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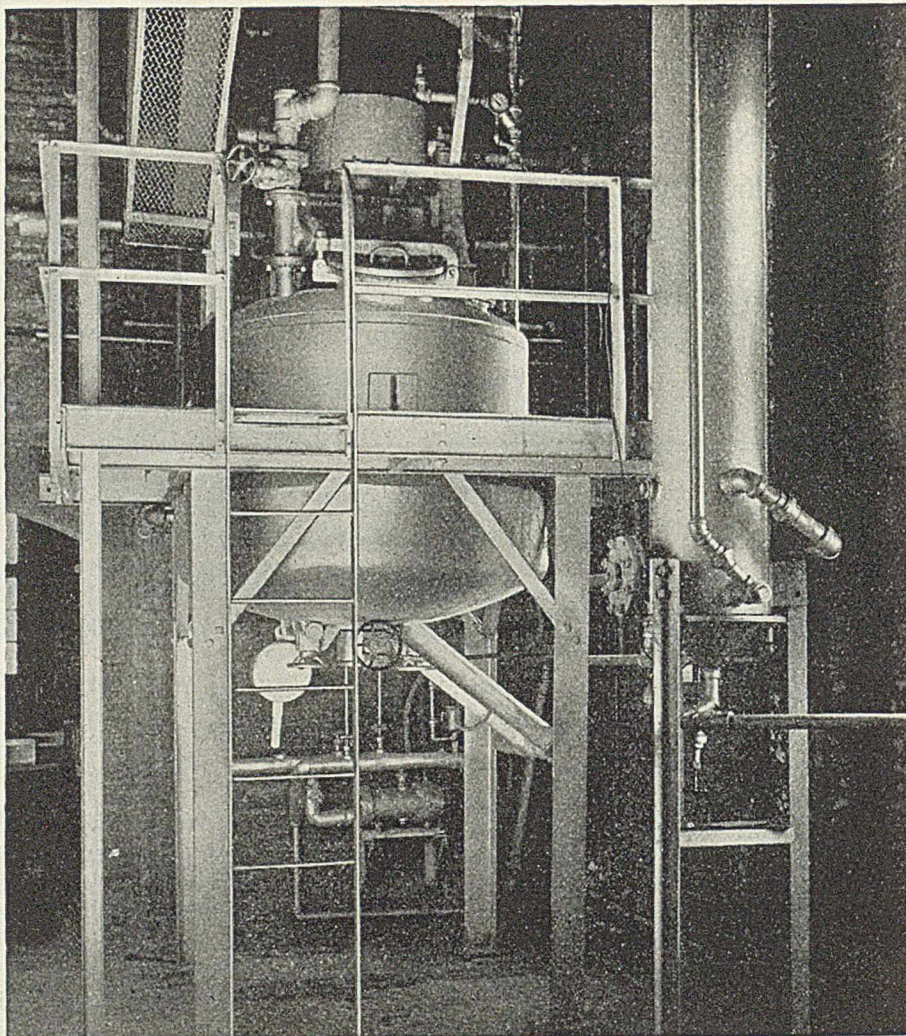
# Pure NICKEL.. and Pure PHENOL!

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Perhaps you have wondered *why* this metal is growing in popularity. If you have read recent reports of studies of the behavior of metals in contact with phenol and cresols\*, you realize that there are sound reasons why Nickel is considered so suitable for the handling of raw materials and for the processing of plastics. Nickel is held to have less discoloring effect than other commercially available metals. And because of its low corrosion rate,

\* *Industrial & Engineering Chemistry, Vol. 26, No. 5. "Corrosion of Metals by Phenols." Also Plastic Products, April, 1934. "Effect of Equipment on Condensation of Plastics."*



*This Nickel-Clad Steel, jacketed pressure kettle with pure Nickel agitator and fittings is used in the processing of phenolic resins at the HEMCO MOLDING DIV. of the BRYANT ELECTRIC COMPANY, Bridgeport, Conn. The equipment was manufactured by the BUFFALO FOUNDRY & MACHINE CO., Buffalo, N. Y.*

Nickel equipment lasts a long time.

Those facts help to explain why pure Nickel and Nickel-Clad Steel have been so widely adopted in the manufacture of phenolic condensation products and resins, for the construction of pressure kettles, agitators, vapor removal equipment, pipe lines, supply tanks and similar equipment. Pure Nickel is also used in equipment handling formaldehyde and in pressure vessels for the manufacture of thiourea.

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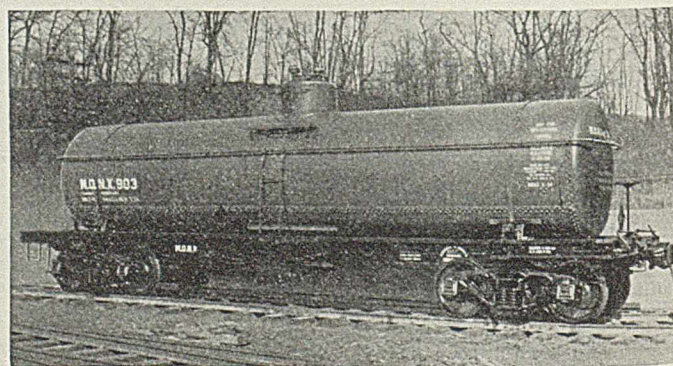
67 WALL STREET, NEW YORK, N. Y.



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*One of the special Nickel-Clad Steel tank cars owned by the American Catalin Corporation, 230 Park Avenue, New York City, for the purpose of shipping phenol. Cars, built by General American Tank Car Co., have 60,000 lbs. capacity and are provided with Nickel coils at bottom for heating.*



*One of two recently built 8000 gallon capacity Nickel-Clad Steel tank cars built by AMERICAN CAR & FOUNDRY COMPANY, 30 Church Street, New York City, for the transportation of phenol for plastic manufacture.*



# THE LISTENING POST

**FELDSPAR**, dug from the earth as a variable mineral, must be given a preliminary processing to make it a uniform material for glazing and glass manufacturing. Weis (page 915) describes not only the mechanical mixing of natural ores for uniformity but also the removal of iron-bearing particles on a modern intense-magnetic separator.

**STERILIZATION** with minute concentrations of silver ions has been recently brought to this country and is being put into practice here after a successful development abroad. Not only do minute concentrations of silver efficiently sterilize water but they also have pronounced effects on alcohol solutions, according to Brandes (page 962).

**BONE CHAR**, widely used as a decolorizing agent, can be made much more efficient by the removal of inert materials normally present, as described by Brown and Bemis (page 918).

**ACID TREATMENT** of deep rock strata to increase porosity and hence increase yields of oil or other subterranean fluids has been successfully used in a large number of wells. Putnam and Fry (page 921) describe new developments in this method of promoting the flow of oil and cite many of the factors which must be considered in its application. It is especially interesting to note that this treatment of oil wells, to date, has increased their yields of oil an average of 448 per cent.

**IRON AND MANGANESE** in water supplies are responsible for many industrial and domestic difficulties. Their removal presents special problems in water treatment since very small concentrations cause trouble. Applebaum and Bretschger (page 925) discuss the methods available for improving water supplies having these impurities and cite numerous cases of successful treatment in industry.

**RUBBER** as we know it today is a very different material from the commercial product of only a few years ago. Among the important properties now controlled by suitable compounding, the aging of rubber articles is especially important. The role of various compounds which affect the aging characteristics of rubber are described by Crawford (page 931) as applied to a variety of rubber products.

**UTILIZATION OF THE BY-PRODUCT GAS** from the large-scale cracking operations of the petroleum industry continues a major problem. To it Egloff and Morrell (page 940) contribute data both from their own observations and from the literature dealing with the character of the gases resulting from various types of cracking and possible uses for them.

**GUM DEPOSITS** in systems for distributing manufactured gas may be formed by the action of minute traces of oxides of nitrogen present in the gas itself. According to Jordan, Ward, and Fulweiler (page 947), the presence of a few parts of nitric oxide in ten million of gas is sufficient to form gum particles to an objectionable extent.

**WASTE WATER DISPOSAL**, always an important problem in chemical industry, presents a difficult series of problems to the petroleum refinery where it carries away many of the plant wastes. Hart (page 965) discusses the solutions of problems arising in an eastern refinery and the methods used to prevent undue contamination of streams.

**COPPER SULFATE**, used to control the growth of algae in raw water supplies, can be removed by precipitating ferric oxide in the water, according to Brockman (page 924), and in this respect ferric floc is superior to alum floc sometimes used.

**CANNED SEA FOOD** may give a positive test for formaldehyde even though this material has not been added. Lunde and Mathiesen (page 974) have investigated this question from the point of view of the Norwegian canning industry and report positive tests for formaldehyde in a variety of marine products.

**SODIUM METAPHOSPHATE**, possessing remarkable ability to soften hard water without precipitation, contributes ease and efficiency to the lowliest of tasks, dishwashing. Long neglected as too simple and humble for serious study, dishwashing has been carefully investigated in the light of the behavior of this newly commercial compound. Schwartz and Gilmore (page 998) suggest ways in which this onerously repetitive household chore can be lightened by the use of detergent mixtures containing sodium metaphosphate.

**REDUCTION OF IRON ORES** by carbon monoxide and the various factors which influence the reaction have been studied by Wetherill and Furnas (page 983) who suggest the methods of calculating the reaction velocities which are applicable to other reactions occurring between a gas and a solid.

**TOBACCO CHARACTERISTICS**, always a mystery to smokers, are very much influenced by the methods of culture and the kind and extent of fertilization, as well as by soil and climate. Garner, Bacon, and Bowling (page 970) discuss the distinctive characteristics of cigar and cigarette tobacco and their influence on the quality of the final product when used by the consumer. Apparently the variations producible by conditions of culture are almost as important as the variety of the seed and the climate in which the plant is grown.

**LUBRICATING PROPERTIES** of petroleum oils appear to be inherent in some constituent which is adsorbed on metal surfaces, according to Rhodes and Lewis (page 1011). These investigators have been unsuccessful in isolating the apparently valuable constituent of oil but have learned a number of interesting and important facts about it.

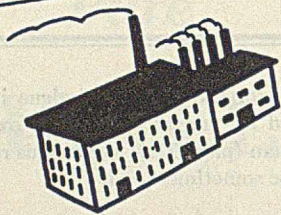
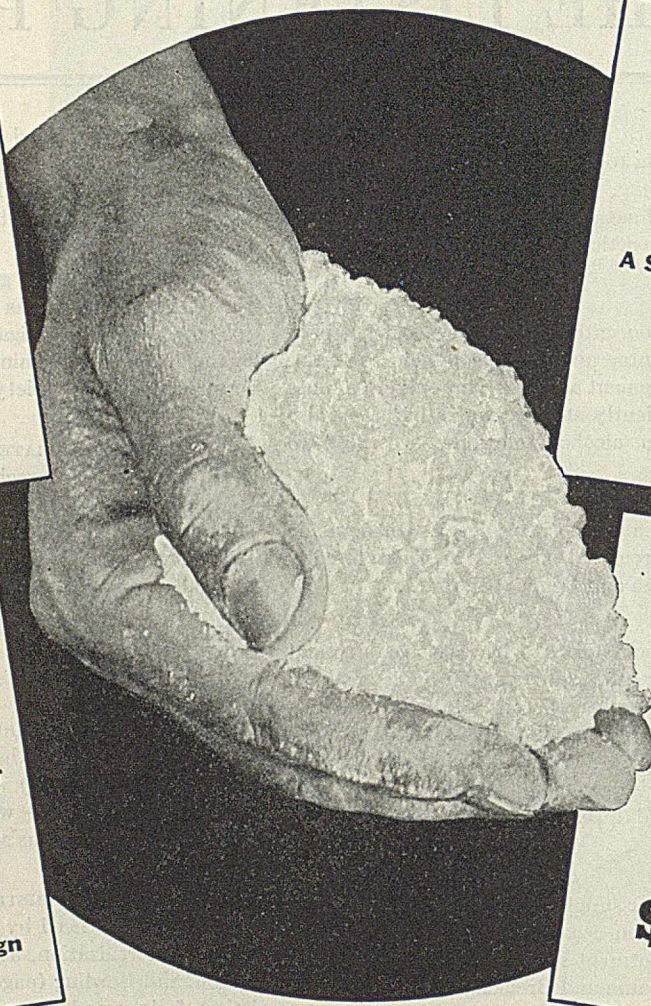
**KETONES** may be made from aliphatic esters by the catalytic action of thoria aëroge, according to Swann, Appel, and Kistler (page 1014) who have succeeded by this method in preparing a number of the ketones of high molecular weight.

**PYROLYSIS OF NATURAL GAS** offers itself as a source of large quantities of styrene and indene from which valuable resins and other polymers are producible. Birch and Hague (page 1008) have prepared both of these compounds in semi-commercial cracking units and discuss here methods of their formation, as well as possible commercial processes.

**CARBON DIOXIDE** apparently forms a solid carbon-oxygen complex when the gas is passed over heated coke, according to Brewer and Reyerson (page 1002). These investigators advance this explanation of irregularities observed in studies made of production of high-hydrogen water gas.

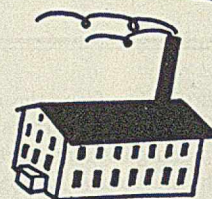






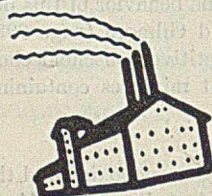
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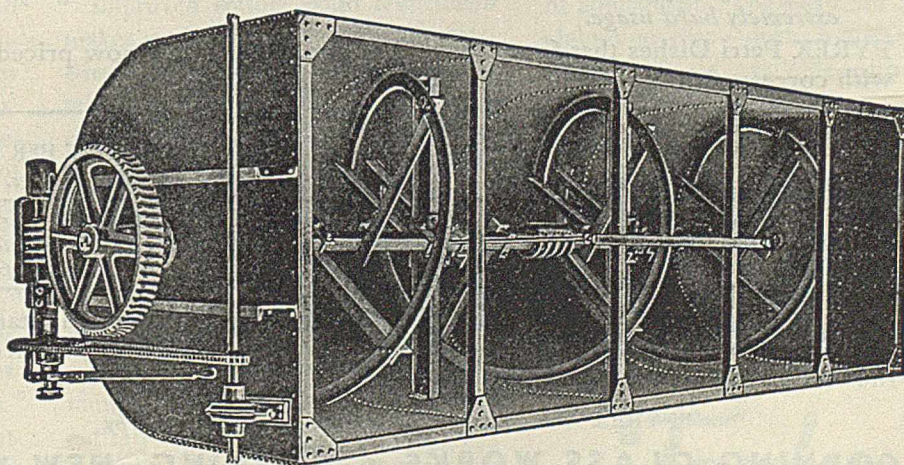
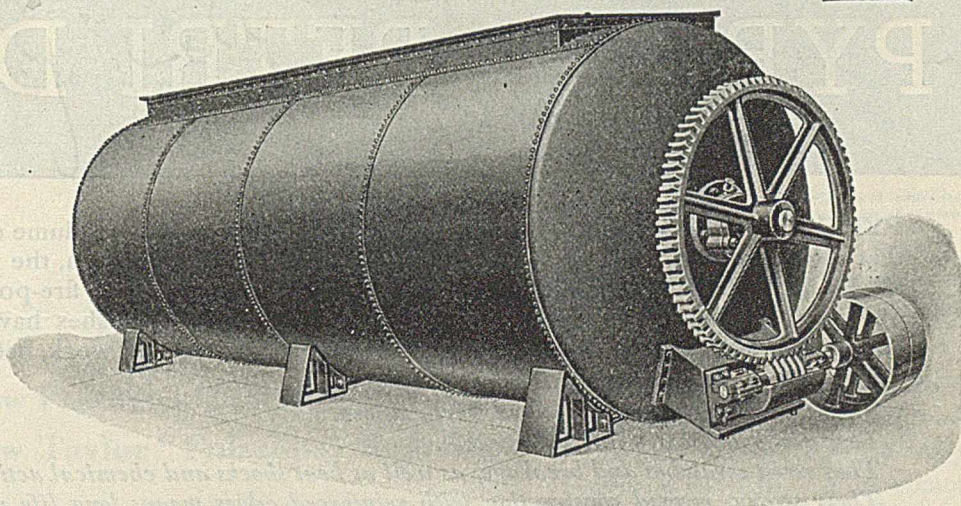
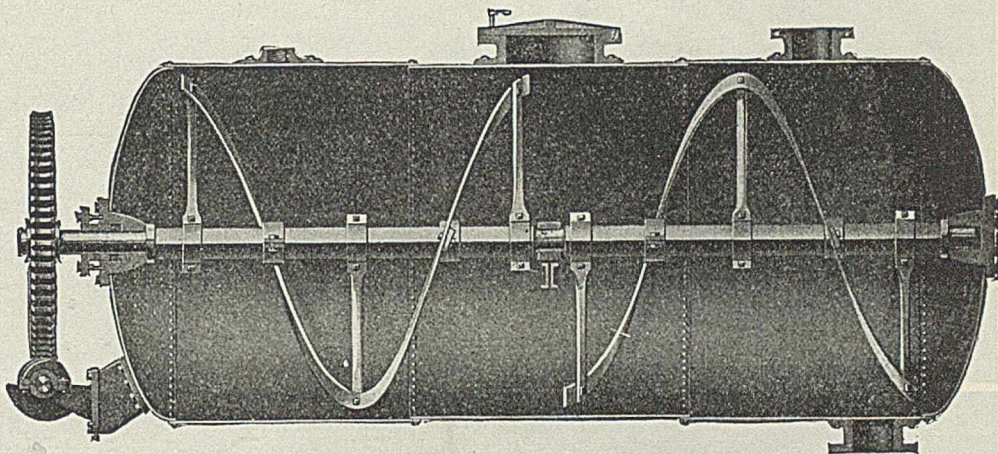


