serve as depolarizers was apparent from the change of color of the solutions during test.

The distribution of attack was very similar to that described for ammonium chloride solutions. The etching was more generally spread over the immersed surface, but the tendency was for the heaviest attack to be near the water line. Again

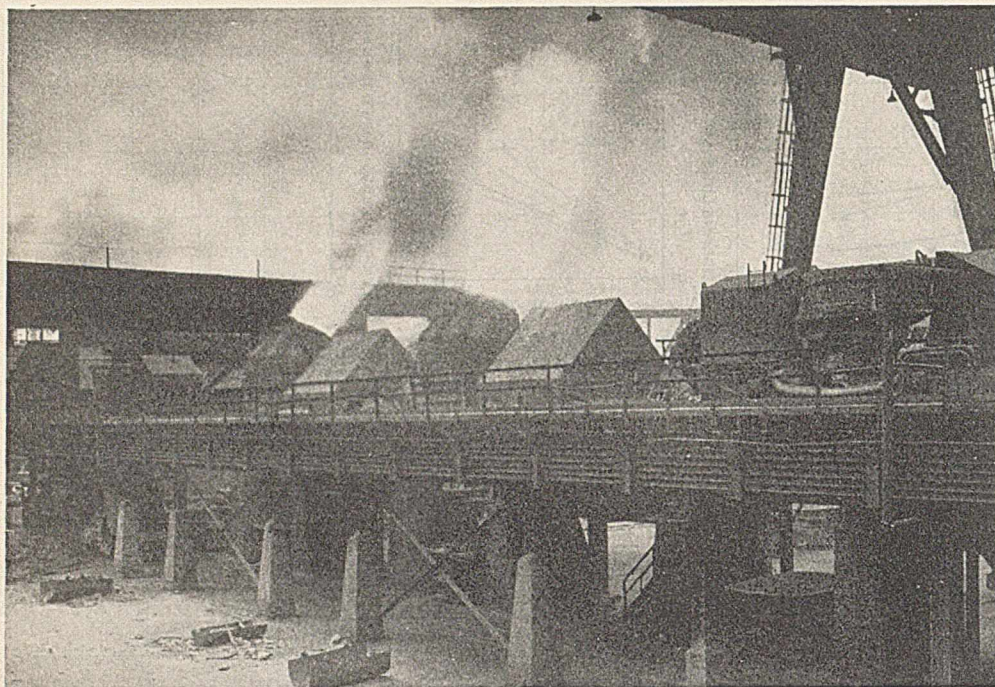
at high concentrations there was a heavy attack above the water level. The attack at the water line was so severe in 2 *N* ferric chloride that the specimen was corroded through in the 48 hours of test.

No corrosion products formed in the aluminum chloride solutions, except in the most dilute solution where a small amount of ferric hydroxide appeared. Gas, probably hydrogen, bubbles were clinging to the metal surface in every case. In chromic chloride solutions no corrosion products were formed at any concentration. The solution lost some of its color during the test, indicating that part of the salt had been reduced. No gas bubbles were noted with this salt. There was a heavy formation of ferric hydroxide in the ferric salt solutions.

TABLE IV. INITIAL CORROSION OF IRON IN SOLUTIONS OF FERRIC, CHROMIC, AND ALUMINUM CHLORIDES

Salt	Normality of Soln.	\bar{X} Mg.	σ Mg.
AlCl ₃	0.0035	12.1	0.33
	0.0524	31.8	4.60
	0.556	31.4	2.32
	2.010	33.3	5.93
CrCl ₃	0.005 ^a	11.5	0.54
	0.05	21.6	0.38
	0.5	72.3	3.79
	2	167.7	6.25
FeCl ₃	0.005 ^a	17.6	0.66
	0.05	63.6	2.27
	0.5	390.0	39.2
	2	1558.5	46.9

^a Approximate.



CONVERTERS

Cadmium and Manganous Chlorides

The results of corrosion tests on iron in solutions of cadmium and manganous chlorides are given in Table V and Figure 9. The weight losses measured for the cadmium chloride solutions are probably not exact because of the deposition of cadmium. However, the discrepancy is small

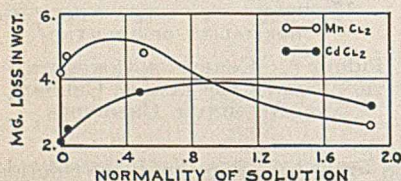


FIGURE 9. CORROSION-CONCENTRATION CURVES FOR MANGANOUS AND CADMIUM CHLORIDES

since the deposits were usually removed readily by light rubbing. The amount of corrosion by chlorides of these weak bases was slight and was of the order of the results in the alkali earth chlorides. The attack, however (Figure 3D), was somewhat different in nature as the entire immersed surface was etched. No evolution of hydrogen was noted in these solutions. A considerable portion of the attack was concentrated above the solution level where a thin film of the liquid had crept up the specimen.

The corrosion products on the specimens in manganous chloride were always dirty reddish brown with little or no black iron oxide present. In the cadmium chloride solutions

TABLE V. INITIAL CORROSION OF IRON IN SOLUTIONS OF CADMIUM AND MANGANOUS CHLORIDES

Normality of soln.	CdCl ₂	
	\bar{X} Mg.	σ Mg.
0.0051	4.1	0.19
0.048	4.5	0.29
0.485	5.6	0.21
1.922	5.2	0.85
MnCl ₂		
0.005	6.2	0.38
0.051	6.7	0.47
0.511	6.8	0.26
1.880	4.6	0.19

the corrosion products were orange-yellow in the dilute solutions and became more yellow as the concentration increased, until at 2 normal they were a bright lemon yellow.

Corrosion in Mixed Chlorides

POTASSIUM AND CALCIUM. The initial corrosion rates of iron were determined in mixtures of calcium and potassium chlorides; the chloride concentration was held constant at 0.25 and 2.0 normal. The results of these tests are given in Table VI and in Figure 10. The addition of small amounts of one salt to the other tends to lower the rate of corrosion. Particularly is this true for small additions of calcium chloride to potassium chloride solutions.

In the 2 N solutions a large portion of the immersed area was etched in calcium chloride solutions (as previously noted) whereas the normal U-shaped attack was formed in potassium chloride solutions. The attacked area in all mixtures was similar to that in calcium chloride; i. e., approximately 80 per cent of the immersed surface was etched. The only exception was the solution of 0.05 N calcium chloride and 1.95 N potassium chloride where the etched area was somewhat less—about 75 per cent. However, even in this solution the attacked area was much larger than in the potassium chloride solution. The rate of penetration was thus decreased much more rapidly than the loss-of-weight figures indicate. Another interesting difference was found in the effect of creepage above the water line. In the high-calcium solutions there was a marked etching of this area. In the range between equal portions of the two salts and 0.05 N calcium chloride-1.95 N potassium chloride, a white deposit (probably calcium carbonate) was formed in this area, and no attack was apparent. The potassium chloride solution neither attacked nor formed a deposit in this area, but rather the iron was left bright and apparently unchanged.

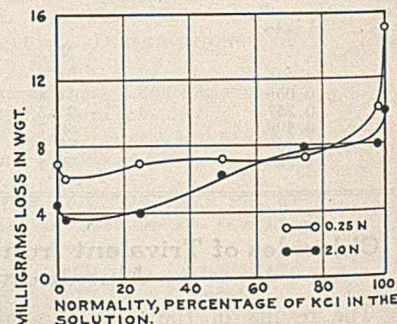


FIGURE 10. INITIAL CORROSION OF MILD STEEL IN SOLUTIONS OF MIXED CHLORIDES OF POTASSIUM AND CALCIUM

There was little or no difference in distribution in the 0.25 N solutions, since all were of the "ideal" U-type. There was, however, a definite though small increase of attacked area as the amount of calcium in the solution was increased. The nature and color of the corrosion products went through a gradual transition from those characteristics of the calcium salts (with a preponderance of yellowish hydroxide) to those of the potassium salt (black and dark green).

POTASSIUM AND AMMONIUM CHLORIDES. Tests similar to those in potassium chloride-calcium chloride solutions were made on potassium chloride-ammonium chloride solutions with constant chloride-ion concentrations of 0.25 and 2.0 normal. The results are given in Table VII and Figure 11. In

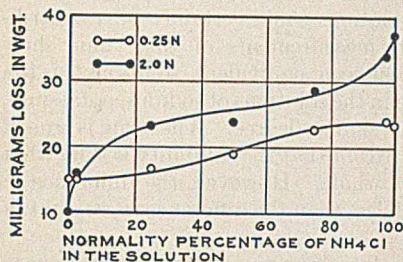


FIGURE 11. INITIAL CORROSION OF MILD STEEL IN SOLUTIONS OF MIXED CHLORIDES OF POTASSIUM AND AMMONIUM

the 0.25 N solutions the rate of corrosion changed gradually from that in potassium chloride to that in ammonium chloride. In the 2.0 N solutions the change of corrosion rate was most rapid with the first small additions of the second salt. The distribution of attack was markedly affected by the mixture of the two salts, one of which corroded iron mainly by hydrogen evolution and the other chiefly by oxygen absorption. The U-type attack was changed to the ammonium chloride type in the 2 N solution with the first addition of ammonium chloride. The major difference between the mixed solutions and pure ammonium chloride was that the area of chief attack, just below the water line, became more and more deeply etched as the concentration of ammonium chloride increased. The lowest concentration of ammonium salt in the 0.25 normal series did not completely alter the U-type of attack. In this solution the major portion of the surface was attacked, but there was a small protected area near the water line. That this particular solution was near the transition point was clearly indicated by the fact that the protected area was not perfectly bright but was covered with interference colors of an advanced order. The presence of such colors would indicate that the margin between protection and attack was very small.

The corrosion products in the mixed solutions resembled those found in pure ammonium chloride solutions. There was some tendency towards a reddish brown color in the 0.25 N solutions with the least amount of ammonium chloride

TABLE VI. INITIAL CORROSION OF IRON IN SOLUTIONS OF MIXED CHLORIDES OF POTASSIUM AND CALCIUM

Normality Ratio, Ca:K	0.25 N Solns.		2.0 N Solns.	
	\bar{X} Mg.	σ Mg.	\bar{X} Mg.	σ Mg.
100:0	7.0 ^a	..	4.5 ^a	..
97.5:2.5	6.1	0.33	3.6	0.16
75:25	7.0	0.47	4.0	0.21
50:50	7.2	0.43	6.3	0.31
25:75	7.3	0.48	7.9	0.24
2.5:97.5	10.2	0.88	8.0	0.90
0:100	15.0 ^a	..	10.0 ^a	..

^a Values taken from Figures 1 and 4.

TABLE VII. INITIAL CORROSION OF IRON IN SOLUTIONS OF MIXED CHLORIDES OF POTASSIUM AND AMMONIUM

Normality Ratio, K:NH ₄	0.25 N Solns.		2.0 N Solns.	
	\bar{X} Mg.	σ Mg.	\bar{X} Mg.	σ Mg.
100:0	15.0 ^a	..	10.0 ^a	0.48
97.5:2.5	15.0	1.09	16.0	0.73
75:25	16.7	1.02	23.3	1.11
50:50	18.9	0.54	28.7	1.14
25:75	22.7	0.80	33.9	1.33
2.5:97.5	23.9	0.45	37.0 ^a	..
0:100	23.5 ^a

^a Values taken from Figures 1 and 6.

and to a dark greenish brown color in the 2.0 N solutions with little ammonium chloride.

CALCIUM AND AMMONIUM CHLORIDES. The results of tests in 0.25 and 2.0 N mixtures of calcium and ammonium chlorides are given in Table VIII and Figure 12. The results were similar in character to those in the ammonium chloride-potassium chloride solutions, although the influence of small additions of calcium chloride was less marked than similar additions of potassium chloride. Further, the distribution of attack and the nature of corrosion products were similar to that of pure ammonium chloride in all the mixtures. The hydrogen-evolution type of attack accounted for the major portion of the corrosion in these solutions.

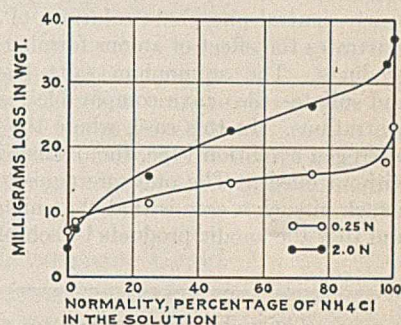


FIGURE 12. INITIAL CORROSION OF MILD STEEL IN SOLUTIONS OF MIXED CHLORIDES OF CALCIUM AND AMMONIUM

TABLE VIII. INITIAL CORROSION OF IRON IN SOLUTIONS OF MIXED CHLORIDES OF CALCIUM AND AMMONIUM

Normality Ratio, Ca:NH ₄	0.25 N Solns.		2.0 N Solns.	
	\bar{X} Mg.	σ Mg.	\bar{X} Mg.	σ Mg.
100:0	7.0 ^a	..	4.5 ^a	..
97.5:2.5	8.4	0.40	7.4	0.24
75:25	11.5	0.33	15.7	1.16
50:50	14.7	0.31	22.7	1.25
25:75	16.2	0.57	26.5	1.51
2.5:97.5	18.0	0.68	33.1	2.34
0:100	23.5 ^a	..	37.0 ^a	..

^a Values taken from Figures 4 and 6.

Salts of Anions Other than Chlorides

The above results indicate that the cation is very influential in determining the initial rate of corrosion in chloride solutions. The influence was so marked, even for neutral electrolytes, that it seemed reasonable to expect other salts of a given metal to give comparable rates of corrosion. This need be true only if the anion forms a soluble primary product (as does chloride) and is nonoxidizing. Consequently, tests were made in solutions of sodium sulfate, sodium iodide, potassium sulfate, and potassium iodide as examples of anions which satisfy the above conditions; in mixtures of monosodium and disodium phosphates and of monopotassium and dipotassium phosphates (nearly neutral), which form a partially soluble anodic product; and in sodium and potassium nitrates which give oxidizing anions. Tests were also made in solutions of magnesium sulfate, calcium nitrate, ammonium nitrate, and ammonium sulfate. The results of these tests are given in Table IX and bear out expectations strikingly. The three potassium salts that obey the two restrictions of forming a soluble primary product and of being nonoxidizing—namely, potassium chloride, potassium sulfate, and potassium iodide—give reasonably comparable results. The corrosion rates in sodium salts of these anions are also in fair agreement. This behavior, coupled with the work of Chapman (4) on potassium fluorides, makes the postulate reasonably well proved. A comparison of the corrosion rates in 0.25 N solutions of magnesium chloride and sulfate adds further support. The results in 0.1 N sodium, potassium, and

calcium nitrates illustrate the influence of an oxidizing salt under the conditions of test. The corrosion was only roughly half of that found in solutions of the chlorides of these metals. The surface of the specimens showed interference colors and other evidence of primary oxidation. The action must be similar in many respects to that in potassium permanganate-potassium chloride solutions (12). The corrosion in the nearly neutral phosphate solutions of sodium and potassium illustrates the effect of anions forming slightly soluble anodic products. The ammonium salts tested—chloride, nitrate, and sulfate—also gave comparable results in equivalent concentrations. In this case, where the major attack is of the hydrogen evolution type, the oxidizing anion appeared to be without effect. The only prerequisite to ensure equality of attack in such a case is that the anion be from a strong acid and that the anodic products be soluble.

TABLE IX. INFLUENCE OF THE ANION ON THE INITIAL CORROSION OF IRON

Normality of Soln.	Anion	Na		K		Ca		Mg		NH ₄	
		\bar{X}	σ	\bar{X}	σ	\bar{X}	σ	\bar{X}	σ	\bar{X}	σ
		Mg.	Mg.	Mg.	Mg.	Mg.	Mg.	Mg.	Mg.	Mg.	Mg.
0.1	Cl	12.1 ^a	..	13.5 ^a	..	7.7 ^a	18.0 ^a	..
0.25	Cl	12.9	0.90	14.5	0.50	4.7	0.29	22.5	1.14
0.25	SO ₄	12.8	0.29	13.6	0.12	4.9	0.31	22.9	1.04
0.25	I	11.2	0.16	13.2	0.29
0.1	NO ₃	6.5	0.42	6.0	0.66	4.0	0.10	17.0	0.87
1 vol. 0.75 N mono-basic phosphate to 1 vol. 0.375 N dibasic phosphate (pH = 6.4)	PO ₄	5.8	0.0	7.7	0.19

^a Values taken from Figures 1, 4, and 6.

Corrosion of Zinc

A few tests were made with zinc in chloride solutions to determine whether the cation also plays a part in determining the corrosion rate of this metal. The results are given in Table X. Zinc B was a commercial grade of zinc for which no analysis was available. The few tests made indicate that the cation plays a marked role in determining the corrosion rate with zinc as well as with iron, but there were differences in the behavior of the two metals. With zinc there was little difference in the amount of corrosion in solutions of sodium and potassium chlorides. The calcium salt, however, gave a much lower loss, the difference being more marked with zinc than with iron. Corrosion in ammonium chloride was unexpectedly slow. The attack was of the hydrogen evolution type, and no corrosion products had formed by the end of 2 days. The purity of the zinc may account for the relatively low rate in this salt.

TABLE X. INFLUENCE OF THE CATION ON THE INITIAL CORROSION OF ZINC IN CHLORIDE SOLUTIONS

Zinc	Normality of Salt	NaCl		KCl		CaCl ₂		NH ₄ Cl	
		\bar{X}	σ	\bar{X}	σ	\bar{X}	σ	\bar{X}	σ
		Mg.	Mg.	Mg.	Mg.	Mg.	Mg.	Mg.	Mg.
A	0.1	32.0	2.08	33.8	1.25	11.3	0.59	13.4	0.14
B	0.25	40.7	0.49	40.6	1.9

Discussion of Results

The experimental results seem to show that the nature of the cation is a definite factor in determining, at least, the initial rate of corrosion of metals under partially immersed conditions. We must bear in mind that in aqueous solutions another cation, hydrogen, is always present, and the concentration of this ion must be taken into account. However, solutions with the same initial hydrogen-ion concentration

give different rates of corrosion, depending solely on the other cation present. Several factors must be considered as possible causes of these differences. They can, perhaps, be discussed more readily if we limit the solutions under consideration to the neutral chlorides, namely, sodium, potassium, lithium, barium, strontium, calcium, and magnesium. The solubility of oxygen in the solutions could certainly be a contributing factor. However, measurements of this value show only small differences between equivalent solutions of the salts. Oxygen is soluble in the solutions of sodium, potassium, and lithium chlorides to a similar degree. The same is true of the alkaline earth group except that the solubility is somewhat less for the group as a whole. However, the difference in oxygen solubility is much less than the difference in amount of corrosion.

The viscosity of the solutions may also influence the rate at which oxygen can reach the surface of the metal and hence influence the rate of attack. The viscosities (13) of the seven chloride solutions under consideration are markedly different, and the differences are in the direction which would influence the corrosion rates in the manner found in the tests. However, if the viscosities of the three potassium salts (chloride, iodide, and sulfate) are compared, the relationship no longer holds true. Other discrepancies are also to be noted and it is apparent that differences in viscosity are not the primary causes of the differences in corrosion rate. In dilute solutions the conductivity is usually an important "rate factor." A comparison of equivalent conductivities (14) of the solutions indicates, if we consider the alkali chlorides in one group and the

alkaline earths in another, that there is a close relationship between this factor and the corrosion rate. However, we must make the division mentioned; otherwise certain discrepancies are evident. For example, dilute lithium chloride solutions have a lower conductivity and yet give a higher corrosion rate than equivalent magnesium chloride solutions. Also the salts of the same cation have different conductivities. It is reasonable to say that the above factors, while undoubtedly influencing the results, are not the primary causes of the differences in corrosion rates.

The one outstanding fact determined by this study is that the stronger the basic properties of the cation, the more rapid is the oxygen-absorption type of corrosion. Further, the more basic the cation, the smaller is the naturally formed anodic or attacked area. The differences in rate of penetration or "conditional velocity" in the different salt solutions are thus even greater than the weight figures indicate. We can further state that the probability that attack will take place is less for the salts of the more basic cations. We would expect, therefore, less tendency towards pitting in solutions of the alkaline earth salts than in those of the alkali salts.

The cause of the differences in total corrosion is difficult to ascribe. Evans and Hoar (5) showed that both the rate of change of cathode potential with amount of total current flowing and the potential of the cathode at zero current determine the corrosion rate of iron under the test conditions described in this paper. A change of either of these factors would influence the corrosion rate. It seems likely that the exchange of cations would influence the cathodic polarization rather than the magnitude of the static potential of the cathode. If this is the true cause of the observed differences, it would mean either that in solutions of calcium chloride, for example, the effective cathodic area is smaller than in potassium chloride solutions of an equivalent strength, or, assuming the cathodic area to be equal the depolarization mechanism is

retarded in some manner in the calcium chloride solutions. In either case the postulate of discrete "active" cathodic areas as put forward by Borgmann and Evans (2) must be considered to receive support.

The increase in the probability of attack (increase in size of anodic area) as one passes from the alkali to the alkaline earth salts is due to a combination of two factors: (a) The rate of production of hydroxyl ions at the cathode is less (lower rate of corrosion), and (b) the bases thus formed are weaker in character. Since the alkali formed is heavier, it flows down the metal surface (8) and maintains the pH high enough in the alkali salt solutions to precipitate *in situ* any iron ions tending to go into solution over a fairly large area, whereas the hydroxides of the alkaline earths would be effective only over smaller areas.

Summary

The variation of the initial corrosion rate with concentration has been measured for a large number of different chloride solutions. The order of increasing corrosiveness of the cations is as follows: magnesium, cadmium, manganese, calcium, strontium, barium, lithium, sodium, potassium, aluminum, ammonium, chromic, and ferric. The rate of attack in neutral solutions was found to depend largely on the nature of the cation, as long as the anion formed a soluble primary product and was nonoxidizing. An explanation, based on the assumption that the cathodic depolarization takes place at discrete "active" points, was given. The cation was assumed to influence either the number of such points or their ability to aid the hydrogen-oxygen reaction.

The corrosion of iron in ammonium, ferric, aluminum, and chromic chlorides was found to take place largely with the evolution of hydrogen or with the reduction of the cation. The attack increased with concentration in all cases, and the presence of an oxidizing cation increased the rate of attack. Ferric chloride was much the most corrosive of any salt tested.

The initial corrosion of iron in mixed solutions was measured. In most cases the first additions of a second salt had the most marked influence on the corrosion rate. The char-

acter and distribution of attack were also often influenced by the presence of a second cation.

The nature of the cation (alkali and alkaline earth metals) was found to have a marked influence on the probability of breakdown and the intensity of attack in the chloride solutions.

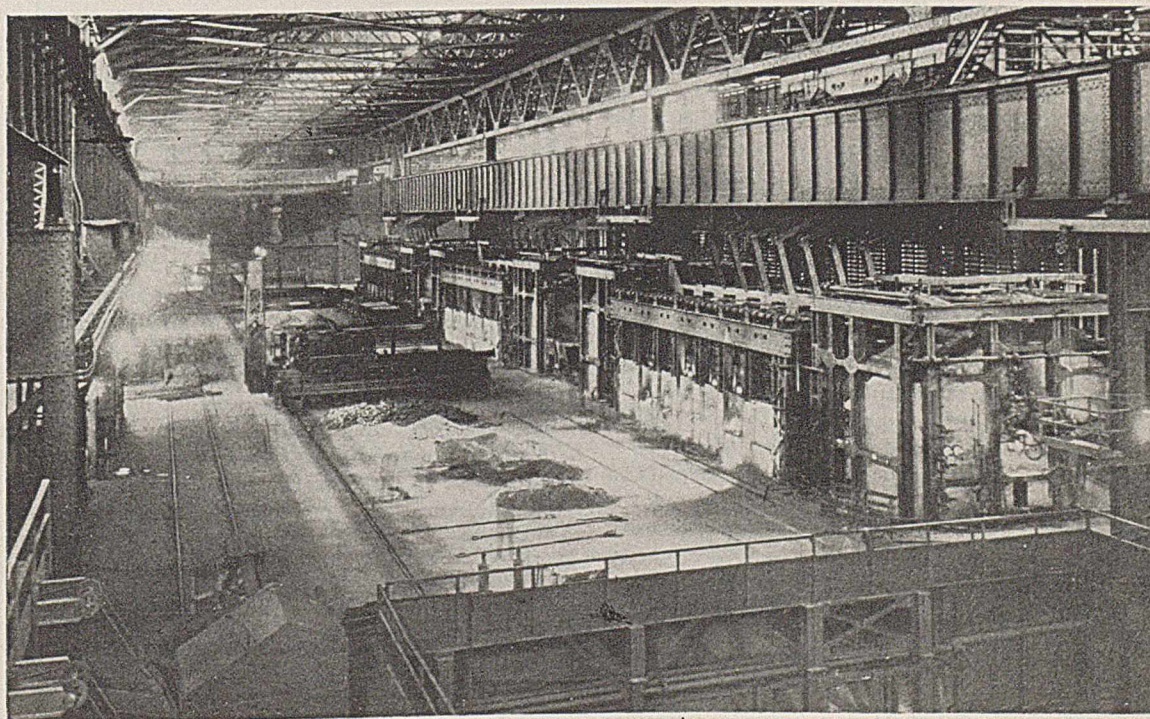
Acknowledgment

The author wishes to thank the Chemistry Department of the University of North Carolina for providing the facilities which made possible the experimental work reported in the paper. The cold-rolled strip steel used in the tests was kindly furnished by F. C. Elder of the American Steel and Wire Company, and the zinc sheet by E. A. Anderson of the New Jersey Zinc Company.

Literature Cited

- (1) Bengough, G. D., *J. Soc. Chem. Ind.*, **52**, 195 (1933).
- (2) Borgmann, C. W., and Evans, U. R., *Trans. Electrochem. Soc.*, **65**, 267 (1934).
- (3) Burns, R. M., *Bell System Tech. J.*, **15**, 20 (1936); Evans, U. R., *J. Franklin Inst.*, **208**, 45 (1929); Evans, U. R., and Hoar, T. P., *Trans. Faraday Soc.*, **30**, 424 (1934).
- (4) Chapman, A. W., *J. Chem. Soc.*, **1930**, 1546.
- (5) Evans, U. R., and Hoar, T. P., *Proc. Roy. Soc. (London)*, **A137**, 343 (1932).
- (6) *Ibid.*, **A137**, 349 (1932).
- (7) *Ibid.*, **A137**, 350 (1932).
- (8) *Ibid.*, **A137**, 355 (1932).
- (9) Friend, J. N., *Iron and Steel Inst. Carnegie Scholarship Mem.*, **11**, 1 (1922).
- (10) Friend, J. N., and Brown, J. H., *J. Iron Steel Inst.*, **83**, 125 (1911).
- (11) Heyn, E., and Bauer, O., *Mitt. kgl. Materialprüfungsamt*, **26**, 200 (1908); **28**, 62 (1910).
- (12) Hoar, T. P., and Evans, U. R., *J. Chem. Soc.*, **1932**, 2477.
- (13) International Critical Tables, Vol. V, pp. 12-19, New York, McGraw-Hill Book Co., 1929.
- (14) *Ibid.*, Vol. VI, pp. 232-8.
- (15) Mears, R. B., and Evans, U. R., *Trans. Faraday Soc.*, **31**, 527 (1935).

RECEIVED March 5, 1937. Presented before the Division of Industrial and Engineering Chemistry at the 93rd Meeting of the American Chemical Society, Chapel Hill, N. C., April 12 to 15, 1937.



OPEN HEARTH

Significance of Low-Temperature Oxidation Products in Anthracite Mine Fire Studies

G. S. SCOTT AND G. W. JONES

U. S. Bureau of Mines, Experiment Station, Pittsburgh, Pa.

The United States Bureau of Mines, as a part of its general program dealing with the causes, behavior, and control of anthracite mine fires, has investigated various means for detecting incipient heating underground and has sought to develop means for determining the trend of the heating once a fire is known to exist.

This report describes apparatus used and tests made on anthracite to determine the amount of oxidation and the composition of the oxidation products when normal dry air is passed through anthracite maintained at temperatures varying from 100° to 350° C. Each

MANY of the suspected heated areas and known active fires in the anthracite region are in the outcrop along ridges at rather high elevations or in broken and caved areas in abandoned and reworked sections that are not accessible for direct inspection and attack.

The fact that these areas are usually inaccessible greatly limits the means available for interpreting what is taking place. The chief and sometimes only source of information is that gained from the chemical composition of the mine gases from the suspected areas.