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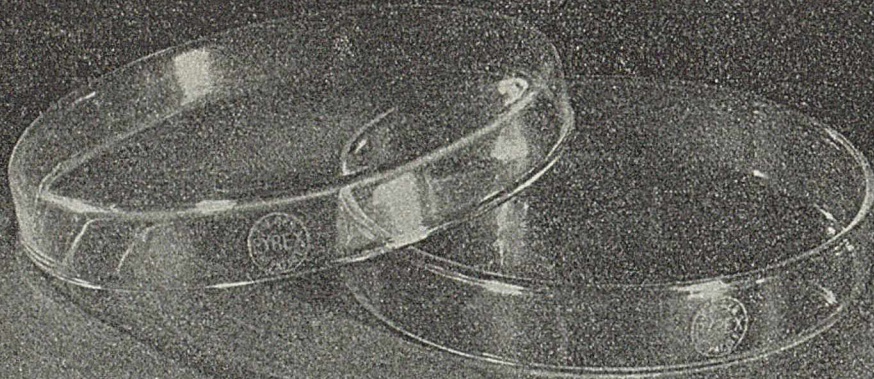
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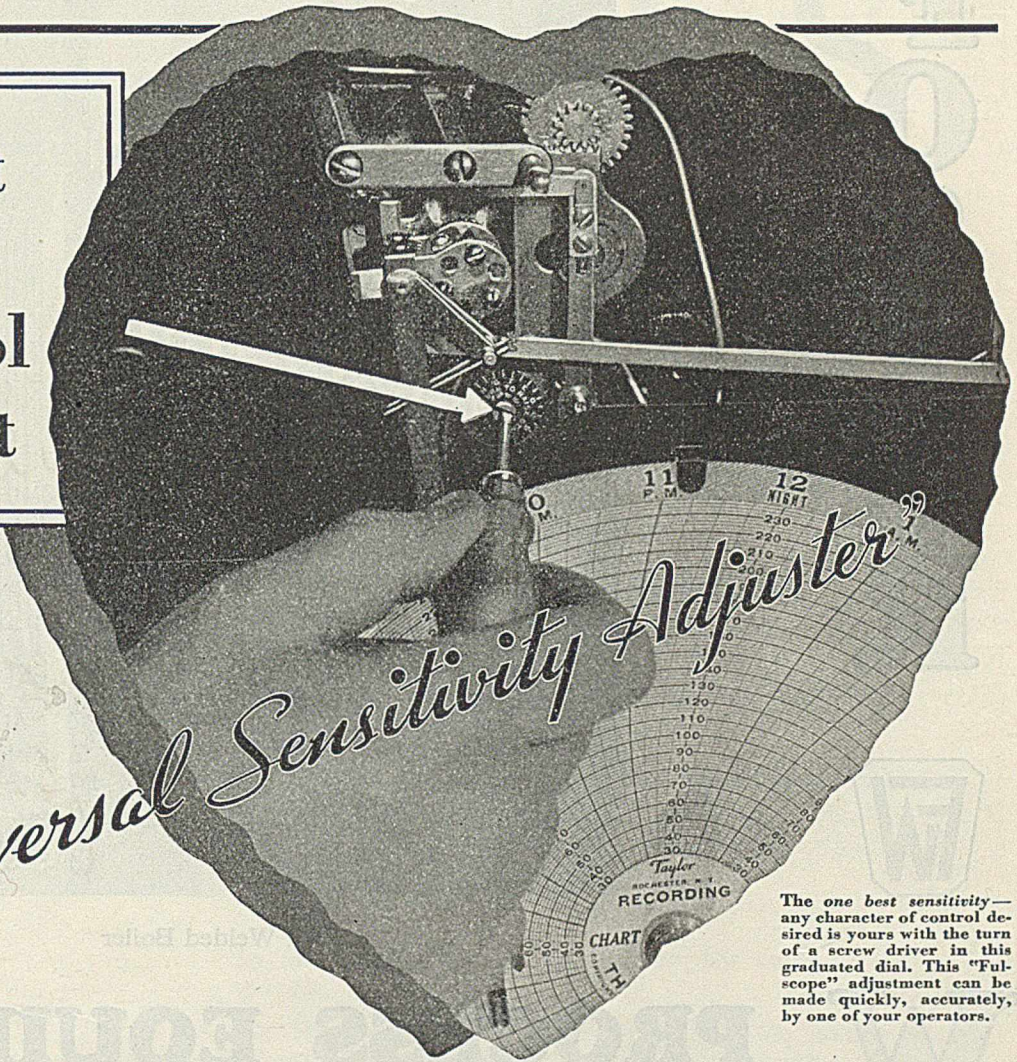
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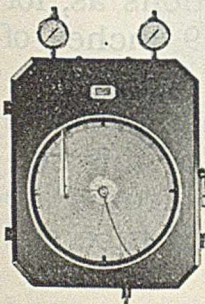
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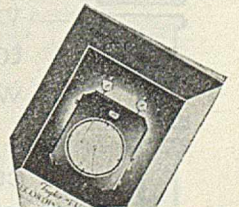


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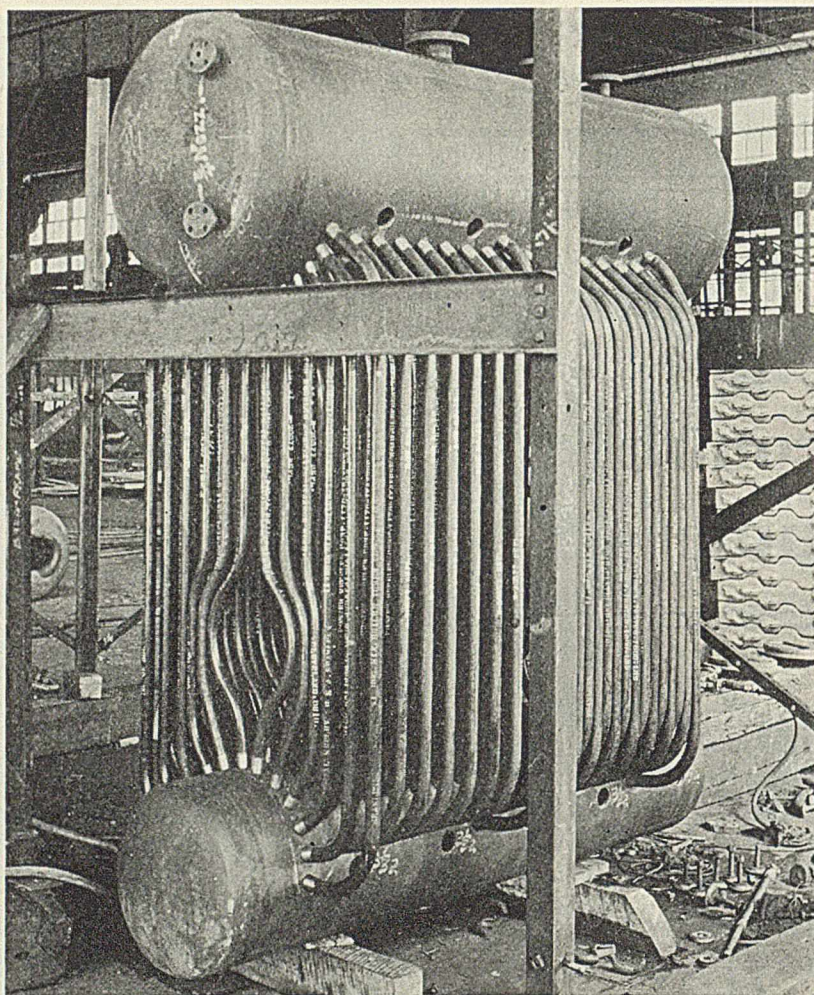
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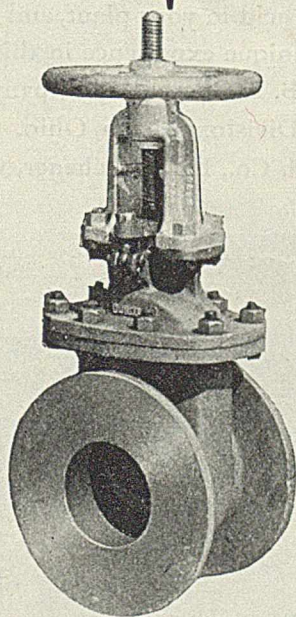
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# HANDLING WASTE ACID

*New use of Goodrich rubber lining conquers costly problem in acid handling*

**V**ULCALOCK Rubber Lining in their pickling tanks proved so outstandingly successful that Inland Steel welcomed the Goodrich suggestion that the same type of lining be applied to their acid sewer.

Chemical stoneware, sawdust packing, pitch covering, everything else had been used, but leakage continued. Leaking acid seeps into the earth, attacks the minerals in the soil, and this causes floors, machinery, even walls to settle or heave. No way had been found to prevent this insidious danger—until rubber lining, applied to a steel sewer by the Vulcalock bonding process, was introduced.

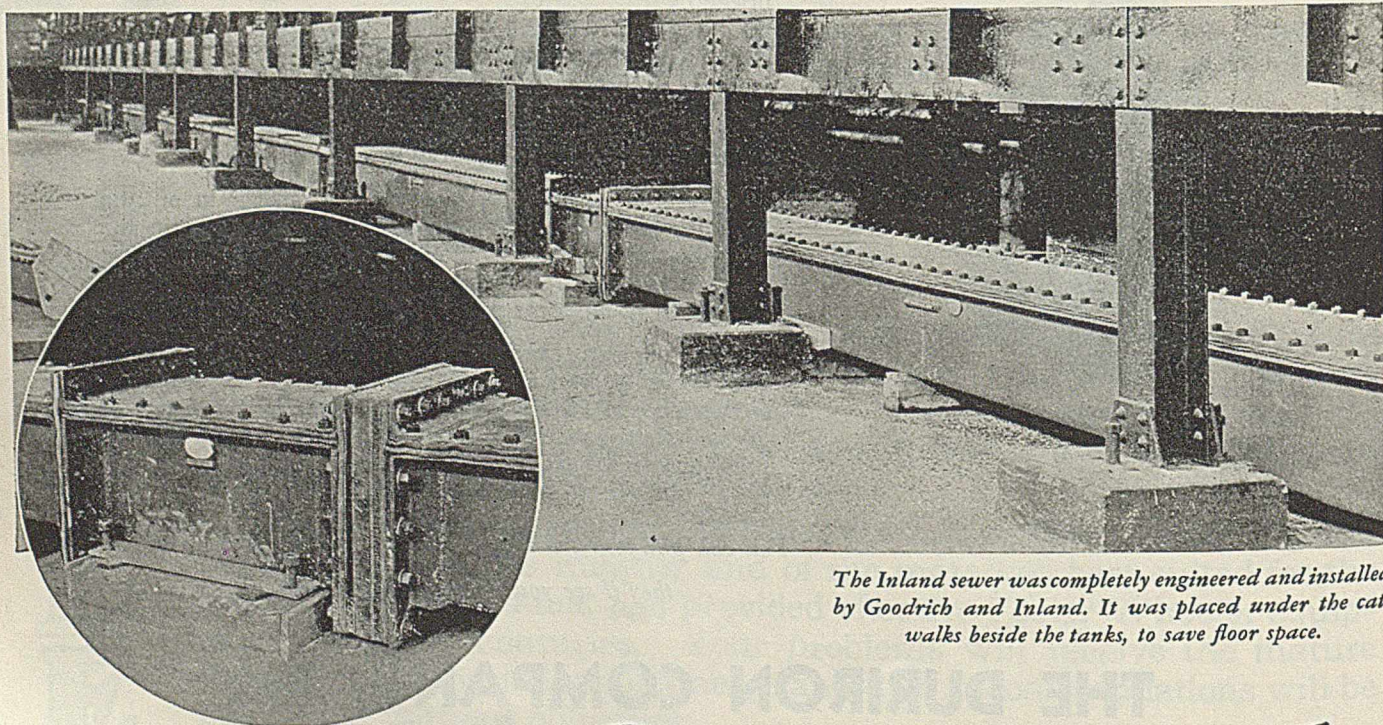
Here was an entirely new development in acid disposal, but Inland and Goodrich engineers worked together as a team in perfecting it. Then this newest application of rubber was installed . . . and immediately all acid leakage was stopped.

Now in the Inland plant the floor is dry, undermining is prevented, time and money formerly spent on sewer repairs are a thing of the past.

## SUGGESTS OTHER USES TO AID IN ACID HANDLING

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The Inland sewer has been so successful that it suggests the possibility of revolutionary new applications of the Vulcalock rubber process to even further serve and save in the handling of acids. Goodrich engineers will be glad to counsel with you on the storage, use and disposition of acid in your plant, and make available to you their unique experience in this branch of industry . . . The B. F. Goodrich Company, Mechanical Rubber Goods Division, Akron, Ohio. In Canada: Canadian Goodrich Co., Ltd., Kitchener, Ont.



*The Inland sewer was completely engineered and installed by Goodrich and Inland. It was placed under the catwalks beside the tanks, to save floor space.*

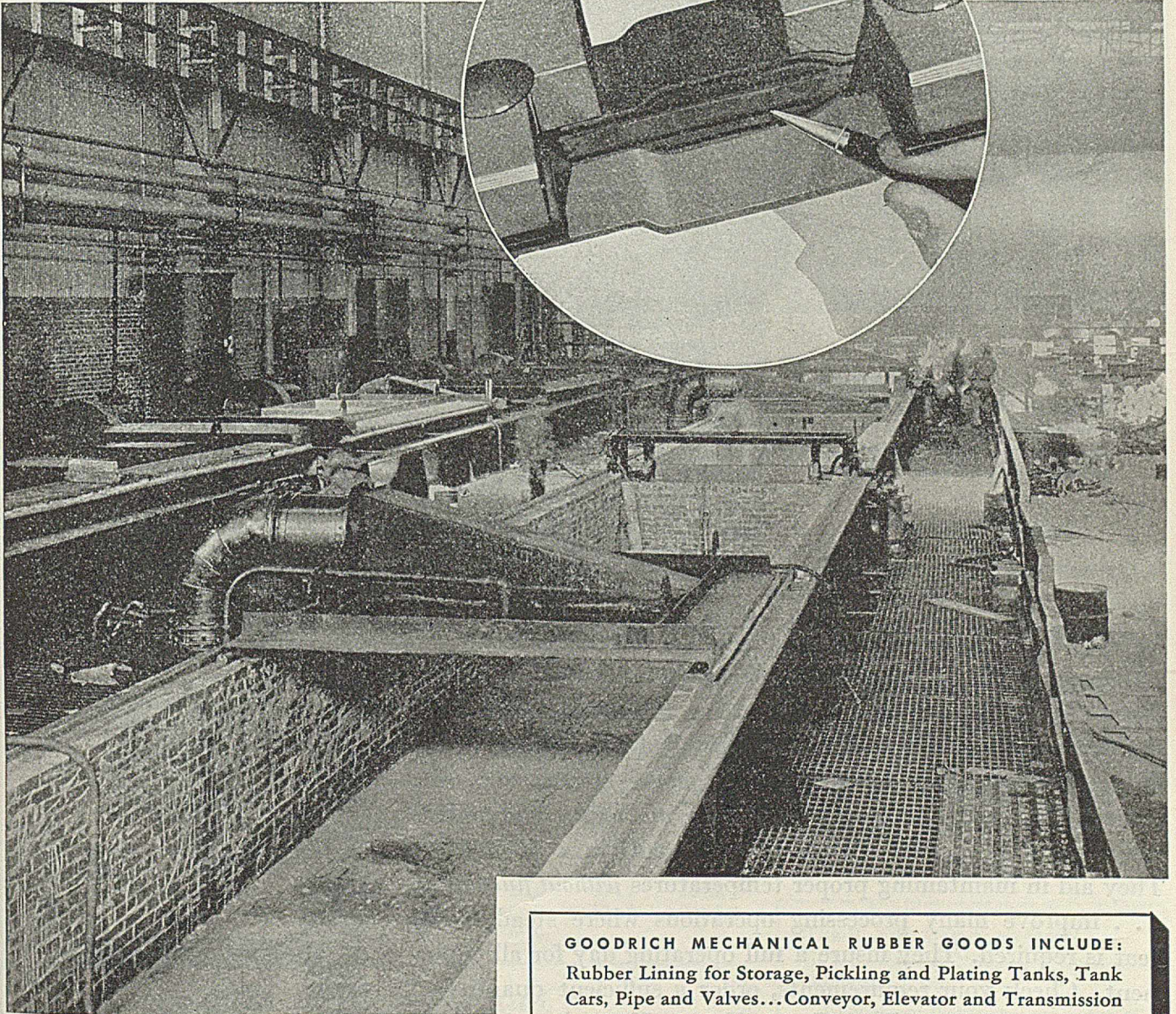
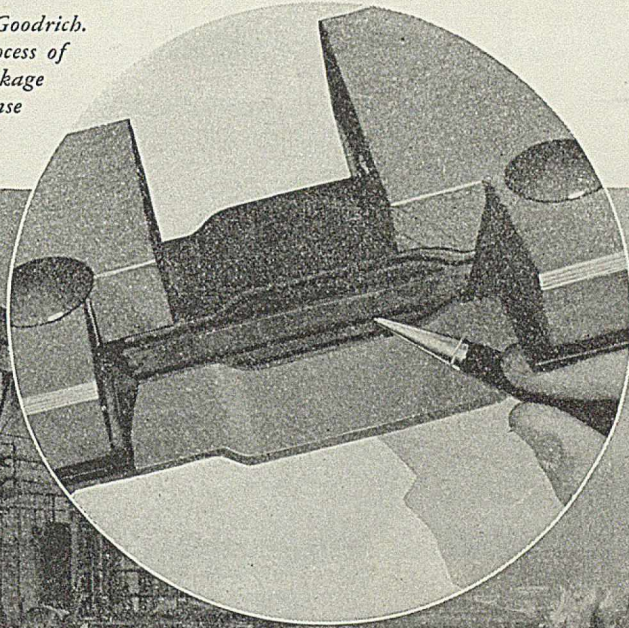
*Steel sewer, lined by the Goodrich Vulcalock process with Goodrich rubber. Note the rubber expansion joint, necessary because the sewer alternately handles cold water and waste acid at 195° F.*

# Goodrich



# MADE SAFE BY VULCALOCK

*Triflex Expansion Joint, designed by Goodrich. This together with the Vulcalock process of lining prevents cracking and acid leakage which is the cause of so much expense and failure when other linings are used.*



*Strip pickling unit at Inland Steel Co., 240 ft. long, 7 ft. wide, about 5 ft. deep. The rubber lining is protected by brick sheathing, in which Triflex rubber expansion joints are used.*

**GOODRICH MECHANICAL RUBBER GOODS INCLUDE:**  
 Rubber Lining for Storage, Pickling and Plating Tanks, Tank Cars, Pipe and Valves... Conveyor, Elevator and Transmission Belting . . . Acid, Air, Steam, Suction and Fire Hose . . . Hard Rubber Goods . . . Packing . . . Molded Rubber Products . . . and a Complete Line of Miscellaneous Rubber Items.

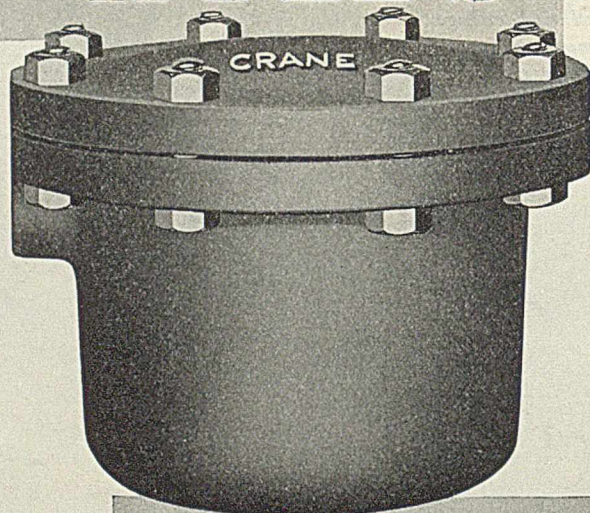
*Rubber Lining*



ALL products problems IN RUBBER



# THIS LITTLE TRAP HOLDS



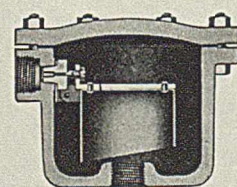
● Crane No. 981 Cast Iron Trap for steam working pressures up to 200 lbs.

● Compare the simplicity of the Crane Inverted Open Float Trap with the complexity of most steam traps. There are no by-passes, thermostats, or petcocks.

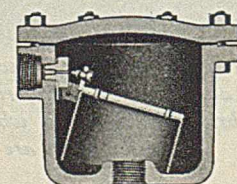


## THE SECRET OF IMPROVED PROCESSING RESULTS . . .

**T**HIS inexpensive piece of equipment . . . so small as to almost escape notice in the average steam line . . . makes all the difference in the returns you get from steam. Properly trapped, with the Crane Inverted Open Float Trap installed at low points in the line, your steam lines will deliver dry, *hotter* steam even over longer distances! Install *enough* of these *automatic*, inexpensive traps and they pay for themselves repeatedly in a single year. They aid in maintaining proper temperatures *without fluctuation* . . . improve many processing operations where steady, *even* heat is required. They insure a full operating day for all equipment. Check your requirements, order a sufficient quantity of Crane Inverted Open Float Steam Traps. Keep them in stock! You'll save money . . . inexpensive as the improvement will be!



TRAP CLOSED—incoming steam under the float buoys it up, keeping outlet closed.



TRAP OPEN—incoming condensate has filled the float, permitting it to sink and open the outlet.

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# HEXACHLORETHANE



## A Solid Chlorinated Hydrocarbon Available in Commercial Quantities . . .

HEXACHLORETHANE offers interesting possibilities in the manufacturing industries. It has been suggested for use in the preparation of synthetic chemicals, safety glass, insecticides, leather, matches, fireworks, paints and varnishes, pharmaceuticals, plastics, coating materials and other products.

### Stable in Storage

Hexachlorethane is stable under conditions of storage. Wood containers with paper liners are satisfactory for storage and shipping.

Hexachlorethane can now be obtained in commercial quantities at reasonable prices.

### Physical Properties

Chemical Formula . . . . .	C <sub>2</sub> Cl <sub>6</sub>
Molecular Weight . . . . .	236.74
Crystal Form . . . . .	Rhombic, tablets
Color . . . . .	Colorless
Odor . . . . .	Pungent, Camphor-like
Density . . . . .	2.0 (appr.)
Melting Point . . . . .	185.6-185.7° C.
Boiling Point (extrapolated from V. P. data) . . . . .	185° C.
Specific Heat, 25° C. . . . .	0.175 g. cal.

### Vapor Pressure

Temp., °C.	Pressure mm. Hg.	Temp., °C.	Pressure mm. Hg.
46.8	3.0	120.5	86.2
59.8	5.5	129.9	127.7
70.0	9.5	140.2	186.6
80.0	15.5	148.6	247.5
84.0	17.5	163.0	402.5
92.8	28.0	174.1	564.5
99.9	36.7	184.3	746.0
112.0	60.0		

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THE R. & H. CHEMICALS DEPT.  
E. I. du Pont de Nemours & Co., Inc.  
Wilmington, Del.

Gentlemen: Please send me technical data on, and sample of, Hexachlorethane. I am interested in using it for

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For Industrial Use: ARTIC\* (Methyl Chloride), Dichlormethane, Chloroform, Carbon Tetrachloride, Dichlorethylene, Trichlorethylene, Tetrachlorethylene, Tetrachlorethane, Pentachlorethane, Hexachlorethane, CYANEGG\* (Sodium Cyanide, min. strength 96%), Case Hardening Mixtures, Metal Cyanides, DUOZINC\* Anodes, Sodium, Formamide, P. A. C.\* Formaldehyde, Paraformaldehyde, Hexamethylenetetramine, Methyl Formate, ALBONE\* C (Hydrogen Peroxide, 100 Vol.), SOLOZONE\* (Sodium Peroxide), Sodium Perborate, Ceramic Decorations, and other chemicals.

\*REG. U. S. PAT. OFF.

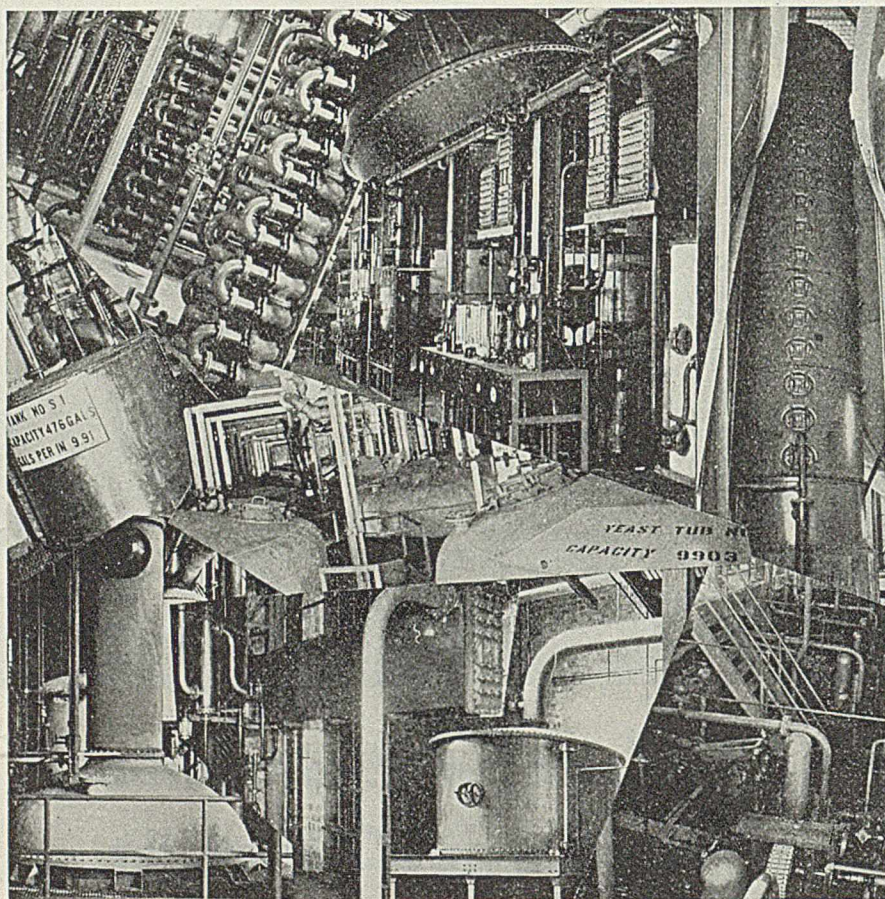
**E. I. DU PONT DE NEMOURS & COMPANY, INC.**  
The R. & H. Chemicals Dept., Wilmington, Del.

District Sales Offices: Baltimore, Boston, Charlotte, Chicago, Cleveland, Kansas City, Newark, New York, Philadelphia, Pittsburgh, San Francisco



# FILE UNDER DISTILLERIES

Grain Cookers  
Drop Tanks  
Yeast Fermenters  
Pure Culture Yeast Apparatus  
Mash Coolers  
Bourbon Whiskey Distilling Equipment  
Rye Whiskey Distilling Equipment  
Rye Whiskey Doubler  
CO<sup>2</sup> Scrubbing Unit  
Still House Proportioning Pumps  
Spent Grain-Ber Heat Interchangers  
Gin Stills



NEW HIRAM WALKER PLANT, WORLD'S LARGEST DISTILLERY

THE SUPREME COURT OF EQUIPMENT RATING

## SPECIFIES VULCAN

The new Hiram Walker Plant at Peoria, Ill., which is now in operation, is the largest grain distillery in the world (with a capacity of 20,000 bushels of grain a day).

The largest distillery project ever conceived, demanded the most modern designing and fabricating that equipment manufacturers could offer.

Vulcan is honored to have Hiram Walker & Sons select over \$300,000 of Vulcan Equipment to perpetuate in the United States, the prestige of the Canadian Parent Company's famous products, Bourbon Whiskey, Rye Whiskey, and Gin.

We are more pleased that Hiram Walker & Sons have identified Vulcan as the leader in grain distilling equipment, in the same way as large concerns in other fields of chemical distilling have recognized Vulcan's advanced designing and fabricating.

Whatever your problem is—a complete plant or a set of valves—you will profit by the advanced Vulcan designing and fabricating. Inquiries are cordially invited.

### WRITE FOR

#### AD NO. 1

Vulcan meters give a better check on distillation.

#### AD NO. 2

Only bubbling cap that fractionates bubbles by cross currents. Much higher contact efficiency.

#### AD NO. 3

\$300,000 of distilling equipment in one plant, designed, fabricated and installed by Vulcan.

#### AD NO. 4

Vulcan,—inventor and perfecter of continuous gin stills.

#### AD NO. 5

Important advances in alcohol beverages now available through Vulcan.

#### AD NO. 6

The large, modern Vulcan laboratory, and processes developed that saved large sums for customers.

#### AD NO. 7

The only continuous plants in America used for direct acetic from wood distilling designed by Vulcan.

#### AD NO. 8

Vulcan condensers,—smaller units, less water cost, no fouling with dirty water.

#### AD NO. 9

Vulcan heat recuperation saves  $\frac{2}{3}$  of heat ordinarily used for solvent recovery.

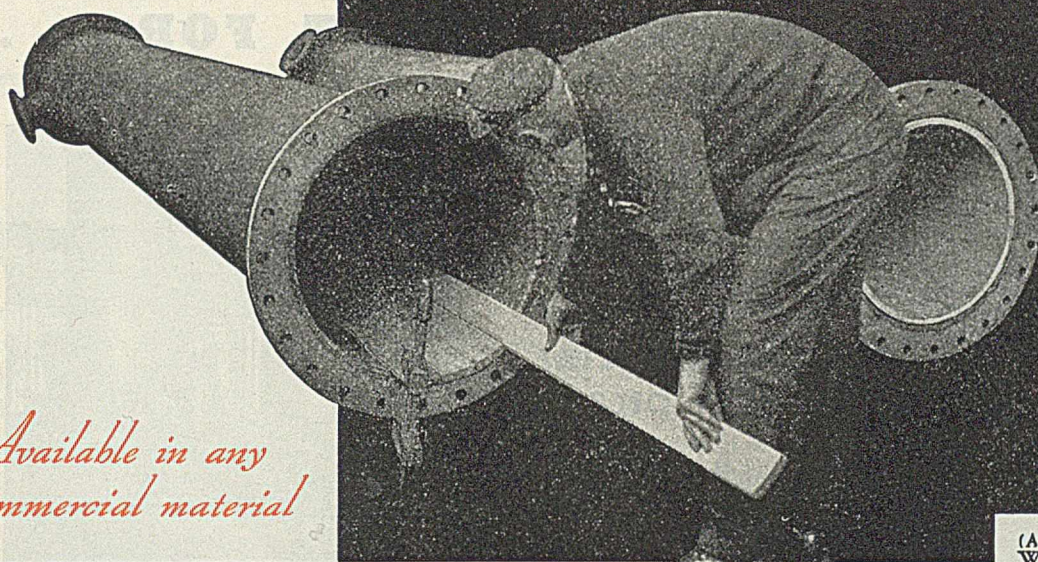
#### AD NO. 10

$\frac{1}{4}$  billion cubic feet of vapor a day go through the slots of all the caps in single Vulcan columns.

**VULCAN COPPER AND SUPPLY**  
C O M P A N Y  
D I S T I L L A T I O N E V A P O R A T I O N  
Cincinnati, Ohio, U. S. A.



# STRUTHERS · WELLS HEAT EXCHANGERS

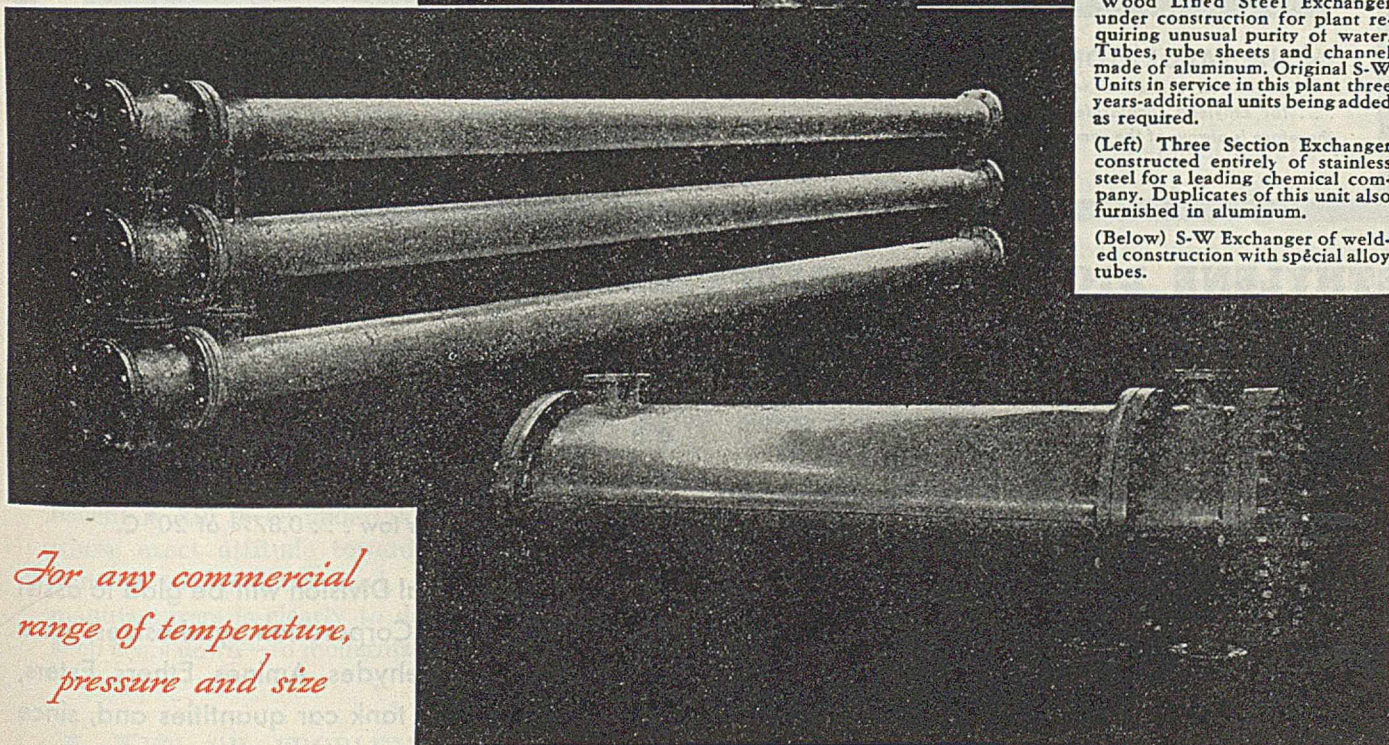


*Available in any  
commercial material*

(Above) Special Struthers-Wells Wood Lined Steel Exchanger under construction for plant requiring unusual purity of water. Tubes, tube sheets and channel made of aluminum. Original S-W Units in service in this plant three years-additional units being added as required.

(Left) Three Section Exchanger constructed entirely of stainless steel for a leading chemical company. Duplicates of this unit also furnished in aluminum.

(Below) S-W Exchanger of welded construction with special alloy tubes.



*For any commercial  
range of temperature,  
pressure and size*

Why not place the splendid design and fabrication facilities of Struthers-Wells at your service in the construction of that next Heat Exchanger?

Here is an organization of master craftsmen skilled in handling all of the special alloys, including stainless steel, aluminum, copper and copper alloys, chrome iron, steel, cast iron or other material . . . here complete annealing and X-ray facilities make possible the construction of Struthers-Wells Heat Exchangers to the most exacting A. S. M. E. Code requirements in any commercial range of size, temperature and pressure.

Complete engineering and research services are available to solve your heat exchange problems. An experienced staff of engineers thoroughly familiar with all phases of vapor, liquid and gaseous heat transfer is at your service.

Your inquiries are invited.

**STRUTHERS-WELLS CO.**

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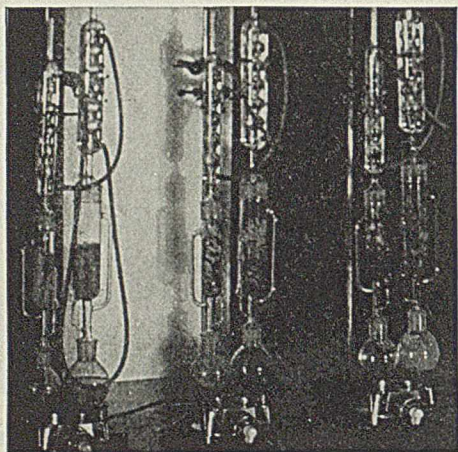
Pressure Stills · Heat Exchangers · Reaction  
Chambers · Stabilizers · Fractionating Columns  
Alloy Steel Equipment



# ETHYLENE DICHLORIDE

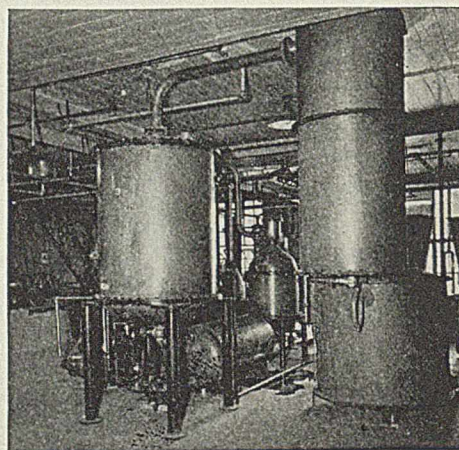
(C<sub>2</sub> H<sub>4</sub> Cl<sub>2</sub>)—B. P. 83.5° C.—10.4 LBS. PER GALLON

## AN EXCELLENT EXTRACTANT FOR . . .



**IN THE LABORATORY** its use means that your plant run will check with your "Soxhlet test" . . . for Ethylene Dichloride is made synthetically, therefore is always of the same never-varying quality.

OILS  
WAXES  
FATS  
RESINS  
ESSENTIAL OILS  
ALKALOIDS  
ORGANIC ACIDS



*Extract Distilling Apparatus — Courtesy F. J. Stokes Machine Co.*

**IN THE PLANT** its use means fewer "control tests" because Ethylene Dichloride comes in the same never-varying quality whether in tank car, or single drum quantities.

## ETHYLENE DICHLORIDE HELPS REDUCE PRODUCTION COSTS

- It is economical in use . . . has lowest specific gravity of commercial chlorhydrocarbon solvents.
- It is easily recovered . . . less than 3% losses in certain commercial extractions.
- It is easily removed from extracted material . . . contains less than 0.001% residue.
- It has excellent solvent properties.
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- Its fire hazard is low . . . flashes at 75° F.
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If your manufacturing problems involve the use of extractants, our Technical Division will be glad to assist you. In addition to Ethylene Dichloride, Carbide and Carbon Chemicals Corporation synthesizes, on a commercial scale, many other Chlorhydrocarbons, as well as Alcohols, Aldehydes, Amines, Ethers, Esters, Glycols, Ketones and other organic chemicals. Most of them available in tank car quantities and, since they are made synthetically, under rigid control, they never vary in quality.