Mine Atmospheres Not Associated with Heating

The difficulties encountered in the application of gas analyses to mine-fire studies are increased by the fact that mine atmospheres not associated with heating contain carbon dioxide and methane and often are depleted in oxygen. This condition is caused by the breathing of men and animals, the oxidation at normal temperatures of coal, carbonaceous rock, timber, and pyrite, the action of acid mine water on carbonates, the evolution of methane from the coal, and the products of blasting. The extent to which the composition of mine air is affected by these constituents depends upon the velocity of air through the workings, the length of air travel, and the chemical and physical nature of the materials along the path of travel. The greatest changes are found in a relatively stagnant atmosphere, such as that from old workings or abandoned sections.

Atmospheres from Hot Zones or Heated Areas

Oxidation processes and the products of the oxidation of bituminous coals have been studied by numerous investigators (7). The oxidation of anthracite at low temperatures and the

test was continued for 72 hours so that the trend of the oxidation process with time could also be ascertained.

Tests made on a high-grade anthracite have shown that the evolved gases and their relative proportions vary with the temperature and offer a means for determining the probable temperature of the coal and thus a means of detecting incipient heating.

Graphs are presented which show the relation of temperature and the more important factors and the practical application of the data to a mine fire in the anthracite region.

products formed by such oxidation, however, have received little attention. The present investigation was made to furnish information along this line. As a part of the work a series of gas samples was taken from various mine-fire areas in the Pennsylvania anthracite region and analyzed for carbon dioxide, oxygen, carbon monoxide, methane, hydrogen, and nitrogen. The results showed that carbon monoxide was present in all cases of known fires, and where the fires were especially active, hydrogen was found also. Therefore it seemed desirable to study the relation of these gases when anthracite is oxidized at various temperatures and under conditions simulating those of a heated area.

Laboratory Investigations

In a previous paper (6) the writers showed by laboratory experiments that the rate of liberation of carbon monoxide by anthracite at temperatures up to the ignition point is roughly proportional to the rate of heat generation by oxidation. In these tests carbon monoxide was not liberated in detectable amounts by anthracite until the temperature of the anthracite exceeded about 200° C. To determine the lowest temperature at which carbon monoxide and hydrogen are liberated by anthracite and the amount of oxygen that reacts with the anthracite at various elevated temperatures when air is passed slowly through it, a special apparatus was designed and assembled to supply the following information:

1. The amount of oxygen that reacts with anthracite at normal and elevated temperatures.
2. The kind, amount, and proportions of the gaseous products evolved when anthracite is oxidized at elevated temperatures.
3. The trend of the reactions at any given temperature over varying periods of time.

4. The initial temperature at which carbon monoxide is evolved.
5. The initial temperature at which hydrogen is evolved.
6. The significance of the carbon monoxide-carbon dioxide ratio of the evolved products as a means of determining the temperature of the anthracite.
7. The significance of the ratio of carbon monoxide to oxygen consumed as a means of determining the temperature of the anthracite.
8. Comparative tests on coals known or suspected of heating spontaneously.

It was decided to study the oxidation by using a small sample of coal varying from 15 to 20 grams in weight. The coal samples were ground and screened; that portion passing through a 20-mesh and caught on a 42-mesh screen was used. Smaller sizes have some advantages because greater areas of surface are exposed for a given weight; but at the higher temperatures the smaller sizes offered too much resistance to permit the required amount of air to be passed through the charge to maintain 15 per cent or more of oxygen in the effluent gases. Normal dried air, rather than pure oxygen, was used to oxidize the anthracite. The rate of passage of air through the sample was kept at a minimum but still sufficient to maintain 15 per cent or more oxygen in the effluent gases. At the lower temperatures (100° and 150° C.) the air rate was approximately 1 liter per hour.

Each test was continued for 72 hours, and analyses and tabulations of results were made every 24 hours.

Apparatus

Figure 1 shows the arrangement of the apparatus:

Motor *A* and pump *B* furnished air for the oxidation. Trap *C*, containing cotton, was used to remove oil carried over from the pump. Towers *E*, *F*, and *G* removed the water and carbon dioxide from the air supply. The rate of air flow was adjusted to the desired rate by regulating valve *D* and indicated by flowmeter *H*. Any water vapor carried over from the flowmeter was caught in drying tower *J*. The temperature inside furnace *L* was determined by means of a Leeds & Northrup Micromax recorder, using an iron-constantan thermocouple, *g*. The evolved products of the oxidation were passed through tubes *M* and *N*, containing Anhydron (magnesium perchlorate), which removed the water; then through tubes *O*, *P*, and *Q*, containing soda lime and Anhydron, which removed the carbon dioxide; then through wet-gas meter *R*; and finally into gas holder *S*, containing 50 per cent glycerol in water as the confining liquid. *K* is a mercury manometer.

Furnace *L*, in which the coal was oxidized, was constructed as follows:

A Duralumin block, *b*, 10 × 10 × 25 cm. in size and having a 44.5-mm. hole drilled down the center, was used. This block was then wrapped with three layers of asbestos paper, *c*, and over this was wound 782 cm. of No. 22-gage Nichrome wire. Insulation was provided by covering the core with 3.8 cm. of 85 per cent magnesia, *e*, and sherardized sheet-iron cover, *f*.

Oxidation tube *a*, containing the coal sample, was made of Pyrex glass, 22 mm. in outside diameter and 178 mm. long. The

coal sample was supported on fine-mesh Nichrome gauze which, in turn, was supported by a short section of glass tubing, as illustrated in Figure 1.

The temperature was controlled by a direct-acting thermostat in series with the furnace winding. A 15-watt lamp bulb connected across the thermostat contacts indicated the operation of the thermostat.

Procedure

The coal sample was poured into sample tube *a* to a depth of 10 cm. The outlet and inlet ends were then closed with rubber stoppers, and the tube and sample weighed. The tube was connected to the purifying train on the intake side and left open to the air on the outlet side. The line was disconnected at regulating valve *D*, and the inlet to tower *E* was connected to a tank of compressed nitrogen gas. The air in the train was then swept out with some 5 or 6 liters of nitrogen. The tube was placed in the furnace and connected to the absorption train. The furnace was maintained at 105° C. while nitrogen gas at a rate of 3 to 6 liters per hour was passed through the tube. The drying period was approximately 6 hours. After drying, the oxidation tube and sample were removed from the furnace without disconnecting from the system and cooled to room temperature. It was then disconnected and weighed.

The nitrogen tank was disconnected and *D* was again connected to tower *E*. Sample tube *a* was connected in the train, the pump motor started, and the nitrogen swept out of the line with air. Tubes *M*, *N*, *O*, *P*, and *Q* of the absorption train were weighed. The gas-meter reading, the barometer, and the room and furnace temperatures were recorded. The oxidation tube was then placed in the furnace, and the time and meter readings were noted. After the passage of about 3 liters of gaseous products through the meter to sweep out the nitrogen, the gas-meter outlet was connected to gas holder *S*. Every 24 hours the oxidation was interrupted to take a complete set of readings and make a complete set of weighings.

Amount of Oxygen Reacting with Anthracite

Table I gives the analyses of the coals used in the tests, and Table II is a summary of the oxidation tests made at temperatures varying from 100° to 350° C. with coal A-16, a high-grade anthracite.

When air was passed through anthracite at laboratory temperatures, the reaction with oxygen was so slight that even during a 72-hour test the amounts of oxygen consumed and carbon dioxide and water vapor evolved were too small to be

determined accurately. It was necessary to heat the anthracite to 100° C. before sufficient reaction took place to ensure trustworthy results.

The rate of oxygen consumption for any given temperature decreased with time for all tests made at the lower temperatures; that is, the number of cubic centimeters of oxygen consumed per day per 100 grams of anthracite was highest during the first day of test, decreased the

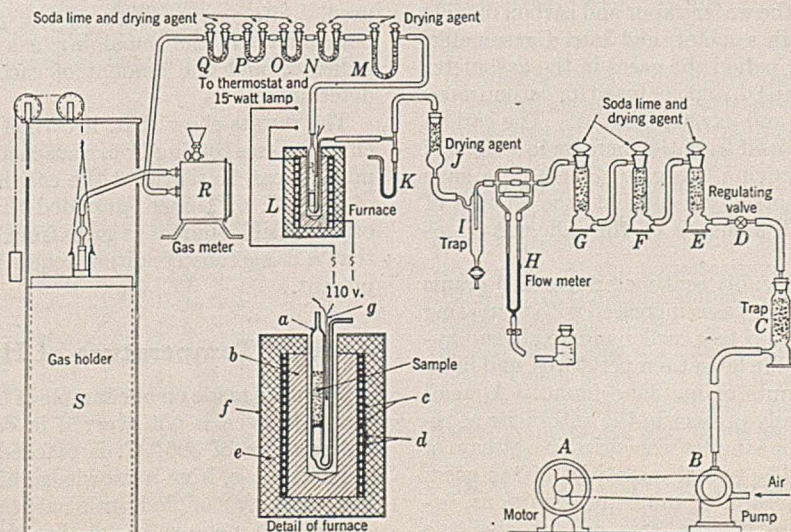


FIGURE 1. APPARATUS FOR DETERMINATION OF OXIDATION RATE OF COAL

TABLE I. ANALYSES OF COALS USED IN OXIDATION TESTS (AIR-DRY BASIS)^a

	A-16 ^b	SB-26 ^c	SB-22 ^d
Moisture	1.2	12.3	5.0
Volatile matter	4.6	33.4	38.5
Fixed carbon	88.3	50.2	44.5
Ash	5.9	4.1	12.0
Hydrogen	2.8	5.7	5.4
Carbon	86.5	64.0	64.9
Nitrogen	1.0	1.5	1.3
Oxygen	3.2	24.4	16.1
Sulfur	0.6	0.3	0.3
Calories	7,767	6,172	6,389
B. t. u.	13,980	11,110	11,500

^a Analyses made in Coal Analysis Section, H. M. Cooper in charge.

^b A high-grade anthracite.

^c A Colorado subbituminous coal.

^d A Washington subbituminous coal.

TABLE II. GASEOUS PRODUCTS OF OXIDATION AT VARIOUS TEMPERATURES (Anthracite sample A-16; ignition temperature = 470° C.; CO inflection point = 372° C.)

Temp. ° C.	Time Days	Gas Volume		Ratio		Gas Compn. (Air-Free)					
		O ₂ consumed Cc./100 g. dry coal/day	CO ₂	CO	CO/CO ₂	CO/O ₂	CO ₂ %	CO %	H ₂ %	CH ₄ %	N ₂ %
100	1	116	13.6	0	3.0	0	0	...	97.0
	2	73	7.6	0	2.7	0	0	...	97.3
	3	53	4.6	0	2.2	0	0	...	97.8
150	1	449	77	3	0.03	0.006	4.4	0.2	0	...	95.4
	2	230	39	3	0.07	0.012	4.3	0.3	0	...	95.4
	3	148	23	3	0.12	0.018	3.9	0.5	0	...	95.6
200	1	1,431	276	58	0.21	0.04	4.8	1.0	0	...	94.2
	2	748	149	41	0.27	0.05	4.9	1.4	0	...	93.7
	3	533	131	50	0.38	0.09	6.0	2.3	0	...	91.7
250	1	2,952	860	206	0.24	0.07	7.0	1.7	0	...	91.3
	2	2,210	814	206	0.25	0.09	8.7	2.2	0	...	89.1
	3	1,798	718	181	0.25	0.10	9.3	2.3	0	...	88.4
300	1	10,650	3,865	896	0.23	0.08	8.6	2.0	0.05	0	89.4
	2	6,950	3,620	1,104	0.30	0.16	11.7	3.6	0.05	0	84.5
	3	7,020	3,640	1,504	0.41	0.21	11.5	4.7	0.05	0	83.8
350	1	24,610	12,350	5,210	0.42	0.21	11.2	4.7	0.1	0	84.0
	2	25,360	18,570	6,020	0.32	0.24	15.4	5.0	0.1	0	79.5
	3	27,300	20,509	7,320	0.36	0.27	15.7	5.6	0.1	0	78.6

second day, and was lowest the third day. This general trend held until a temperature of 300° C. was reached, when it was found that although less oxygen reacted the second day, the third day showed an actual increase. At a temperature of 350° C. the amount of oxygen reacting showed an increase over that of each previous day.

Gaseous Products Evolved

The gases leaving the heated anthracite were passed through absorbents where the water vapor and carbon dioxide were removed, then through a meter, and into a gasometer. At the end of each 24-hour period the gases in the gasometer were thoroughly mixed, sampled, and analyzed for carbon monoxide, hydrogen, methane, and oxygen content. The carbon dioxide content was determined from the increase in weight of the absorbent used for removing this gas. These data gave information that made it possible to calculate the amount of oxygen consumed and the amounts of the different gases evolved.

The actual quantities, in cubic centimeters per 100 grams of coal per day, of the different gases increased with increasing temperature, as should be expected; carbon monoxide and hydrogen were not evolved at the lowest temperatures, and in no case were detectable amounts of methane found. A small amount of methane, originally present in the anthracite as received, was evolved when the samples were dried in a stream of nitrogen gas at 105° C. The actual quantities of the gases are not so important in interpreting mine-fire conditions, because analyses of mine-fire atmospheres cannot give the quantities of the different gases evolved but only their rela-

tive proportions. The gases can be best interpreted when recorded on an air-free basis. The air-free analyses of the gases are so given in Table II. The air-free analyses vary, for a given temperature, with the period of time elapsed from the start of the test. Tests made at temperatures of 100° and 150° C. showed that the carbon dioxide present decreased as the test extended from one day to the next. At all temperatures from 200° to 350° C. the carbon dioxide content increased with the time of test.

The carbon dioxide content of the air-free products was also very low at the lower temperatures; the average concentration at 100° C. was 2.9 per cent. This is in agreement with work done by Haldane and Makgill (4), who obtained similar results with bituminous coals.

The concentration of carbon dioxide in the air-free products increased with the temperature and at 350° reached 15 to 16 per cent. These findings, in conjunction with the carbon monoxide and hydrogen contents, which also increased with temperature, enabled a prediction to be made as to the probable average temperature of a mass of heated anthracite from the chemical composition of the air-free products. Any interpretation or prediction made must, however, consider all three constituents. It is well known that many oxygen-depleted atmospheres in mines at normal temperatures may contain from 2 to 20 per cent or more carbon dioxide in the air-free products and thus carbon dioxide considered by itself is entirely useless for estimating the temperature of heated anthracite.

Initial Temperature of Carbon Monoxide Evolution

When air was passed through heated anthracite, carbon monoxide was not evolved in detectable quantities until a temperature of 150° C. was reached. At the higher temperatures the carbon monoxide content was determined by analyzing the gases on a Bureau of Mines Haldane gas-analysis apparatus (1) supplemented by the pyrotannic acid method (5). The limit of analysis for carbon monoxide by the pyrotannic acid method is about 0.01 per cent by volume in the products. To determine the carbon monoxide in concentrations below 0.01 per cent a carbon monoxide indicator (Mine Safety Appliances Company) with a special scale covering a range from 0.001 to 0.01 per cent carbon monoxide was used. After an analysis of the gas in the gasometer had been made, all the remaining gas was passed through the indicator and the amount of carbon monoxide present was determined.

The results show that, if carbon monoxide is found in the effluent gases coming from a suspected section of an anthracite mine, it can be said that the coal has reached a temperature of 150° C. or higher (provided that carbon monoxide from other possible sources as gases from explosives are absent) and that a dangerous condition requiring immediate attention is present.

Initial Temperature of Hydrogen Evolution

The tests made on one sample of high-grade anthracite show that hydrogen is not evolved in detectable amounts until a temperature of 300° C. is reached. This observation is of value because, from a knowledge of the presence of hydrogen in a mine air sample from a suspected heated area, a prediction can be made as to whether the temperature of the area is above or below 300° C.

TABLE III. GASEOUS PRODUCTS OF OXIDATION FROM VARIOUS COALS AT ELEVATED TEMPERATURES

Sample No.	Temp. ° C.	Time Days	Gas Volume			Ratio		Gas Compn. (Air-Free)					Ignition Temp. ° C.	CO Inflection Point ° C.	Remarks
			O ₂ concn. Cc./100 g. dry coal/day	CO ₂	CO	CO/CO ₂	CO/O ₂	CO ₂ %	CO %	H ₂ %	CH ₄ %	N ₂ %			
A-16	100	1	116	13.6	0	3.0	0	0	0	97.0	470	372	High-grade anthracite
		2	73	7.6	0	2.7	0	0	0	97.3			
		3	53	4.6	0	2.2	0	0	0	97.8			
SB-26	100	1	1,743	318	64	0.20	0.04	4.5	0.9	0	0.2	94.4	186	141	Colo. subbituminous
		2	854	202	48	0.23	0.05	5.7	1.3	0	1.0	92.0			
		3	680	172	40	0.26	0.07	6.2	1.6	0	0.8	91.4			
A-16	150	1	449	77	3	0.03	0.006	4.4	0.2	0	0	95.4	470	372	High-grade anthracite
		2	230	39	3	0.07	0.012	4.3	0.3	0	0	95.4			
		3	148	23	3	0.12	0.018	3.9	0.5	0	0	95.6			
SB-22	150	1	5,325	992	280	0.28	0.053	4.6	1.3	0	0.3	93.8	234	204	Wash. subbituminous
		2	2,668	713	200	0.28	0.075	6.5	1.8	0	0.3	91.4			
		3	2,050	607	176	0.29	0.086	7.1	2.1	0	0.3	90.5			
SB-26	150	1	6,410	2,170	368	0.17	0.06	8.1	1.4	0	0.1	90.4	186	141	Colo. subbituminous
		2	3,835	1,300	368	0.28	0.10	4.3	2.3	0	0	89.6			
		3	2,722	1,042	360	0.34	0.13	8.9	3.1	0	0	88.0			
A-16	200	1	1,431	276	58	0.21	0.04	4.8	1.0	0	0	94.2	470	372	High-grade anthracite
		2	748	149	41	0.27	0.05	4.9	1.4	0	0	93.7			
		3	533	131	50	0.38	0.09	6.0	2.3	0	0	91.7			
SB-22	200	1	13,820	4,320	1,304	0.30	0.094	7.5	2.3	0	0	90.2	234	204	Wash. subbituminous
		2	7,180	2,993	984	0.33	0.137	9.6	3.2	0	0	87.2			
		3	6,060	2,750	808	0.31	0.133	10.4	3.1	0	0	86.5			

Significance of Carbon Monoxide-Carbon Dioxide Ratios

Graham and others (3) made use of the ratios of carbon monoxide to carbon dioxide, carbon monoxide to oxygen consumed, and carbon dioxide to oxygen consumed for detecting the heating of coal and for determining when a fire has been extinguished. The ratios of carbon monoxide to carbon dioxide and carbon monoxide to oxygen consumed were investigated, and the values are given in Table II.

The data show that the carbon monoxide-carbon dioxide ratio varies widely for the same temperature with the time elapsed from the start of the test; for example, in the case of the tests made at 150° C. the ratio for the first day was 0.03, for the second day 0.07, and for the third and last 0.12. The same general trend is shown for most of the tests, but in spite of these variations there is an increase in the ratio as the temperature of oxidation increases. The values are erratic and are rather useless for the purpose of predicting the temperature of the anthracite through which air may be passing at elevated temperatures.

Significance of Carbon Monoxide-Oxygen Consumed

The carbon monoxide-oxygen consumed ratios for the different tests made at elevated temperatures are also given in Table II. They show erratic values for the same oxidation

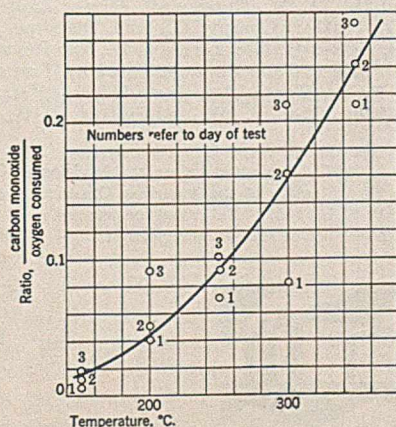


FIGURE 2. CARBON MONOXIDE-OXYGEN CONSUMED RATIO vs. TEMPERATURE

TABLE IV. APPLICATION OF GAS ANALYSES AND CHART TO A COOLING MINE-FIRE AREA IN PENNSYLVANIA ANTHRACITE REGION

Days after sealing:	6	45	51	65	76	210
Analysis of gases, %:						
CO ₂	2.4	2.3	1.3	1.8	3.9	..
O ₂	7.4	2.1	0.7	0.4	0.3	..
CO	2.6	0.5	0.6	0.4	0.15	..
CH ₄	16.7	36.9	43.9	45.7	27.7	..
N ₂	70.9	58.2	53.5	51.7	67.95	..
Air- and methane-free gases, %:						
CO ₂	4.1	4.3	2.5	3.4	5.5	..
CO	4.5	0.9	1.1	0.8	0.2	..
N ₂	91.4	94.8	96.4	95.8	94.3	..
CO/O ₂ consumed	0.23	0.038	0.045	0.06	0.011	..
Hot zone temp., ° C.:						
Based on CO ₂	160	160	100	130	200	..
Based on CO	335	180	200	180	130	..
Based on CO/O ₂	340	180	200	210	140	..
Thermometer reading, ° C.	19
Estd. av. temp., ° C.	340	180	200	195	150	..

temperature and, in general, increase with the elapsed time of oxidation. The values increase with temperature at a higher rate than the carbon monoxide-carbon dioxide ratios; as indicated in Figure 2, the ratios may be of value in interpreting and predicting the temperature of anthracite undergoing oxidation at elevated temperatures.

Oxidation of Coals That Heat Spontaneously

Oxidation tests of 72 hours' duration were made on coals other than anthracite at selected temperatures to obtain data comparable with those of the high-grade anthracite. These results are given in Table III. They have special significance in connection with the anthracite investigation, in that they show the rate at which oxygen reacts with anthracite as compared with other coals known or suspected of heating spontaneously. At the same temperatures the amount of oxygen absorbed by the subbituminous coals is far in excess of that absorbed by anthracite. In general, it has been found that the subbituminous coals absorbed from ten to fifteen times as much oxygen in a given time as the anthracite, showing the anthracite to have a far higher resistance to oxidation at the lower temperatures and therefore less liability to heat spontaneously.

Likewise the air-free gaseous products and also the carbon monoxide-carbon dioxide and carbon monoxide-oxygen consumed ratios of the subbituminous coals are different from those of anthracite at a given temperature. Therefore

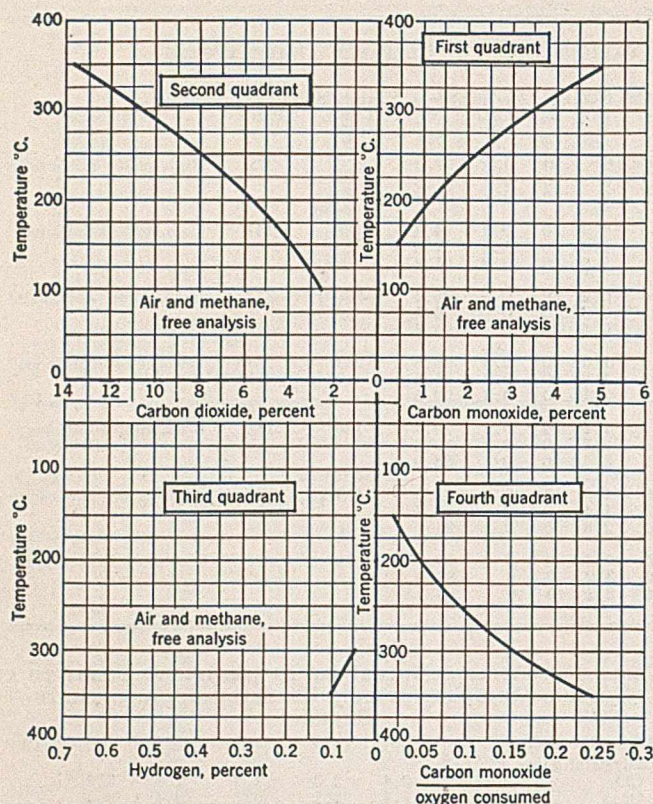


FIGURE 3. DATA FOR ESTIMATING THE TEMPERATURE OF ANTHRACITE WHEN OXIDIZED WITH AIR

the data obtained on anthracite cannot be used at all for predicting the temperature or change of temperature in an area of subbituminous coal suspected or known to be heating.

Also appreciable amounts of carbon monoxide were evolved at 100° C., and it is not unlikely that minute amounts may be liberated at ordinary temperatures. No hydrogen was evolved in any of the tests made up to 200° C., the highest temperature tested. Methane was found in some of the tests as shown in Table III, but the amounts are small and close to the experimental error of analysis.

General Summary

The oxidation tests made on a high-grade anthracite to determine the amount of oxygen consumed, the amounts of carbon dioxide, carbon monoxide, hydrogen, and methane evolved when air was passed through samples of the coal at different elevated temperatures, showed that the evolved gases and their relative proportions vary with the temperature and offer a means for determining the probable temperature of the coal and of detecting incipient heating. The following factors are most important: (a) the initial temperature at which carbon monoxide is liberated, (b) the initial temperature at which hydrogen is liberated, (c) the percentage of carbon dioxide and carbon monoxide in the air-free products, and (d) the ratio of the carbon monoxide to the oxygen consumed.

These relations, taken from experimental data obtained on one sample of high-grade anthracite, are shown in Figure 3. In predicting the temperature from the relations given, it is

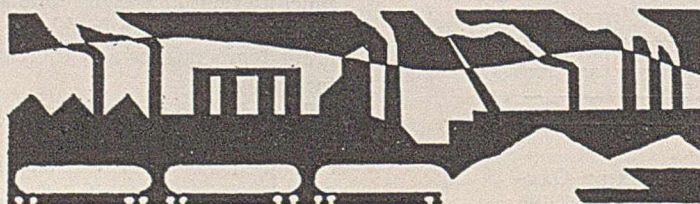
necessary to consider all four variables in arriving at a given conclusion. The curves in Figure 3 are divided into four quadrants. The first gives the relation between the carbon monoxide percentage of the air- and methane-free products and the indicated temperature; the second gives the relation between the carbon dioxide content in the air- and methane-free products and the temperature; the third gives the relation between the hydrogen and the temperature; and the fourth gives the ratio of the carbon monoxide to the oxygen consumed, and the temperature.

To illustrate a practical application of the graphs, Table IV shows analyses of mine atmospheres from a sealed fire area and temperatures estimated from these analyses by application of the data of Figure 3. The sealed area was opened after about 200 days from the time of final sealing (2). This was an especially gaseous mine, and the steady decrease in oxygen and increase in methane with time gives proof of the efficiency of the sealing. There is a reasonably good check between the temperature estimated from the air-free carbon monoxide content and the carbon monoxide-oxygen ratio, but the temperatures estimated from the air-free carbon dioxide are lower. This is attributed to the known fact that anthracite absorbs considerable quantities of carbon dioxide. The data in Figure 3 do not extend above 350° C. However, cases of active combustion at higher temperatures may arise in which the carbon monoxide, hydrogen, and methane produced by the oxidation processes are burned by additional air at or above their ignition temperature. These reactions at the higher temperatures are now being investigated.