*You are cordially invited to visit the Union Carbide and Carbon Corporation Exhibit in the Hall of Science at Chicago's 1934 A Century of Progress Exposition*

**CARBIDE AND CARBON CHEMICALS CORPORATION**

Producers of Synthetic Organic Chemicals

30 East 42nd Street, New York, N. Y.



Unit of Union Carbide  and Carbon Corporation



# Industrial AND ENGINEERING Chemistry

VOLUME 26  
NUMBER 9

SEPTEMBER  
1934

HARRISON E. HOWE, EDITOR

## The Editor's Page

**M**ODERNIZE. Huge extensions of federal credit to stimulate business activity continue to loom large in the economic picture and must by their very size affect all industry. Present proposals to encourage the spending of billions on the rehabilitation of homes seem at first glance unlikely to influence seriously the chemical industry, but closer analysis reveals a host of chemical products—things the popularizers of the science delight to describe—which will be required in significant quantities in such a program. One need only consider paints, plasters, stuccoes, wall paper, refrigeration, air-conditioning, rubber-covered electric wiring, and heat insulation to realize that such a revival of building, quite as surely as any other pronounced return to normal business, will reflect itself in demand for chemical industry's products.

Speed of spending is of the essence of the administration's plans and consequently one may reasonably anticipate that demand will rise to a sudden peak and that, unless precautions are taken in advance to prevent it, prices may be forced up to prohibitive levels.

If no other reason existed for embodying the latest and best in plants operated on lean schedules during recent years, this one should suffice. When, in addition, the problem of tariff trading for agriculture's benefit is still to be undertaken by an administration whose exact attitude toward the chemical industry remains to be determined, the course of chemical manufacturers is clearly to do everything possible to keep costs down—to modernize until it hurts.

**M**EN OR PROBLEMS? In 1919 arrangements were made whereby the National Research Council, through a fellowship board, undertook to administer funds supplied by the Rockefeller Foundation for the support of a system of National Research fellowships in physics, chemistry, and mathematics. As much as \$155,000 a year has been available for this work, although the appropriation for 1934-35 is but \$75,000. In the report published this year, 427 were on the rolls as active or

retired fellows. Of these, 165 were credited to physics, 167 to chemistry, and 95 to mathematics. It seems pertinent after 15 years to inquire whether this experiment has been successful and should be continued.

The purposes of these fellowships are stated as: (1) opening of a scientific career to large numbers of able investigators and their more thorough training in research, thus meeting an urgent need of our universities and industries; (2) increase of knowledge of the fundamental principles of physics, chemistry, and mathematics, upon which the progress of all the sciences and the development of industry ultimately depend; (3) creation of more favorable conditions for research in the educational institutions of this country. The fellowship board, made up of men distinguished in their sciences, has devoted a large amount of arduous labor in the selection of fellows from the numerous candidates and in following their work as it progresses in the several institutions. Recently the board has had the services of a part-time field secretary who, by visits to the institutions from which fellows come and in which they work, has obtained first-hand information concerning the operation and results of the fellowship program.

The purposes clearly indicate that the primary object has been the confirmation of men of unusual equipment in research. The plan was launched at a time when pure research was seriously threatened by the bid of industry for the best men to enter its laboratories and devote their talents to developing processes and products more likely to be described first in the patent literature than in the scientific periodicals of the world.

To visualize, initiate, and complete fundamental scientific problems, whether they be in industry or in academic halls, requires brilliant individuals. When such enter industrial laboratories they usually devote their talents to a narrow field, where it is unlikely that anything of fundamental importance or of interest to science in general may be developed. If, however, the university be chosen as the place for continued work, the researcher will apply his efforts to investigations, the results of which not only will benefit science but will contribute to useful knowledge. Not one chemical industry, but any or all, may draw upon this.



As it is, there is a feeling in some quarters that, even now, chemistry suffers somewhat because so many of the men who might have become heads of departments in our academic institutions at that time preferred a career in industry, with the result that there is a noticeable scarcity of leaders to undertake departmental responsibility. The move, then, through fellowships to develop promising young men and women in scientific research was wise and offered great possibilities.

To what extent the goal has been achieved must be found in the record of those who have enjoyed these fellowships. We find that, of the 352 who have retired from the fellowships and undertaken other work, 260 are now in universities, 3 continuing research, 20 in the employment of the Government, 51 in the industries, 8 in institutional work, and 10 who have given no recent information. Coming particularly to chemistry, 32 are in the industries, 11 in government employ, 8 in institutional work, 3 have made no recent report, and 83 are in universities. Of these, 37 have achieved the rank of assistant professor or above. A study of the present positions and scientific standing of past National Research fellows shows that a very large majority of them have justified their respective appointments. Indeed, the proportion of successful fellows is greater than one might have imagined, in view of the difficulties involved in making selections, although it is to be expected that, with so large a number of individuals chosen, a few mistakes would be made.

When the operation of the fellowship program began, there were numerous applications for opportunities to work abroad, and a considerable number of such appointments were made. At times as much as \$30,000 was spent annually on this class of fellowships because, particularly in the fields of theoretical physics and chemistry, there was the conviction that the best facilities for such studies were to be found in Europe. At the present time, however, comparatively few fellows apply for work abroad, and only three or four per year are appointed. The reason for this rather remarkable change is that during the 15-year period centers of research in theoretical physics, chemistry, and mathematics have been developed in America to such an extent that it is no longer necessary or even desirable for fellows to go abroad to find opportunities for study. The operation of the fellowship program can be credited to an important degree with the development of such favorable opportunities as now exist in America.

We believe that the careful study of the report will lead to the conclusion that science is under a considerable debt to the Rockefeller Foundation for the funds, to the National Research Council for assuming their administration, and particularly to the fellowship board for the meticulous care with which it has discharged its considerable duty.

We would repeat that the program primarily has been to develop men and secondarily to add to our knowl-

edge. It would be an error, in our judgment, to reverse this policy and seek men fitted for research along specialized lines. Unquestionably there is greater need for some types of information than for others, but the man truly grounded in his science can be placed upon special problems with greater assurance of success than if from the beginning of his intensive training he had been held to one particular channel. Then, too, an error in the selection of a research worker for a special task is far more likely to be committed than in the choice of one capable of receiving that broad fundamental training which will enable him later to take up various tasks with assurance and enthusiasm.

It is to be hoped, therefore, that the policies of the fellowship board, which certainly have proved successful, may be continued without material change. If we need information of special kinds, let us train men and better men, with confidence that it is by these means that such objectives are attained. Furthermore, it is most important that the fellowship program should be extended. Its worth has been demonstrated, and many men of unusual promise at the threshold of their careers need the support which it affords if they are to continue in fundamental work. We urge the continuation of the enterprise as a whole on an expanding scale.

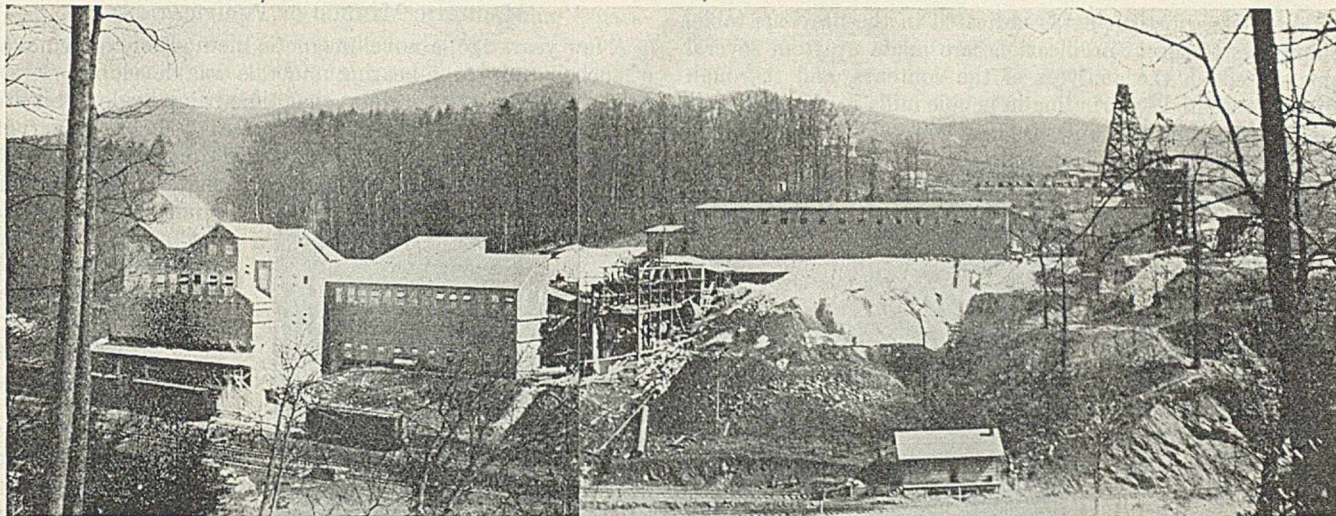
..

**WHAT IS WANTED?** A distinct service to the industries concerned, as well as to members of our profession, can be rendered if a way is found to apprise the individual of the problems awaiting solution. We invite industrial organizations to advise us of such needs as may confront them regarding products, processes, waste elimination, new uses, etc., which they would be willing to have us pass on (anonymously if they so prefer) to men, some of whom are unemployed but who are both willing and capable of undertaking certain investigations. We offer to print a statement of such problems, or otherwise to submit them to chemists desirous of giving them serious attention.

But this service will also work in the reverse direction. There are doubtless chemists who have ideas worthy of careful consideration who do not know either the firm or individuals with whom they should get in contact. We propose to offer assistance to such individuals and undertake to transmit to those who might be interested such disclosures as are made in an effort to get together men of science and of business.

While this is a somewhat ambitious program and may easily place an additional burden upon our small office staff, we believe that it is a constructive enterprise. An exchange of ideas is not a new thought but if, by its promotion, we can contribute to the accomplishment of but a few things, we shall regard the effort as having been worth while. Your inquiries and ideas are solicited.





FELDSPAR PLANT OF THE TENNESSEE MINERAL PRODUCTS COMPANY, MINPRO, N. C.

## Modern Processing of Feldspar

J. H. WEIS, United Feldspar Company, New York, N. Y.

**F**ELDSPAR is a generic term for a group of alkali aluminum silicate minerals used principally by the ceramic industry in glass, pottery, and porcelain enamel. Commercial feldspars are mixtures of two basic feldspars: potash spar (microcline),  $K_2O \cdot Al_2O_3 \cdot 6SiO_2$ , and soda spar (albite),  $Na_2O \cdot Al_2O_3 \cdot 6SiO_2$ , with small amounts (generally less than 10 per cent) of lime spar (anorthite),  $CaO \cdot Al_2O_3 \cdot 2SiO_2$ .

### COMPOSITION OF FELDSPAR

Since feldspar is a pegmatite mineral, it is generally associated with quartz, and, although attempts are made to remove all of this mineral, it is not always possible to do so because of the low value of crude feldspar and the physical characteristics of the deposit which may preclude hand-cobbing or sorting to remove quartz. Fortunately, quartz is not generally considered an impurity, as it is a normal ingredient in ceramic batches, but its presence lowers the quality of the particular feldspar. The quartz content ranges up to 30 per cent, the average feldspar containing about 15 per cent.

Other minerals present in lesser amounts (generally less than one per cent) include muscovite mica, kaolin, and minor amounts of garnet, biotite mica, and tourmaline. The presence of the last three minerals is especially harmful as they contain much iron and cause specks and poor color in the finished ware.

A typical commercial feldspar has the following chemical composition:

SiO <sub>2</sub>	68.5	MgO	Trace
Al <sub>2</sub> O <sub>3</sub>	17.9	K <sub>2</sub> O	10.2
Fe <sub>2</sub> O <sub>3</sub>	0.1	Na <sub>2</sub> O	2.5
CaO	0.4	Loss on ignition	0.3

This analysis indicates the presence of all of the three types of feldspar previously mentioned as shown by the potash, soda, and lime content. Some of the loss on ignition may be caused by mica and kaolin which contain water of composition, and the presence of iron-bearing minerals affects the ferric oxide content.

All three types of feldspar (microcline, albite, and anorthite) usually occur in the same mine or deposit, and individual crystals generally contain all three feldspars in solid solution.

It is apparent, therefore, that by virtue of its mineral associations feldspar is an impure, variable mineral in the mine and must be carefully handled during mining and processing to insure uniformity of the final product. Likewise, much variation can be expected in the composition of feldspar on account of its association with other minerals and its method of formation. For example, some parts of the deposit may be higher in albite than other parts, and, as the albite content materially influences the fusibility of a feldspar, there would be considerable variation in this important property of the feldspar from that deposit unless the sodium oxide content (derived from albite) were controlled.

Skilful pickers can generally sort out the various grades of feldspar with the free quartz content and type of spar as the basis. For example, the following analyses represent four typical feldspars produced from one mine and sorted by hand on a picking belt (1):

PRODUCT	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	K <sub>2</sub> O	Na <sub>2</sub> O	Loss	TOTAL
Potash spar 1	66.40	18.70	0.09	0.56	11.53	2.63	0.16	100.07
Potash spar 2	68.52	17.65	0.10	0.54	10.22	2.67	0.18	99.88
Soda spar 1	72.01	16.66	0.11	1.12	5.33	4.58	0.23	100.04
Soda spar 2	72.95	16.85	0.15	1.55	1.58	6.81	0.16	100.05
Flint (quartz)	98.29	1.08	0.03	0.36	...	..	0.05	99.81
Mica <sup>a</sup>	45.2	39.5	..	..	11.8	..	4.5	100.00

<sup>a</sup> Theoretical composition.

The above analyses indicate the great differences to be expected in feldspar from a single deposit, and, as producers must obtain crude spars from several deposits in order to lengthen the life of the individual mines, it is apparent that the problem of supplying uniform feldspar to the consumer is not simple. Chemical control must be used, and the crude spars from individual mines are segregated in bins and processed individually to avoid mixing or contamination with others of different composition. After separately crushing and drying, each batch of feldspar is mechanically sampled on the way to 80-ton mix bins, and the sample is analyzed



for all of its constituents as indicated in the previous table. Shipments to meet specifications are made up from several bins, based on the analyses of the contents, and thorough mixing is assured by grinding in pebble mills in closed circuit with vibrating screens and air classifiers. The finished product is again checked during processing with a mechanical sampler for fineness of particle size, chemical analysis, and fusing characteristics. By this method of chemical control it is possible to produce and furnish to the consumer uniform grades of feldspar which meet rigid specifications. Losses in ware caused by using the wrong type of feldspar are thus avoided.

As previously mentioned, feldspar is associated with various other minerals, some of which must be removed as completely as possible to make the product usable in industry. Some of these harmful impurities are biotite (black mica), garnet, and tourmaline, and their presence, even in amounts less than one per cent, causes black specks in the finished ware. These impurities are iron-bearing minerals, and often much crude spar must be discarded as waste because of their presence; otherwise, expensive hand-cobbing is necessary to remove them.

#### MAGNETIC METHOD OF PURIFICATION

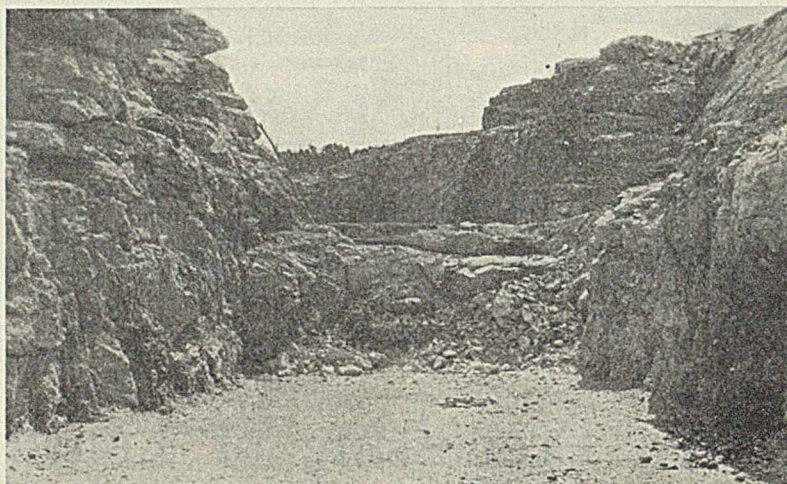
A few years ago, a novel magnetic method for the removal of such harmful iron-bearing minerals was developed (2, 3). Magnetic separations were at that time being made of biotite mica and other feebly magnetic materials, such as garnet and tourmaline, but the muscovite or white mica which also

contains iron oxide in small quantities was not responding to the magnetic forces then employed. The new method of magnetic separation by high-intensity induction, however, separates minerals formerly considered quite nonmagnetic.

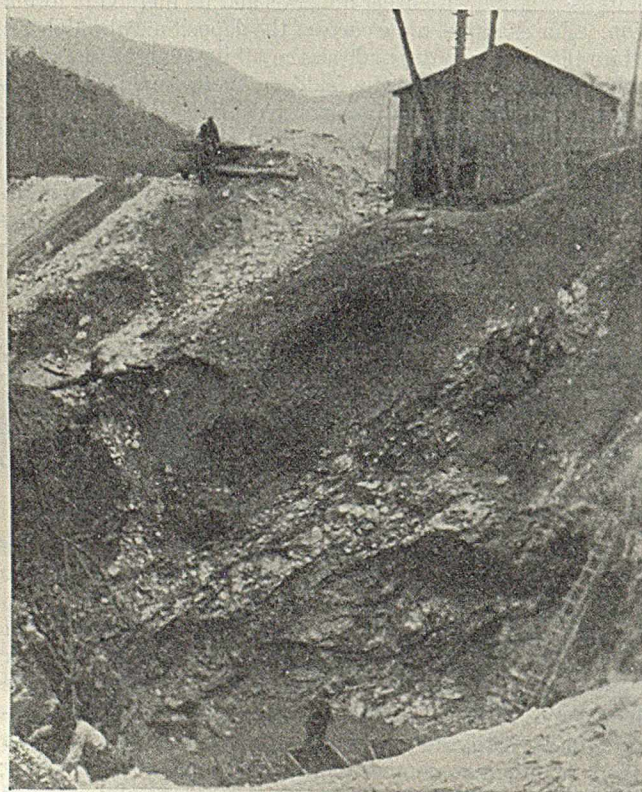
To appreciate how the line of demarcation between feebly magnetic and nonmagnetic substances has been so far shifted as to be practically wiped away, it should be understood that the magnetic force

acting on a particle is proportional to the square of the field strength which is for this purpose increased nearly twenty fold normal. An ordinary permanent magnet has a field strength of the order of 800 gauss (lines of force per square centimeter), while modern magnetic separators employ field strengths as high as 15,000 gauss.