Literature Cited

- (1) Burrell, G. A., and Seibert, F. M., U. S. Bur. Mines, *Bull.* 197 (1926).
- (2) Dever, P. H., *Coal Age*, 37, 187-90 (1932).
- (3) Graham, J. I., *Colliery Guardian*, 140, No. 3610, 902-4 (March 7, 1930) and No. 3611, 1008-9 (March 14, 1930); Thomas, W. M., Jones, T. D., and Graham, J. I., *Ibid.*, 146, No. 3774, 776-9 (April 28, 1933) and No. 3775, 822-3 (May 5, 1933); Starrow, J. T., and Graham, J. I., *Ibid.*, 128, No. 3327, 873-4 (Oct. 3, 1924) and No. 3328, 833-5 (Oct. 10, 1924); Morgan, C. E., *Ibid.*, 152, No. 3925, 529-32 (March 20, 1936), No. 3926, 584-7 (March 27, 1936), No. 3927, 634-5 (April 3, 1936), and No. 3932, 868-9 (May 8, 1936).
- (4) Haldane, J. S., and Makgill, R. H., *Trans. Inst. Mining Engrs.* (London), 172-85 (1932-3).
- (5) Sayers, R. R., Yant, W. P., and Jones, G. W., U. S. Bur. Mines, *Rept. Investigations* 2486 (1923).
- (6) Scott, G. S., and Jones, G. W., *IND. ENG. CHEM.*, 29, 106-8 (1937).
- (7) Sinnatt, F. S., *Trans. Am. Inst. Mining Met. Engrs.*, 71, 189-210 (1925); Winnill, T. F., *Trans. Inst. Mining Engrs.* (London), 46, 563-91 (1913-14); Parr, S. W., and Milner, R. T., *IND. ENG. CHEM.*, 17, 115-17 (1925); Newall, H. E., *Fuel*, 14, 34-42 (1935); Graham, J. I., *Trans. Inst. Mining Engrs.* (London), 66, 41-57, 145-53 (1923-4); Schmidt, L. D., and Elder, J. L., *IND. ENG. CHEM.*, 28, 1346-53 (1936); Lamplough, F. E. E., and Hill, A. M., *Trans. Inst. Mining Engrs.* (London), 45, 629-57 (1913); Charpy, G., and Descorps, G., *Compt. rend.*, 178, 1588-9 (1924); Davis, J. D., and Reynolds, D. A., U. S. Bur. Mines, *Tech. Paper* 409 (1928); Francis, W., and Wheeler, R. V., *Trans. Am. Inst. Mining Met. Engrs.*, 71, 165-75 (1925); Parr, S. W., and Hobart, F. B., 71, 216-26 (1925).

RECEIVED March 1, 1937. Presented before the Division of Gas and Fuel Chemistry at the 93rd Meeting of the American Chemical Society, Chapel Hill, N. C., April 12 to 15, 1937. Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)



Reliability of Common Types of Thermocouples

D. QUIGGLE, C. O. TONGBERG, AND M. R. FENSKE
The Pennsylvania State College, State College, Pa.

THE usefulness and convenience of thermocouples for measuring temperatures are obvious. Although they are used extensively in industrial equipment to centralize the measurement and recording of a variety of temperatures at important points not readily accessible in an apparatus, they are also finding extensive use in research work, in laboratory control work, and in analytical work where temperature is a property to be measured with at least reasonable accuracy. Since the accuracy and reliability of the electrical equipment used to read or record the electromotive forces produced by thermocouples appear to be more definitely known than the characteristics of the thermocouples themselves, this work has been undertaken to help to some extent in determining what happens under certain conditions of treatment to some of the commonly used types of thermocouples.

In work of this nature the question naturally arises as to whether or not it is necessary to calibrate each individual thermocouple when the wires come from the same spools, how much deviation there is in the same type of thermocouple made of wires from different lots, and what effect heating the thermocouples to different temperature levels has on their electromotive force-temperature relationship. Although various investigators mention factors which tend to affect the electromotive force-temperature relationship of different types of thermocouples (1, 3, 5-7, 9-12), actual experimental data are very limited. Roeser and co-workers state that the guarantee limits on chromel-alumel thermocouples have been fixed by the manufacturers at $\pm 2.8^{\circ}\text{C}$. (5°F .) in the range 0° to 350°C . and at ± 0.75 per cent in the range 350° to 1250°C . Roeser and co-workers tested a considerable number of chromel-alumel thermocouples and found them to fall within these limits. They state (6) that, inasmuch as practically all base metal thermocouple wire produced in this country is annealed or given a "stabilizing heat treatment" by the manufacturer, such treatment is generally considered sufficient, and it is seldom found advisable to anneal the wire further. White and co-workers (9, 11) published articles in 1910 on the general reliability of thermocouples and the proper means of selecting homogeneous thermocouple wires. They give electromotive force-temperature relationships of two copper-constantan thermocouples between the temperatures of 0° and 100°C .

The ordinary user of thermocouples is seldom concerned with preliminary examination or preparation of his thermocouple wires, such as making homogeneity tests and annealing, and it is for him that the data presented here on copper-copel,

The results obtained seem to indicate that for the temperature range, for the size of wires, and for the conditions under which the tests were made: (1) Heat treatment of copper-copel, copper-constantan, and chromel-alumel thermocouples above about 200°C . causes them to indicate temperatures which are different from those before heat treatment, the discrepancy, in general, being greater the higher the temperature of heat treatment; moreover, measurements of lower temperatures show, in general, less discrepancy than measurements of higher temperatures. (2) Heat treatment of copper-copel and copper-constantan thermocouples at temperatures between about 200°C . and 300 - 350°C . causes them to indicate a higher temperature than before such heat treatment; heat treatment above 300 - 350°C . causes them to indicate a lower temperature. It may be concluded that copper-copel and copper-constantan thermocouples possess a rather high degree of reliability if used in the temperature range 0° to 200°C .

copper-constantan, and chromel-alumel thermocouples are principally intended. Although copel wire is generally considered to belong to that class of wires known as constantan, a considerable difference was found in the electromotive force-temperature relationships of the copper-copel and copper-constantan thermocouples investigated, because of the difference in composition of copel and constantan. (Those made with constantan gave, up to 200°C ., about 91 per cent of the e. m. f. values given by those made with copel.) The copel wire was obtained from the Hoskins Manufacturing Company and had a composition of 55 per cent copper and 45 per cent nickel; the constantan wire was purchased from the Leeds & Northrup Company and had a composition of about 53.6 per cent copper, 44.4 nickel, 1.6 manganese (the remaining 0.4 per cent being impurity).

Calibration of Thermocouples

In this work thermocouples were calibrated either at fixed points, such as the boiling points, freezing points, and

transition points of pure substances, or by comparison with standard thermocouples. In the latter case either a copper block or a boiling liquid was used as the source of heat.

To determine any desired number of points over a temperature range of 0° to 450° C., the copper block shown in Figure 1 was found suitable:

It was made by casting a 23-kg. piece of electrolytic copper so that it measured 9 cm. square and 32 cm. long. Cast in the copper block were two 500-watt iron-sheathed heating coils located close to the outside; two 9.5-mm., two 6.4-mm., and one 4.7-mm. Shelby steel tubes, placed close together in the middle to serve as thermocouple or thermometer wells; and a coil of 6.4-mm. Shelby steel tubing to facilitate cooling the block, when necessary, by blowing air through it. This unit was placed in a heavy galvanized iron can 18 cm. in diameter and 40 cm. long, the space between the block and the container being filled with Sil-O-Cel.

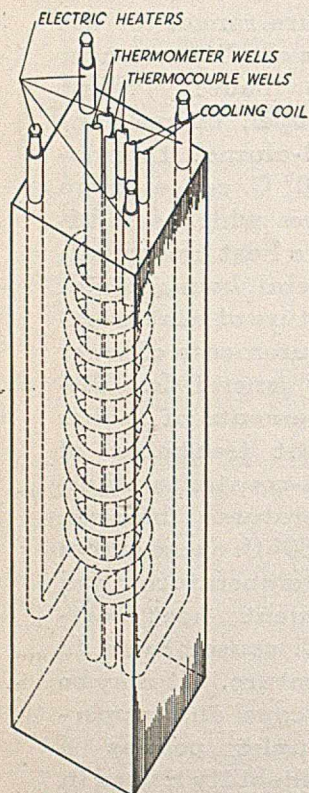


FIGURE 1. COPPER BLOCK

peratures to be read to $\pm 0.05^\circ$ C. with thermocouples developing electromotive forces of the order of magnitude of those of copper-constantan or copper-copel.

If the equation of the e. m. f. vs. temperature for the thermocouple is known, and if the curvature of the over-all calibration curve is not excessive, it has been found convenient, if fairly accurate readings from a curve are desired, to assume that a straight-line relation exists between e. m. f. and temperature over 5° C. intervals, plotting the curve in sections as shown in Figure 2 instead of in one long curve. The type of plot shown in Figure 2, using a scale of 1 mm. for 0.1° C. and 20 mm. for 0.1 millivolt, is used in this laboratory for copper-copel thermocouples, since it is possible to plot the range 0–300° C. on a chart 46×50 cm.

Standard thermocouples used in this laboratory, many of which have been calibrated by the Bureau of Standards, are checked occasionally against fixed points such as the transition point of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ at 32.38° C. (2, 5, 8, 11) and the boiling points (at 760 mm. of mercury pressure) of *n*-hexane at 68.7° C., *n*-heptane at 98.4° , water at 100.0° , *n*-octane at 125.6° , and naphthalene at 217.96° .

In calibrating a thermocouple (or thermometer) it may be placed either in the tube containing the standard thermocouple or in one of the other tubes, the tips touching the bottom in either case. Because of the high heat conductivity of the copper, the bottoms of all the tubes are at the same temperature. Readings may be obtained both on heating and cooling the block, if desired. Previously determined values of the amount of current necessary to keep the block at any desired temperature level facilitates manipulation. It is not, however, necessary to wait for the block to come to a constant temperature, unless some one definite temperature is desired. With such a large mass the temperature changes slowly, unless a large amount of heat is used to raise the temperature quickly from one level to another. A double-pole, double-throw switch enables readings to be taken rapidly, first with one couple and then with the other; if on going back to the first couple the reading is the same, it shows that the temperature of the block has been constant during that period. A Leeds & Northrup No. 8662 portable precision potentiometer with a lower scale range of 0 to 16 millivolts enables tem-

All thermocouples for accurate work are made either by soft soldering the hot junction, using a nonacid flux if the wire is fine, or by silver soldering, using borax as a flux. In either type of soldering the thermocouple is never held in an open flame, a soldering iron being used as the heat transfer medium. When using the higher melting silver solder, one end of the iron is heated while the molten solder and flux are allowed to run down onto the opposite end. By dipping the clean ends of the wires to be soldered into this molten mass while pressing them at the same time against the hot iron to furnish plenty of heat, a firm, neat junction is readily obtained.

Cold junctions are maintained at 0° C. by means of a stiff slush of finely crushed ice and water in a Dewar flask. Experience has shown the necessity of periodically replacing the melted ice with more finely crushed ice inasmuch as over a period of a few hours equilibrium may no longer exist between the water and ice; the latter rises to the top of the water and thus allows the water in the bottom of the Dewar flask to warm up gradually.

Method of Checking Thermocouples

The easiest means of checking the thermocouples was to determine the e. m. f. at two temperatures by means of liquids boiled in a modified Cottrell boiling point apparatus previously described (4). In each determination a standard thermocouple was always present to allow the true temperature of the boiling solution to be known. Inasmuch as all checking was done at the prevailing atmospheric pressure, the change in temperature with pressure of the boiling solution was obtained from the temperatures as given by the standard couple. Knowing the change in electromotive force per degree for the particular type of couple being checked, e. m. f. readings could be corrected, if necessary, for any slight change which might occur in the boiling temperature due to barometric pressure change from 731 mm., which seemed to be the most prevalent during all the tests. Thus

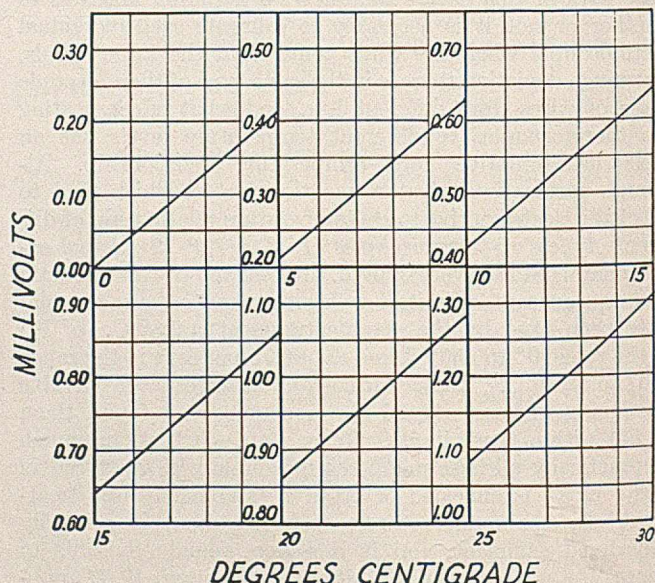


FIGURE 2. COPPER-COPEL THERMOCOUPLE CALIBRATION

all readings were put on the same barometric basis. In checking the thermocouples, two liquids were used; toluene served to give values at 109.2° C., and a cut obtained from the fractionation of triisobutylene gave values at 177.7° C., both at a barometric pressure of 731 mm.

The thermocouples to be checked were carefully tied to a sillimanite tube so that they did not touch one another, and

the tips were directly exposed to the mixture of boiling liquid and vapor impinging upon them. As many as four thermocouples in addition to the standard could be handled at once in this way; a series of double-pole, double-throw knife switches facilitated connection with the potentiometer.

In this type of calibration the ultimate purity of the boiling liquid is unimportant with the type of boiling point apparatus used as long as no liquid is withdrawn during calibration. For this reason such a method serves as an easy means of calibrating thermocouples at temperatures up to 200° or even 225° C. For example, a series of hydrocarbon fractions might be used as the boiling liquids, or points could be obtained from a petroleum fraction or other liquid having a relatively wide boiling range by removing a little product at a time, thus progressively increasing the boiling point. Similarly, results might be obtained by boiling liquids at a series of different pressures.

Agreement of Thermocouples

In determining the agreement of thermocouples made from the same and from different spools of wire, the copper-copel thermocouples were made from No. 30 B & S gage enameled copper wire (John A. Roebing's Sons Company) and No. 26 B & S gage enameled copel wire (Hoskins Manufacturing Company); the chromel-alumel thermocouples were made from No. 22 B & S gage asbestos-covered wire (Leeds & Northrup Company). The following table shows that the copper-copel thermocouples made from the same spools of wire agree within 0.1° C. up to a temperature of about 180° C:

Thermocouple No.	Agreement at 109.2° C.		Agreement at 177.0° C.	
	E. m. f. Millivolts	Deviation from standard ° C.	E. m. f. Millivolts	Deviation from standard ° C.
2 (standard)	5.151	...	8.837	...
1	5.151	0.0
3	5.151	0.0
4	5.147	-0.1	8.833	-0.1
5	5.149	-0.05	8.832	-0.1
6	5.149	-0.05	8.832	-0.1
7	5.147	-0.1	8.832	-0.1

A copper-copel thermocouple made from a different spool of copel wire read 1.9° C. lower than the standard copper-copel couple (No. 2) at 109.2° C.

The following table shows that at 109.2° C. the chromel-alumel thermocouples made from the same spools of manufacturer's matched wire differ from one another considerably more than do the copper-copel thermocouples; this behavior might be expected where copper wire is known to be of high purity, thus making that half of the couple wholly reproducible.

Thermocouple No.	E. M. F. Millivolts	Deviation from Standard ° C.
1 (standard)	4.546	...
2	4.529	-0.45
3	4.522	-0.6
4	4.548	+0.05
5	4.547	0.0
6	4.528	-0.45

Thermocouples made from different spools of chromel and alumel wire (but from manufacturer's matched wires) may give readings which are considerably different at the same temperature (109.2° C.).

Thermocouple No.	E. M. F. Millivolts	Deviation from Standard ° C.
1 (standard)	4.546	...
7	4.440	-2.55
8	4.487	-1.4
9	4.470	-1.7

Table I shows that the difference in e. m. f. of the two chromel-alumel thermocouples tested (manufacturer's

matched wires) is practically proportional to the e. m. f. This is usually true of thermocouples of the same general class. No previous heat treatment was given to these thermocouples before testing as shown. Despite the deviation shown between the two thermocouples, they do come within the manufacturer's specifications for such wires;¹ the values shown here fall on either side of the manufacturer's calibration for chromel-alumel thermocouples. In this range a deviation of $\pm 2.8^\circ \text{C.}$ ($\pm 5^\circ \text{F.}$) from the specified values is allowable. It should be remembered that the chromel-alumel thermocouple is primarily a high-temperature couple and gives good results at high-temperature levels where thermocouples of the copper-constantan type are not suitable.

TABLE I. VARIATION AT DIFFERENT TEMPERATURE LEVELS OF CHROMEL-ALUMEL THERMOCOUPLES MADE FROM DIFFERENT SPOOLS OF WIRE

Thermocouple No.	True Temp. ° C.	E. M. F. Millivolts	Deviation ° C.
2		2.087	
7	50.9	2.041	1.1
2		4.529	
7	109.2	4.440	2.15
2		6.399	
7	154.9	6.287	2.75
2		7.211	
7	175.0	7.073	3.4

Changes in Electromotive Force-Temperature Relationships

Whether or not a thermocouple will give the same e. m. f. reading for a given temperature after having been heated to some higher temperature level is important if accurate results are desired. White (9, 11) showed that the vital part of a thermocouple is that along which there is a temperature gradient, since it is that part which mainly determines the calibration and constancy. If the thermocouple is always immersed to the same extent in the hot medium, and if the temperature distribution in the temperature gradient from the hot medium to the cooler medium is always the same, there is no change in the electromotive force-temperature relationship with heating and use even if the wires are not homogeneous over this section. However, it is seldom that the ordinary user of thermocouples—unless it be in some industrial process where units are run under fixed conditions—does not vary one or both of these important items.

Although some authorities on thermocouples advise annealing the wires before use, most users feel that this is unnecessary. To determine how different types of thermocouples changed on heating, they were treated in the previously described copper block for varying periods of time at different temperature levels; the e. m. f. was determined, both before and after the heat treatment, in the boiling point apparatus. By checking the thermocouples in the boiling point apparatus where the depth of immersion was only about 11 cm. as compared with the 37-cm. length heated in the copper block, the change in the electromotive force-temperature relationship due to any inhomogeneity in the wire was easily determined. This was true because a large part of the wire which had been subjected to heat treatment in the copper block was, when checked in the boiling point apparatus, located in the temperature gradient section. If the wires over this section had been perfectly homogeneous and unaffected by heat treatment, no difference in the electromotive force-temperature relationship would have been found. Since

¹ Hoskins Manufacturing Company's catalog on chromel wire.

TABLE II. CHANGE IN ELECTROMOTIVE FORCE-TEMPERATURE RELATIONSHIPS OF THERMOCOUPLES AFTER HEAT TREATMENT

Thermo- couple No.	Change at 109.2° C.		Change ^a at 177.0° C.		Heat Treatment	Thermo- couple No.	Change at 109.2° C.		Change at 177.0° C.		Heat Treatment
	E. m. f. Millivolts	ΔT ° C.	E. m. f. Millivolts	ΔT ° C.			E. m. f. Millivolts	ΔT ° C.	E. m. f. Millivolts	ΔT ° C.	
Copper-Copel Thermocouples						Chromel-Alumel Thermocouples					
4	5.147	...	8.833	...	Before heating	3	4.522	Before heating
	5.158	+0.2	8.852	+0.35	10 hr. at 315° C.		4.540	+0.45	Heated to 430° C. and cooled; total time, 10 hr.
6	5.149	...	8.832	...	Before heating						
	5.159	+0.2	8.847	+0.25	10 hr. at 315° C.						
	5.159	+0.2	8.852	+0.35	20 hr. at 315° C.						
5	5.149	...	8.832	...	Before heating		4.539	+0.45	Heated to 430° C. as above and 10 hr. at 315° C.
	5.125	-0.45	8.788	-0.8	Heated to 430° C. and cooled; total time, 10 hr.						
							4.539	+0.45	Heated to 430° C. as above and 20 hr. at 315° C.
7	5.147	...	8.832	...	Before heating						
	5.159	+0.25	8.844	+0.2	10 hr. at 235° C.						
	5.158	+0.25	8.851	+0.35	10 hr. at 235° C. and 10 hr. at 285° C.	4	4.548	Before heating
					10 hr. at 235° C., 10 hr. at 285° C., and 10 hr. at 360° C.		4.547	0.0	10 hr. at 315° C.
	5.135	-0.2	8.809	-0.4	10 hr. at 235° C., 10 hr. at 285° C., and 10 hr. at 360° C.		4.551	+0.05	20 hr. at 315° C.
					10 hr. at 235° C., 10 hr. at 285° C., 10 hr. at 360° C., and 10 hr. at 430° C.	5	4.547	...	7.318	...	Before heating
	5.110	-0.7	8.761	-1.25			4.559	+0.25	7.339	+0.5	10 hr. at 235° C.
							4.555	+0.15	7.332	+0.35	10 hr. at 235° C., 10 hr. at 285° C., 10 hr. at 360° C.
							4.560	+0.30	7.345	+0.65	10 hr. at 235° C., 10 hr. at 285° C., 10 hr. at 360° C.
							4.562	+0.35	7.347	+0.7	10 hr. at 235° C., 10 hr. at 285° C., 10 hr. at 360° C., 10 hr. at 430° C.
Copper-Constantan Thermocouples						Chromel-Alumel Thermocouples					
1	4.694	...	8.041	...	Before heating						
	4.696	+0.05	8.053	+0.25	10 hr. at 315° C.						
2	4.693	...	8.040	...	Before heating						
	4.696	+0.05	8.049	+0.15	10 hr. at 285° C.		4.528	...	Not determined	...	Before heating
	4.696	+0.05	8.046	+0.1	10 hr. at 235° C., 10 hr. at 285° C.		4.541	+0.35	7.316	...	10 hr. at 360° C.
					10 hr. at 235° C., 10 hr. at 285° C., 10 hr. at 360° C.		4.547	+0.5	7.317	...	10 hr. at 285° C., 10 hr. at 360° C., 10 hr. at 430° C.
	4.684	-0.2	8.030	-0.2							
	4.682	-0.25	8.019	-0.4							

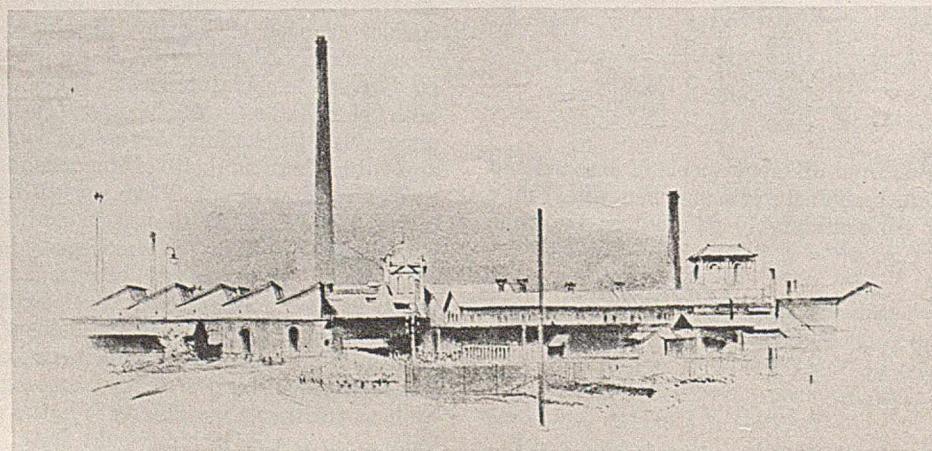
all the thermocouples were treated and tested in exactly the same manner, the results are directly comparable, though they would not necessarily hold for thermocouples tested in a different manner.

The thermocouples tested had never before been heated above 180° C. In some instances they were the same as were previously tested to determine how thermocouples made from the same spools of wire varied from one another. The copper-copel and chromel-alumel thermocouples were in all cases of the same size and description as those previously used, whereas the copper-constantan thermocouples were made from No. 22 B & S gage asbestos-covered constantan wire (Leeds & Northrup Company) and No. 18 cotton-covered copper bell wire. Table II summarizes the results obtained on copper-copel, copper-constantan, and chromel-alumel thermocouples.

Literature Cited

- (1) Eichelberger, W. C., *J. Am. Chem. Soc.*, 56, 800 (1934).
- (2) Foote, P. D., Fairchild, C. O., and Harrison, T. R., Bur. Standards, *Technol. Paper* 170, 23, 64-74 (1921).
- (3) Pacific Gas Assoc. Comm., *Gas Engineers' Handbook*, 1st ed., p. 551, New York, McGraw-Hill Book Co., 1934.
- (4) Quiggle, D., Tongberg, C. O., and Fenske, M. R., *IND. ENG. CHEM., Anal. Ed.*, 6, 466 (1934).
- (5) Reilly, J., and Rae, W. N., "Physico-Chemical Methods," 2nd ed., pp. 283, 444, New York, D. Van Nostrand Co., 1932.
- (6) Roeser, W. F., Dahl, A. I., and Gowens, G. J., *Bur. Standards J. Research*, 14, 239, 247 (1935).
- (7) Walger, O., and Lorenz, F. R., *Z. tech. Physik*, 11, 242 (1930).
- (8) Webb, T. J., and Lindsley, C. H., *J. Am. Chem. Soc.*, 56, 874 (1934).
- (9) White, W. P., *Phys. Rev.*, 31, 135 (1910).
- (10) White, W. P., *Rev. Sci. Instruments*, 4, 142 (1933).
- (11) White, W. P., Dickinson, H. C., and Mueller, E. F., *Phys. Rev.*, 31, 159 (1910).
- (12) Wood, W. P., and Cork, J. M., "Pyrometry," p. 27, New York, McGraw-Hill Book Co., 1927.

RECEIVED December 14, 1936.



Courtesy, CIBA

Minimizing Wood Shrinkage and Swelling

The hygroscopicity and subsequent swelling and shrinking of dry wood are decreased by heating in various gases above thermal decomposition temperatures. Greater reductions in hygroscopicity are obtained in an oxidizing than in a reducing atmosphere for the same heating conditions; but, by increasing the temperature, equal reductions in hygroscopicity can be obtained in reducing atmospheres. The darkening of the wood on heating appears to vary directly with the resulting reduction in hygroscopicity, regardless of heating conditions. Soaking in water after heating has but a slight tendency to restore the original hygroscopicity. Heating wood in water-saturated atmospheres has no permanent effect upon the swelling and shrinking.

FOR a long time it has been recognized that excessive heating of wood reduces its hygroscopicity. Tiemann (10) found that heating air-dry wood in superheated steam to about 150° C. for 4 hours reduced the subsequent moisture absorption by 10 to 25 per cent with but relatively small reductions of the strength, except for red oak which showed a reduction in crushing strength and modulus of rupture of about 60 per cent. An unpublished Forest Products Laboratory report (1) shows that heating black gum in dry air at 205° C. for 6 hours reduces the subsequent hygroscopicity to almost half of its original value with only a slight accompanying decrease in its strength. Koehler and Pillow (5) and Pillow (6) heated air-dry Sitka spruce and ash to 138° C. for 1 to 8 days and obtained reductions in the equilibrium moisture content at several different relative humidities for the longer time of heating of 30 to 40 per cent with accompanying reductions in the crushing strength of 15 to 25 per cent and reductions

¹ Other papers in this series appeared in April, 1935, page 401, in December, 1935, page 1480, and in October, 1936, page 1164.

Effect of Heating in Various Gases¹

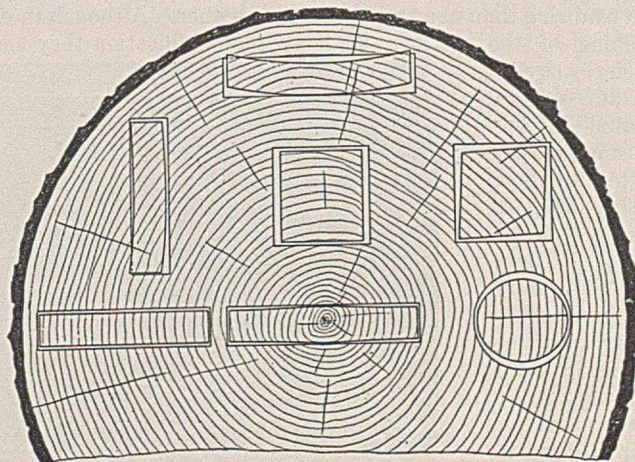
ALFRED J. STAMM AND L. A. HANSEN
Forest Products Laboratory, Madison, Wis.

in the toughness of 50 to 75 per cent. Data of Greenhill (3) on the relation between maximum strength of beech in tension perpendicular to the grain and the moisture content at different temperatures indicate that the loss of strength on heating of the wood decreases with a decrease in moisture content to a negligible value for very dry wood. Although the temperature range covered by these data is below the temperatures required to obtain appreciable antishrink efficiencies, they indicate the possibility that less loss in strength will occur if the wood is adequately seasoned at normal kiln temperatures before being subjected to the higher temperatures required to reduce its subsequent swelling and shrinking.

Heating Experiments

The purpose of this preliminary research was to confirm this loss of hygroscopicity of wood which occurs on heating, and to determine its permanence and how it is affected by the medium in which heating occurs.

Sections of white pine 9 cm. long in the tangential direction (the direction of maximum swelling), 2 cm. radially, and 0.6 cm. in the fiber direction, were used. The short dimension in the fiber direction ensured rapid attainment of moisture equilibrium and made possible the cutting of a number of adjacent sections from the wood with a minimum variation of structure from section to section. Four specimens were suspended in a small steel bomb that was heated on the outside by an electrical resistance coil and lagged with asbestos insulation. The temperature was determined by a thermocouple inserted into a well in the wall of the bomb. The temperature was controlled manually to about 2° C. When the specimens were heated in gases other than air, the bomb was evacuated and the gas admitted several times to ensure the elimination of air. The moisture content of wood used in the tests was about 6 per cent. When the heating was carried out in presence of water vapor, a large excess of water over that necessary to saturate the specimens was placed in the bottom of the bomb.



CHARACTERISTIC SHRINKAGE AND DISTORTION OF FLATS, SQUARES, AND ROUNDS AS AFFECTED BY THE DIRECTION OF THE ANNUAL GROWTH RINGS

Effect of Gases

Table I gives the effect of heating the white pine sections in different dry atmospheres upon the subsequent swelling and shrinking. Measurements were made of both the tangential dimension change and the weight change occurring when the specimens were alternately brought to equilibrium with 30 and 90 per cent relative humidity in humidity rooms held at 26.7° C. The specimens were exposed 2 weeks at each relative humidity, which proved adequate for the attainment of equilibrium. The antishrink efficiencies are calculated on the basis of the reduction in dimensional change or weight change between 90 and 30 per cent relative humidity. These changes

TABLE I. EFFECT UPON ANTISHRINK EFFICIENCY OF HEATING DRY WOOD IN VARIOUS GASES AND SUBSEQUENT SOAKING IN WATER FOR 5 DAYS

Gas	Temp. ° C.	Time of Heating Hr.	Antishrink Efficiency			
			—Before Soaking ^a —		—After Soaking ^b —	
			Tangential dimension basis %	Weight basis %	Tangential dimension basis %	Weight basis %
Hydrogen	165	0.25	5.9	6.3	2.8	1.8
	205	2.00	16.0	17.0	11.5	11.4
	260	2.00	32.0	32.0	31.8	31.2
Illuminating gas	165	0.25	8.2	8.5	6.3	4.8
	205	2.00	18.0	19.0	14.0	13.2
	205	6.00	20.6	19.0	19.6	17.6
Air	165	0.25	8.3	6.4	4.9	4.4
	205	2.00	17.5	19.0	14.0	12.3
	205	6.00	23.2	21.2	22.0	21.0
Oxygen	165	0.25	10.0	12.0	7.0	6.1
	205	2.00	20.7	21.0	15.4	13.6
	205	6.00	28.0	30.0	28.7	27.2

^a In terms of retardation of the dimension and weight changes, for the average of four specimens, per unit change of the untreated controls when alternately brought to equilibrium with 30 and 90 per cent relative humidity.

^b Based upon the second humidity change cycle as the first is appreciably affected by hysteresis (11).

are referred to the corresponding change for the control. The sections heated in dry atmospheres were soaked in water for 5 days after the humidity cycles were complete and then subjected again to the humidity change cycles. Only the second subsequent humidity cycle was used in the calculations, since the first would involve a higher desorption curve due to the soaking and thus give results affected by the sorption hysteresis (11). The same is true for sections heated in the presence of water. The first cycle gave appreciable negative efficiencies because of this hysteresis effect.

Heating the sections for as short a time as 15 minutes at 165° C., a temperature at which thermal decomposition was just becoming appreciable, gave definite antishrink efficiencies in all the dry gases. Increasing the temperature and the time of heating increased the antishrink efficiency. In each case the efficiency was greater in an oxidizing than in a reducing atmosphere. Subsequent soaking of the sections in water reduced the antishrink efficiency by a relatively constant amount, regardless of the heating conditions. Sections heated in the presence of water vapor gave very small uncorrelatable antishrink efficiencies after the first cycle, part of the values being positive and part negative (average antishrink efficiency 0.25 per cent, mean deviation 1.1 per cent). These values for all the temperatures and times may be considered within experimental error of being zero; that is, heating in water vapor has no effect upon the antishrink efficiency after the first humidity change cycle.

The sections heated at 165° C. were but slightly darkened without a perceptible difference in appearance between the sections heated in the various gases. The darkening was more appreciable after heating for 2 hours at 205° C. and

still more so after the time was increased to 6 hours. In each of these cases the darkening obtained by heating in the different gases increased in the following order: hydrogen, illuminating gas, air, and oxygen. The specimens heated to 260° C. in hydrogen, however, were as dark as those heated for 6 hours at 205° C. in oxygen. The darkest specimens were about the color of unfinished walnut. The antishrink efficiency appears to parallel the darkening of the wood, irrespective of the temperature and the gas used.

Although part of the antishrink efficiency may have been due to oxidation in the cases where the wood was heated in air and oxygen, it is hard to imagine that this was a major factor since equal efficiencies can be obtained by heating in hydrogen at a slightly elevated temperature. The phenomenon can best be explained on the basis of thermal decomposition. Loss of water of constitution is the first thermal reaction. If this loss were due to the formation of an ether linkage between two adjacent cellulose chains through adjacent hydroxyl groups, the loss in hygroscopicity could be readily explained. Not only would the hygroscopicity be reduced because of the substitution of the less hygroscopic ether group for the more hygroscopic hydroxyl groups, but also because of the parallel bonding of the cellulose chains. Staudinger (9) showed that the formation of such bridges between the chains in polystyrene resins with *p*-divinylbenzene, cuts down the swelling tremendously even when only enough *p*-divinylbenzene is used to form a single bridge for several thousand molecules of monomeric styrene. Just an occasional cross link evidently cuts down appreciably the tendency for water to be taken up

between structural chains. The formation of ether linkages between the hygroscopic hydroxyl group not only explains the decreased hygroscopicity of wood heated in dry atmospheres but also the fact that heating in the presence of a large excess of water vapor causes no change in hygroscopicity. The presence of an excess of water vapor would depress the thermal reaction in which water is evolved according to the principle of LeChatelier and thus markedly reduce the tendency to form the ether bridges. If the change in hygroscopicity were merely a physical change, such as that postulated by Urquhart (11) to explain hysteresis, soaking of the specimens in water should largely restore their original hygroscopicity. This investigator believes that the free hydroxyl groups of cellulose, which are originally satisfied to a large extent by water, draw closer together on drying and finally mutually satisfy one another. Although these bonds are only partially broken on rehumidification they should be largely broken on soak-



PARQUETRY FLOORING OFFERS POSSIBILITIES OF CHEMICAL TREATMENT TO MINIMIZE SWELLING AND SHRINKING

ing in water and the active groups again satisfied by water. The reversible part of the antishrink efficiency—that is, the difference between the antishrink efficiency obtained directly after heating and that subsequent to soaking in water—is practically constant, regardless of heating conditions. This part is undoubtedly due to a physical effect such as that given by Urquhart (11). The physical mutual satisfaction of hydroxyl groups evidently increases until the free water is rather completely removed but does not increase on further heating.

These preliminary results indicate that the antishrink efficiency resulting from the excessive heating of dry wood in several common gases is sufficiently great and permanent to warrant a more extensive investigation in which the strength properties are simultaneously studied. Although this method of minimizing the swelling and shrinking of wood does not

appear to be so effective as methods previously described (2, 4, 7, 8), its possible value rests on the fact that it would be relatively inexpensive.

Literature Cited

- (1) Betts, N. D., Forest Products Lab., *File No. 2B468* (1916).
- (2) Browne, F. L., *IND. ENG. CHEM.*, **25**, 835 (1933).
- (3) Greenhill, W. L., *J. Council Sci. Ind. Research*, **9**, 265 (1936).
- (4) Hunt, G. M., U. S. Dept. Agr., *Circ. 128* (1930).
- (5) Koehler, A., and Pillow, M. Y., *Southern Lumberman*, Dec. 19, 1925, 219.
- (6) Pillow, M. Y., *Wood Working Ind.*, Oct., 1929, 8.
- (7) Stamm, A. J., and Hansen, L. A., *IND. ENG. CHEM.*, **27**, 1480 (1935).
- (8) Stamm, A. J., and Seborg, R. M., *Ibid.*, **28**, 1164 (1936).
- (9) Staudinger, H., *Trans. Faraday Soc.*, **32**, 323 (1936).
- (10) Tiemann, H. D., *Lumber World Rev.*, **28**, No. 7, 10 (1915).
- (11) Urquhart, A. R., *J. Textile Inst.*, **20**, 125T (1932).

Treatment with Sucrose and Invert Sugar

ALFRED J. STAMM

The treatment of wood with sucrose and invert sugar solutions greatly reduces the subsequent shrinkage. Shrinkage takes place when the relative vapor pressure under which the specimens are dried is less than the relative vapor pressure of the treating solution at the concentration attained when evaporation has proceeded to the fiber-saturation point. The large reduction in shrinkage to the oven-dry condition is due to the deposition of sugar within the swelling structure. This reduction

in shrinkage can be calculated from the partial specific volume of sugar in the concentration attained within the swollen structure on the basis that this concentration becomes equal to the corresponding bulk concentration.

Invert sugar reduces the dimension changes of wood to a greater extent than sucrose and should serve as a good antishrink agent under conditions that will not be too conducive to the leaching of the sugar from the wood.

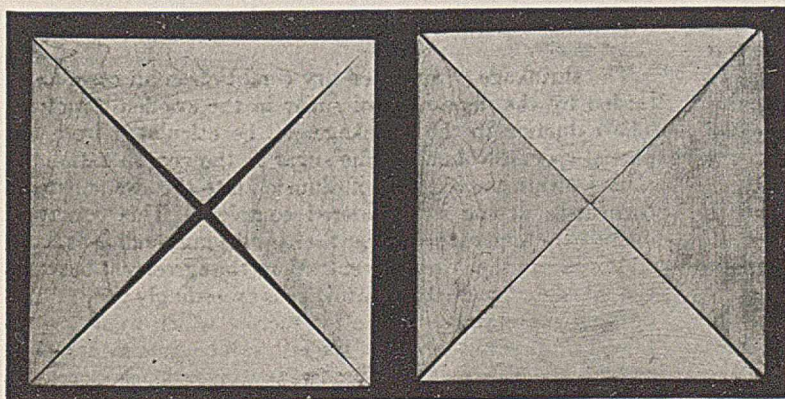
THE treatment of wood with sugar solutions dates back to the Powell patent of 1904 (7). Powell did not consider the stabilization of the dimensions of the wood but was rather interested in the prevention of decay. The following year Tiemann showed that sugar materially reduces the shrinkage of wood as a result of the retention of the solution. Further measurements made by him in 1928 are summarized by Hunt (4). Antishrink efficiencies (the reduction

of the dimension changes of the treated specimens per unit dimension change of the controls) of better than 70 per cent were obtained between the saturated and the air-dry condition for specimens treated with concentrated sugar solutions.

This research was undertaken to determine more definitely the effect of sugar treatment upon the shrinking of wood and to find out if the shrinkage is governed by the same principles as were found to hold for salt treatment (9). It was also desirable to determine the dimension stabilization of wood treated with invert sugar compared to that treated with sucrose, since invert sugar had been shown by Dittmar (3) to be considerably more hygroscopic than sucrose, and by Leete (5) and Pike (6) to increase the moisture retention of paper when used in only moderate concentrations.

Experimental Procedure

Thin sections of northern white pine, 2 mm. in the fiber direction and 4.4 cm. in the other two directions, were used for these measurements. Oven-dry sections were weighed, and the tangential and radial dimensions determined. The sections were then soaked in water or sugar solutions, with intermittent applications of suction to remove the air. After soaking for 3 days to permit diffusion of the sugar into the fine structure, the sections were brought to equilibrium with the decreasing relative vapor pressures of



UNTREATED WOOD SHOULD BE DRIED TO THE MOISTURE CONTENT PREVAILING IN SERVICE TO PREVENT SUBSEQUENT SHRINKAGE OR SWELLING
Left, wood put in service too wet; right, too dry.

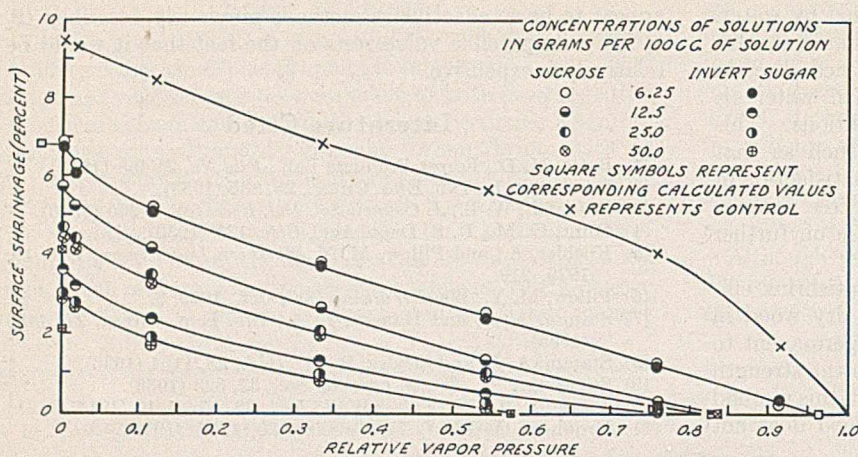


FIGURE 1. SHRINKAGE vs. RELATIVE VAPOR PRESSURE FOR NORTHERN WHITE PINE SECTIONS SATURATED WITH SUCROSE AND INVERT SUGAR

91.2, 75.8, 54.1, 32.9, and 11.7 per cent. These vapor pressures were obtained by drawing air at room temperature (approximately 25° C.) through towers containing saturated solutions of barium chloride, sodium chloride, manganese chloride, magnesium chloride, and lithium chloride, respectively, and then through open dishes of the saturated salt solutions placed on the bottom of vacuum desiccators which served as the humidity chambers. Air was drawn through the system under a reduced pressure of about half an atmosphere at the approximate rate of 10 liters per hour. Under these conditions the theoretical relative vapor pressures in equilibrium with the saturated salt solutions were virtually attained. Experiments showed that the 2-week humidification period used for conditioning was ample for obtaining equilibrium. The sections were then dried at room temperature over phosphorus pentoxide for 2 weeks, followed by oven drying over phosphorus pentoxide for 3 days at 110° C. The sections were weighed and measured after each of these periods.

Relation of Shrinkage to Relative Vapor Pressure

The sum of the tangential and the radial shrinkage in per cent (the approximate surface shrinkage) from the soaked condition to equilibrium with the various relative vapor pressures are plotted against the relative vapor pressure in Figure 1 for the average of three water-saturated sections and three sections completely filled with each of four different concentrations of sucrose and invert sugar solutions. The relative vapor pressure effective in drying over phosphorus pentoxide at room temperature under the conditions of these measurements was estimated from the shrinkage occurring from equilibrium with phosphorus pentoxide to the oven-dry condition, using the relationships of moisture content to relative vapor pressure and of linear moisture content to shrinkage. Completely water-swollen sections were found to swell only 0.1 per cent further on a surface swelling basis when enough sugar was added to the water in which the sections were soaking to bring the equilibrium concentration of liquid up to 50 grams per 100 cc. of solution. The shrinkage of the sugar-treated sections on drying can thus be referred to the shrinkage of the controls without involving a green dimension correction.

Figure 1 shows that the treatment of the wood sections with sugar solutions depresses the equilibrium shrinkage in a similar manner to that previously found for treatment with salts (9). The zero shrinkage and zero relative vapor pressure points (square symbols) correspond to the similar circular symbols and represent calculated points. The zero shrinkage points were calculated on the basis of the concentration of the solutions virtually attaining the same concentration within the swelling structure of the cell wall as the bulk concentration. The completely saturated sections contained 214 per cent water on the basis of the dry weight of the wood; the

fiber-saturation point on the same basis from the shrinkage data (Figure 2) is 28.5 per cent. In evaporating the free water from the wood, the volume is thus decreased 7.5 fold. Since the dimensions of the wood are virtually unaffected by the presence of the sugars, this last figure represents the increase in concentration of sugar solution occurring when a saturated section is dried to the fiber-saturation point. The relative vapor pressure in equilibrium with this concentration was obtained from the relative vapor pressure-concentration relations for sucrose given in the International Critical Tables, and the similar relation for invert sugar given by Dittmar (3). Initial sucrose concentrations of 12.5 grams per 100 cc. of solution and above give concentrations above saturation after evaporation. The sucrose will thus be deposited in the cell cavities, even if diffusion into the swollen structure is complete. The saturated solution gives a relative water vapor pressure of 83.5 per cent. Invert sugar is considerably more soluble than sucrose; hence in the higher concentrations it shows a greater depression of the relative vapor pressure. There is no definite solubility limit for invert sugar, since there is a gradual transition from a viscous solution to a glass. In concentrations above approximately 85 per cent, diffusion should be negligibly small, however, so that this has been considered as the limiting concentration for these calculations.

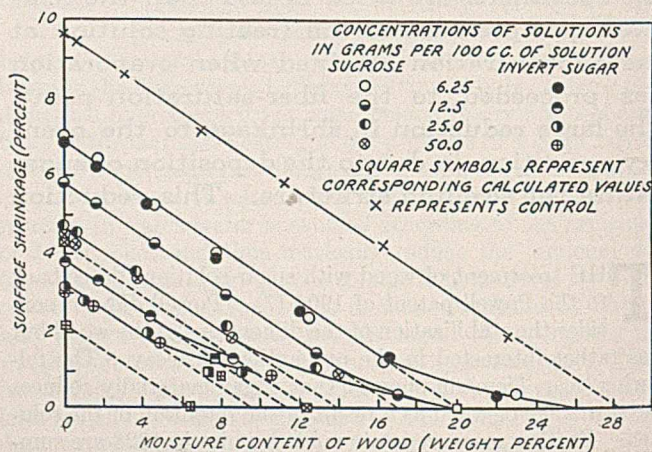


FIGURE 2. SHRINKAGE vs. MOISTURE CONTENT FOR NORTHERN WHITE PINE SECTIONS SATURATED WITH SUCROSE AND INVERT SUGAR

The shrinkage to the oven-dry condition in all cases is retarded by the deposition of sugar in the swollen structure. The reduction in the shrinkage can be calculated from the partial specific volume of the sugar in the concentration attained within the cell wall, if diffusion into the swollen structure upon drying is considered complete. This condition seems to be approached under the slow drying conditions used. In the case of the lower concentrations the agreement between the calculated and actual shrinkage is exceedingly good. The limiting shrinkage reduction for sucrose which would be attained if the solution within the cell wall became saturated is approached as a limit as the initial concentration is increased. The agreement for invert sugar is not quite so good, presumably because of less efficient diffusion of the solute into the cell wall as a result of the high viscosity of the solution. The general good agreement of the experimental and calculated

values of both ends of the curves indicates definitely that the concentrations within the cell wall approach closely the external bulk concentrations.

The data indicate that invert sugar is considerably superior to sucrose for the antishrink treatment of wood. In both cases nothing is gained by increasing the initial concentration above 25 grams per 100 cc. of solution for this particular wood with a green density of 0.35. For high-density woods this concentration should be somewhat increased. The antishrink efficiencies obtained with these sugars are superior to those obtained with the salts previously reported (9) because the curves are flatter. That is, the sugars with their high specific volume in solution show a larger reduction in the final shrinkage and a correspondingly larger relative vapor pressure at which shrinkage begins. The dimensional-change protection obtained with sugars is greatest over the relative humidity range of about 50 to 100 per cent. Over the range 20 to 50 per cent there is very little protection, even when the higher concentrations of invert sugar are used. Under actual use conditions, however, the stabilization of the dimensions may be better than Figure 1 indicates because the treated wood comes to equilibrium more slowly than the untreated and hence cannot respond as readily to humidity fluctuations.

Relation of Shrinkage to Moisture Content

In Figure 2 the data are plotted on the basis of surface shrinkage vs. moisture content of the dry wood. The relationship is practically linear with constant slope, as previously reported for wood and wood treated with various salts (8, 9). Except near the fiber saturation point the shrinkage seems to be a constant function of the moisture lost, irrespective of the sugar treatment. The calculated minimum moisture content for zero shrinkage was determined by multiplying the partial specific volume of water in the sugar solution when evaporation was carried to the fiber saturation point by the moisture content of the fiber saturation point. In each case these points fall on the extended lines through the experimental points. The specimens treated with the higher concentrations of invert sugar show a more pronounced deviation from the linear relationship at the higher moisture contents than those treated with sucrose. This behavior is due to the excess of invert sugar deposited in the coarse capillary structure holding water at relative vapor pressures above 22 per cent (3). A correction for the water held in this way by the excess invert sugar was made for the sections in equilibrium with a relative vapor pressure of 30 per cent. The corrected points represented by the square symbols fall practically on the extended straight lines. In the case of the sucrose no such correction need be made below a relative vapor pressure of 83.5 per cent.

Relation of Moisture Content to Relative Vapor Pressure

Figure 3 gives the relation between moisture content and relative vapor pressure. As the variation of moisture content with concentration for any given relative vapor pressure condition is relatively small and shows no definite trend with changes in concentration, average values have been plotted. The curves show that the equilibrium moisture contents are only slightly increased by the presence of sugar in concen-

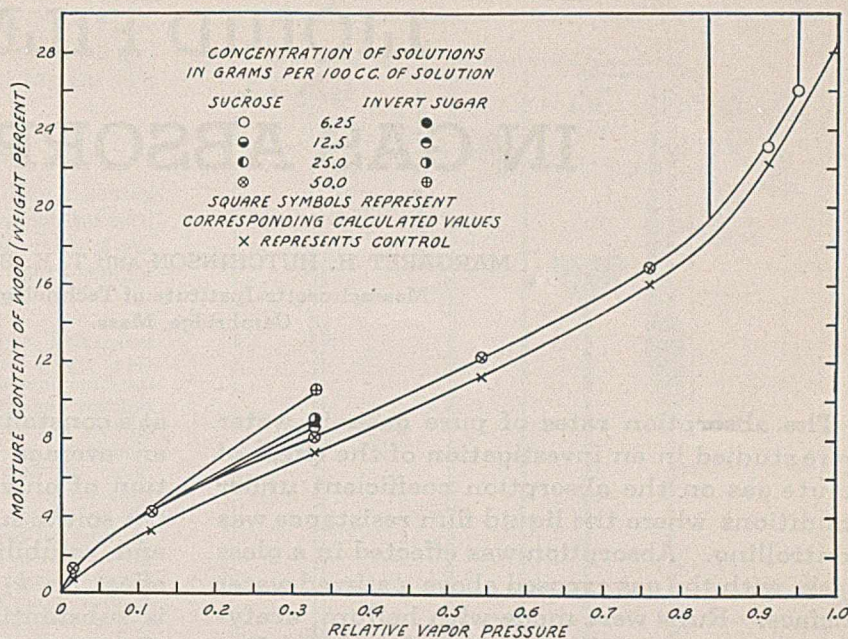


FIGURE 3. MOISTURE CONTENT vs. RELATIVE VAPOR PRESSURE FOR NORTHERN WHITE PINE SECTIONS SATURATED WITH SUCROSE AND INVERT SUGAR

trations that will not cause deposition of sugar in the coarse capillary structure and relative vapor pressures that will not permit this sugar to take on water. In the case of the higher concentrations of invert sugar, the increased moisture contents are due to water being held by the sugar in the coarse capillary structure. This behavior is in agreement with data of Barkas (1) for 4 per cent sucrose absorption, the data of Bateson (2) for 28 per cent sorbitol absorption by wood, and the data of Leete (5) for 2 per cent invert sugar absorption by paper. For comparison with the data of these authors, the 6.25 grams of sugar per 100 cc. of solution and multiples thereof used in the treatments reported here correspond to 13 per cent sugar on the basis of the dry weight of the wood and the corresponding multiples.

The data show that invert sugar in concentrations not exceeding about 25 grams per 100 cc. of solution serves as a good inexpensive antishrink agent for wood which is to be subjected to the higher relative humidity conditions. The difficulty involved in its practical use, however, seems to be in keeping the sugar in the wood and the tacky feeling that the wood assumes at high relative humidities. This difficulty can be largely avoided by minimizing the amount of sugar deposited in the coarse capillary structure.

Literature Cited

- (1) Barkas, W. W., *Proc. Phys. Soc. (London)*, 48, 1 (1936).
- (2) Bateson, R. G., *Chem. Trade J.*, 99, 493 (1936).
- (3) Dittmar, J. H., *IND. ENG. CHEM.*, 27, 333 (1935).
- (4) Hunt, G. M., *U. S. Dept. Agr., Circ.* 123 (1930).
- (5) Leete, J. F., *Paper Mill*, 58, No. 28, 21 (1935).
- (6) Pike, N. R., *Paper Trade J.*, 102, No. 5, 39 (1936).
- (7) Powell, W., *U. S. Patent* 755,240 (March 22, 1904); *Official Gaz. U. S. Pat. Office*, 109, 917 (1904).
- (8) Stamm, A. J., *IND. ENG. CHEM.*, 27, 401 (1935).
- (9) Stamm, A. J., *J. Am. Chem. Soc.*, 56, 1195 (1934).

RECEIVED February 23, 1937. Presented before the Division of Cellulose Chemistry at the 93rd Meeting of the American Chemical Society, Chape Hill, N. C., April 12 to 15, 1937.



LIQUID FILM IN GAS ABSORPTION

MARGARET H. HUTCHINSON AND T. K. SHERWOOD

Massachusetts Institute of Technology,
Cambridge, Mass.

The absorption rates of pure gases in water were studied in an investigation of the effect of solute gas on the absorption coefficient under conditions where the liquid film resistance was controlling. Absorption was effected in a glass flask, with the gas exposed above a stirred water surface. Runs were made with helium, acetylene, nitrogen, oxygen, carbon dioxide, sulfur dioxide, and chlorine.

At high stirrer speeds k_L is approximately proportional to the 0.6 power of the speed. In this range the results for eight different gases

at a constant stirring speed of 171 r. p. m. gave an average k_L of 3.2 with a maximum deviation of only about 20 per cent. Properties of the solute such as molecular weight, diffusivity, and solubility in water appear to have little effect on k_L , and it may be concluded that k_L is substantially independent of the nature of the solute gas.

At low speeds and at rest the coefficients for the several gases studied were influenced by natural convection effects and were independent of stirrer speed.

GAS absorption is a diffusional process involving the transfer of material from the gas to the liquid phase. As in most problems involving interphase transfer of material, the film concept is of value as an aid in visualizing the resistances encountered in both phases near the phase boundary, although the exact structure of the surface films is not known. Gas and liquid film resistances are additive, and each is represented as the reciprocal of the individual film coefficient, k_G or k_L . The rate of interphase transfer is given by the Lewis-Whitman equation (14):

$$N_A = k_G(p_G - p_i) = k_L(C_i - C) = K_G(p_G - p_L) = \frac{K_L(C_G - C)}{K_L(C_G - C)} \quad (1)$$

where N_A = rate of transfer of solute, gram moles/sq. cm./hour
 p_G = partial pressure of solute in main body of gas, atm.
 p_i = partial pressure of solute at gas-liquid interface, atm.
 p_L = equilibrium vapor pressure of solute corresponding to concentration of main body of solution, atm.
 C = concentration of solute in main body of solution, gram moles/cc.
 C_i = concentration of solute at gas-liquid interface, gram moles/cc.
 C_G = equilibrium concentration of solute corresponding to partial pressure p_G in gas, gram moles/cc.

Film coefficients k_L and k_G and over-all coefficients K_L and K_G are defined by this equation. Where Henry's law applies (C_i equals $H p_i$), these are related by the equation:

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{1}{H k_L} = \frac{1}{H K_L} \quad (2)$$

The application of the Stefan equation for molecular diffusion to the transfer of material across the gas film has been suggested by Lewis and Chang (13), and tested by comparison with absorption and vaporization data by Hanks and McAdams (10) and by Sherwood and Gilliland (19). The latter workers show that coefficient k_G is proportional to the 0.56

power of the molecular diffusivity for the case of vaporization into a turbulent gas current, in a wetted-wall column. Their correlation has not been tested for packed towers but is presumably of value in the design of absorption equipment for one solute gas when data for another gas in similar equipment are available.