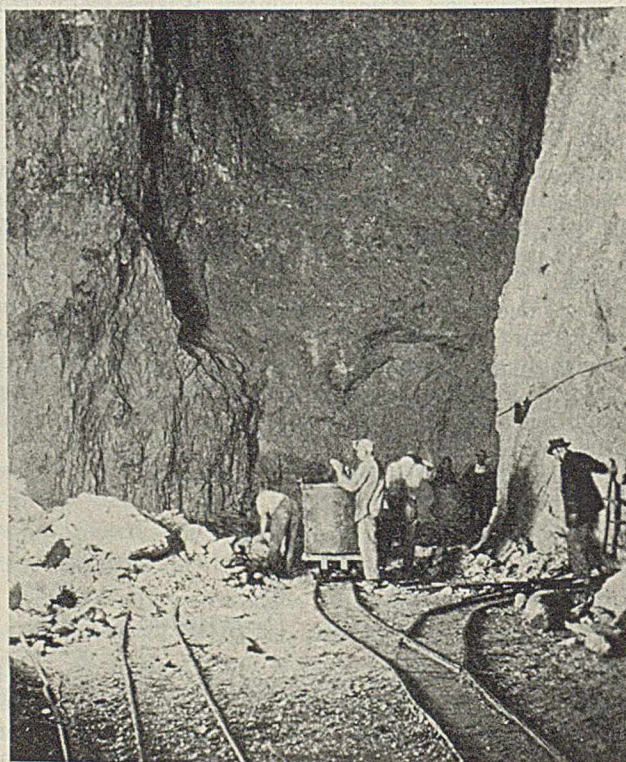
Magnetic separation, like nearly all other separating methods, depends on the density of the particles as well as on the particular physical property characteristic of the method



OPEN-CUT MINING OF FELDSPAR SHOWING PEGMATITE DIKE



TYPICAL OPEN-PIT MINING OF FELDSPAR



LOWER LEVEL OF DEER PARK FELDSPAR MINE, SPRUCE PINE, N. C.



(magnetic susceptibility). All particles undergoing separation react to two forces, one of which is gravity. The other force acts in a direction different from that of gravity, and therefore the direction of the resultant force is determined by the ratio between the special force employed and gravity. Although the special force may be and usually has been exerted upward, directly opposed to gravity, it may be partly or entirely horizontal.

In magnetic separation both vertical and horizontal forces have been used. The older machines in general were vertical force types, but the newer and more sensitive machines employ horizontal forces.

The magnetic separator of high-intensity induction consists of an electromagnetic coil and core from which core pole pieces extend in front of laminated rotors. A closing path of iron is provided behind these rotors, which, therefore, are in the working air gap of the electromagnetic circuit and hence are induced magnets. The material is fed to the rotors by means of a chute, and the more magnetic particles cling to this induced magnet an instant longer, starting their fall from the face of the revolving rotor a little farther along the periphery than do less magnetic particles.

The raw feed is given several successive treatments in the same magnetic separator, each treatment occurring in a stronger magnetic flux density until finally a finished product is left which has not responded to the strongest of these forces. Prior to magnetic treatment the material is crushed through 8 mesh and sized by screens so that the magnetic separator is not expected to remove 8-mesh and 150-mesh particles at the same time. This sizing varies with different minerals

for best results. The feed material must be dry and free-flowing although not necessarily bone dry. The method, apparently, is applicable to a wide variety of products.

In the past it was extremely difficult to meet specifications of glass manufacturers for low iron content before the development of this method, because hand selection could not be depended upon to sort feldspars with the required accuracy. Furthermore, impurities are sometimes concealed within a block or piece of crude rock so that they cannot be detected by eye. On this account feldspar shipments formerly contained varying amounts of iron, ranging from 0.5 to 0.13 per cent ferric oxide. Through the

use of this novel process it is now possible to produce feldspar with a uniformly low iron content ranging from 0.05 to 0.06 per cent from crudes containing up to 0.15 per cent.

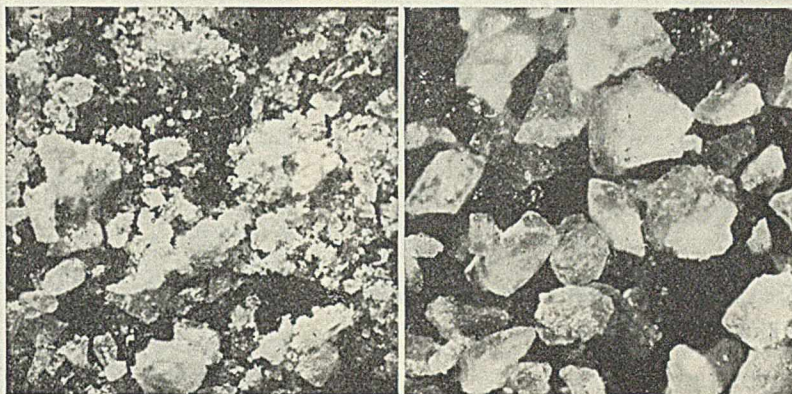
The development of this magnetic concentration process for use in the feldspar industry has made possible the use of crudes which formerly were discarded because of their high content of iron-bearing impurities. It has also served to eliminate the wide variation in iron content of hand-selected spars so that a product with a uniformly low iron content can now be supplied to the glass, pottery, and enamel industries. To these industries, feldspar of uniformly low iron content means higher quality ware by avoiding specks and poor color in the finished product, an important point in the manufacture of glistening white porcelains, tiles, glass, china, and other ceramic ware.

Thus, a natural mineral of highly variable composition can be converted into a high-grade product of the greatest uniformity. Specifications for various purposes can be met with great exactness.

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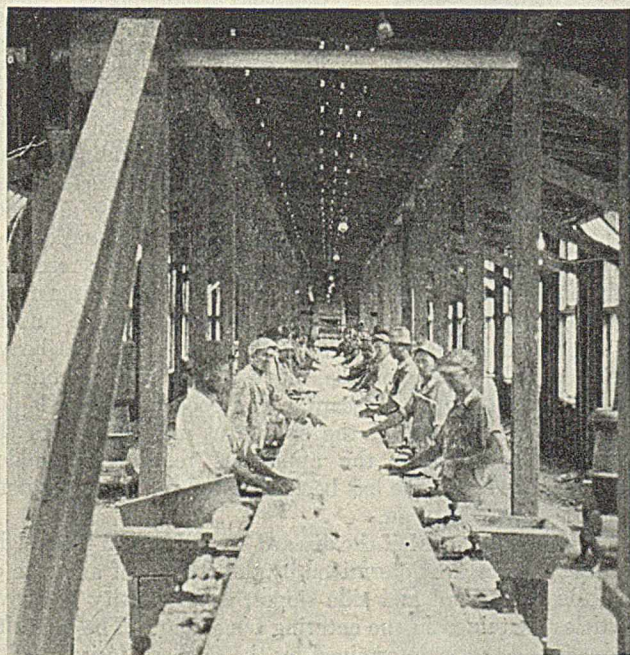
- (1) Burgess, B. C., *Bur. Mines, Circ.* 6488 (1931).
- (2) Frantz, S. G., and Jarman, G. W., Jr., *Trans. Am. Inst. Mining Met. Engrs.*, 102, 122-30 (1932).
- (3) Weis, J. H., *J. Am. Ceramic Soc.*, 14, 413 (1931).

RECEIVED June 27, 1934.



PHOTOMICROGRAPHS OF FELDSPAR (X18)

Left: Ground feldspar as formerly supplied to the glass industry. Right: Granular feldspar free from iron minerals.



CLASSIFYING CRUDE FELDSPARS ON A PICKING BELT



CABLEWAY DELIVERING FELDSPAR TO PLANT ACROSS THE RIVER, MINPRO, N. C.



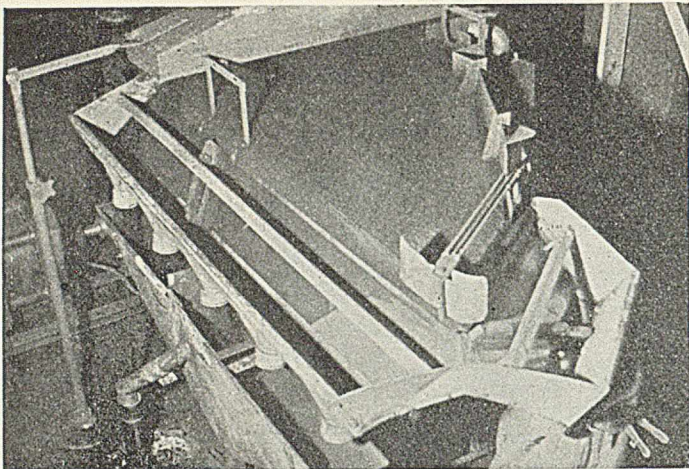


FIGURE 1. DUST HOOD AND FEEDER

## Removal of Inert Material from Bone Char

JAMES M. D. BROWN AND WATSON A. BEMIS  
Revere Sugar Refinery, Charlestown, Mass.

**I**N THE cane sugar refining industry of the United States the amount of bone char in active circulation in the refineries is probably in excess of 50,000 tons. In addition there is a tremendous amount in constant use in the corn products and kindred industries; smaller quantities are employed in the refining of petrolatums, the filtration of paraffin, and the making of medicinal white oils. As this product is generally the only decolorizing agent used, it is important that it be kept at its maximum degree of efficiency both in ash and color adsorption ability.

It is rather strange, in so far as the sugar industry is concerned, that little practical research on this problem has been done. This is probably due to the fact that the majority of the refineries have an excess of bone char over their actual requirements and because it is difficult to interpret the complex reactions of bone char in terms of refinery practice.

Impurities having no adsorptive value collect in the bone char system continually; the usual method of screening or air separation removes only the dust and smaller particles which have a high adsorption value but are likely to hinder filtration, and leaves behind the useless inert material such as iron scale from the char containers, hard poreless portions of bone having little or no adsorptive value, and pieces of glass, concrete, sand, small gravel, small pieces of tramp iron, and other debris. All of these for some unaccountable reason appear to gravitate to the bone char system and, owing to the practice of removing only the smaller particles by screening, accumulate over a period of years to a sizable portion of the total volume of bone char in service.

### BONE CHAR SEPARATOR

Magnetic pulleys have sometimes been used to remove tramp iron, but the authors have found that this is only a

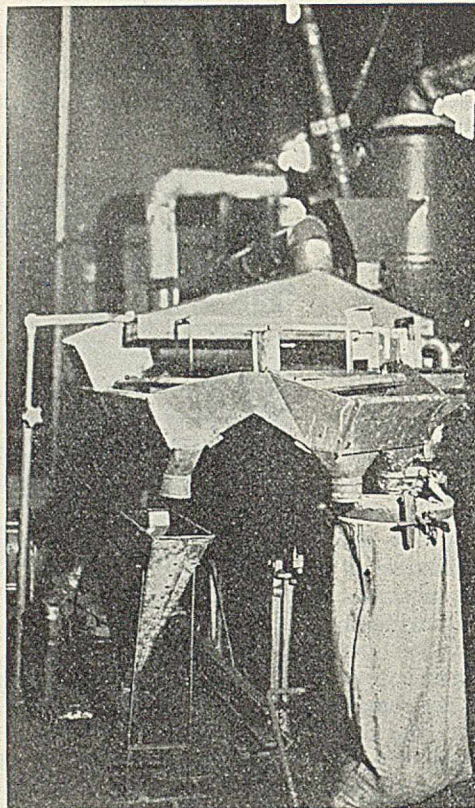


FIGURE 2. FEED CONTROL, DUST COLLECTOR, AND DISCHARGE

minor portion of the undesirable material present in service char. This company has installed and is operating as part of its bone char equipment a specific gravity char separator designed and built by Sutton, Steele and Steele, Inc., of Dallas, Texas. With the aid of this apparatus material can be removed from the bone char system which is of absolutely no value to the refinery but the presence of which is a continual and appreciable item of expense owing to waste of power in heating and circulating.

In general, the bone char separator consists of a grass-hopper conveyor plus an adjustable screened deck through which a powerful current of air passes. The deck surface consists of a perforated plate through which air is blown at the rate of 1700 to 3100 cubic feet per minute, the rate being determined by the type of char to be cleaned. Deck baffles about one inch apart run practically the entire length of the deck. The deck moves about  $\frac{3}{16}$  inch longitudinally four hundred times a minute. (This rate is variable between 330 and 400 vibrations per minute.) The sidewise and endwise slopes of the deck are also variable. The bone char is fed onto the deck and the dust is collected at the receiving end through a dust hood, fan, and cyclone arrangement. The lighter particles of bone char are raised by the current of air high enough to drift over the baffles and the heavy particles, independent of size, move toward the far end and are discharged there as discard. The good bone char is discharged over the side of the apparatus and returns to the system. Operation of the apparatus requires no added labor after the machine has been adjusted for whatever bone char it is desired to clean.

The rate of removal of the discard bone char and the weight per unit volume are determined by the volume of air, rate of feed, degree of end and side slopes, and quantity of heavy particles contained in the entering bone char. The quantity of dust collected is determined by the fineness desired. The amount of air used to convey this material is regulated by a



sliding damper. A 5-horsepower motor is required to operate the entire unit.

Bone chars of varying densities and degrees of activity may be obtained at will by varying the lateral or longitudinal tilt of the table and by varying the air flow through the perforated deck. The fineness of the dust removed may be controlled and varied by raising or lowering the dust hood and by varying, with the damper, the volume of air sucked into the dust-collecting system.

TABLE I. TYPICAL AVERAGE ANALYSES OBTAINED FROM ACTUAL OPERATION

	SERVICE BONE CHAR	DISCARD MATERIAL	DUST REMOVED
Weight, lb./cu. ft.	56	88	49
C, %	7.57	1.40	6.30
CaCO <sub>3</sub> , %	4.32	5.37	7.65
CaSO <sub>4</sub> , %	1.12	0.35	1.39
CaS, %	0.24	0.18	0.34
Fe, %	0.28	0.41	0.47
Insol. in HCl (other than C), %	0.51	4.14	0.78
Color adsorption, %	94	9	94
Ash adsorption, %	34	3	35
Bone phosphate of lime, %	79.2	84.1	77.9
SCREENING (per cent)			
On 10	0.1	0.0	6.2
On 14	8.3	18.2	21.6
On 20	32.3	49.6	22.7
On 28	29.9	26.9	49.5
On 35	17.3	4.8	
On 48	6.9	0.4	100.0
Through 48	5.2	0.1	
	100.0	100.0	

TABLE II. RESULTS OF TEST RUNS

Run No.	4	8	1	7	2	6	3	9	12-A	ORIGINAL SERVICE BONE CHAR	DUST REMOVED
Weight, lb./cu. ft.	58	73	77	80	81	83	87	88	90	56	49
Color adsorption, %	91	78	19	17	17	16	13	12	8	94	93
Ash adsorption, %	37	31	17	10	12	12	3	7	5	34	33
Discard, % of feed	3.4	4.9	6.0	3.6	3.0	3.7	4.0	4.3	1.7	..	1.0
Lb. per hour feed	3300	1800	1200	2200	1200	2100	3000	3400	4500	..	..

Figures 1 to 4 show the table in operation. Figure 1 is taken from above and shows the dust hood in the upper center; the feeder is under the right-hand end of the dust hood. The volume of the overflow is distinctly shown as the bone char flows into the hopper on the left-hand side of the machine. The discard trough is over the receiving bag shown at the lower right.

Table II gives the results of test runs giving discard char at varying weights per unit volume.

Figure 5 shows the average color and ash adsorption values of different portions of service char at varying weights per cubic foot as obtained by the use of the bone char separator.

It has been demonstrated that particle size is not necessarily a measure of the quality of bone char, although the discard consists mostly of the larger particles as shown by the screen tests; it is equally true that not all large particles

are inactive; therefore a screening separator is not dependable.

These discard particles are extremely hard and therefore do not wear down as do the usual particles of bone char and so do not become fine enough to be screened out. On the contrary, because of their hardness and abrasive action, they cause the active particles to wear down more rapidly than would be the case if they had not been allowed to accumulate.

This material, in occupying space in the char filters that might be replaced by active bone char, cuts down the efficiency of the bone char system.

The high content of bone phosphate indicates that the discard particles are composed mostly of dense, poreless, inactive bone fragments accumulated over a period of years. Tests have shown that this material has a high degree of resistance to attrition.

Under present operating conditions the discard amounts to about one ton of material having color and ash adsorption values of 10 and 5 per cent, respectively, and one-half ton of fine dust per 24 hours.

A feed of 7000 pounds per hour has been experimentally used on this machine and a satisfactory separation obtained, but a feed of 3000 pounds per hour with a discard rate of three per cent and a dust removal of 1 per cent gives a consistent maximum weight per cubic foot with low adsorption values for the discard material. The discard is controlled

by keeping the weight between 86 and 90 pounds per cubic foot. Bone char of this density has adsorption values of approximately 10 per cent color and 5 per cent ash ad-

sorption.

The above discard rates were obtained on a service char which has been in use over a period of years. The bone black replacement under ordinary operating conditions should amount to less than 0.5 per cent of the bone char re-verified.

The ash and color removal values are determined by heating together in a flask submerged in a water bath at 170° F. a weight of char equivalent to the solid content of a sugar solution of 47.5° Brix for 4 hours. The flasks are shaken at each half-hour period with a rotary motion. The results are compared with a bone char having a definite, high-adsorption value which is regarded as standard by this laboratory. (All adsorption values are calculated by using the results obtained on the standard laboratory char and laboratory sugar solution under the usual routine adsorption procedure in use in this laboratory.)