A similar study of the effect of diffusing solute on liquid film coefficient k_L has not been made. Table I summarizes the published results obtained by various workers on small-scale laboratory tests; although in the majority of cases the gases used were sufficiently insoluble so that liquid film resistance probably controlled, only the data of Schwab and Berninger cover more than two gases absorbed under similar conditions. These workers absorbed the pure gases in a 100-cc. buret filled with 90 cc. of water. The buret was rotated about a central axis perpendicular to its length, and after each rotation (requiring about 20 seconds) the total pressure in the gas bubble was measured. Only the calculated results are reported, and these are apparently valueless because the vapor pressure of water at temperatures as high as 80°C. was ignored in the calculations. The values given in Table I were obtained by recalculating the results, starting with the incorrect values calculated by Schwab and Berninger. Although the method followed is believed to be correct, the results can be considered approximate at best, since some of the solubility data used were widely different from the best values in the literature and could not be corrected in the recalculation. Furthermore, it was necessary to use single values for gas volume and interphase surface in the recalculation, although it was stated by the investigators that these quantities varied from one run to another.

The present investigation was undertaken with the purpose of studying the effect of solute on the liquid-film resistance (or coefficients). Eight different gases were absorbed in water at 25°C. in batch experiments in a small stirred vessel. The gas film resistance was eliminated as a factor by two means: (a) by using only pure solute gases, with essentially no inerts

to build up a film,¹ and (b) by using relatively insoluble gases, for which the Henry's law constant, H , is small and the liquid film resistance $1/Hk_L$ is large compared with the gas film resistance $1/k_G$ (Equation 2).

Apparatus and Procedure

Figure 1 illustrates the apparatus used. The essential features of the design are similar to those of the apparatus used by Davis (6) for his measurements of the initial rates of absorption of carbon dioxide by water and by dilute sodium carbonate solutions.

The absorption flask, which had a volume of 83 cc., had sealed at the bottom a tube 73 cm. long in which the glass stirrer shaft turned. At the top of the flask a ground-glass junction connected it to capillary tubing leading to the gas buret and vacuum pump. The suction tubing joining the stirrer sleeve to a parallel vertical glass tube held mercury to seal the flask from the atmosphere. Through this U-tube the stirring mechanism could operate freely. The flexibility of both the section of mercury seal and that of the stirring mechanism at the bottom of the U-tube permitted the absorption flask to be lowered for refilling.

In Davis' apparatus, the mercury level was just above the end of the glass stirrer shaft and liquid filled the clearance space between shaft and sleeve. This mixed with the main body of solution at a slow and unknown rate. In the present work this difficulty was avoided by raising the stirring motor to such a height that the mercury level would be only a few centimeters below the absorption flask.

The stirrer propeller, which was 2 cm. below the surface of the liquid, was curled into an S-shape so that it would pass through the neck of the flask, slightly more than 1 cm. in diameter. Coupled to the stirrer shaft at the bottom was a section of flexible steel shafting, and to this was attached a $3/16$ -inch (4.8-mm.) solid steel shaft which passed up through the other arm of the U-tube. Above the mercury level this shaft was coupled

¹ The experiments were conducted at constant temperature and total pressure, the rate of absorption being obtained from the reduction in total volume. Since the gas was saturated with water vapor throughout the test, there was no possibility that water vapor might concentrate in the gas film.

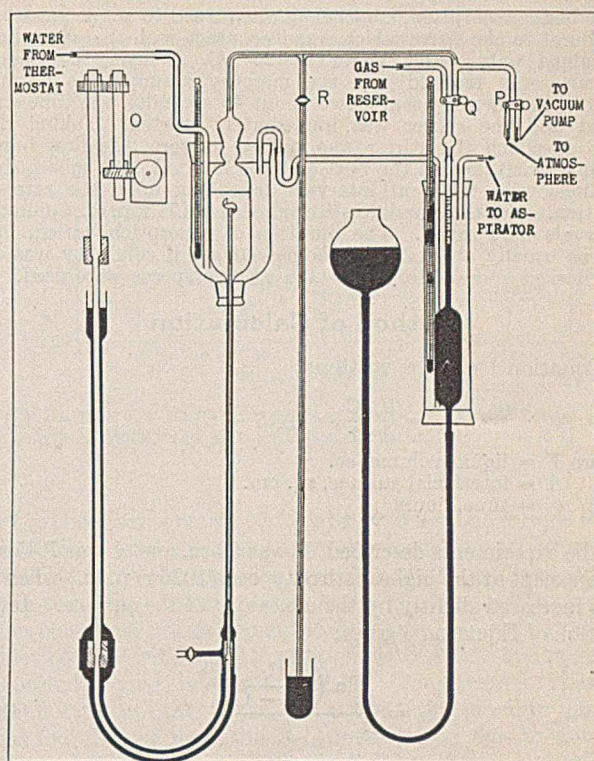


FIGURE 1. SKETCH OF APPARATUS

to one of two parallel shafts driven by a synchronous motor. The stirring speed could be varied by varying the diameter ratio of the spur gears transmitting power between the two shafts; the other shaft was driven by the motor through a 10 to 1 speed reduction gearing.

When the flask was under atmospheric pressure, the mercury depth was 93 cm. A depth in excess of the normal barometric height of mercury was necessary to ensure a mercury seal when the flask was under a vacuum. A mercury reservoir at the top of the mercury column on the motor side was made by using an enlarged cross section. It was found that the suction tubing expanded very slightly under the mercury pressure during the first part of a run. However, the reservoir provided for this slight expansion, and the resulting error in the measurement of gas volume was negligible.

By means of the two-way stopcock, P , the gas space of the flask could be connected to either the vacuum pump or the atmosphere. The two-way stopcock, Q , could connect either the absorption flask or the gas supply to the gas buret. A 2-cc. buret was used for the four very slightly soluble gases. This had a bulb attached to hold enough gas to refill the evacuated gas space at the start of a run. For the other gases a 100-cc. buret of uniform cross section was used. Atmospheric pressure was maintained in the gas system by means of a mercury leveling bottle which could be raised or lowered with a crank. Stopcock R , which could connect the gas system to a barometer, was left closed during all the runs, since pressure changes could be satisfactorily observed by the mercury level in the mercury seal. Both the absorption flask and the gas buret were surrounded by water jackets at $25 \pm 0.1^\circ \text{C}$.

At the start of a run the absorption flask was filled with 50 cc. of freshly boiled distilled water, and the vacuum pump was started with the gas buret cut off from the gas system. Over a period of about half an hour the pump was turned on at intervals to boil the water at 25°C ., so that all the air might be driven from the gas space.

In the meantime, gas from the reservoir (where it stood at approximately atmospheric pressure and in contact with water) had been drawn into the gas buret to a predetermined mark. Here it was allowed to remain for half an hour at exactly atmospheric pressure and 25°C . A small layer of water over the mercury in the buret permitted the gas to become saturated with water vapor at the exact conditions of the experiment. This precaution was necessary in order that the initial buret reading as well as the final one might correspond to saturation with respect to the water. This also prevented cooling of the water in the flask by evaporation at the start of the run.

TABLE I. SUMMARY OF RESULTS OF PREVIOUS INVESTIGATORS

Investigator	Conditions	Gas	kL^*
Absorption into Stirred Solutions			
Davis and Crandall (7)	100 cc. water, 400 r. p. m., 25°C .	O_2	7.9
		CO_2	10
	30 cc. water, 200 r. p. m., 25°C .	O_2	13
	30 cc. tetrachloroethane, 200 r. p. m., 25°C .	O_2	30
Whitman and Davis (21)	4000 cc. water, 60 r. p. m., 20°C .	O_2	3.3
		SO_2	3.6
Guyard and Tobler (9)	Water at 20°C ., 200 r. p. m., horizontal churn-like stirrer	CO_2	23**
		C_2H_2	26**
Bohr (4)	92 cc. water, 250 r. p. m., 25°C ***	CO_2	10
Davis (6)	100 cc. water, 158 r. p. m., 25°C .	CO_2	10
Becker (3)	Quiescent water, 20°C .	Air	0.4
Bubbling			
Schwab and Berninger (17)	10-cc. bubbles through a water column, 25°C ***	O_2	20
		H_2	26
		CO_2	21
		C_2H_2	22
		C_2H_4	23
		N_2O	23
Adeney and Becker (1)	Tip of 15-cc. bubble through a water column, 25°C .	Air	230
	Side of 15-cc. bubble, 25°C .	Air	32
		O_2	31
Ledig and Weaver (12)	Small bubbles through water, 25°C .	CO_2	72
Other Absorption Methods			
Conant and Scherp (5)	Shaking 400 times a min., 15 cc. water, 25°C .	O_2	83
		H_2	130
	Shaking 15 cc. oleic acid soln., 25°C .	O_2	72
		H_2	97
	Shaking 5 cc. tetrachloroethane, 25°C .	O_2	76
		H_2	100
	5 cc. bromobenzene, 25°C .	O_2	93
Whitman, Long, and Wang (22)	0.1-cc. water drops through gas	CO_2	260
	Drops at time of formation	CO_2	338
Naess and Moyes (15)	Wetted wall column, 25°C .	CO_2	36

* Unit of $kL = \frac{\text{gas quantity}}{\text{hr.} \times \text{sq. cm.} \times (\text{gas quantity/cc. liquid})}$ or $\frac{\text{cm.}}{\text{hr.}}$

** Possible gas film resistance.

*** Interpolated to given temperature.

To begin absorption, stopcock *Q* was turned to admit gas from the buret to the space which was in contact with the water and contained only water vapor at 25° C. When atmospheric pressure was reached and the mercury assumed its normal level in the mercury seal (after about 45 seconds), the time was noted and the stirrer was immediately started. Taking the time at which the stirrer was started as zero, the first buret reading was taken at the next possible interval, and subsequent readings were taken at intervals depending upon the rate of solution. For the standard stirring speed of 171 r. p. m., 5-minute intervals were taken. The duration of absorption varied, but it was usually about 2 or 3 hours—longer if solubility was to be checked and shorter when high stirring speeds were used.

Method of Calculation

Equation 1 may be written:

$$N_A = \frac{V}{A} \frac{dC}{d\theta} = k_L(C_i - C) \quad (3)$$

where *V* = liquid volume, cc.
A = interfacial surface, sq. cm.
 θ = time, hours

In the experiments described, *V* was 50 cc. and *A* was 7.35 sq. cm., except at the highest stirrer speed (1025 r. p. m.) when *A* was increased slightly by the concavity of the surface. Integration of Equation 3 gives:

$$k_L = \frac{V}{A} \frac{\ln \left(\frac{C_i}{C_i - C} \right)}{\theta} \quad (4)$$

The results of each run were plotted as (*C_i - C*) vs. θ on semi-logarithmic coordinate paper, and *k_L* was calculated from the average slope of the line obtained. Since the equation involves a ratio of concentrations, the units employed are not important, and it was found convenient to let *C* represent cc. of gas per 50 cc. of solution. Figure 2 shows data plotted in

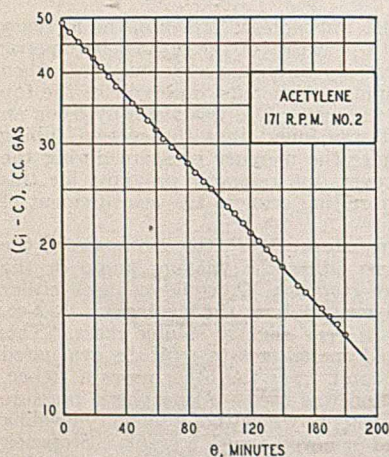


FIGURE 2. SEMILOG PLOT OF DATA FROM REPRESENTATIVE RUN

this way; the example is that of a run using acetylene with a stirrer speed of 171 r. p. m. In almost every case the lines obtained were essentially straight, and there was little difficulty in determining the slope to be employed in calculating *k_L*. In the absorption of acetylene, however, it was found that, at stirrer speeds of 27 r. p. m. and less, the curves were concave upwards when plotted as in Figure 2. The values reported for acetylene correspond to the slope of the line in the early part of the run and hence to initial absorption rates. In most cases it was convenient to carry the absorption roughly halfway to saturation, although at high stirrer speeds some tests were continued to over 95 per cent saturation.

Results

Absorption of carbon dioxide, acetylene, oxygen, and hydrogen was studied over a wide range of stirrer speeds. Additional tests using helium, nitrogen, sulfur dioxide, and chlorine were made at a constant stirrer speed of 171 r. p. m. The results are reported in Table II, which gives the stirrer speed and the calculated values of *k_L* obtained for each gas. The results are also shown in Figure 3, where *k_L* is plotted

against stirrer speed, using logarithmic coordinates. In order that a comparison may be made with the other data, the points representing *k_L* for unstirred liquid are plotted at an abscissa of 1 r. p. m. The curves consist of two branches: a horizontal section in the region of low turbulence and a straight section with a slope of 0.6 at stirrer speeds above 100 r. p. m. The values of *k_L* for the several gases fall in a different order in the two regions.

TABLE II. SUMMARY OF CALCULATED VALUES OF *k_L* FOR THE ABSORPTION OF PURE GASES AT 25° C.

Stirrer Speed R. p. m.	Run No.	<i>k_L</i>	Av. <i>k_L</i> Cm./hr.	Stirrer Speed R. p. m.	Run No.	<i>k_L</i>	Av. <i>k_L</i> Cm./hr.
Hydrogen				Oxygen			
0	1	0.56		0	1	0.47	
	2	0.44	0.50		2	0.36	0.41
13	1	0.31		13	1	0.36	0.36
	2	0.43	0.37	76	1	1.17	
171	1	3.8			2	1.24	1.20
	2	3.8		171	1	3.08	
	3	3.8	3.8		2	2.92	
1025	1	11.6			3	3.01	3.00
	2	11.8	11.7	486	1	5.52	
Helium				Carbon Dioxide			
171	1	3.7		0	1	1.45	
	2	4.3			2	1.47	1.46
	3	3.8	3.9	13	1	1.44	1.44
Acetylene				Sulfur Dioxide			
0	1	0.26		171	1	2.77	
	2	0.26	0.26		2	2.72	
13	1	0.27		486	1	4.87	
	2	0.28	0.28		2	4.80	4.84
27	1	0.33	0.33	1025	1	8.11	
76	1	1.46			2	8.60	8.35
	2	1.43	1.45	Nitrogen			
171	1	3.01		171	1	2.5	
	2	2.88			2	2.9	
	3	3.01	3.00		3	2.6	
486	1	5.65			4	2.2	2.6
	2	5.60	5.63	Chlorine			
1025	1	8.46		171	1	2.77	
	2	8.51			2	2.86	2.8
	3	8.60	8.52				

Since the upper branches of the curves of Figure 3 are straight and parallel, the results at 171 r. p. m., where data on eight gases were obtained, may be assumed to be representative of the results in this region. Values of *k_L* at this stirrer speed are given in Table III, together with values of diffusivity, heats of solution, and solubility. Although the two largest *k_L* values were obtained with the gases having the two largest diffusivities in water, it is evident that the variation of *k_L* with *D* is relatively small. Figure 4 shows *k_L* plotted against molecular weight for the eight gases.

The high point for sulfur dioxide may be explained if it is assumed that the lower horizontal branch of the curve of *k_L*

TABLE III. COMPARISON OF RESULTS AT 171 R. P. M. WITH PHYSICAL PROPERTIES OF SOLUTE GASES

Gas	Mol. Weight	Diffusivity at 20° C. Sq. cm./day	Gas Soly. ^a at 25° C. Cc./50 cc. H ₂ O	Heat of Soln. G. cal./g. mole	<i>k_L</i> Cm./hr.
Hydrogen	2	5.1 ^b	0.97	1420	3.8
Helium	4	4.9 ^c	0.55		3.9
Acetylene	26	1.6 ^b	48.9	4100	3.0
Nitrogen	28	1.6 ^b	0.80		2.6
Oxygen	32	1.8 ^b	1.55	3300	3.0
Carbon dioxide	44	1.5 ^b	40.2	4800	2.7
Sulfur dioxide	64	2.2 ^c	1780	8560	3.7
Chlorine	71	1.2 ^b	114	5300	2.8

^a Values from International Critical Tables and various sources in the literature. The values for the first six gases were checked roughly (within 5 per cent) by continuing absorption for 15 hours or more.

^b Selected by Arnold (2) as the most reliable, based on a study of values reported in the literature. For hydrogen the latter vary from 3.14 to 8.44 sq. cm. per day.

^c Calculated from the empirical equation given by Arnold (2).

for sulfur dioxide *vs.* stirrer speed continues at a value of 3.7 to some stirrer speed greater than 171 r. p. m. The transition to the upper branch would presumably occur in the vicinity of 200 to 300 r. p. m. so that the upper branch of the sulfur dioxide curve would fall near the upper branch of the carbon dioxide curve. Under such circumstances k_L for the sulfur dioxide would be in agreement with k_L for the other gases if a plot similar to Figure 4 were constructed for a stirrer speed in excess of that at which the break occurs in the sulfur dioxide curve.

If the results at 171 r. p. m. are plotted as k_L *vs.* diffusivity, using logarithmic coordinates, the best line has a slope of about 0.25. It is apparent from Table III, however, that the results fall in two groups, with hydrogen and helium at one extreme and the other gases (except sulfur dioxide) grouped at the other extreme. The coordinates of two points representing the two groups are $k_L=2.8$ at $D=1.5$ sq. cm. per day, and $k_L=3.85$ at $D=5$ sq. cm. per day. Visualizing the liquid film to be made up of a stagnant layer in which the mechanism of transfer is molecular diffusion, and an eddy layer in which the transfer is independent of molecular diffusivity, we may write:

$$\frac{1}{k_L} = \frac{x}{D} + R_E \quad (5)$$

where x = effective thickness of laminar layer
 R_E = resistance of eddy layer

Substituting the representative values given above and solving, $x = 0.0087$ cm. and $R_E = 0.218$. Hence the eddy layer represents 84 per cent of the total resistance when D is 5, and 61 per cent of the total when D is 1.5 sq. cm. per day. These proportions are of interest, although valid only for the apparatus tested.

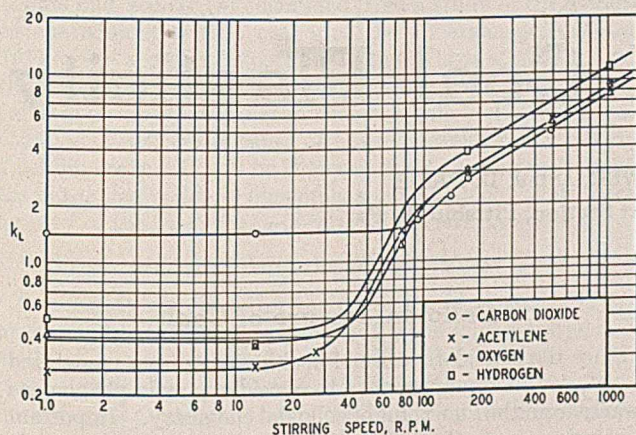


FIGURE 3. EFFECT OF STIRRER SPEED ON ABSORPTION COEFFICIENT k_L

As noted in Figure 3, the order of solution rates is changed at low stirrer speeds, and k_L is not a simple function of the diffusivity. In this region natural convection comes into play and the results, although reproducible, are difficult to explain. If convection currents were due primarily to thermal effects, it would follow that k_L in this region should fall in order of the product of solubility times heat of solution. This product is large for carbon dioxide and acetylene, and low for oxygen and hydrogen. The lack of correlation is indicated by the fact that k_L is highest for carbon dioxide and lowest for acetylene, the results for oxygen and hydrogen lying between. Convection currents set up due to the different density of the saturated surface layer may explain the results, although such density differences are probably extremely slight. Data are not available on the densities of saturated solutions of these gases, but the estimated molecular densities of the solute

molecule fall in the same order as the values of k_L in this region. Faulty temperature control does not appear to be a factor, since the results at the lowest stirrer speeds could be reproduced after an interval of several weeks.

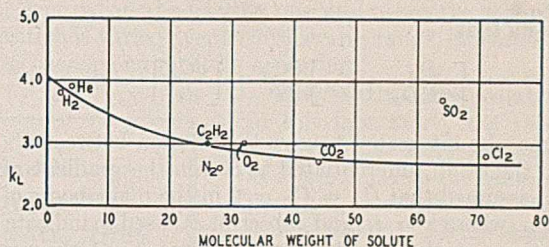
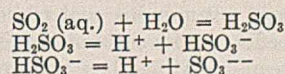


FIGURE 4. RELATION BETWEEN MOLECULAR WEIGHT OF SOLUTE GAS AND k_L AT A STIRRER SPEED OF 171 R. P. M.

Carbon dioxide reacts with water, and the acid formed tends to ionize. At the concentration corresponding to saturation at 25° C., however, less than one per cent of the dissolved gas is in the form of the hydrate (8, 11, 16, 20), and the ionization constants are extremely low. Both sulfur dioxide and chlorine react with water to an appreciable extent and might be expected to give higher values of k_L . The results for chlorine fall in with the other gases, and although k_L for sulfur dioxide was found to be high, this is believed to be due to another effect, already explained. Table I shows that Whitman and Davis found k_L larger for sulfur dioxide than for oxygen. If the equilibria involved are assumed to be reached rapidly, it may be shown that the absorption of either sulfur dioxide or chlorine may be interpreted by means of the Lewis-Whitman Equation 1. An outline of the derivation for sulfur dioxide follows. The derivation for chlorine is similar but somewhat more complicated.

Derivation of Diffusion Equations for Simultaneous Absorption and Chemical Reaction

This derivation is based on that of Sherwood and Roberts (18) for the corresponding case in the gas film when equilibrium is maintained between N_2O_4 and NO_2 . The absorption of sulfur dioxide by water will be treated as a case of true diffusion in a stagnant aqueous layer. The reactions are:



The dissociation of HSO_3^- is small compared with that of H_2SO_3 , and will be neglected. H_2SO_3 and HSO_3^- diffuse together, and Fick's law may be written for the diffusion of each:

$$\begin{aligned} N_B &= -D_B \frac{dC_B}{dx} \\ N_A &= -D_A \frac{dC_A}{dx} \end{aligned}$$

where x = distance in direction of diffusion, cm.
 N = rate of diffusion, gram moles/(sec.)(sq. cm.)
 D = diffusion coefficient
 C = concentration, gram moles/liter

Subscripts $B, A = H_2SO_3$ and HSO_3^- , respectively

As the two diffuse, the H_2SO_3 dissociates since the equilibrium between the acid and its ions is presumably reached extremely rapidly; therefore equilibrium may be assumed at any plane x . By a material balance,

$$dN_B = -dN_A$$

whence
$$D_B \frac{d^2 C_B}{dx^2} = -D_A \frac{d^2 C_A}{dx^2}$$

and since by the assumed equilibrium,

$$C_B = KC^2 A \quad \text{and} \quad dC_B = 2KC_A dC_A$$

it follows that

$$\left[\frac{D_A}{2KD_B} + C_A \right] \frac{d^2 C_A}{dx^2} + \left[\frac{dC_A}{dx} \right]^2 = 0$$

This may be integrated to give the relation between C_A and x , and the result differentiated to obtain the gradient of C_A . If it is assumed that $C_A = C_B = 0$ in the main body of the solution, where $x = x_2$, and subscript i is used to indicate concentrations at the liquid surface, where $x = 0$, the result is

$$(N_B)_{x=x_2} = -D_B \left(\frac{dC_B}{dx} \right)_{x=x_2} = 0$$

$$(N_A)_{x=x_2} = KD_B \frac{C_{A_i}^2}{x_2} + D_A \frac{C_{A_i}}{x_2} = \frac{D_B}{x_2} C_{B_i} + \frac{D_A}{x_2} C_{A_i}$$

For the assumed case of absorption into pure water, the rate of total transfer is seen to be the same as if each diffused without reacting. If it be assumed that the two diffusivities are equal, the total rate of H_2SO_3 plus HSO_3^- transfer is proportional to the concentration of total ionized and un-ionized H_2SO_3 at the interface. If the various assumptions are allowed, then it follows that the absorption of sulfur dioxide may be treated in the same manner as the absorption of an inert gas which does not react with water.

In the derivation outlined, the existence and diffusion of sulfur dioxide in the liquid phase are neglected. It is apparent that the reaction between sulfur dioxide and water to form

H_2SO_3 can be treated in a manner analogous to that employed for the simultaneous diffusion of H_2SO_3 and HSO_3^- . If the diffusivities of sulfur dioxide and H_2SO_3 are assumed to be equal, it follows that the sum of the sulfur dioxide plus H_2SO_3 can be treated as a single solute, referred to as H_2SO_3 in the derivation.

In the case of chlorine the equilibrium condition involves a cube instead of a square, but the line of reasoning and conclusions reached are similar.

Literature Cited

- (1) Adeney and Becker, *Phil. Mag.*, 38, 317 (1919); 39, 385 (1920).
- (2) Arnold, *J. Am. Chem. Soc.*, 52, 3937 (1930).
- (3) Becker, *Phil. Mag.*, 45, 581 (1923).
- (4) Bohr, *Ann. Physik*, 68, 500 (1899).
- (5) Conant and Scherp, unpublished work at Harvard Univ., reprinted by Davis and Crandall.
- (6) Davis, *IND. ENG. CHEM.*, 25, 1023 (1933).
- (7) Davis and Crandall, *J. Am. Chem. Soc.*, 52, 3757 (1930).
- (8) Fraunholt, *J. chim. phys.*, 21, 400 (1924).
- (9) Guyer and Tobler, *Helv. Chim. Acta*, 17, 257 (1934).
- (10) Hanks and McAdams, *IND. ENG. CHEM.*, 21, 1034 (1929).
- (11) Higbie, *Trans. Am. Inst. Chem. Engrs.*, 31, 365 (1935).
- (12) Ledig and Weaver, *J. Am. Chem. Soc.*, 46, 650 (1924).
- (13) Lewis and Chang, *Trans. Am. Inst. Chem. Engrs.*, 21, 127 (1928).
- (14) Lewis and Whitman, *IND. ENG. CHEM.*, 16, 1215 (1924).
- (15) Naess and Moyes, *Mass. Inst. Tech.*, chem. eng. thesis, 1925.
- (16) Saal, *Rec. trav. chim.*, 47, 264 (1928).
- (17) Schwab and Berninger, *Z. physik. Chem.*, 138A, 55 (1928).
- (18) Sherwood, "Absorption and Extraction," New York, McGraw-Hill Book Co., 1937.
- (19) Sherwood and Gilliland, *IND. ENG. CHEM.*, 26, 1093 (1934).
- (20) Thiel and Strohecker, *Ber.*, 47, 945, 1061 (1914).
- (21) Whitman and Davis, *IND. ENG. CHEM.*, 16, 1233 (1924).
- (22) Whitman, Long, and Wang, *Ibid.*, 18, 363 (1926).

RECEIVED April 1, 1937.

Characteristics of Coal Plasticity

R. G. ATKINSON, R. E. BREWER, AND J. D. DAVIS

U. S. Bureau of Mines, Experiment Station, Pittsburgh, Pa.

THE behavior of bituminous coal while it is plastic has considerable effect on its carbonizing properties; therefore the Bureau of Mines has undertaken studies on plasticity at its Pittsburgh Experiment Station in connection with a survey of the gas-, coke-, and by-product-making properties of American coals. In addition to the carbonizing properties, the chemical, physical, and petrographic characteristics of the coals studied are determined, so that the plastic properties may be correlated with them. Previous papers (8, 9) showed rough correlation of results of plastic measurements with other properties, particularly with coking power. The purpose of the present paper is to present the results of recent experimental work that throw further light on the mechanism of coal plasticity during coking.

In this work plasticity was determined by the Davis plastometer (8). The resistance to stirring, or torque, observed by this method is a function of temperature and is roughly proportional to the viscosity of the heated coal mass. The term "plasticity," as broadly applied in fuel technology, includes all of the fluid phenomena that occur during the heating of coal up to and through the plastic range. This "plastic range," as commonly defined and used here, refers to the entire range of temperature, or time, throughout which coal, when heated in the absence of air, exists in a semifluid state.

Colloidal Nature of Coal

Since the colloidal nature of coal has long been recognized (1, 11, 18), it is appropriate to consider plastic phenomena largely from the viewpoint of colloidal chemistry. Important conclusions as to the origin of the structural constituents in coal have been reached from microscopic and ultramicroscopic studies (13, 17, 18, 20). The use of the Spierer lens by Thiessen (18) gave conclusive evidence of the colloidal nature of coal. His Spierer photographs (18) of coal of different ranks show the arrangement and size of the micelles dispersed in it. Figure 1 is a thin cross section of bituminous coal from the Pittsburgh bed photographed by means of the Spierer lens system using vertical illumination. The oriented micelles found in the coal are clearly seen. It has also been observed that this micelle structure is carried through into the coke. Figure 2 shows a Pittsburgh bed by-product coke. This photograph of a polished section of the coke was taken by means of vertical illumination using a Leitz short-mount apochromatic objective.

From the colloidal point of view coal may be looked upon as a coagel (1) in which the micelles and no doubt other particles are dispersed. Agde and Hubertus (1, 2) showed that a considerable proportion of the coal can be dispersed in certain

solvents (probably with some depolymerization of the larger coal molecules). Of particular importance is their observation that certain high-boiling primary tar oils are good dispersing agents. This fact has a bearing on plasticity because of the presence of such oils in the mass while the coal is plastic. A further observation of these authors is that "solvation" (solation) by a good dispersing agent is invariably preceded by the swelling of the coagel or solid coal.

Heating coal in the absence of air causes part of its constituents to melt and other parts to produce liquids by decomposition. When these liquids are present in large enough amounts, they disperse the solid colloidal particles of coal to form an organophilic sol commonly called the plastic state. Extended preheating in the preplastic range decomposes the liquid-forming material to such an extent that within the plastic temperature range there may no longer be left a sufficient quantity in which to disperse the solids. A high rate of heating through the preplastic range increases the amount of fluid material causing solvation and therefore some coals (bordering on the range of coking rank) form a much better coke when heated at a high rate than when coked by normal operation. Plastometer tests indicate that increasing the time of heating in the plastic range will decrease the quality of coke formed from a given coal. The formation of the colloid sol called the plastic state is a delicate process and depends greatly on the thorough dispersion of the constituents of the coal.

Agde and Winter (3) concluded from a study of the softening characteristics that coal must be an organogel; Seyler (16) derived a similar hypothesis from the laws of plastic flow, which he states are valid for plasticity of coking coals. Agde and Hubertus (2) postulated that the colloidal structure of bituminous coal is the cause of flowing, swelling, and caking of coking coals. It will be shown in the following sections of this paper that colloidal phenomena must play important roles in many of the phenomena observed in plasticity studies.

Formation of Liquid Material in Coal

A necessary condition for the causation of plasticity is the forming of liquids which wet and soften the solid material and finally disperse the micelle and other material into a sol. These liquids may be formed by the melting of certain definite chemical compounds or by cracking very large molecules to form molecules that are liquid at the prevailing temperature. Experiments conducted by the Bureau of Mines show that the liquids formed by both melting and decomposition are essential for the phenomena of plasticity of many coals. Figure 3 shows the results of a plastometer test made on Powellton coal, a high-volatile A coal (4) with plastic properties typical of those occurring in that group. The upper curve indicates that Powellton coal fuses at 404° C., reaches its maximum fluidity at about 452°, and has solidified into coke at 492°. The heating rate from 200° C. to the end of the test is given by the time-temperature curve shown in the lower part of Figure 3. The following table shows the fusion point of Powellton coal determined by the plastometer method, using various heating rates:

Heating Rate, ° C./Min.	Fusion Point, ° C.
1.5	410
4.5	404
17.0	403

The sharpness with which these fusion points can be reproduced, even when the heating rate and hence the rate of decomposition is varied over a considerable range, indicates that melting phenomena must be occurring.

With nearly all the coals tested in this laboratory, the rate of gas evolution increases sharply at approximately the same temperature at which the coal becomes plastic. Figure 4 shows the total gas evolved from a number of coals as they are heated at an approximately constant rate of 4° C. per minute. A point is marked on each curve which corresponds to the fusion temperature of the coal. The coals tested were described in an earlier paper (8). The remarkable coincidence that their fusion points are all so close to the temperature at which the rate of gas evolution becomes appreciable suggests that part of the liquid materials necessary for causing solvation are formed by thermal decomposition. That is, the cracking indicated by the production of hydrogen, methane,

etc., causes some of the solid coal molecules to form smaller molecules which are liquid at the prevailing temperature.

Figure 5 gives some information on the decomposition that occurs at a temperature slightly below the fusion point. This figure represents a plastometer test in which Powellton coal was heated at a constant temperature of 392° C. for 7 hours and 40 minutes. At the end of that time the temperature was increased through the plastic range at a constant rate. The resistance curve does not have any "fluidity range," and the maximum resistance is much less than that shown by the normal plastic range curve (Figure 3). Experience in the Bureau of Mines laboratory indicated that a plastometer curve showing no fluidity and a low maximum resistance is to be expected when a low degree of fusion takes place in the coal. Further preplastic heat treatment gives a further reduction in plasticity, until finally after a sufficiently prolonged heating

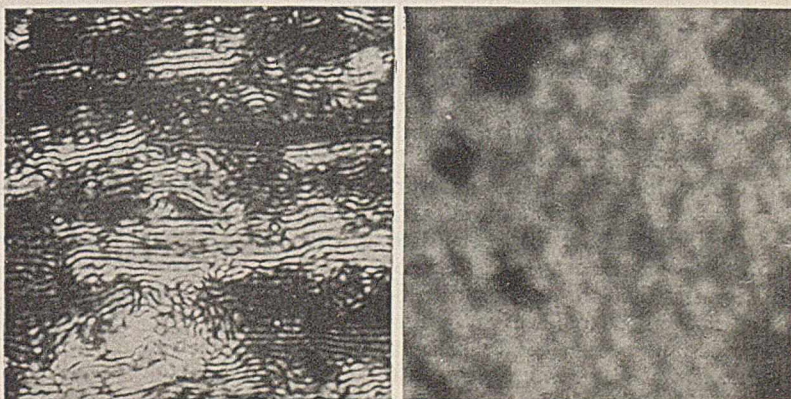


FIGURE 1 (Left). THIN CROSS SECTION OF PITTSBURGH BED COAL ($\times 1000$)
FIGURE 2 (Right). COKE FOR PITTSBURGH BED ($\times 3000$)

period the fusibility of the coal is completely destroyed. These same effects were observed on a number of coals in this laboratory, and Audibert (6) reported similar results for pellets of coal heated in a dilatometer tube.

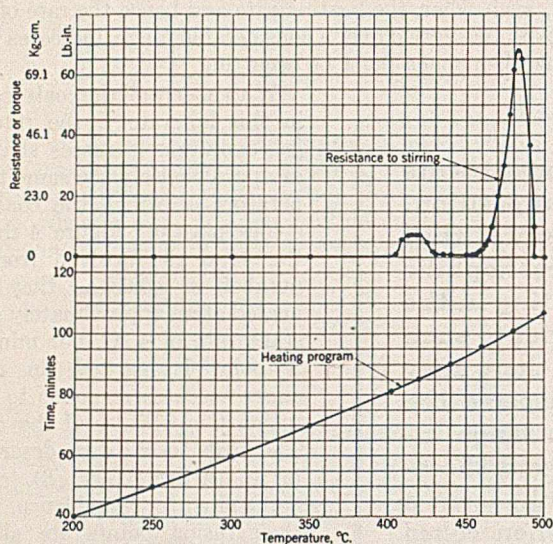


FIGURE 3. PLASTOMETER TEST ON POWELLTON COAL

These facts may be interpreted to mean that the preheating decomposes the liquid-forming material to such an extent that within the plastic temperature range there is no longer a sufficient quantity in which to disperse the solids. Warren (19) showed that slow heating in the preplastic range reduces the yield of tar which a coal is capable of giving. A further experimental fact, which bears on the dependence of degree of dispersion of the solids on the amount of liquid available, is the yield of tar obtainable in the Fischer low-temperature assay. Here the over-all rate of carbonization is very high, and the yield of tar is higher than in any industrial method of low-temperature carbonization. Dispersion of the solids takes place with all coals within the range of coking rank. The coke is well fused, but because of the high rate of evolution of gases and vapors it is often very porous and hence poor in quality.

Nature of the Plastic State

While coal is being heated to the beginning of the plastic range, the organophilic nature of the micelles present causes much of the liquid formed to remain adsorbed on the solid surfaces and distributed throughout the intercellular space. The solid particles are progressively softened by this liquid until finally the whole mass coalesces and forms a colloidal solution called the plastic state. The formation of this colloidal solution is probably an intricate process and one that may be easily disturbed, as indicated in the following series of experiments. These show that a relatively small amount of liquid may be a determining factor in whether a coal may or may not exhibit plasticity and that the physical distribution of the materials in the coal is of great importance.

This evidence was obtained by preheating in the plastometer at a rate of 4.5° C. per minute up to 395° C., a considerable quantity of a high-volatile A coal (4) of 410° C. fusion point (Upper Cedar Grove bed), and then treating the preheated coal as follows: A portion of the preheated coal was tested in

the plastometer by again heating at a rate of 4.5° C. per minute. In this test the preheated coal fused and passed through a normal plastic range. Another portion of the preheated coal was extracted thoroughly with benzene at about 30° C. The benzene extracted about 2.5 per cent of a brown material which was solid at room temperature. A portion of the preheated extracted coal was then tested in the plastometer and found to be infusible. Since benzene at 30° C. should have no chemical effect on the natural coal substance, it was concluded that the 2.5 per cent of material extracted was a necessary part of the liquid materials that cause solvation. The extract was added to some of the extracted coal, first in approximately the same and then in somewhat greater proportions than were present in the original coal. Both mixtures of extract and extracted coal were found to be infusible. That such mixtures are not fusible is presumably due to the fact that the physical distribution of the liquid-forming constituents in the prepared mixture of extract and extracted coal is not the same as in the unextracted preheated coal. These experiments indicate that a particularly thorough dispersion of the constituents must exist if coal is to have the property of being converted into the plastic state.

To learn approximately how fluid a coal may become during its plastic state, the plastometer was charged with a heavy transmission lubricant of about 14,000 centipoises viscosity at 20° C. A resistance reading of about 0.2 pound-inch (0.23 kg.-cm.) was obtained at 20° C. In comparing this resistance reading with that obtained with coals, it is found that several typical high-volatile A coals show two or three times greater viscosity, even at their temperature of maximum fluidity. The coals, other than the high-volatile A group, which do become plastic are much more viscous than the oil tested.

Relation of Plasticity to Coking Power

One of the main objectives of research on plasticity is to find the relation between the plastic behavior of coals and the strength of the coke they will produce. Previous work (12) showed that, in general, a high maximum resistance in the plastometer test connotes strong coke and vice versa. The

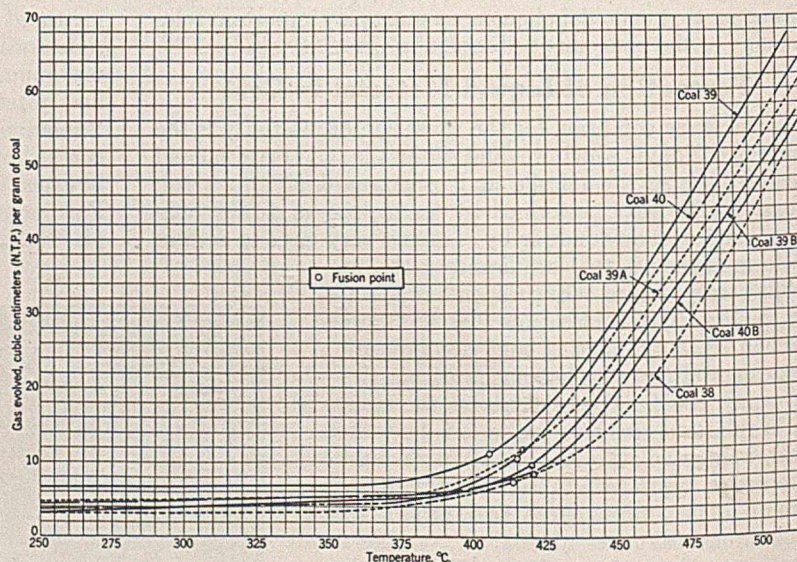


FIGURE 4. GAS EVOLVED FROM COALS HEATED AT RATE OF 4° C. PER MINUTE

plastometer resistance is not closely proportional to coking power but, where there are moderately wide differences in coking power, the plastometer curve will usually indicate that such differences exist. Obviously, there must be some fluidity of a coal within the plastic range of temperatures if it is

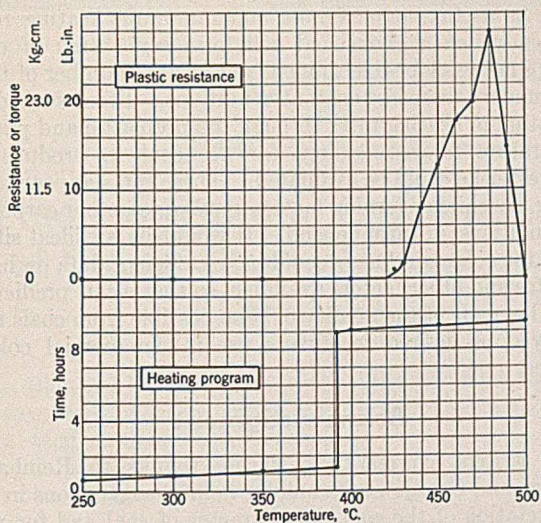


FIGURE 5. EFFECT OF PREHEATING TREATMENT ON PLASTIC RANGE OF POWELLTON COAL

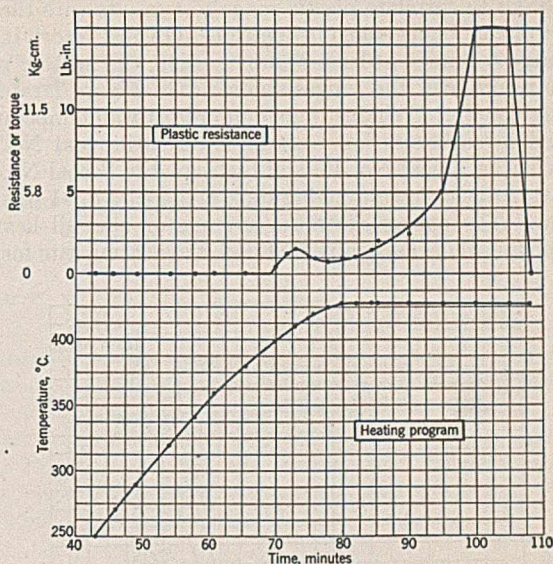


FIGURE 6. PLASTICITY RANGE OF DOROTHY COAL AT 430° C.

to produce coke of characteristic structure. The cell structure and fissures in a piece of by-product coke show clearly that it has passed through a stage of more or less complete fusion. Fluidity in excess of the amount required to bring about these desired objectives, however, has been shown to be detrimental to the strength of the coke (5, 8, 9). German writers speak of a good coke as having been well fused in the process of formation. A coal which, because of its inherent properties or because of unfavorable carbonizing conditions, does not fuse well will produce what is known to coke men as a pebbly coke. In such coke some of the pieces of coal have not been assimilated by the rest of the charge; that is, they have not been sufficiently well fused. The amount and character of the liquid required to complete such fusion or, perhaps better, to disperse completely the infusible colloidal particles of the coal, may sometimes be favorably changed by other carbonizing conditions (7, 10).

The plastic range curve—e. g., Figure 3—breaks off very sharply at the point of maximum resistance where the transformation into coke occurs. Since coking power varies approximately with maximum resistance in the plastometer, this fact offers a means of studying the effect of manner of heating through the plastic range on coking power. To determine this relation, a series of tests was made in the plastometer by heating progressively through the plastic range at a rate comparable with rates used in an industrial coke oven, and then another series using the same coals with the time of heating extended considerably. This was done by bringing the temperature in the plastometer up to 430° C. at the normal rate and holding it constant at that point through the rest of the plastic range. Figure 6 shows the results of a test on Dorothy bed (high-volatile A) coal in which the temperature was held constant after it had reached 430° C. The general shape of the resistance curve obtained in this manner is similar to the curve obtained by the test method where the temperature is increased continuously throughout the experiment. Table I shows the data obtained by both series of

tests. The maximum resistance is decreased in all cases by the long-time heating of the second method, indicating that the coke resulting from such treatment would be weak. The magnitude of the effect differs for different coals, which can be explained by saying that some coals are more sensitive to heat treatment than others. Actually, we do not have to make this assumption because it is well known from by-product practice that low-rank coals must be coked rapidly if good coke is to be obtained.

Effect of Heating Rate

Among the many coals studied in this laboratory, a few showed no fusion in the routine plastometer test, although fair cokes were formed when the same coals were carbonized at 500° C. in the Bureau of Mines-American Gas Association retort. Such coals, however, showed fusion in the plastometer when heated at a sufficiently high rate. The over-all heating rate in the BM-AGA retort and in commercial coke ovens is usually less than 1° C. per minute. The heating rate through the temperature range 350° to 500° C. (the important range affecting coke formation) is, however, much higher. Moreover, coal in the retort or oven is under some pressure, which tends to force the individual particles together. On the other hand, the coal charge in the plastometer is being constantly stirred during heating, tending to minimize or prevent fusion. For these reasons it is sometimes necessary to use higher heating rates than normal to bring about fusion of certain coals in the plastometer. Indiana No. 4, a high-volatile C coal (4), illustrates this type of coal. When carbonized in the BM-AGA 13-inch (33-cm.) retort at 500° C., this coal produced a coke with a 1.5-inch (3.8-cm.) shatter index of 65.7 and a 1-inch (2.5-cm.) tumbler index of 32.5. The coal showed no fusion under the normal rate of heating in the plastometer. With an over-all heating rate of 9.6° C. per minute, fusion resulted.

TABLE I. DURATION OF PLASTICITY

Coal No.	Fixed Carbon ^a %	Continuous Temp.-Rise Tests		Constant-Temp. Tests				Portion of time before start of solidification %		
		Temp. range ° C.	Time Min.	Temp. ° C.	Time Min.	Max. resistance				
						Lb.-in.	Kg.-cm.			
42	66.6	405-99	26.6	70	81	430	60	53	61	31
44	66.3	404-92	25.8	68	78	430	38	19	22	44
46	66.1	411-90	22.0	34	39	430	32	33	38	50
43	63.6	407-94	24.0	23	27	430	38	15	17	56

^a Rank: dry and free of mineral matter.

In order to correlate plastic range test results with the behavior of coal being coked in the BM-AGA test retort, it was necessary to know, at least approximately, the heating rates in the retort over the ranges studied. In Figure 7 rates of heating are plotted against maximum retort wall temperature as used in carbonization tests of low-volatile coal No. 41, high-volatile A coal No. 46, and high-volatile B coal No. 19; the latter was of lowest coking rank and coal No. 41 was the highest. The curves show the average or over-all heating rate for the whole carbonizing period, the heating rate for the

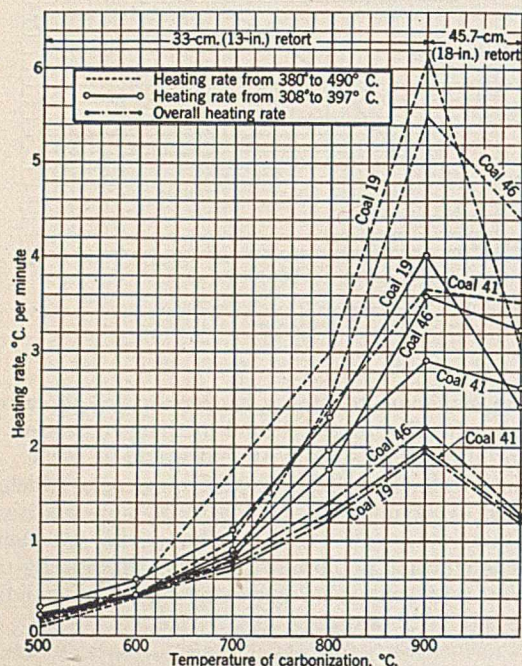


FIGURE 7. RELATION OF RATE OF HEATING TO RANK OF COAL

preplastic range, which is taken as 308° to 398° C., and the heating rate for the plastic range, which is 380° to 490° C. The heating rates apply to a retort of 33-cm. (13-inch) diameter for maximum carbonizing temperatures of 500°, 600°, 700°, 800°, and 900° C. Rates are also shown for the 45.7-cm. (18-inch) diameter retort at the maximum carbonizing temperature of 900° C. It is shown that:

1. All heating rates increase with the maximum carbonizing temperature used, but the increase through the preplastic and plastic ranges is greater than that of the average or over-all rate. All heating rates for the 45.7-cm. retort are slower than those for the 33-cm. retort at the same carbonizing temperature—900° C.

2. Although the three coals selected cover about the entire range of coke-making rank, there is little difference in the average coking rate, the maximum difference being about 0.3° C. per minute applying to the 33-cm. retort at a carbonizing temperature of 900° C. However, in general, the heating rates in the preplastic and plastic ranges do vary with the rank of the coal, being most rapid for the lowest rank coal (No. 19). The heating rate through the plastic range is more rapid than in the preplastic range.

The increases in heating rates for the lower rank bituminous coals through their preplastic and plastic temperature ranges, above those shown by higher rank coals under conditions of similar thermal input, have been attributed to their more highly exothermic character (15). In fact, many high-volatile C, high-volatile B, and lower ranking high-volatile A coals have been successfully coked commercially by employing higher heating rates than are customarily used with higher rank coals (14). It appears, therefore, that increased heating rates through the preplastic and plastic temperature ranges are advantageous when coking lower rank bituminous coals.

The limits for the maximum and minimum heating rates between which a given coal will form some kind of coke must of necessity be determined from a large number of tests made under otherwise constant conditions. From such data the optimum heating rates through the preplastic and plastic temperature ranges required for the coal to produce its strongest coke could be evaluated. These rates appear to be among the chief governing factors upon which other carbonizing conditions, in turn, depend. It would be an ideal situation if the coking industry could have sufficient data on heating rates and other factors available, so that a fair prediction might be made of the quality of coke possible from coals now employed or desired for future use in commercial coking practice.

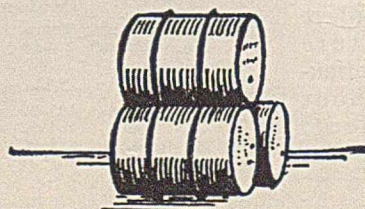
Acknowledgment

The writers express their sincere thanks to Reinhardt Thiessen and George C. Sprunk for helpful suggestions in the interpretation of the colloidal character of coal and for permission to use Figures 1 and 2 from their work.

Literature Cited

- (1) Agde, G., and Hubertus, R., *Braunkohlenarchiv*, No. 46, 1-30 (1936).
- (2) Agde, G., and Hubertus, R., *Brennstoff-Chem.*, 17, 149-50 (1936).
- (3) Agde, G., and Winter, A., *Ibid.*, 15, 126-9 (1934).
- (4) Am. Soc. Testing Materials, *Proceedings*, 35, Pt. I, 847-53 (1936).
- (5) Audibert, E., *Fuel*, 8, 225-43 (1929).
- (6) Audibert, E., *Rev. ind. minérale*, 6, 115-36 (1926); *Fuel*, 5, 229-44, esp. 231 (1926).
- (7) Audibert, E., and Delmas, L., *Ibid.*, 6, 131-40, 182-9, esp. 188 (1927).
- (8) Brewer, R. E., and Atkinson, R. G., *IND. ENG. CHEM., Anal. Ed.*, 8, 443-9 (1936).
- (9) Davis, J. D., Jung, F. W., Juettner, B., and Wallace, D. A., *IND. ENG. CHEM.*, 25, 1269-74 (1933).
- (10) Davis, J. D., and Reynolds, D. A., *Ibid.*, 18, 838-41 (1926); *Mining Met. Investigations, U. S. Bur. Mines, Carnegie Inst. Tech., Mining Met. Advisory Boards Coöp. Bull.* 55, 1-10 (1932).
- (11) Fernor, L., *Fuel*, 8, 16-29 (1929).
- (12) Fieldner, A. C., and Davis, J. D., *U. S. Bur. Mines, Monograph* 5, 105 (1934).
- (13) Lehmann, K., and Stach, E., *Glückauf*, 66, 289-99 (1930).
- (14) Ovitz, F. K., *U. S. Bur. Mines, Bull.* 138 (1917).
- (15) Parr, S. W., and Francis, C. K., *Univ. Ill. Eng. Expt. Sta., Bull.* 24 (1908); Parr, S. W., and Olin, H. L., *Ibid.*, 60 (1912), 79 (1915); Parr, S. W., and Layng, T. E., *J. IND. ENG. CHEM.*, 13, 14-17 (1921); Parr, S. W., *Gas Age-Record*, 50, Pt. II, 531-4 (1922).
- (16) Seyler, C. A., *Colliery Guardian*, 142, 401-4, 488-90, 577-9 (1931).
- (17) Seyler, C. A., *Fuel*, 2, 217-18 (1923).
- (18) Thiessen, Reinhardt, *IND. ENG. CHEM.*, 24, 1032-41 (1932).
- (19) Warren, W. B., *Ibid.*, 27, 1350-4 (1935).
- (20) Winter, H., *Kolloid-Z.*, 19, 8-11 (1916), 42, 233-42 (1927); *Glückauf*, 55, 545-50 (1919), 58, 1533-9 (1922), 63, 483-92 (1927), 64, 653-8 (1928); *Fuel*, 2, 78-82 (1923), 3, 134-9 (1924); *Braunkohle*, 23, 605-13 (1924).

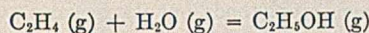
RECEIVED March 1, 1937. Presented before the Division of Gas and Fuel Chemistry at the 93rd Meeting of the American Chemical Society, Chapel Hill, N. C., April 12 to 15, 1937. Published by permission of the Director U. S. Bureau of Mines. (Not subject to copyright.)



CORRESPONDENCE

Thermodynamic Calculation of Vapor-Phase Hydration of Ethylene

SIR: Bliss and Dodge (2) recently published the results of a direct, experimental determination of the equilibrium constants at several temperatures for the reaction:



From their results and the earlier experimental data of Stanley, Youell, and Dymock (14), they thus derived the general free-energy equation,

$$\Delta F^\circ = -9600 + 28.2 T \quad (1)$$

for this gas-phase reaction and then calculated the corresponding equilibrium constants at intervals of 100° between 400° and 700° K. This experimental investigation is a valuable contribution, and it is to be hoped that Dodge and his collaborators will continue to make such equilibria studies for other organic reactions.

The present writer, however, cannot agree with the statements of Bliss and Dodge regarding the thermodynamic calculation of the equilibrium constant from thermal data. Among other things they say: "Sanders and Dodge (13) reviewed the situation on the thermodynamic calculation of the equilibrium constant and came to the conclusion that this method was of little value because of the widely divergent results obtained. The present authors have made further calculations using other combinations of thermal data, some of which became available after the earlier paper was published. The results confirm the conclusions already reached."

This writer feels that such statements were justifiable four years ago when the paper by Sanders and Dodge was written, because the thermal data then available for ethylene were distinctly unreliable. However, the situation has greatly improved during the past two years, principally because of the excellent combustion studies of Rossini at the National Bureau of Standards, and today it is possible to calculate quite reliable equilibrium constants for this reaction from the thermal data alone. The object of the present communication is to demonstrate this point.

From the combustion value of Rossini (11) for ethyl alcohol vapor (336,780 ± 100 calories), that of Rossini (12) for ethylene (337,280 ± 70 calories), and the heat of vaporization of water (10,499 ± 3 calories) at 298.1° K. given by Giauque and Stout (5), we obtain $\Delta H_{298} = -11,000 \pm 130$ calories for the reaction in question. The entropy of liquid ethyl alcohol at 298.1° K. is 38.40 ± 0.30 entropy units (E. U.) according to Kelley (7). The heat of vaporization of ethyl alcohol is taken as 10,120 calories per mole by Rossini (11); the corresponding entropy of vaporization thus becomes 33.95 ± 0.07 E. U. Flock, Ginnings, and Holton (4) give 0.0771 atmosphere for the vapor pressure of ethyl alcohol at 298.1° K.; hence the entropy change for compressing the saturated vapor to the standard pressure of 1 atmosphere is -5.09 ± 0.005 E. U. Combination of these data then yields $S^\circ_{298} = 67.3 \pm 0.31$ E. U. for alcohol vapor at the hypothetical pressure of 1 atmosphere. Taking the estimate of Parks (8) for the entropy of ethylene ($S^\circ_{298} = 52.3 \pm 0.3$ E. U.) and Gor-

don's value (6) for gaseous water ($S^\circ_{298} = 45.10 \pm 0.005$ E. U.), we obtain $\Delta S^\circ_{298} = -30.1 \pm 0.5$ E. U. for this reaction.