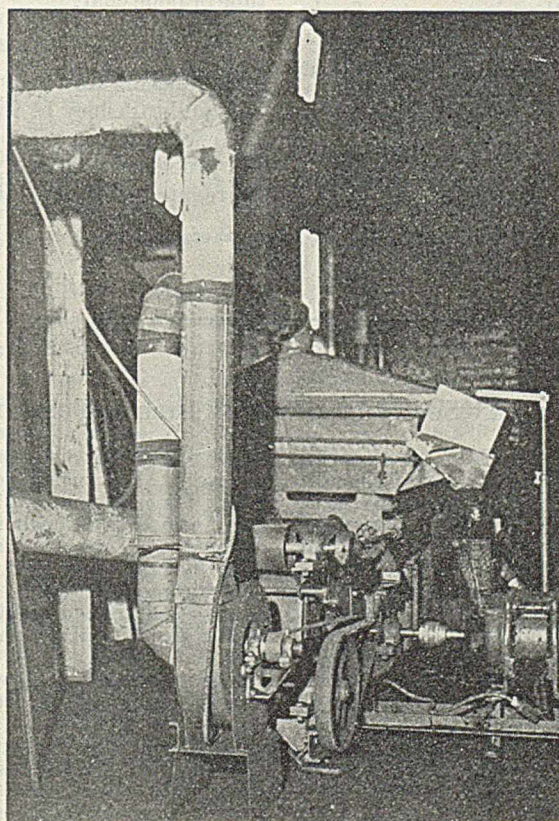


FIGURE 3. FEED END, DRIVE MECHANISM, BLOWER, AND DUST COLLECTOR SYSTEMS



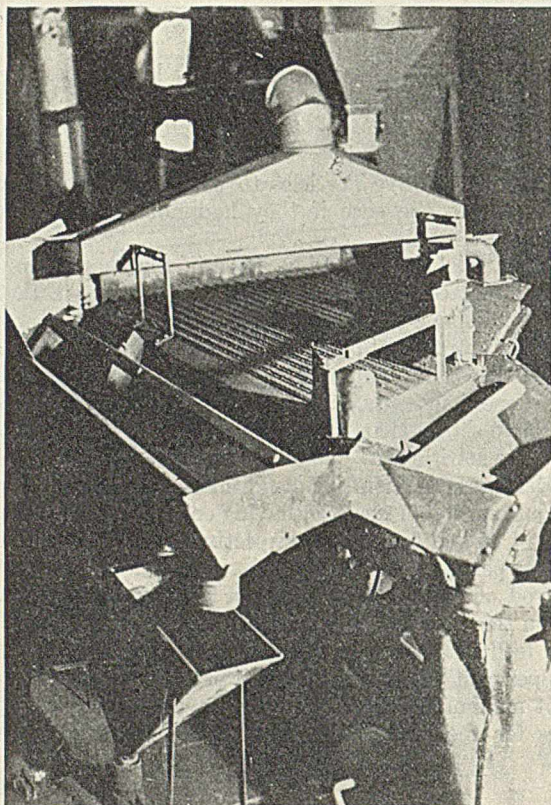


FIGURE 4. NAKED TOP DECK OF APPARATUS

The separator has run with practically no attention (except changing the bags as filled), and the results obtained have been consistent. The deck is swept clean daily as a precautionary measure against bone char slivers which have a tendency to embed themselves in the openings of the screen and should be brushed out before they become too firmly embedded.

The performance of the apparatus has been so consistent that it is possible to take off any portion of bone char with the deflectors and obtain comparable figures for density and weight over the full weekly period of operation of the apparatus and also to transfer char from primary to secondary service char in this manner, using a slow constant rate and thus insuring even distribution of the transferred portion.

A small quantity of inert bone particles is present in new char and may be separated with this machine before the char is put in service or removed in the routine manner from the service char after the addition of the new bone char to the service char.

A sufficient number of tests on this phase of the question to supply evidence convincing enough to determine which method is the more economical have not yet been made.

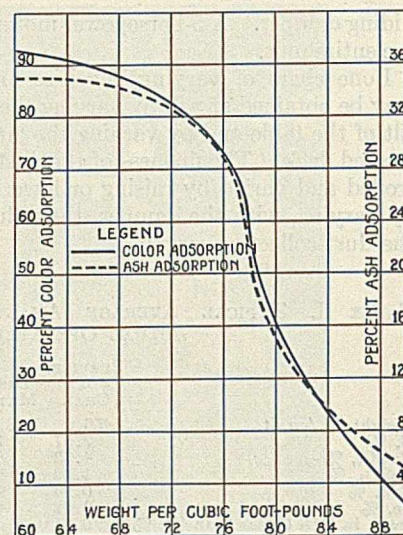


FIGURE 5. AVERAGE COLOR AND ASH ADSORPTION IN RELATION TO WEIGHT PER CUBIC FOOT

#### ADVANTAGES OF INSTALLATION

The following advantages, which tend to increase the efficiency of the bone char system, may be attributed to the use of this installation: removal of useless débris from bone char; removal of inert bone char and its replacement with new active bone char; increase in active area per bone char filter; saving in heat and power; inhibition of attrition of active particles; and removal of dust.

With this machine bone char may be graded into or from various service chars in the bone char system, or, as mentioned, a definitely determined portion may be continuously transferred from one service char to another without loss of time or bone char.

#### ACKNOWLEDGMENT

The authors are deeply grateful to Sutton, Steele and Steele, Inc., and to Ashley L. Sheppard of that company for the time and effort they have expended in helping to work out details and problems connected with the adaptation of this unit to the requirements of the bone char system.

RECEIVED June 11, 1934.

### MEXICAN SUGAR INDUSTRY IN STRONG POSITION

The strict control exercised by the Sugar Producers Association of Mexico in connection with production and sale of sugar in that country has placed the local sugar industry in the most favorable position it has known for years, according to a report to the Commerce Department from Assistant Commercial Attaché Glover, Mexico City.

The association was organized in 1932 following the crisis in the Mexican sugar industry which began in 1930, in which year production was in excess of consumption, selling prices below production costs, and sugar producers unable to obtain finances. Since the association was organized at the instance of the Mexican Government, it has had complete supervision over sales. Last year, it exported surplus sugar to the amount of 100,000 tons, after which it managed to stabilize prices on the home market. The association also organized a bank to advance money to growers. This greatly relieved the financial crisis existing in the sugar industry.

Mexico's normal consumption of sugar amounts to approximately 200,000 tons annually, but now that conditions are good

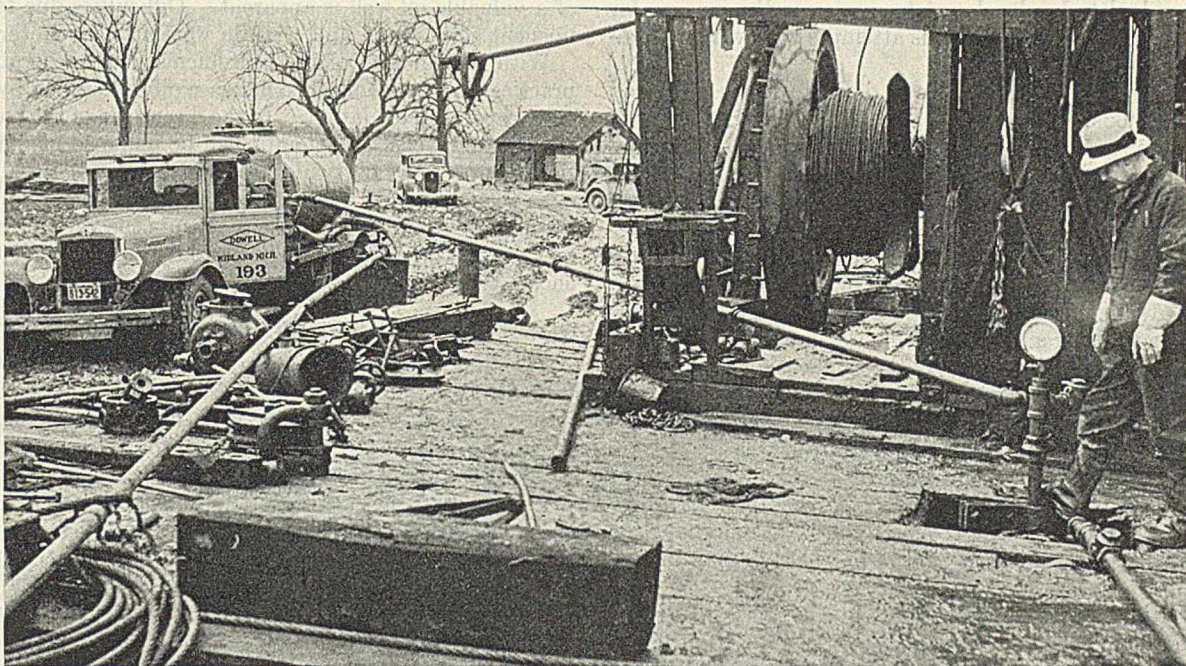
in all sections of the country, consumption will probably be increased. The sugar association has recently taken steps to increase domestic consumption by means of a well-planned educational campaign throughout the country, a movement which undoubtedly will meet with at least a fair degree of success in view of the favorable economic situation at present prevailing there.

Mexican sugar output in the season which has recently closed amounted to 180,000 tons, which, with the carry-over from 1933, makes a total amount of available sugar in excess of 200,000 tons.

In all probability, this will fall between 12,000 and 20,000 tons short of the market's requirements, but the Sugar Producers Association believes that there will be no necessity to import sugar because of early grinding during the latter part of the year.

Mexico is a high-cost sugar-producing country, and for that reason it is essential for the welfare of the sugar industry to regulate consumption to meet the domestic demand, as it is impossible for Mexican sugar successfully to compete in world markets.





A DOWELL SERVICE UNIT IN OPERATION

## Chemically Controlled Acidation of Oil Wells

SHERMAN W. PUTNAM, Dowell Incorporated, AND WILLIAM A. FRY, Dow Chemical Company, Midland, Mich.

THE past three years have witnessed the acid treatment of approximately three thousand lime wells in the United States and Canada for the purpose of increasing oil production. The acid treating, or, as it is popularly known today, acidation or acidizing of wells, has resulted in successful treatments in a large percentage of cases, especially in the areas containing the purer limestones of Michigan, Texas, Oklahoma, Kansas, Louisiana, Ohio, Illinois, Kentucky, and Ontario. The increased oil production due to these acid treatments ranges from a few to over one thousand barrels per well per day, averaging 448 per cent increase for all of the wells treated to date.

Several papers have already been published on the acidation of oil wells, but they have dealt mainly with field experience and production. An article by the Pure Oil Company (6) notes the early acid treatments of oil wells in the Michigan field near Mt. Pleasant. Swindell (7) discusses field conditions relative to acid treating and results in the Seminole area. Cunningham (3) gives the history and results of the first acid treatments. He also discusses the chemical reactions, treatments, and value of acidizing *vs.* shooting of wells. Best (1) describes the technical knowledge necessary if the wells are to be acidized in a scientific manner to assure the maximum increase in production. The article also discloses the various methods of introducing acid into the well and problems on water control. Covell (2) has shown that the use of acid to stimulate oil production from Michigan lime wells requires a study of several factors: an analysis of the formation to be treated, the selection of a suitable type of acid and its amount, the time of treatments with respect to date of well completion, and finally an economic analysis of the results.

The object of this paper is to present the chemical background and laboratory developments required to give the

acidation of oil wells its present status. There was no progress of commercial importance in this field until a scientific study of the problem had been made in the laboratory, even though as early as 1894 lime wells were treated with uninhibited concentrated hydrochloric acid for the purpose of increasing oil production. Most people connected with the oil industry are familiar with the patent issued to Frasch (4) which specified the use of hydrochloric acid in limestone formations. Since that time practically every commercial field has had, at one time or another, some producer attempt the application of acid treatment in an effort to increase the porosity of the rock and eventually increase oil production.

### DEVELOPMENT OF ACIDATION

The control and technic, both by chemical and physical means, of directing the acid into the well and thus making it a constructive agent rather than a destructive one was not perfected on a commercial scale until about 1932. The work which led to the practical development of chemically controlled acidation of oil wells began in 1929, owing to the demand for increased production of natural brine which forms the basis of raw materials for The Dow Chemical Company. The demand for more natural brine brought the problem to the attention of both the chemical and physical research laboratories in order to develop a method of opening up the crevices of producing rock other than by the use of explosives.

The brine is produced for the most part from a sandstone of very high silica content, which contains a small percentage of calcareous material. Being a chemical company, its first thoughts were to find an acid which would be effective. As is the usual procedure on any research problem, the literature was searched, with the conclusion that all previous attempts to acid-treat wells had met with failure. The experiments were begun with the full knowledge that some-



thing new had to be developed to overcome the reasons for the failure of the several previous attempts with various commercial acids.

The research work was narrowed down to the use of acid by two methods: In the first place, it was fed into the well along with a stream of brine which carried the brine and acid mixture back into the producing formation. It was hoped that the acid would react with calcareous material in the rock and thus increase its porosity.

For the second method a charge of acid was fed directly into the well, and a certain head of brine or oil pumped in on top. At first the difference in head of the two fluids was relied upon to bring about sufficient pressure to feed the acid back into the rock, and later, by the application of mechanical pressure, this was more completely accomplished.

The lack of a large percentage of calcareous rock in or adjacent to the brine formation prevented the treatment from showing very great promise for improved production. However, for a well which had previously been discarded as a non-profitable producer, it was possible to increase its production some 25 per cent, thereby making the well a paying investment.

In addition to the research which developed into the two major methods described above, work was carried on to determine the best type of acid to use, as well as the strength of acid which could be used. Hydrochloric acid was looked upon with favor because it was commercially available and because soluble salts were formed as a result of its reaction with limestone. At the same time there were drawbacks which required much study before it was possible to put this acid into practical use.

The problem of acid strength became of far more importance than occasional observation in the beginning had indicated. For instance, highly concentrated hydrochloric acid put into a well, with little or no water, did two things: It worked so rapidly in some formations that it did not penetrate into the pores any distance but merely increased the size of the bottom of the hole; and the water formed by the reaction back into the pores of the rock was not sufficient to dilute the calcium chloride salt to the point where it could be easily brought out and open up the formation for increased production. In other words, it had a greater tendency to seal the well than to open it.

Connected directly with the problem of strength of acid was the necessity of developing an inhibitor which would retard or eliminate the action of the acid on the metals employed in the well but at the same time would not retard the action on the formation to be attacked.

During these experiments on the brine-producing sand formation, neighboring oil well owners became interested, and, as a result of the combined efforts of The Dow Chemical Company and The Pure Oil Company, oil production was increased. The patents relating to this procedure taken out by both companies were licensed to Dowell Incorporated (5). The oil, however, was produced from a limestone formation at a much greater depth than the brine. The results obtained were interesting, if not phenomenal, from the start. However, the apparent possibility of making an error of a few feet one way or another in depth when working at a distance of over a half-mile, immediately suggested the possibilities of chemical action taking place where it might do harm rather than good.

In many wells the casing used to close off the upper water formation from the oil-producing sand is embedded in a limestone formation and apparently is sealed at this point. However, since there is as great a possibility of the acid's attacking the seat of the casing in the limestone formation as there is of its attacking the limestone which produces the oil, the need of a careful diagnosis and expert control in the treatment

of a valuable oil well is apparent. Difficulties due to water, unspent acid, plugs, and paraffin were also encountered.

With the solution of these problems, it then became both practical and economical to increase oil production by chemically controlled acidation. In the discussion of the treatment given to oil wells, no attempt will be made to give an exact treatment for any particular well, since every well is different, even though it is an offset in the same pay formation. However, an attempt will be made to discuss the various materials and reasons for using them in various types of wells that are encountered.

#### SELECTION OF INHIBITOR

The first and unquestionably the most important factor from the standpoint of economical oil well treatment is the inhibitor used. Inhibitors for acids have been used for metal pickling to retard the action of acids for a great many years. The word "retard" is used advisedly, as that is the exact function which these partial inhibitors perform. No attempt was made to eliminate the action of acid on metal entirely but merely to slow it down, as the pieces of metal were taken through the bath and brought out at the other end of the line.

In the early work the well-known arsenic compounds were used, but it was found that they were not sufficiently inhibiting to prevent excessive losses due to acid attack on the metallic surfaces. It finally developed, in order to assure safety, that two or three materials had to be used in the same solution to accomplish the desired inhibition. At the present time both organic and inorganic inhibitors are used, of both the soluble and insoluble types. The value of the inhibitor lies in its long-time protection of the equipment against possible acid pocketing at various points in the casing and tubing, such as joints, casing seats, etc.

The entire situation would be comparatively easy for the oil companies to cope with if the tubing and casing were destroyed or badly attacked within the first 30-day period. Even though actual operation on a commercial scale has been going on since 1932, when many oil well owners bought carboys of acid and dumped it into wells, those wells are being lost 2 years later as a result of using uninhibited acid. Unquestionably the percentage of lost wells due to the use of uninhibited acid is greater after 1 or 2 years than of those which are ruined within the 30- to 60-day period after initial treatment.

One of the most corrosive agents known is iron chloride, formed by the action of hydrochloric acid on iron. It embeds itself under the oil film and continually permits corrosion to take place. No oil well owner should permit the use of any treatment on a well without first testing the inhibiting qualities of the acid employed. It should be insisted upon that, prior to forcing the acid into the well, a few cubic centimeters should be drawn off into a test tube in which a piece of clean iron is placed and allowed to stand for 15 to 30 minutes to determine whether the gas bubbles continue to be evolved and therefore whether corrosion will take place. Many experiments were made in connection with the use of old tubing and casing that were partially corroded with paraffin and oil sludge to determine the possibility of the use of uninhibited acid. Experiments have been conducted by flushing with oil first, then putting in acid, and following with the second oil treatment in order to clear the tubing. Both of these procedures would, undoubtedly, work satisfactorily if the tubing could be guaranteed to have a uniform coating that would not be washed off as a result of mechanical action so that the acid would not remain in joints or on the sides and thus reach the steel and attack it.

One company used an inhibited acid which caused corrosion at the rate of 0.108 pound loss per square foot per day. The hydrochloric acid alone causes a loss of 0.210 pound per

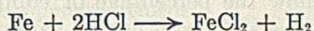


square foot per day, whereas the inhibitor used in all Dowell acids limits it to only 0.001 pound per square foot per day.

#### SELECTION OF ACID

The next item of particular importance is the selection of a suitable acid and the determination of the most satisfactory concentration to be used. To acidize a well successfully, the products of the reaction of the acid and the pay formation must be soluble in water, and the acid must be sufficiently dilute to hold the products of the reaction in solution. Hydrochloric acid was selected as the most suitable acid because of its rapid action on lime formations and the fact that it forms sufficiently soluble salts. Fifteen per cent was found to be the most satisfactory concentration for general well treatment. This concentration of acid gives a 22 per cent calcium chloride solution when completely reacted with the limestone and is thus well within the limits of the saturation concentrations for all likely temperatures. The inhibited hydrochloric acid, called

Dowell X, reacts with the pay formation, forming calcium chloride, carbon dioxide, and water, but prevents the reaction,



to the extent of 99 per cent.

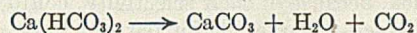
The XX acid is the same as the X acid but contains a catalyst particularly effective in connection with dolomitic formations which are mixtures of magnesium and calcium carbonates. The action of hydrochloric acid on magnesium carbonate is slow and consequently does not accomplish the desired results except when an accelerating agent is present.

The XF acid is an inhibited, free-flowing hydrochloric acid and is used particularly in limestone formations where the rock pressure is low. In certain types of formation where this is the case, the regular acid can be forced back into the pores of the rock, but the products of reaction do not come out. The difficulty is that the acid acting on the limestone forms carbon dioxide and calcium chloride solution which exist side by side in the pores. The pressure required to force such an interspacing of gas and liquid from the pores is considerable and is dependent on four factors: (1) size of pores, (2) surface tension of the neutralized acid, (3) force of attraction between the neutralized acid and the walls of the pores, and (4) number of gas-liquid groups.

The XF acid was developed to reduce the pressure necessary to make the gas-liquid products of reaction flow more easily. This was accomplished by adding to the regular X acid, materials which would reduce the surface tension of the resulting brine or spent acid. Most technical men in the oil industry are familiar with the Jamin test which can be demonstrated easily with a capillary tube, filling it with alternating liquid and gas bubbles. A pressure is then applied and measured with a manometer in the system. Using neutralized XF acid, the manometer shows that only one-tenth the pressure is necessary to force it from the capillary tube as compared with the regular material.

The XG acid is an inhibited blend which is particularly

adapted for the cleaning out of casings and tubings where "gyp" formation is prevalent.<sup>1</sup> Gyp is generally formed in wells that contain brine and have high rock pressure. The calcium is present in the brine as the acid carbonate, and, as it approaches the surface, the pressure is reduced and carbon dioxide liberated. The bicarbonate is thus converted into the carbonate and deposited in the upper length of tubing, as indicated by the following formula:



As soon as the X acid comes in contact with the gyp it reacts, liberates carbon dioxide, and immediately channels so that most of the acid drops to the bottom of the well unreacted. The XG acid is the regular X acid treated with an agent which causes foaming simultaneously with the formation of calcium chloride and the evolution of carbon dioxide. The foaming tends to buoy up the column of acid in the tubing and allow more time for reaction.

A great deal of work has been done and results have been

obtained with hydrofluoric acid, especially for the sand type of well. However, it is well known that hydrofluoric acid reacts with sand to form silica gel in the bottom of the well, which stops up the well rather than increases the flow. Methods of eliminating this trouble have been developed, but, owing to their present status in the Patent Office, details cannot be given now. However, in the treating of sand wells, it must be taken into consideration that the results cannot be expected to be as phenomenal as in the limestone treatments where the rock formation provides channels and crevices, making it possible oftentimes to open an untapped pool or pocket of oil which would not be touched under the ordinary methods; with sand formation there is a certain amount of uniformity existing that, at best, will allow only an increase in the rate of production rather than the total amount to be recovered.

One of the most important accessories to well treatment is what is known as a blanket. In the normal treatment of a well, the tendency is for the acid to work straight down or, at least, on a downward curve rather than out into the formation. With a water layer underneath the oil-bearing strata, a considerable amount of care must be exercised to prevent the bringing in of water to the exclusion of the oil. One of the greatest hazards, aside from the effect on equipment in oil well treating, is the bringing in of water in excess of that being produced at the well at the time of treatment. In the original research work on the problem it was found that, by using a 40° Bé. calcium chloride solution to fill the lower section of the pay or the bottom of the hole, the X acid could be directed to the upper layers of the formation. The acid following the blanket does not penetrate it but floats on top. There is no chemical action involved but an adjustment of gravity which increases the protection to the well.

In addition to the problems encountered in the treating

<sup>1</sup> "Gyp" is a term used in the oil industry which has been erroneously derived from the word "gypsum." Gyp as found in the oil field is a definite calcium carbonate, whereas gypsum is calcium sulfate.



SMALL TRUCK EQUIPPED WITH 500-GALLON TANK AND HIGH-PRESSURE PUMP



of brine wells, paraffin presents an additional difficulty in oil wells. There are two types of paraffin solvents which were developed to be used in connection with well treating—one at the time of well treating, the other for well maintenance. It is definitely known that there is selectivity among solvents. Therefore, it was necessary to obtain paraffin samples from various fields all over the country and to put them through the laboratory tests to determine the various solvents which, because of their selectivity, could be used in blending satisfactory materials for paraffin work.

Owing to the amount of insoluble material mixed with paraffin, it was necessary to develop the solvent with selectivity from the standpoint of solvent power and with the proper gravity for maintaining the insoluble materials in suspension so that they could be brought to the top of the well rather than be deposited at the bottom. The use of any of the petroleum products alone, while being good solvents and the natural solvents for paraffin deposits at the bottom of the hole, may cause trouble because of the insoluble materials present. Solvent Red, which is blended, is technically correct from the standpoint of gravity and selectivity, and excellent results have been obtained in various fields with it. The second type of paraffin solvent is one with organic acid so that it will attack the paraffin and the limestone. It is used where the hole has been covered with paraffin and the pores of rock stopped up around and near the surface. This is used during the treatment with beneficial results.

Other factors to be considered in well treatment are the

use of special plugs, protections for the lead plugs that are already set in the hole, the proper method of protection for the casing seat, which may or may not be cemented, and particularly the known dimensions of the pay formation.

The above factors have been determined from actual well work, and in addition the technic for the handling of these various reagents has been developed by carefully trained men who are put in the field to do the actual diagnosing of the well.

The successful results without damage to wells or equipment through the use of materials and methods described above indicate the aid of chemistry in the oil industry.

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## Removal of Copper Sulfate from Water by Ferric Floc

C. J. BROCKMAN, University of Georgia, Athens, Ga.

COPPER sulfate has been used for years to control algae growth in municipal raw-water supplies. A previous paper (1) reported the adsorption of copper sulfate by aluminum floc; considerable quantities of copper were completely removed by treating the water with alum, provided the filtered water possessed a pH of 6.3 or above.

In continuing this work it was of interest to know what effect the ferric floc would have on the removal of copper in the filtering process. It is well known that ferric floc is more insoluble at lower pH values than alum floc. We are not concerned here with coagulation in pH ranges over 7.0 because considerable copper alone without iron or alum coagulants will be removed by the floc, probably as a basic salt.

A 0.01 molar solution was prepared by dissolving 1.116 mg. of good-grade ferric ammonium sulfate in 1 liter of distilled water. A solution having a concentration of 0.1 mg. of copper ion per cc. was made by dissolving 0.3928 gram of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in 1000 cc. of distilled water. The buffer solutions were prepared according to Clark's method (2) from disodium and monosodium phosphate. These solutions were used in 50-cc. volumes at a definite pH, to which were added, in order, the copper sulfate solution with stirring, and then the solution of ferric ammonium alum with stirring. These solutions then stood 1 to 4 hours until the floc had settled. The supernatant liquid was filtered by decantation so that only about 40 cc. ran through, and very little of the floc appeared on the filter paper. Of these 40 cc., 10 cc. were used for the determination of copper by the ferrocyanide method and 10 cc. for the colorimetric determination of pH (3).

In some cases at the lower pH range there was considerable residual iron in the solution which interfered with the deter-

mination of copper by the ferrocyanide method. In these cases the iron and copper were separated by means of strong ammonium hydroxide; this is the usual procedure. The following data show the percentage of copper removed by various concentrations of ferric floc at various pH values:

TEST No.	pH	BUFFERED WATER		FILTERED WATER	
		Ferric soln. P. p. m.	Copper soln. P. p. m.	pH	Cu removed %
1	6.8	159.3	14.3	6.4	100
2	6.8	279	12.5	6.1	100
3	6.8	368	11.1	5.0	100
4	6.8	20.7	8.9	6.5	100
5	6.8	0.0	8.9	6.8	93
6	6.6	159.3	14.3	6.3	100
7	6.6	171.8	7.2	6.2	100
8	6.6	182	1.6	6.3	100
9	6.6	20.7	8.9	6.4	97
10	6.6	0.0	8.9	6.4	93
11	6.0	159.3	14.3	5.2	92
12	6.0	171.8	7.2	5.2	100
13	6.0	182	1.6	5.2	100
14	6.0	20.7	8.9	5.9	100
15	6.0	0.0	8.9	6.0	63
16	5.6	159.3	14.3	<3.8	92
17	5.6	171.8	7.2	<3.8	100
18	5.6	182	1.6	<3.8	100
19	5.6	20.7	8.9	5.5	88
20	5.6	0.0	8.9	5.5	56
21	6.4	159.3	14.3	5.8	100
22	6.4	159.3	14.3	5.4	100
23	6.4	182	1.6	<3.8	100
24	6.4	20.7	8.9	6.3	94

Comparison of the above results with those obtained in the previous paper (1) indicates that the iron floc is more efficient in removing copper ions from solution than is the aluminum floc. The pH range for this removal is wider, and smaller concentrations of iron will effect complete removal of copper ions. Copper ions have been completely removed from water at a pH value of 3.8; this was impossible with the aluminum floc.

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# Removal of Iron and Manganese from Water

S. B. APPLEBAUM, The Permutit Company, New York, N. Y., AND M. E. BRETSCHGER, Buffalo Electrochemical Company, Buffalo, N. Y.

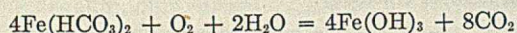
**I**RON and manganese in water supplies in amounts greater than 0.3 to 0.5 p. p. m. cause difficulties (13) in industry and the home. Chief among these are unpleasant taste, unsightly stains, and troublesome deposits.

Iron and manganese give an astringent, metallic taste to drinking water; this causes trouble in cooking in the home, in the canning industry, and in the production of beverages.

Yellow to black stains are formed by the precipitation of iron and manganese. This is noticeable in the staining of porcelain basins, bathtubs, bottles, glasses, and china, and also in the washing of linens, in textile plants, in paper mills, and in the manufacture of raw water ice where concentrations in the core accentuate the difficulty. Many reagents react with iron and manganese to form precipitates, such as tannin in leather which forms black iron tannates as fast as ink. This occurs also in dyeing in textile plants.

Iron and manganese deposit on coils in cooling systems, requiring expensive cleaning and reducing cooling efficiency. In municipal distribution systems such deposits increase the friction through the pipes and increase pumping costs. At sudden high rates of flow the deposits are loosened and cause turbid water. The growth of iron bacteria, such as *Crenothrix* (?), is promoted by iron and manganese. These organisms accumulate in stringy, slimy masses and produce disagreeable tastes and odors on decomposing.

In general, iron and manganese may be removed from well waters by two methods. The first is by oxidation (8) to the higher oxides and hydrates. These are insoluble and can therefore be removed by filtration. The iron oxidation reaction is as follows:



The manganese oxidation reaction is similar; the two factors involved in this reaction are introduction of oxygen and liberation of carbon dioxide. The second method for removing iron and manganese is by base exchange through zeolite without oxidation.

## FACTORS INTERFERING WITH OXIDATION REACTIONS

Usually the oxidation reactions of the first method take place quite readily. In such cases, frequently, it suffices for the water to stand in contact with the air for a few hours, and its crystal clear condition (when drawn) changes to a milky

*A description of some of the difficulties caused by iron and manganese both in industry and the home is given. The general methods of iron and manganese removal consist of (1) oxidation and filtration and (2) base exchange. The oxidation reactions are interfered with by a number of factors, such as the presence of free carbon dioxide, low total solids, low pH value, organic matter, etc.*

*The various types of iron and manganese removal plants consist of: (1) the simplest form of aeration followed by filtration, (2) more thorough aeration for removal of free carbon dioxide followed by filtration, (3) aeration followed by basin settling and final filtration, (4) aeration, lime feeding, basin settling, and filtration, (5) same as (4) using special coagulants, (6) oxidation and filtration by manganese zeolite, and (7) removal of iron and manganese by sodium zeolite through base exchange without oxidation.*

*The design of iron removal plant selected for any given water and set of engineering conditions requires experimental study, both in the laboratory and in the field. Four cases of actual iron removal installations, and results and experiences obtained with them are given.*

and then brownish turbidity, which finally settles out as a precipitate. The first method of iron removal thus closely follows the reaction that occurs in Nature.

However, many waters do not thus respond readily to this oxidation reaction. Discussion of some of the interfering factors follows.

**FREE CARBON DIOXIDE.** Since carbon dioxide is formed on the right-hand side of the oxidation reaction, the presence of high amounts of carbon dioxide or any acid in the original water interferes with this reaction's going to completion (11). Many waters do contain interfering amounts of carbon dioxide. In those cases it is necessary to remove the carbon dioxide either by thorough aeration or addition of alkalies or both.

The type of thorough aeration necessary to remove carbon dioxide differs from the type of aeration required merely for introduction of oxygen for the oxidation reaction. The latter involves the addition of only 0.14 p. p. m. of oxygen

per 1 p. p. m. of iron. Such small amounts of oxygen can be introduced by sniffing air into the suction of well pumps or by a compressor, or by adding small amounts of oxidizing chemicals. But with high interfering amounts of carbon dioxide present, a more thorough aeration than sniffing is required.

**LOW TOTAL SOLIDS.** In general, the well waters of high bicarbonate hardness in the Middle West respond readily to this oxidation reaction. With waters low in total solids, however, even a thorough removal of the carbon dioxide by efficient aeration usually does not suffice, and additional steps are required.

**LOW PH VALUE.** Iron and manganese in acid waters are usually present as sulfates and require the addition of alkalies to raise the pH value above 8 or 9 before filtration.

**ORGANIC MATTER.** Iron or manganese present in organic combinations resist removal by aeration and filtration. In such cases special coagulants, agitating devices for acceleration of floc formation, and sedimentation basins are necessary before filtration.

**EXCESSIVE AERATION.** Excessive aeration (2, 16) sometimes interferes with complete removal of iron and manganese, especially manganese. In such cases better results have been obtained by restricted aeration, limiting the absorption of oxygen to a fraction of saturation.

**MANGANESE.** In general, manganese (15) is more difficult to remove than iron and requires higher pH values. It



oxidizes more slowly and requires long detention periods in basins, together with addition of special reagents for complete formation of manganic precipitates; often its presence also causes the iron to resist oxidation and precipitation.

#### TYPES OF IRON AND MANGANESE REMOVAL PLANTS

The type of treatment plant required is determined by a number of factors such as: character of the water, especially the interfering factors present; engineering conditions; and

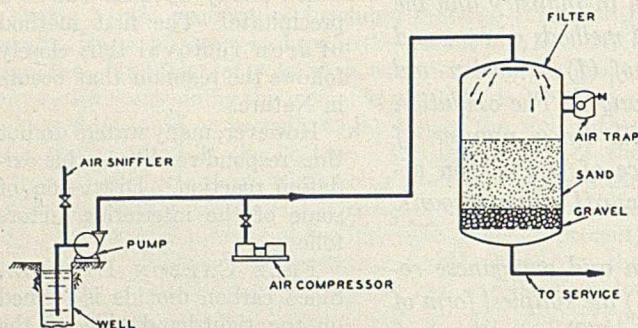


FIGURE 1. IRON AND MANGANESE REMOVAL FILTER WITH AIR SNIFFLER OR COMPRESSOR

the purpose for which water is used and the degree of iron or manganese removal required. Classification of the various types of iron and manganese removal plants follows.

**WATERS LOW IN CARBON DIOXIDE, RESPONDING READILY TO OXIDATION.** Figure 1 shows the usual type of plant employed for such waters, where the amounts of iron or manganese are not excessive. The small amount of oxygen needed for the oxidation reaction is introduced by sniffing air into the well pump. An air trap releases any excess of air from the side of the filter above the filter bed. The use of a pressure filter as shown avoids repumping, but gravity filters may be used.

If the amounts of iron and manganese present were so high that they would tend to clog the filter and require excessive filter washing, in time the iron and manganese would penetrate the filter bed and slip through into the effluent. Therefore, in such cases a contact filter is used ahead of the final filter. This contact filter uses coarse granules with greater storage capacity between the grains. Frequently the contact filter is arranged so that the bed is not submerged and is thus exposed to the air. Here also by using pressure shells repumping is avoided, but gravity filters may be employed if desired.

The final filter should be run at rates of not over 2 to 3 gallons per square foot per minute. If sand is employed as the filtering medium, a coarser sand may be used than in ordinary filtration practice because the iron and manganese hydroxide coatings on the grains act as catalytic agents, and the entire bed is in action rather than the surface alone. It is therefore necessary to season the bed directly after installation until sufficient coating forms on the grains. Owing to the greater penetration of iron and manganese into the bed, it is advisable to use air wash to assist the water wash in cleaning the bed.

**WATERS HIGH IN CARBON DIOXIDE REQUIRING CARBON DIOXIDE REMOVAL BY ALKALI FEED OR EFFICIENT AERATOR BEFORE FINAL FILTRATION.** In this case Figure 1 may be employed, provided an alkali feed is installed to neutralize the carbon dioxide. Otherwise some type of efficient aerator should precede the filter. Aeration is more economical than alkali addition because no chemical costs are involved.

Figure 2 shows a coke tray aerator. The receiving basin below the aerator provides additional time to complete the

oxidation reaction. The basin also serves to catch precipitates that may slough off the coke at times. No air trap is required on the filter because no excess air is present.

Coke aerators have the advantage of catching some of the iron and manganese on the rough coke surfaces which act as catalysts in accelerating the oxidation reaction. However, the coke tends to clog in time, and periodic washing and replacement are required.

Other types of aerators may be employed (6). A vertical pipe spouting upward is the simplest aerator, but the water is insufficiently broken up. To increase the dispersion as well as contact time between air and water, tables or trays may be added below the riser. In general, the action of any aerator consists in exposing the water to the air in thin films, jets, or drops so that each particle of water contacts air low in carbon dioxide content. Sometimes steps are used or a riffle board—i. e., an inclined surface with obstructions to flow. Tricklers similar to coke aerators may be employed, using brick or stone instead of coke, or using merely wooden boards arranged in staggered tiers. When wells are pumped by air lift, the air bubbles frequently suffice to provide efficient aeration. A popular form of aerator for larger plants consists of spray nozzles similar to spray pond cooling systems.

Instead of sprinkling the water through the air, air may be blown through the water. Frequently the engineering conditions prevent lifting the water high enough to drop through an aerator, whereas it is possible to install an air grid in a basin below ground level and blow air up through the water. The cost of blowing low-pressure air must be compared with the cost of pumping the water against the additional head consumed by the trickling type of aerator.

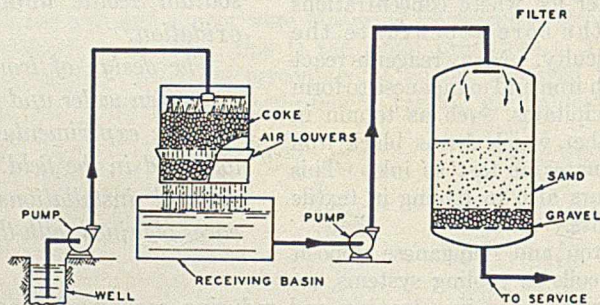


FIGURE 2. COKE AERATOR AND FILTER

Figure 3 shows the theoretical amount of air that must be blown through water to decrease the amount of carbon dioxide to any desired amount. These curves were drawn for a temperature of 59° F. For other temperatures corrections must be applied as shown in Table I.

To use Figure 3, start at the base with the original amount of carbon dioxide in the water and pass vertically up to the curve showing the final carbon dioxide desired. Then pass horizontally to the amount of air at the left. Multiply the theoretical amount of air thus obtained by a factor for temperature (Table I) and a factor for aerator efficiency.

TABLE I. CORRECTION FACTORS<sup>a</sup>

TEMP. ° F.	CORRECTION FACTOR	TEMP. ° F.	CORRECTION FACTOR
32	1.70	95	0.56
41	1.40	104	0.49
50	1.18	113	0.44
59	1.00	122	0.39
68	0.86	140	0.29
77	0.74	212	0
86	0.63		

<sup>a</sup> The theoretical volume of air determined from Figure 3 for 59° F. must be multiplied by these factors for other temperatures.