Accordingly, the free-energy change at 298.1° K. becomes:

$$\Delta F^\circ_{298} = -11,000 + (298.1)(30.1) = -2030 \pm 200 \text{ calories} \quad (2)$$

The corresponding equilibrium constant for the vapor-phase hydration of ethylene at 298.1° K. is $K_p = 3080$ with a probable maximum uncertainty of about 40 per cent.

What is really desirable is a general free-energy equation (similar to Equation 1) which will be valid over a range of temperatures. If ΔC_p for the reaction is assumed to be zero, Equation 2 yields the simple general form:

$$\Delta F^\circ = -11,000 + 30.1 T \quad (3)$$

This assumption of zero value for ΔC_p represents only a rough first approximation, but the resulting equation cannot involve us in serious error if we do not try to apply it too far above 298° K.

A more reliable ΔC_p value is obtainable with the equation,

$$\Delta C_p = -6.43 + 0.0133 T \quad (4)$$

which the writer derived from the following heat-capacity relations:

$$\text{C}_2\text{H}_4(\text{g}); C_p = 3.68 + 0.0224 T$$

$$\text{H}_2\text{O}(\text{g}); C_p = 7.25 + 0.0023 T$$

$$\text{C}_2\text{H}_5\text{OH}(\text{g}); C_p = 4.50 + 0.038 T$$

In this case the linear equation for ethylene conforms within 1.1 per cent to the experimental values of Eucken and Partz (3) and of Beeck (1) between 290° and 573° K., and that for steam agrees within 0.8 per cent up to 750° K. with the highly accurate statistical C_p values published by Gordon. The equation for ethyl alcohol vapor is the one derived previously by Parks and Huffman (10), mainly from Regnault's specific heat value at 437° and Thibaut's value at 623° K. It is undoubtedly the weakest point in the present calculations, since the C_p values thereby obtainable may, perhaps, be in error by 5 per cent. With the data in Equations 2 and 4 the general free-energy equation

$$\Delta F^\circ = -9674 + 6.43 T \ln T - 0.00665 T^2 - 9.01 T \quad (5)$$

was derived by the usual thermodynamic procedures (9). This should be appreciably more accurate than Equation 3 between 300° and 700° K.

TABLE I. COMPARISON OF ΔF° AND K_p VALUES

T ° K.	ΔF°			Derived $K_p \times 10^3$		
	Equation 1	Equation 3	Equation 5	Equation 1	Equation 3	Equation 5
298.1	-1,200	-2,030	-2,030	759	3,080	3,080
400	1,680	1,040	1,069	120	270	260
500	4,500	4,050	4,139	10.7	16.9	15.5
600	7,320	7,060	7,206	2.14	2.68	2.36
700	10,140	10,070	10,249	0.68	0.71	0.63

In Table I the writer compares the free-energy values calculated by Equations 3 and 5 with those obtainable from the equation of Bliss and Dodge (Equation 1). Undoubtedly the values given by Equation 1 are the more reliable at 500°, 600°, and 700° K., since at these temperatures they are closely related to the experimentally measured equilibrium constants; those given by Equations 3 and 5 are safer at 298° and 400° K. However, it is clear from these data that the new equations, especially 5, are

in fair agreement with the results of the equilibrium studies. This fact is also brought out by the comparison of the equilibrium constants derived from the three free-energy equations, as tabulated in columns 5, 6, and 7.

A direct comparison of the results obtainable from Equations 3 and 5 with the experimentally measured equilibrium constants of Bliss and Dodge provides still another way of testing the exactness of the thermodynamic calculation of the equilibrium. At 623° K. Bliss and Dodge found $K_p = 0.00149$, whereas Equation 3 gives 0.00190 and Equation 5, 0.00167. At 651° K. their experimental value was 0.00126 as against 0.00129 by Equation 3 and 0.00114 by Equation 5. In the writer's opinion this agreement, especially with Equation 5, is very satisfactory and serves to indicate quite fairly the potentialities of the thermodynamic calculation of equilibria.

Literature Cited

- (1) Beeck, O., *J. Chem. Phys.*, 4, 680 (1936).
- (2) Bliss, R. H., and Dodge, B. F., *IND. ENG. CHEM.*, 29, 19 (1937).
- (3) Eucken, A., and Partz, A., *Z. physik. Chem.*, 20B, 184 (1933).
- (4) Fiock, E. F., Ginnings, D. C., and Holton, W. B., *Bur. Standards J. Research*, 6, 881 (1931).
- (5) Giauque, W. F., and Stout, J. W., *J. Am. Chem. Soc.*, 58, 1144 (1936).
- (6) Gordon, A. R., *J. Chem. Phys.*, 2, 65 (1934).
- (7) Kelley, K. K., *J. Am. Chem. Soc.*, 51, 779 (1929).
- (8) Parks, G. S., *Chem. Rev.*, 18, 325 (1936).
- (9) Parks, G. S., and Huffman, H. M. "Free Energies of Some Organic Compounds," A. C. S. Monograph No. 60, pp. 23-5, New York, Chemical Catalog Co., 1932.
- (10) *Ibid.*, p. 125.
- (11) Rossini, F. D., *Bur. Standards J. Research*, 13, 189 (1934).
- (12) *Ibid.*, 17, 635 (1936).
- (13) Sanders, F. J., and Dodge, B. F., *IND. ENG. CHEM.*, 26, 208 (1934).
- (14) Stanley, H. M., Youell, J. E., and Dymock, J. B., *J. Soc. Chem. Ind.*, 53, 205T (1934).

GEORGE S. PARKS

STANFORD UNIVERSITY, CALIF.
April 2, 1937

SIR: Parks points out that the free-energy change for the ethylene hydration reaction can now be calculated from thermal data with considerable confidence. This has been made possible largely by the new value of the heat of combustion of ethylene obtained by Rossini at the Bureau of Standards. Our work on the experimental study of this reaction was completed more than a year before this value was published, and our paper was submitted nearly 6 months prior to its publication. Consequently at the time that our calculations for the paper were made, our pessimistic statement about the value of the thermodynamic calculation may have been justified.

It is true, however, that prior to the submission of our paper the data on heat of combustion of ethane obtained by Rossini (3) and on heat of hydrogenation of ethylene by Kistiakowsky (1) permitted a more accurate calculation of the free energy of hydration than had been possible at the time our work was started. These data were used by Parks (2) to compute a value for the free energy of ethylene formation—namely, 15,820 in the usual units. If this value is combined with the best data on ethyl alcohol and water (the same data used by Parks in his communication), the value of -1790 is obtained for the standard free energy of the hydration reaction in the vapor phase. This is to be compared with Parks's value of -2030 as given above. The equilibrium constant, K_p , at 700° K., based on the former ΔF° value, is 1.62×10^{-3} compared to 2.36×10^{-3} given by Parks. Considering the circumstances, this is good agreement and on this basis the statement of Bliss and myself was certainly too pessimistic.

I would be one of the last to belittle the value of thermodynamics in the prediction of chemical equilibrium, and I am glad to have Parks correct any false impression that our paper may have created.

We may conclude that the equilibrium conditions for the ethylene hydration reaction, at least at low pressures, are well established as a result both of the recent work on heats of reaction and absolute entropy and of the direct experimental measurements of the equilibrium constants. It would appear desirable to continue the attack on organic reaction equilibria along both of these lines. I hope that Parks and his co-workers and Rossini, to mention only a few of the investigators on the thermodynamic side, will continue to supply accurate thermal data. I should also like to point out that, even if we can calculate from thermal data the equilibrium constant for a given reaction, it will still be desirable to carry out direct experimental studies of the same reaction. This is not only because of the desirability of having check results by independent methods, but also because we learn a great deal about the reaction from the direct experimental study that cannot be obtained from the thermodynamic calculations. For example, the important practical questions of pressure, temperature, and catalyst to realize a rate of reaction that permits an approach to equilibrium, and of the extent of side reactions, are answered only by an experimental investigation.

Literature Cited

- (1) Kistiakowsky, G. B., Romeyn, H., Jr., Ruhoff, J. R., Smith, H. A., and Vaughan, W. E., *J. Am. Chem. Soc.*, 57, 65-75 (1935).
- (2) Parks, G. S., *Chem. Rev.*, 18, 325-34 (1936).
- (3) Rossini, F. D., *Bur. Standards J. Research*, 13, 21 (1934).

BARNETT F. DODGE

YALE UNIVERSITY,
NEW HAVEN, CONN.
May 17, 1937

Correction

Attention is called to an article by C. D. West [*J. Am. Chem. Soc.*, 59, 742 (1937)] on "Optical Properties and Polymorphism of Paraffins" where the author points out an error in the article by Page [*IND. ENG. CHEM.*, 28, 856 (1936)] on "Commercial Paraffin Waxes."

In Table II of Page's article the ordinary and extraordinary refractive indices are reversed, so that the column $n_o - n_e$ is actually $n_e - n_o$, and the mean refractive index n is incorrect. Table VI is therefore incorrect also. Table VII, corrected, is given here.

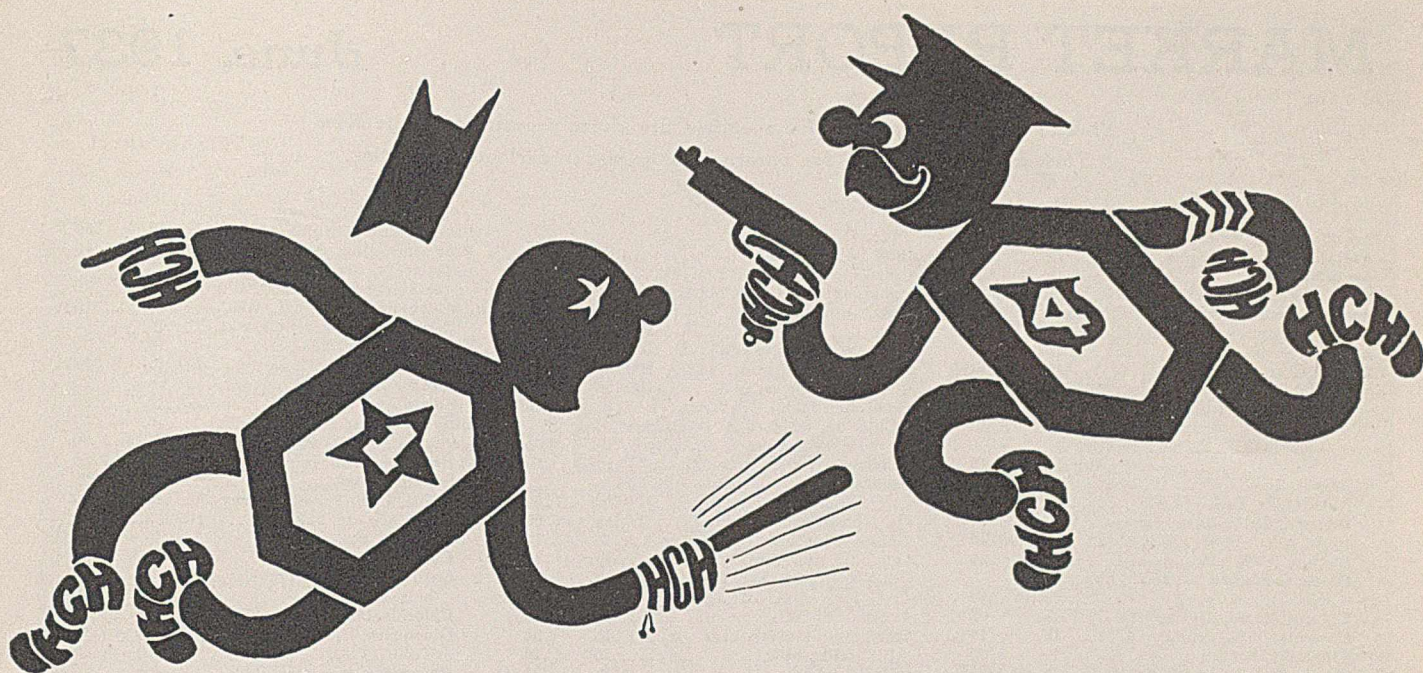
TABLE VII. TRUE DENSITY OF, AND VOLUME PER CENT AIR IN, SOLID COMMERCIAL PARAFFIN WAXES

M. P. of Wax ° F.	° C.	r_D at 20° C.	Temp.		n (Obsvd.)	d_1 (Obsvd.)	d_2 (Calcd.)	$d_2 - d_1$	Vol. % Air
			° F.	° C.					
121	49.4	0.3343	50	10.0	1.5153	0.900	0.902	0.002	+0.23
			60	15.6	1.5136	0.897	0.899	0.002	+0.23
126	52.2	0.3342	50	10.0	1.5179	0.911	0.906	-0.005	-0.55
			60	15.6	1.5155	0.909	0.902	-0.007	-0.77
131	55.0	0.3339	50	10.0	1.5182	0.912	0.907	-0.005	-0.55
			60	15.6	1.5160	0.909	0.904	-0.005	-0.55
136	57.8	0.3341	50	10.0	1.5213	0.917	0.911	-0.006	-0.55
			60	15.6	1.5197	0.914	0.909	-0.005	-0.41
141	60.6	0.3337	60	15.6	1.5214	0.914	0.913	-0.001	-0.10
			70	21.1	1.5192	0.911	0.909	-0.002	-0.22

The difference between the calculated and observed densities now becomes so small as to be attributable to experimental error.

J. M. PAGE, JR.

STANDARD OIL COMPANY (INDIANA),
CASPER, WYO., May 13, 1937



HI, SERGEANT

The chemical sergeant is now on call when you need him for gum inhibiting jobs that are too hard for the chemical cop to handle

The sergeant has a number - he is U O P Inhibitor No 4 The cop is No 1

The chemical cop is on duty in more than a score of refineries, inhibiting thousands of barrels of cracked gasoline every day - doing a good job

But sometimes he gets up against it

In such cases call the chemical sergeant

They dont come too tough for him - that's why he rates chevrons

Considering the money he saves you, the chemical sergeant, like the chemical cop, really works for nothing - and boards himself

Universal Oil Products Co
Chicago, Illinois



Dubbs Cracking Process
Owner and Licensor

MARKET REPORT

June, 1937

These prices unless otherwise specified are those prevailing in the New York market, June 15, for commercial grades in carload quantities.

Acetaldehyde, drums, c/l, wks. lb.	.14	Wood, <i>see</i> Methanol		Bromobenzene, drums..... lb.	.50
Acetaldol, 50-gal. drums..... lb.	.27	Aldol, 95%, drums, c/l..... lb.	.21	Bromoform, jars..... lb.	1.40
Acetamide, tech., c/l, drums..... lb.	.32	Alpha-naphthol, bbls..... lb.	.52	Butyl acetyl ricinoleate, drums..... lb.	.24
Acetanilide, U. S. P., powd., bbls..... lb.	.25	Alpha-naphthylamine, bbls..... lb.	.32	Acetate, drums, c/l, frt. allowed. lb.	.10
Acetic anhydride, drums, frt. allowed. lb.	.13	Alum, ammonia, lump, bbls., wks. 100 lbs.	3.00	Aldehyde, drums, c/l, wks..... lb.	.16½
Acetone, drums, wks, c/l, frt. allowed. lb.	.06	Chromic, casks, wks..... 100 lbs.	7.00	Carbinol, norm., drums, wks..... lb.	.60
Acetphenetidin, bbls..... lb.	1.30	Potash, lump, bbls., wks..... 100 lbs.	3.00	Carbinol, sec., wks..... lb.	.60
Acid, abietic..... lb.	.09¾	Soda, bbls., wks..... 100 lbs.	3.25	Lactate, drums..... lb.	.22½
Acetic, 28%, c/l, bbls..... 100 lbs.	2.53	Aluminum, metal, N. Y..... lb.	.20	Oleate, drums..... lb.	.25
56%, c/l, bbls..... 100 lbs.	4.75	Chloride, anhyd., commercial, wks., drums extra, c/l..... lb.	.05	Stearate, drums..... lb.	.26
Glacial, c/l, drums..... 100 lbs.	8.70	Stearate, 100-lb. bbl..... lb.	.19	Butyraldehyde, drums, wks..... lb.	.35½
Glacial, U. S. P., c/l, carboys 100 lbs.	13.75	Sulfate, comm'l, bags, wks., frt. equal..... 100 lbs.	1.80	Cadmium, metal, cases..... lb.	1.20
Acetylsalicylic, U. S. P., bbls..... lb.	.50	Iron-free, bags, wks..... 100 lbs.	2.00	Bromide, 50-lb. jars..... lb.	1.56
Anthranilic, tech., bbls..... lb.	.75	Aminoazobenzene, 100-lb. kegs..... lb.	1.15	Sulfide, boxes..... lb.	.90
Benzoic, tech., bbls..... lb.	.43	Ammonia, anhydrous, cyl., wks..... 50,000-lb., frt., tanks, wks..... lb.	.04½	Caffeine, U. S. P., 5-lb. cans..... lb.	2.10
Boric, tech., bbls..... ton	95.00	Ammonia, aqua, 26°, tanks, wks., contained NH..... lb.	.04½	Calcium acetate, bags..... 100 lbs.	2.25
Butyric (99%), drums, wks..... lb.	.22	Ammonium acetate, kegs..... lb.	.26	Arsenate, bbls..... lb.	.06¾
Chloroacetic, mono-, tech., bbls., wks..... lb.	.16	Bifluoride, bbls..... lb.	.16	Carbide, drums..... lb.	.05
Chlorosulfonic, drums, wks..... lb.	.03½	Bromide, bbls..... lb.	.35	Carbonate, U. S. P., precip., 175-lb. bbls..... lb.	.06½
Chromic, 99%, drums..... lb.	.14¾	Carbonate, tech., bbls..... lb.	.08	Chloride, bags, flake, c/l, deliv..... ton	22.00
Cinnamic, bottles..... lb.	2.85	Chloride, gray, bbls..... 100 lbs.	5.50	Glucanate, U. S. P..... lb.	.50
Citric, U. S. P., cryst., bbls..... lb.	.25	Lump, casks..... lb.	10½	Tech..... lb.	.28
Cresylic, H. B., c/l, wks., frt. equal, drums..... gal.	.91	Iodide, 25-lb. jars..... lb.	3.25	Phosphate, monobas., bbls..... lb.	.07½
Formic, 90%, cbys., N. Y..... lb.	.11	Linoleate, bbls..... lb.	.11	Tribas., bbls..... lb.	.06½
Furoic, tech., drums..... lb.	.35	Nitrate, tech., cryst., bbls..... lb.	.10	Calomel, 100-lb. drums..... lb.	1.59
Gallic, tech., bbls..... lb.	.65	Oleate, bbls..... lb.	.04	Camphor, Jap., slabs..... lb.	.55
H, bbls., wks..... lb.	.50	Oxalate, kegs..... lb.	.22½	Carbazole, 70-80%, bbls..... lb.	.60
Hydriodic, 57%, 5-lb. bot..... lb.	2.65	Persulfate, cases..... lb.	.21	Carbon bisulfide, drums, c/l..... lb.	.05
Hydrobromic, 10%, U. S. P., cbys., wks..... lb.	.18	Phosphate, dibasic, tech., bbls..... lb.	.07½	Carbon black, bags, c/l..... lb.	.05
Hydrochloric, 20°, tanks, wks. 100 lbs.	1.10	Stearate, anhyd., drums..... lb.	.26	Carbon dioxide, liq., cyl..... lb.	.06
Hydrofluoric, 30%, bbls., wks..... lb.	.07	Sulfate, bulk, wks..... ton	26.50	Carbon tetrachloride, drums..... lb.	.05½
60%, bbls., wks..... lb.	.15	Amylene, tanks, wks..... lb.	.09	Casein, stand. gr., bbls..... lb.	.13
Hydrofluosilic, 35%, bbls., wks..... lb.	10½	Amyl acetate, tech., from pentane, tanks, frt. allowed..... lb.	.11½	Cellulose acetate, bbls..... lb.	.08½
Hypophosphorus, 30%, U. S. P., 5-gal. demis..... lb.	.75	Chloride, normal, drums, wks..... lb.	.56	Cerium oxalate, kegs..... lb.	.28
Koch, bbls..... lb.	.36	Chlorides, mixed, tanks, wks..... lb.	.06	Charcoal, willow, powd., bbls..... lb.	.06
Lactic, 22%, dark, bbls..... 100 lbs.	2.50	Mercaptan, drums, wks..... lb.	1.10	China clay, bulk..... ton	8.00
44%, light, bbls., wks..... 100 lbs.	6.50	Oleate, l. c. l., drs., wks..... lb.	.25	Chloral hydrate, drums..... lb.	.80
Linoleic, drums..... lb.	.16	Stearate, l. c. l., drs., wks..... lb.	.26	Chlorine, liq., c/l, cyl.*..... lb.	.055
Maleic, powd., drums..... lb.	.30	Aniline oil, drums..... lb.	.15	Chlorine, tanks..... 100 lbs.	2.15
Mixed, tanks, wks..... N unit	.06½	Anthracene, 80-85%, casks, wks..... lb.	.75	Chlorobenzene, mono-, drums..... lb.	.06
S unit	.0085	Anthraquinone, subl, bbls..... lb.	.65	Chloroform, tech., drums..... lb.	.20
Naphthenic, S. V. 120-200, drums. lb.	.07	Antimony, metal..... lb.	.14¾	Chromium acetate, 20° soln., bbls..... lb.	.05
Naphthionic, tech., bbls..... lb.	nom.	Chloride, cbys..... lb.	.17	Coal tar, bbls., wks..... bbl.	7.25
Nitric, c. r., cbys..... lb.	.10½	Oxide, bbls., c/l..... lb.	.16½	Cobalt oxide, bbls..... lb.	1.67
Nitric, 36%, c/l, cbys., wks..... 100 lbs.	5.00	Salt, dom., kegs..... lb.	.23¾	Copperas, c/l, bulk..... ton	12.00
Oxalic, bbls., wks..... lb.	.10¾	Sulfide, golden, bbls..... lb.	.22	Copper, metal, elec..... 100 lbs.	14.00
Phosphoric, 50%, U. S. P..... lb.	.12	Arsenic, metal, kegs..... lb.	.42	Copper carbonate, bbls., 52/54%..... lb.	.18
Picramic, kegs..... lb.	.65	Red, kegs, cases..... lb.	.15¾	Chloride, bbls..... lb.	.15
Picric, bbls., c/l..... lb.	.35	White, c/l, kegs..... lb.	.03	Cyanide, drums..... lb.	.37
Pyrogallic, tech., bbls..... lb.	.90	Barium carbonate, bbls., bags, wks. ton	44.00	Oxide, black, bbls..... lb.	nom.
Salicylic, tech., bbls..... lb.	.33	Chloride, bbls., wks..... ton	72.00	Sulfate, c/l, bbls..... 100 lbs.	5.15
Sebacia, tech., drums..... lb.	.37	Dioxide, drs., wks..... lb.	.11	Cotton, soluble, bbls..... lb.	.40
Stearic, d. p., bbls., c/l..... lb.	12½	Hydroxide, bbls..... lb.	.04¾	Cream of tartar, bbls..... lb.	.17¾
Sulfanilic, tech., 250-lb. bbls..... lb.	.17	Nitrate, casks..... lb.	.07	Crotonaldehyde, drums, c/l..... lb.	.26
Sulfuric, 66%, c/l, cbys., wks. 100 lbs.	1.25	Thiocyanate, 400-lb. bbls..... lb.	.27	Cyanamide, bulk, Atlantic ports..... Ammonia unit	1.15
66°, tanks, wks..... ton	15.50	Barytes, floated, 350-lb. bbls., wks. ton	23.65	Diaminophenol, kegs..... lb.	3.80
60°, tanks, wks..... ton	12.00	Benzaldehyde, tech., drums..... lb.	.60	Diamylamine, drums, c. l., wks..... lb.	.47
Oleum, 20%, tanks, wks..... ton	18.50	Benzidine base, bbls..... lb.	.70	Diethylene glycol, drums, wks..... lb.	.08½
Tannic, tech., bbls..... lb.	.26	Benzol, tanks, wks..... gal.	.16	Diamyl ether, drums, wks..... lb.	.08½
Tartaric, U. S. P., cryst., bbls..... lb.	.23¾	Benzoyl chloride, drums..... lb.	.40	Diamyl oxalate, lc-l., drs., wks..... lb.	.30
Tungstic, tech., kegs..... lb.	2.75	Benzyl acetate, F. F. C., bottles..... lb.	.55	Diamyl phthalate, tanks..... lb.	.20½
Valeric, c. r., 10-lb. bot..... lb.	2.50	Chloride, tech., drums..... lb.	.30	Diamyl sulfide, drums, wks..... lb.	1.10
Alcohol, ethyl from molasses, 190 proof, bbls..... gal.	4.13	Beta-naphthol, bbls..... lb.	.23	Dianisidine, bbls..... lb.	2.25
Amyl, from pentane, tanks..... lb.	.123	Bismuth, nitrate, cases..... lb.	1.20	Dibutoxyethylphthalate, wks, drums..... lb.	.35
Secondary, tanks..... lb.	.08¾	Oxychloride, kegs..... lb.	2.95	Dibutyl ether, drums, wks..... lb.	.30
Butyl, drums, c/l, wks., frt. allowed..... lb.	.10	Subnitrate, 25-lb. jars..... lb.	1.22	Dibutyl phthalate, drums, wks., frt. allowed..... lb.	.21
Cinnamic..... lb.	2.50	Blanc fixe, dry, bags, c/l..... ton	60.00	Dibutyl tartrate, drums..... lb.	.35
Denatured, No. 11, comp. denat., c/l, drums..... gal.	.35	Bleaching powder, drums, wks. 100 lbs.	2.00	Dichloroethyl ether, drums, c/l, wks. lb.	.15
Diacetone, tech., c. l., drums..... lb.	.12¾	Bone ash, kegs..... lb.	.06	Dichloropentanes, tanks, wks..... lb.	no prices
Furfuryl, tech., 500-lb. drums, c/l. lb.	.30	Bone black, bbls..... lb.	.08¾	Diethanolamine, drums, wks..... lb.	.31
Isocamyl, drums..... lb.	.27	Borax, bags..... ton	42.00	Diethylaniline, drums..... lb.	.50
Isobutyl, ref., drums..... lb.	.09½	Bordeaux mixture, drums..... lb.	.10	Diethylene glycol, drums, wks..... lb.	.22
Isopropyl, ref., 91%, drums, frt. allowed..... gal.	.39½	Bromine, cases..... lb.	.30	Monobutyl ether, drums, wks..... lb.	.26
				Monoethyl ether, drums, wks..... lb.	.16
				Diethylene oxide, drums, wks..... lb.	.20
				Diethyl carbinol, drums, wks..... lb.	.60
				Diethyl phthalate, drums..... lb.	.19

* F. O. B. destination.

(Continued on page 40)



A Picture...

OF THE MAGNIFICENT, NEW MELLON INSTITUTE IS NOT NECESSARY



Every scientist can visualize the imposing Greek "Temple of Science." It has made "news" for the profession of scientific research.

Alberene Stone Equipment was installed in the original Mellon Institute 24 years ago, and in practically every important laboratory built since that time . . . Therefore, it was the obvious choice for the new Mellon Institute, and we are proud to continue this distinguished name on our "Roll Call."

"If . . .

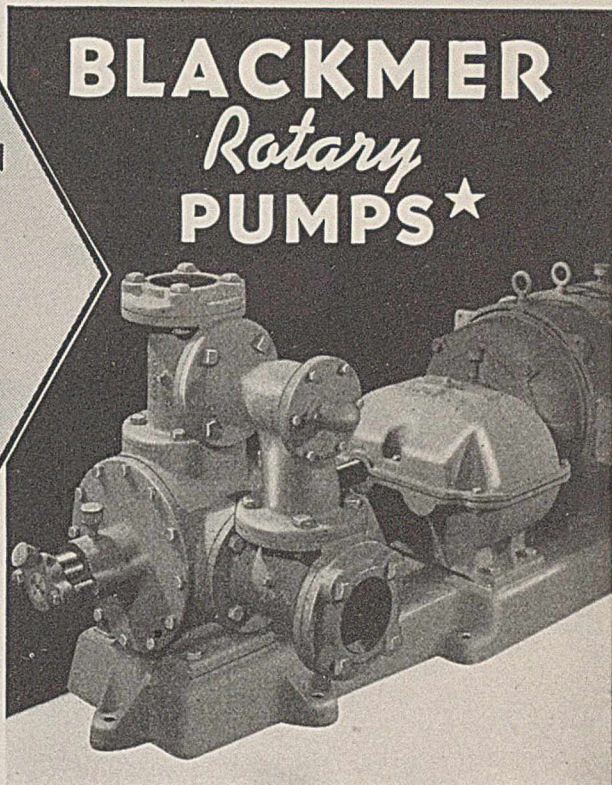
there was a better material for the purpose, Alberene Stone would not have been used."

MARKET REPORT (continued from page 38)

Diethyl sulfate, tech., drums, wks.	lb.	.13	Meta-nitroaniline, bbls.	lb.	.67	Pyridine, drums	gal.	1.30
Diglycol oleate, light, bbls.	lb.	.24	Meta-phenylenediamine, kegs.	lb.	.80	Pyrocatechin, c. p., drums	lb.	2.15
Dimethylamine, pure 25.40% sol.— 100% basis, drums	lb.	.95	Meta-tolylenediamine, bbls.	lb.	.65	Resorcinol, tech., kegs.	lb.	.75
Dimethylamine, frt. allowed E. Miss., drs., c. l.	lb.	1.00	Methanol, pure, synthetic, drums, wks., frt. allowed, c/l.	gal.	.38	Rochelle salt, bbls., U. S. P.	lb.	.15½
Dimethylaniline, drums	lb.	.26	Tanks, wks., frt. allowed.	gal.	.33	R salt, bbls.	lb.	.52
Dimethyl ethyl carbinol, drums, wks. lb.	lb.	.60	Methyl acetone, tanks, wks., frt. allowed.	gal.	.41	Saccharin, cans.	lb.	1.70
Dimethylsulfate, drums	lb.	.45	Chloride, cylinders.	lb.	.36	Salt cake, bulk.	ton	12.00
Dimethyl phthalate, drums, wks., frt. allowed.	lb.	.21	Formate, 1 c. l., drs., frt. allowed. lb.	lb.	.39	Salt peter, gran., bbls.	lb.	.06
Dinitrobenzene, tech., drums	lb.	.16	Hexyl ketone, drs., tech., wks.	lb.	.60	Silica, ref., bags.	ton	22.00
Dinitrochlorobenzene, bbls.	lb.	.16½	Laotate, 1 c. l., drs., frt. allowed. lb.	lb.	.30	Silver nitrate, 16-oz. bot.	oz.	.32½
Dinitronaphthalene, bbls.	lb.	.35	Propyl carbinol, drums, wks.	lb.	.60	Soda, ash, 58%, light, bags, contract, wks.	100 lbs.	1.23
Dinitrophenol, bbls.	lb.	.23	Salicylate, cases.	lb.	.42	Soda, caustic, 76%, solid, drums, contract, wks.	100 lbs.	2.60
Diphenyl.	lb.	.15	Michler's ketone, kegs.	lb.	2.50	Sodium abietate, drums.	lb.	.08
Diphenylamine, bbls.	lb.	.31	Monoamylamine, drums, c. l., wks. lb.	lb.	.62	Acetate, flake, bbls.	lb.	.04½
Diphenylguanidine, bbls.	lb.	.35	Monoethanolamine, drums, wks.	lb.	.31	Alginate, drums.	lb.	.69
Epsom salt, tech., bbls., c/l., N. Y.	100 lbs.	1.90	Monomethylamine, drums.	lb.	.65	Antimoniate, drs.,	lb.	.15½
Ether, conc., drums	lb.	.09	Naphthalene, crude.	100 lbs.	2.30	Benzoate, tech., bbls.	lb.	.40
Ether, nitrous, bot.	lb.	.75	Nickel, metal.	lb.	.35	Bicarbonate, bbls.	100 lbs.	1.75
Ethyl acetate, 85-88%, tanks, c/l., wks., frt. allowed.	lb.	.06½	Nickel salt, single, bbls.	lb.	.13	Bichromate, casks.	lb.	.06½
Acetoacetate, 110-gal. drums, wks., frt. allowed.	lb.	.27½	Double, bbls.	lb.	.13	Bisulfite, bbls.	lb.	.03½
Bromide, drums	lb.	.50	Niter cake, bulk.	ton	nom.	Bromide, bbls., U. S. P.	lb.	.31
Carbonate, 90%, 50-gal. drums. gal.	gal.	1.85	Nitrobenzene, drums.	lb.	.08	Chlorate, cryst., bags.	lb.	.06½
Chlorocarbonate, carboys.	lb.	.30	Nitrogen solution unit.	unit	1.04	Chloride, bags.	ton	14.80
Chloride, drums	lb.	.22	Octyl acetate, tanks, wks.	lb.	.15	Cyanide, cases.	lb.	.16½
Ether, absolute, 50-gal. drums.	lb.	.50	Oil, castor, No. 1.	lb.	.10	Fluoride, bbls.	lb.	.07½
Formate, 1 c. l., drs., frt. allowed. lb.	lb.	.31	China wood, bbls.	lb.	.13	Metallic, drums, 12½-lb. bricks. lb.	lb.	.19
Methyl ketone, drums.	lb.	.07	Cocoon, tanks.	lb.	.05½	Metasilicate, cryst.	100 lbs.	2.75
Ethylbenzylamine, 300-lb. drums.	lb.	.86	Cod, N. F., bbls.	gal.	.52	Metasilicate, gran., bbls.	100 lbs.	2.15
Ethylene dichloride, drums, wks., frt. allowed.	lb.	.05½	Corn, crude, tanks, mills.	lb.	.08½	Naphthenate, drums.	lb.	1.12
Ethylenechlorohydrin, anhyd., drums, wks.	lb.	.75	Cottonseed, oil refined, bbls.	lb.	.11	Naphthionate, bbls.	lb.	.52
Glycol, c/l., wks.	lb.	.17	Linseed, boiled, bbls.	lb.	.114	Nitrate, crude, bulk, N. Y.	ton	25.50
Monobutyl ether, drums, wks.	lb.	.20	Menhaden, crude, tanks.	gal.	.45	Nitrite, bbls.	lb.	.07
Monoethyl ether, drums, wks.	lb.	.16	Neat's-foot, pure, bbls.	lb.	.13½	Perborate, bbls.	lb.	.14½
Monoethyl ether acetate, drums, wks.	lb.	.14	Oleo, No. 1, bbls.	lb.	.13	Phosphate, disodium, bags. 100 lbs.	lb.	1.70
Monomethyl ether, drums, wks.	lb.	.18	Olive oil, denat., bbls.	gal.	1.50	Phosphate, trisodium, bbls. 100 lbs.	lb.	2.05
Oxide, cylinders, wks.	lb.	.50	Foots, bbls.	lb.	.11½	Picramate, kegs.	lb.	.65
Feldspar, bulk.	ton	11.00	Peanut, crude, tanks.	lb.	.08½	Prussiate, bbls.	lb.	.10
Fluorspar, 98%, bags.	ton	nom.	Perilla, drums.	lb.	.11½	Silicate, drums, tanks, 40°. 100 lbs.	lb.	.80
Formaldehyde, bbls.	lb.	.05½	Rapeseed, denat., bbls.	gal.	.95	Silicofluoride, bbls.	lb.	.06
Formaniline, drums.	lb.	.37½	Red, bbls.	lb.	.11½	Stannate, drums.	lb.	.36
Fuller's earth, bags, c/l., mines.	ton	10.00	Soy bean, crude, tanks.	lb.	.095	Sulfate, anhyd., bags.	100 lbs.	1.45
Furfural, drums, tech., contract, works.	lb.	.10	Sperm, 38°, bbls.	lb.	.10	Sulfide, cryst., bbls.	lb.	.02½
Glauber's salt, bbls.	100 lbs.	1.05	Whale, bbls., natural, refined.	lb.	.105	Solid, 60%.	lb.	.03
Glycerine, c. p., drums.	lb.	.22	Ortho-aminophenol, kegs.	lb.	2.15	Sulfocyanide, bbls.	lb.	.28
Glyceryl phthalate, drums.	lb.	.30	Ortho-dichlorobenzene, drums.	lb.	.06	Thiosulfate, reg., cryst., bbls.	lb.	.024
Glycol phthalate, drums.	lb.	.29	Ortho-nitrochlorobenzene, drums.	lb.	.28	Tungstate, tech., kegs.	no prices	
Stearate, drums.	lb.	.23	Ortho-nitrophenol, bbls.	lb.	.85	Strontium carbonate, pure, bbls.	lb.	.30
G salt, bbls.	lb.	.45	Ortho-nitrotoluene, drums.	lb.	.07	Nitrate, bbls.	lb.	.07½
Hexamethylenetetramine, tech., drums.	lb.	.35	Ortho-toluidine, bbls.	lb.	.14	Peroxide, 100-lb. drums.	lb.	1.25
Hydrogen peroxide, 100 vol., ebys.	lb.	.20	Paraldehyde, 110-50-gal. drums.	lb.	.16	Sulfur, bulk, mines, wks.	ton	18.00
Hydroquinone, kegs.	lb.	.90	Para-aminophenol, kegs.	lb.	1.05	Sulfur chloride, drums.	lb.	.03
Indigo, synth., liq., bbls.	lb.	.16½	Para-dichlorobenzene.	lb.	.16	Sulfur dioxide, commercial, cyl.	lb.	.07
Iodine, resubl. jars.	lb.	1.50	Para-formaldehyde, cases.	lb.	.34	Sulfuryl chloride, drums.	lb.	1.0
Iron acetate, liq., 17°, bbls., c/l.	lb.	.03	Paraldehyde, tech., drums.	lb.	.16	Tetrachloroethane, 50-gal. drums.	lb.	.08
Iron chloride, cryst., bbls.	lb.	.05	Para-nitraniline, drums.	lb.	.45	Thiocarbamilid, bbls.	lb.	.20
Isobutyl carbinol (128-132° C.), tanks.	lb.	.32	Para-nitrochlorobenzene, drums.	lb.	.23½	Tin.	lb.	.55½
Kieselguhr, bags, Pac. Coast, wks.	ton	22.00	Para-nitrophenol, bbls.	lb.	.35	Tin tetrachloride, anhydrous, drums, bbls.	lb.	.28
Lead, metal, N. Y.	100 lbs.	6.00	Para-nitrosodimethylaniline, bbls.	lb.	.92	Oxide, bbls.	lb.	.58
Lead acetate, drs., white.	lb.	.13½	Para-nitrotoluene, bbls.	lb.	.35	Titanium dioxide, bbls., wks.	lb.	.16½
Arsenate, drs.	lb.	.11½	Para-phenylenediamine, bbls.	lb.	1.25	Toluene, tanks.	gal.	.30
Oxide, litharge, bbls., 20-ton lots. lb.	lb.	.07½	Para-tertiary amyl phenol, drums, c/l., wks.	lb.	.26	Triamylamine, drums, c. l., wks.	lb.	.77
Peroxide, drums.	lb.	.46	Para-toluidine, bbls.	lb.	.56	Triamyl borate, 1 c. l., drs., wks.	lb.	.27
Red, bbls., 20-ton lots.	lb.	.08½	Paris Green, 250-lb. kegs.	lb.	.22	Tribromophenol, cases.	lb.	1.10
Sulfate, bbls.	lb.	.07	Perchloroethylene, drs., frt. allowed. lb.	lb.	.10½	Tributyl citrate, 1 c. l., drs., frt. al- lowed.	lb.	.45
White, basic carb., bbls.	lb.	.07½	Phenol, drums.	lb.	.13½	Phosphate, 1 c. l., drs., frt. allowed. lb.	lb.	.50
Lime, hydrated, bbls.	100 lbs.	.85	Phenolphthalein, yellow, drums.	lb.	.85	Trichloroethylene, drums, wks., frt. allowed.	lb.	.089
Lime, live, chemical, bbls., wks.	280 lbs.	1.70	Phenylethyl alcohol, 1-lb. bot.	lb.	3.75	Tricresyl phosphate, tech., drs.	lb.	.24½
Lithopone, bbls.	lb.	.04½	Phloroglucinol, tech., drums.	lb.	15.00	Triethanolamine, drums, wks., frt. allowed.	lb.	.26
Magnesite, calcined, 500-lb. bbls., wks.	ton	60.00	c. p., drums.	lb.	20.00	Trihydroxyethylamine oleate, drums. lb.	lb.	.40
Magnesium, metal, wks.	lb.	.30	Phosphorus, red, cases.	lb.	.40	Stearate.	lb.	.35
Magnesium carbonate, bags.	lb.	.06½	Oxychloride, 175-lb. cylinders.	lb.	.16	Trimethylamine, drs., frt. allowed E. Miss., c. l.	lb.	1.00
Chloride, drums.	ton	39.00	Trichloride, cyl.	lb.	.16	Triphenylguanidine, drums.	lb.	.58
Fluosilicate, cryst., bbls.	lb.	.10	Phthalic anhydride, bbls.	lb.	.14½	Triphenyl phosphate, drums.	lb.	.34
Oxide, U. S. P., light, bbls.	lb.	.36	Platinum, metal, solid.	oz.	68.00	Tungsten, tech., powder.	lb.	nom.
Manganese chloride, bbls.	lb.	.09	Potash, caustic, drums.	lb.	.06½	Urea, crystals.	lb.	.0475
Dioxide, 85-90%, bbls.	ton	51.50	Potassium acetate.	lb.	.06	Vinyl chloride, 16-lb. cylinders.	ton	1.00
Sulfate, casks.	lb.	.07	Bicarbonate, gran., bbls.	lb.	.10	Whiting, bags.	ton	7.00
Manitol, pure, cryst., cs., wks.	lb.	1.48	Bichromate, casks.	lb.	.08½	Xylene, 10°, tanks, wks.	gal.	.30
Mercury bichloride, cryst., 100 lbs.	lb.	1.22	Binoxalate, bbls.	lb.	.23	Xylidine, drums.	lb.	.36
Mercury, flasks, 76 lbs.	flask	97.00	Bromide.	lb.	.31	Zinc, metal, E. St. Louis.	100 lbs.	6.75
			Carbonate, 80-85%, calc., casks.	lb.	.05½	Zinc ammonium chloride, bbls.	lb.	.0465
			Chlorate, cryst., kegs.	lb.	.09½	Chloride, granulated, drums.	lb.	.05
			Chloride, crystals, bbls.	lb.	.04	Oxide, Amer., bbls.	lb.	.06½
			Cyanide, cases.	lb.	.55	Perborate, 100-lb. drums.	lb.	1.25
			Meta-bisulfite, bbls.	lb.	.15	Peroxide, 100-lb. drums.	lb.	1.25
			Muriate, fert., bulk, per K ₂ O unit.	lb.	.53½	Stearate, bbls.	lb.	.20
			Permanganate, drums.	lb.	.18½	Zinc dust, bbls., c/l.	lb.	.0865
			Prussiate, red, casks.	lb.	.35			
			Yellow, casks.	lb.	.15			
			Titanium oxalate, bbls.	lb.	.32			

The
STARTING POINT
 for **LOWEST**
PUMPING COSTS

Handling Anything from Ether
 to Tar . . . from Toothpaste to
 Dog Food--to Sulphuric Acid



BLACKMER
Rotary
PUMPS★

**PUMP CAPACITIES UP TO 700 G. P. M.
 AT HEADS UP TO 75 POUNDS**

Shown above is a BLACKMER Integrated, the last word in complete rotary pumping outfits.

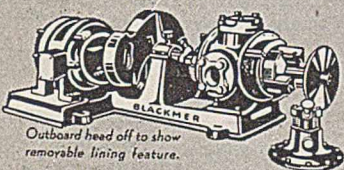
The advantages of BLACKMER Integrations are many. First, unique design gives perfect coordination of working parts. Thus higher overall efficiency — lower operating cost.

Second, the design and construction permit a high degree of standardization — also enable us to include as standard equipment features ordinarily classed as special. Thus lower first and installation costs.

Third, maintenance is reduced to minimum, due to simplicity and because all parts, except the motor, are BLACKMER built — the highest quality in the industry.



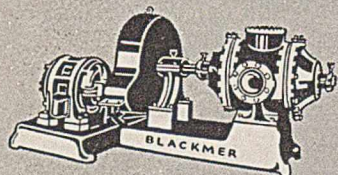
The pumps furnished on BLACKMER Integrations are BLACKMER Rotaries available in various standard constructions. Without going outside our standard line, you can choose pumping units for almost any requirement (note two other standard arrangements at left). Here again is marked economy, as compared with special equipment. Try BLACKMER once, and we will have another satisfied user added to our long customer list. Use Coupon



Outboard head off to show removable lining feature.

LINED PUMPS

Exclusive BLACKMER development — built with replaceable lining and end discs — no wear on pump casing. All working parts renewed at **LOW COST** without disturbing pipe connections. Ideal for pumping corrosive and abrasive liquids, where ordinary equipment is short lived.



STEAM-JACKETED

Rotary Pumps with steam-jacketed heads for handling very viscous liquids and materials semi-solid at room temperatures. Use these pumps, add heat to your pipe lines, and **SAVE MANY DOLLARS** in operating costs.

5
FEATURES

COMPLETE

A BLACKMER Integrated Unit includes rotary pump, base, drive, motor, bypass and strainer—complete outfit.

COMPACT

Capacities considered, Integrated Units are smaller than older types—can be installed in very close quarters.

SIMPLE

Not one complicated part! Any mechanic can service a BLACKMER Integrated.

STANDARD MOTOR

Design permits use of standard high-speed motor—considerable saving in first cost.

3-POINT BASE

Installation easy by use of 3-point Support Base—misalignment troubles eliminated.

★ **"Bucket" Design = Economy**

Moving parts in any BLACKMER Pump consist of the rotor and a set of swinging buckets. In operation the buckets swing outward, in light contact with the pump case—receiving the brunt of all wear. But as the buckets wear, they swing out farther, thus taking up their own wear **AUTOMATICALLY** and maintaining an efficient performance seal.

When replacement of buckets is finally necessary, they can be quickly inserted in the pump without disturbing pipe connections. And the new buckets never total more than 5% of original pump cost. Reason No. 1 for BLACKMER'S amazing economy!

LET US SHOW YOU

BLACKMER PUMP COMPANY

1841 Century Ave., Grand Rapids, Michigan

Without obligation, send complete details covering _____ BLACKMER Rotary Pumps for service as indicated: *how many?*

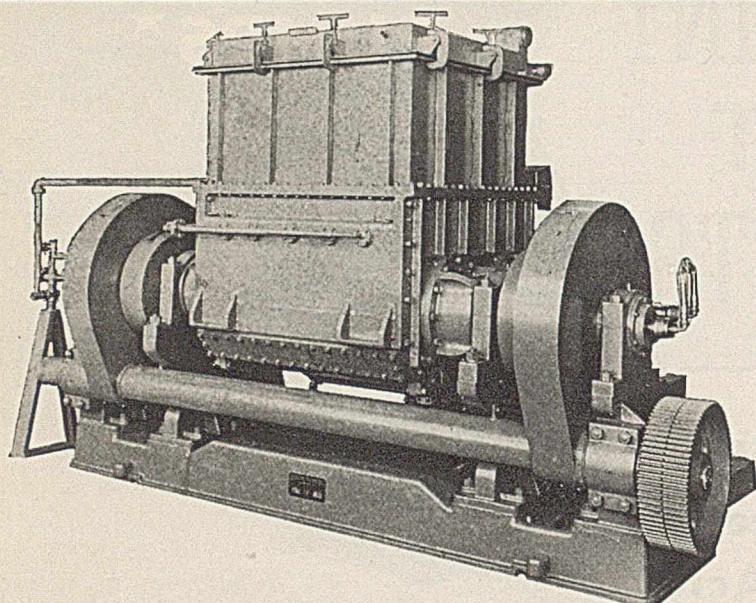
Material to be handled _____

Gallons per minute per pump _____

NAME _____

ADDRESS _____

FOR *unusually tough* MIXES



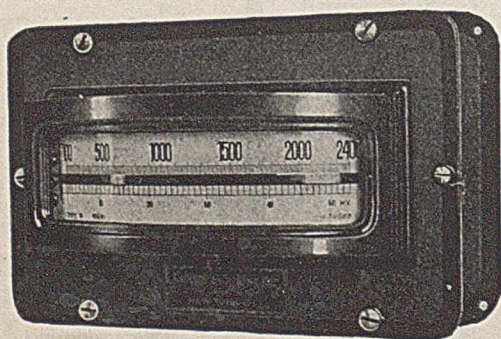
BAKER PERKINS SIZE 18 HEAVY DUTY UNIVERSAL MIXER.
Working capacity 290 gals. Total capacity 650 gals.

BAKER PERKINS

WERNER & PFLEIDERER DIVISION
General Offices and Factory, Saginaw, Mich.
Sales Offices:
New York Chicago Saginaw San Francisco



Why do customers re-order
The Engelhard Type W-1
Indicating Pyrometer?



- It is provided with zero adjustment.
- It has an exclusive frictionless moving system.
- It is extremely sensitive, responding to slightest change in e.r.f.
- It will withstand severe shocks.
- It has no lag and no overrun.
- It is a high resistance instrument.

Know with Engelhard Accuracy

Write Dept. P.

CHARLES ENGELHARD, INC.

90 Chestnut St.

Newark, N. J.

Manufacturers of Gas Analyzers, Pyrometers, Resistance Thermometers, Exhaust Gas Analyzers, Combustion Indicators.

LAMOTTE CHEMICAL CONTROL SERVICE



LAMOTTE UNIVERSAL pH OUTFIT

This compact LaMotte outfit is readily portable, yet it covers a wide pH range. Can be supplied with any 3, 4, 5, 6, 7 or 8 sets of LaMotte Permanent Color Standards and will therefore cover any desired part of pH range, 0.2-13.6. Applicable to all types of research and industrial pH work. Accurate to 0.1 pH. Excellent for use with highly colored or turbid solutions.

Price \$35.00 to \$60.00 f. o. b. Baltimore, Md.

LAMOTTE PERMANENT COLOR STANDARDS

These sealed liquid standards are unquestionably the most accurate type made, since all other types are made by matching against such standards. They have the great advantage of permitting a comparison of a test sample and standard of a similar medium and identical color elements. Available over the entire range from 0.2-13.6 pH in intervals of 0.2 pH. Packed in sets of 9, plus a tube of distilled water.

Set of 10 ampoules \$5.00 f. o. b. Baltimore, Md.

LAMOTTE

CHEMICAL PRODUCTS CO.

Originators of Practical Application of pH Control
414 Light St. Baltimore, Md.

Subscription Rates

American Chemical Society Publications

1. Journal American Chemical Society..... \$ 8.50
2. Chemical Abstracts..... 12.00
3. **Industrial and Engineering Chemistry.**
 - a. Industrial Edition..... \$5.00
 - b. News Edition..... 1.50
 - c. Analytical Edition..... 2.00
 - 3a and 3c together..... 6.00
 - 3a, 3b and 3c (i. e., complete journal)... 7.50

10% discount for combinations of 1, 2 and (or) 3 (complete).
Postage to foreign countries outside the Pan American Postal Union extra as follows: 1, \$1.50; 2 and 3 (complete), \$2.10 each. Canadian postage one-third these rates.

BACK NUMBERS AND VOLUMES

	Single Numbers, when available, each major publication.....	\$ 0.75
}	J. Am. Chem. Soc., Vols. 29-58, each.....	\$ 9.00
	Chemical Abstracts	
	Vols. 1-30, incl. both Decennial Indexes	615.00
	Vols. 8, 9, 10, 11, 12, 13, 14, 15; each	20.00
	Vols. 16-30; each.....	15.00
	Ind. and Eng. Chem., Vols. 9-28; each Vol.....	9.00
	Ind. and Eng. Chem. Sets, Vols. 1-28*.....	252.00
	Index to Vols. 1-20, J. Am. Chem. Soc.....	1.00
	Index to Chem. Abst., ordered separately each Vol.....	2.50
	2nd Decennial Index to Chemical Abstracts—5 Vols.....	50.00

Members, for personal use (sets excepted), are allowed a discount of 20%.

* *The News Edition and Analytical Edition are not included in back volume price for INDUSTRIAL and ENGINEERING CHEMISTRY. Price \$2.00 and \$3.00 each, respectively, when available. Single numbers of the News Edition, 10 cents each; Anal. Ed., 75 cents each through Vol. 8, 1936; 50 cents each thereafter.*

Advance payment is required in all cases and must be made by check or postal order payable in American exchange (dollars).

1. Journal American Chemical Society
Proceedings, Vol. 2 and Vols., 29-58, only available. Some single numbers of other volumes can still be supplied.
2. Chemical Abstracts
Volumes 1-7 will be sold as complete volumes only in sets of Vols. 1-30, including the 1st and 2nd Decennial Indexes.
3. Industrial and Engineering Chemistry
Volumes 1 to 8 sold only as complete sets of Vols. 1-28, inclusive.

DOMESTIC SHIPMENTS. Single copies are sent by mail. Full volumes, and sets are sent in the United States and Canada express collect.

FOREIGN SHIPMENTS. Foreign shipments will be sent by mail either at purchaser's risk or by registered mail at postage cost, plus 5% of invoice, additional for registry; minimum charge, 75 cents. Large shipments will be delivered, if desired, to responsible forwarding agents in New York free, further charges to be paid by the purchaser on receipt.

The Society will not be responsible for loss due to change of address unless notification is received ten days in advance of issue. Claims for non-receipt must be made within 60 days of date of issue. "Missing from files" cannot be accepted as evidence of non-receipt. If change of address means a change of position, please indicate its nature.

Members or subscribers desiring their Journals or Abstracts forwarded from an old address should always notify their Postmaster and leave necessary postage.

The names of members and subscribers, whose Journals cannot be delivered by the Post-Office Department, will be cut off the mailing list at once, and will not be restored until correct addresses have been furnished.

In the absence of other information, the notices of change of address received from the Post-Office Department will be considered as correct, and the mailing list changed accordingly.

All communications relating to subscriptions or back issues should be addressed to

CHARLES L. PARSONS, Business Manager, Mills Building, Washington, D. C.

Announcing

The Reactions of Pure HYDROCARBONS

Gustav Egloff

Director of Research, Universal Oil Products Company, Chicago

A. C. S. Monograph, No. 73

DR. EGLOFF'S treatise is primarily a critical correlation of the widely scattered work on the reactions of pure hydrocarbons which should do much to point the way toward furthering the usefulness of these substances and products.

Almost unbelievable quantities of hydrocarbons are naturally available all over the world, appearing as gases, liquids and solids and forming the basis for many of the largest industries. The natural gas and manufactured gas industries handle billions of cubic feet of gaseous hydrocarbons daily, while the petroleum industry is guardian over fabulous volumes of gases, oils, waxes and asphalts. The coal industry in its turn has within its scope an estimated quantity of some 7,000 billion metric tons of coal and lignite, starting material containing valuable hydrocarbons of which all manner of use may be made. Moreover, hydrocarbon oil to the estimated amount of 300 billion barrels is potentially present in oil shale deposits.

There are seven distinct hydrocarbon groups outlined for the purposes of this book:—paraffins, olefins, acetylenes, aromatics, cycloparaffins and cycloolefins, and terpenes. Each group is individual in its properties, its reactions toward various agencies, thermal, electrical and catalytic; and its reactivity with other hydrocarbons or with unrelated substances. Despite these characteristics, however, each group is capable of being produced from most of the other hydrocarbon groups, and is equally capable of producing its fellow hydrocarbon groups under varying and, to a high degree, controllable conditions. Natural gas in the United States which is available at the rate of billions of cubic feet per day is made up of methane, ethane, propane, and butanes.

The outstanding example of naturally occurring hydrocarbon mixtures is to be found in the crude petroleum of the world. The compositions of these oils, 1,500,000,000 barrels of which were produced in 1935 alone, vary widely for different geographical locations and for different depths of production within the same field.

Obviously a book dealing with such a vast subject can never be "complete" in the strict sense of the word. For that reason Dr. Egloff and his co-workers have included especially thorough bibliographies as a guide for more detailed study of each chapter.

Not only technologists in such industries as petroleum, gas, rubber, plastics, naval stores and synthetic organic chemical products will find it essential, but it should also be of the greatest possible interest for research workers throughout the realm of organic chemistry.

NOTE—Because of the limited space available, the table of Contents is omitted here. Our circular containing full details will be sent upon receipt of your request.

897 pages

Illustrated

Price, \$16.75

Reinhold Publishing Corporation, 330 West 42nd St., New York, U.S.A.