If the water supply is high in carbon dioxide and in iron and manganese, it is frequently advisable to install a contact



filter between the aerator and final filter. With very high iron and manganese present, a settling basin may even be desirable instead of the contact filter.

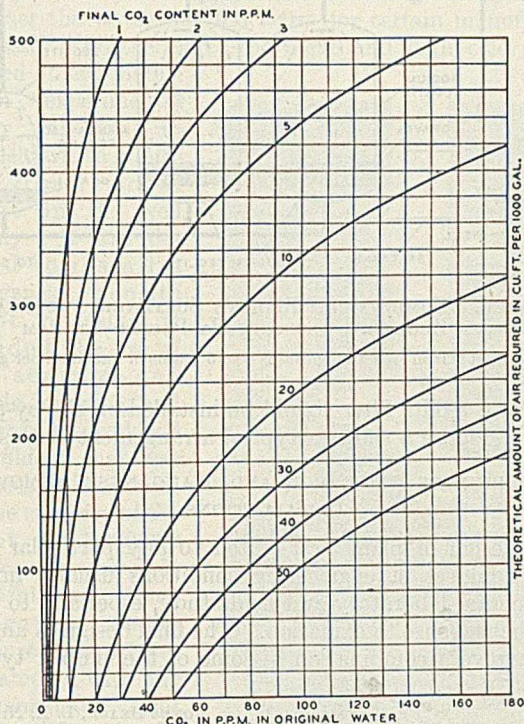


FIGURE 3. THEORETICAL AMOUNT OF AIR REQUIRED TO REMOVE CARBON DIOXIDE FROM WATER AT 59° F.

WATER OF LOW pH VALUE THAT DOES NOT READILY RESPOND TO OXIDATION EVEN AFTER THOROUGH AERATION. Figure 4 shows the type of plant required. Lime is usually employed to raise the pH value for larger plants, soda ash for smaller plants. Lime, however, usually gives better results because of the coagulating effect of the calcium carbonate precipitate formed. But lime increases the hardness, and where this is not desired soda ash is preferred. An agitating chamber is shown for floc acceleration. The settling basin has a sludge remover. Contact filters are usually not required because of the settling basin.

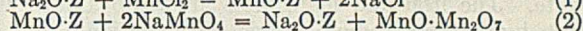
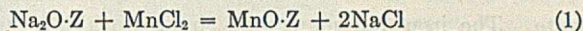
WATER CONTAINING IRON AND MANGANESE IN ORGANIC COMBINATIONS. In this case coagulants are required.

Sometimes aluminum sulfate will suffice, provided the pH value of the water is adjusted to within the optimum range. Frequently lime alone may suffice if added in sufficient excess to raise the pH value. In some cases, as at Elizabeth City, N. C., a complicated treatment (12) was found necessary, consisting of: (a) primary coagulation at pH of 8.8 to 9.8 with lime and potassium permanganate, (b) secondary coagulation at pH of 5.8 with chlorinated copperas and alum, and (c) agitation for floc acceleration, settling, and filtration, followed by alkali addition after filtration to raise the pH above 7.0.

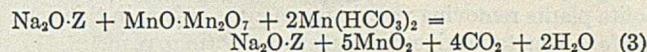
The treatment suited to any given case will depend on the type of organic compound present. Derivatives of citric, malic, tartaric, or humic acid may be present (1). These

derivatives do not respond alike to the same coagulant. In some cases activated carbon has been found very effective, in others, prechlorination. The best treatment must be determined by experiment. The treatment plant should therefore be designed so that the pH values may be altered at will at various stages in the process and also so that different coagulants may be added.

**MANGANESE ZEOLITE.** This zeolite (4) has been found very effective in the removal of iron and manganese from water, especially where complete removal is desired for industrial purposes. Manganese zeolite consists of sodium zeolite that has been treated by manganous chloride to convert it to manganous zeolite by base exchange and then oxidized by sodium or potassium permanganate. The reactions involved in this production of manganese zeolite may be written as follows (Z stands for zeolite):



The higher oxides of manganese formed in reaction 2 are really carried by the zeolite on the surface of the grains. The zeolite proper acts as an active carrier and catalytic reagent. The oxides themselves do the work of iron and manganese removal. These oxides give up oxygen to the water for the necessary oxidation reactions, thus:



After the higher oxides have given up most of their available oxygen in this manner, they are reoxidized by passing permanganate solution through the bed. The amount of permanganate required is about 0.01 pound per 1000 gallons for the average water. One or two regenerations per week are usually sufficient, although daily backwashings are desirable.

Figure 5 shows a typical manganese zeolite layout. The contact filter ahead of the manganese zeolite units is used whenever the amounts of iron and manganese are high. The manganese zeolite removes completely the residual iron and manganese left in the effluent of the contact filter.

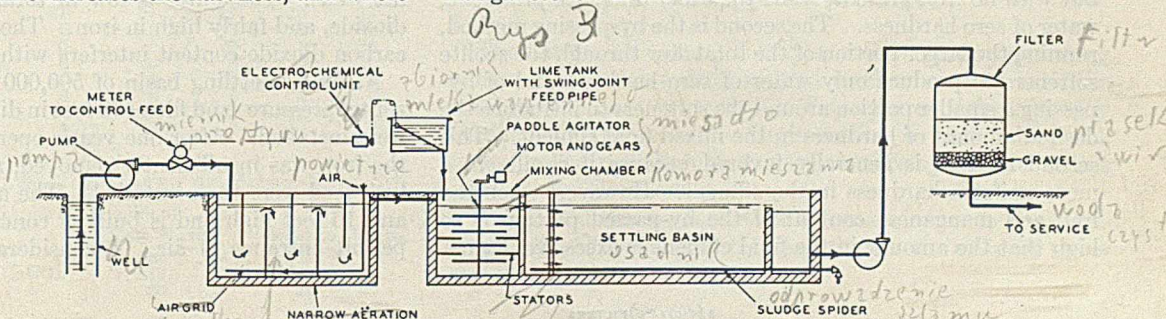


FIGURE 4. COMBINATION PLANT FOR AERATION (BY AIR GRID), LIME TREATMENT, MIXING, SETTLING, AND FILTRATION FOR IRON AND MANGANESE REMOVAL

**SODIUM ZEOLITE FOR IRON AND MANGANESE REMOVAL BY BASE EXCHANGE.** Sodium zeolite of certain types may be economically employed to remove iron and manganese by base exchange at the same time that the zeolite is softening the water (10). In fact, zeolite continues to remove iron and manganese by base exchange after the usual water-softening run is ended and the salt regeneration of the softener is required (19). This action in what is called the "twilight zone" of zeolite softener operation may be explained by the fact that calcium zeolite has the power of exchanging its calcium for iron and manganese. During softening, the sodium zeolite is converted to calcium zeolite. After the end of the softening run the calcium zeolite is converted to iron and manganese



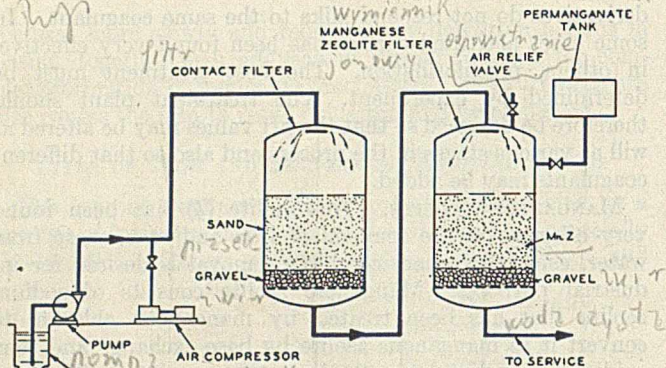


FIGURE 5. CONTACT FILTER AND MANGANESE ZEOLITE FILTER

zeolite. The iron and manganese are removable from the zeolite by the usual sodium chloride regeneration.

When zeolite is used for iron and manganese removal by base exchange, the iron should be maintained in ferrous form and the manganese in manganous form. Therefore, well waters should not be exposed to air before the zeolite treatment.

This iron and manganese removal property of sodium zeolite is frequently utilized as its main function. There are many zeolite plants removing very high amounts of iron in this way. The following table gives typical examples (in p. p. m.):

Plant	MOORESTOWN, N. J.		DES MOINES, IOWA		FT. WAYNE, IND.		JONES BEACH, L. I., N. Y.	
	Raw	Softened	Raw	Softened	Raw	Softened	Raw	Softened
Hardness as CaCO <sub>3</sub>	43	0	393	0	430	0	169	0
Iron as Fe	28	0.1	14	0.1	8	0.1	20	0.1

In the field of municipal water softening, it is often desired to soften the water by zeolite and yet to produce an effluent of not below 4 to 5 grains of hardness per gallon. To accomplish this partial softening by zeolite and yet provide an iron-free effluent, two methods are available. The first is the twilight-zone method, overrunning the zeolite softeners so that some of the units are allowing hardness to slip through but with no iron present, while the other units are producing water of zero hardness. The second is the by-passing method, running the larger portion of the total flow through the zeolite softeners to produce only water of zero hardness and of by-passing a smaller portion around the softeners to introduce the desired amount of hardness in the mixed final effluent. This second method is generally favored because it results in a more uniform hardness in the effluent. However, when the iron and manganese content of the by-passed portion is so high that the amount in the final effluent is excessive, then a

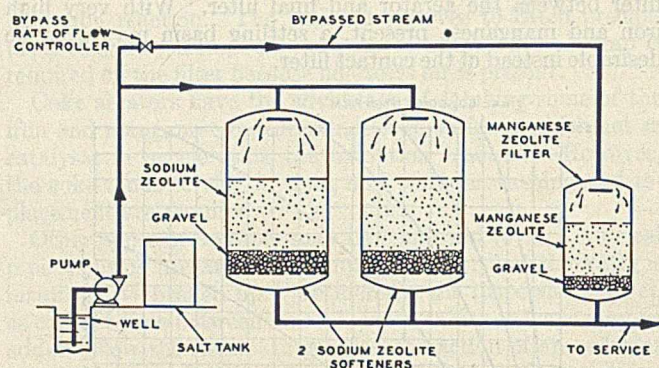


FIGURE 6. COMBINATION ZEOLITE SOFTENER AND MANGANESE ZEOLITE FILTER ON BY-PASSED STREAM

Final effluent is iron-free and contains 4 to 5 grains of hardness per gallon.

manganese zeolite filter should be installed on the by-passed stream. Figure 6 shows a typical arrangement of this kind.

### EXPERIENCES WITH IRON AND MANGANESE REMOVAL INSTALLATIONS

The design of plant best suited to any particular water supply and set of engineering conditions usually involves experimental laboratory and field study, especially to determine the response to oxidation. The final design in any case may involve a combination of some of the simpler types of

plants previously mentioned. It is therefore of interest in conclusion to describe four existing installations, especially to show how the design selected fitted the water and engineering requirements and also to give operating experiences, some of which are of a novel character.

**STEEL PLANT IN THE EAST.** The steel company furnishes 2,000,000 gallons per day of water to a near-by town from air-lift wells. The water is low in total solids, high in carbon dioxide, and fairly high in iron. The low pH value and high carbon dioxide content interfere with the oxidation reaction.

At first a settling basin of 500,000 gallons and three horizontal pressure sand filters (8 feet in diameter and 22 feet long) were installed. After one year's operation it was found that the iron was insufficiently removed, and a coke aerator and lime feed were then installed. The aerator is 21 feet square and 16 feet high and is built of concrete with air louvers to permit entrance of air. A considerable excess of lime was required to accomplish satisfactory iron removal.

Table II shows the results obtained by using increasing amounts of lime.

**MANGANESE ZEOLITE PLANT IN A WESTERN PAPER MILL.** The water supply consists of wells about 200 feet deep. Formerly, air lift was used and the water was re-pumped to a gravity sand-filter plant. This air-lift system

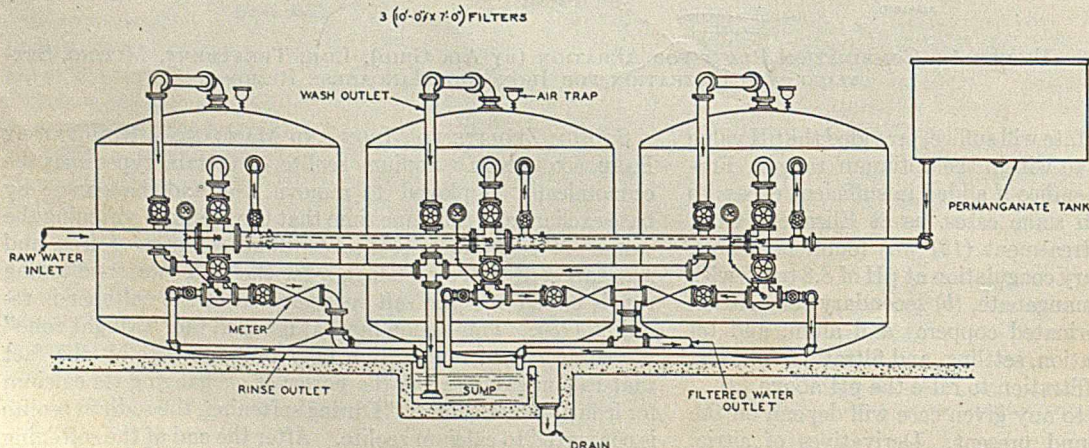


FIGURE 7. MANGANESE PERMANGANATE IRON AND MANGANESE REMOVAL PLANT



proved excessively costly to operate, and it was replaced by motor-driven turbine pumps. It was then found that the filters failed to remove the iron, and the mill turned to a pond water supply. This pond supply was satisfactory in winter, but in summer the water was too warm for certain manufacturing processes. Furthermore, the algae and high color present proved objectionable.

An experimental study was made in the field with a miniature iron-removal plant on the well supply. It was decided to install a manganese zeolite plant because it avoided the use of coke aerators and double pumping, and because it produced an effluent that was practically iron-free.

The capacity of the plant is 1,000,000 gallons per day. It consists of three manganese zeolite pressure units, 10 feet in diameter, with one permanganate tank for regeneration 7 feet in diameter. Figure 7 shows the elevation of the plant.

The analyses of the raw and treated waters are given in Table III.

TABLE II. EFFECT OF EXCESS LIME

	(In parts per million)		FILTERED WATER WITH INCREASING AMOUNTS OF LIME		
	RAW WATER	AERATED WATER	26	30	38
Hardness as CaCO <sub>3</sub>	21	21	26	30	38
Methyl orange alkal. as CaCO <sub>3</sub>	9	9	16	20	30
Phenol alkal. as CaCO <sub>3</sub>	0	0	0	5	20
Causticity as CaCO <sub>3</sub>	0	0	0	0	10
Free CO <sub>2</sub>	30	6	3	0	0
Chlorides as Cl	8	8	8	8	8
Sulfates as SO <sub>3</sub>	12	12	12	12	12
Iron as Fe	6-12	4-5	2-3	1-2	0.1

TABLE III. ANALYSES OF WATER OF PAPER MILL

	(In parts per million)	
	RAW WATER	TREATED WATER
Total hardness as CaCO <sub>3</sub>	212	203
Methyl orange alkalinity as CaCO <sub>3</sub>	223	220
Free CO <sub>2</sub>	30	29
Chlorides as Cl	9	9
Sulfates as SO <sub>3</sub>	8	8
Iron as Fe	1-3	0-0.05
Color	50	5-10

As a result of installing this manganese zeolite plant, savings in formaldehyde and chlorine resulted, and a paper of improved quality was obtained.

**COMBINED IRON REMOVAL AND SOFTENING BY BASE EXCHANGE THROUGH SODIUM ZEOLITE.** In the town of Bamberg, S. C., a deep iron-bearing well is pumped by a multi-stage pump at the rate of 250 gallons per minute. An existing concrete settling basin and gravity sand filter had failed to remove the iron satisfactorily. The basin had cracked and needed a roof to prevent algae growths, and the filter needed renovation.

A study was made of the first cost and operating cost of installing a zeolite softener as compared with that of a coke aerator and caustic soda feed ahead of their existing basin,

plus the repairs required on the basin and filters. The first costs of the two systems were about equal. The operating cost of the zeolite softener was greater by several hundred dollars a year, but as compensation the effluent would be free from iron and also from hardness. The zeolite softener was installed.

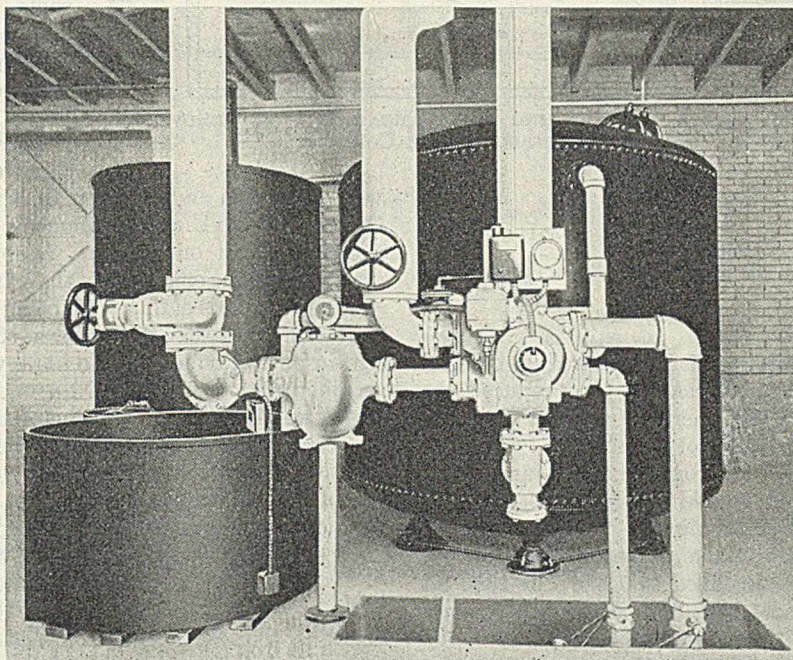


FIGURE 8. AUTOMATIC SOFTENER SIMILAR TO THE BAMBERG UNIT

The softener equipment is 8 feet in diameter and is fully automatic (3, 5); i. e., it regenerates itself automatically. This not only saves labor of attendance but also insures mechanical control of the softener so that it is always regenerated on time. Salt is saved by avoiding regeneration before the end of a run and by mechanical, accurate salt measurement.

The cycle of operations of a zeolite softener consists of softening, backwashing, salting, and rinsing. In manually operated zeolite softeners, a nest of seven individual valves

is needed to control the operation. In place of this nest of valves, the automatic unit employs a multiport single valve, having a rotary flat disk with ports so arranged that by turning the disk to four successive positions, the four operations of a complete cycle are carried out. The control mechanism is so arranged that the duration of each operation of a complete softening cycle can be separately adjusted and controlled.

The flat rotary valve (14) employs a new principle of using a hard-rubber valve disk, rotated in close contact with the stationary bronze port plate. This insures tightness, easy turning, and ruggedness. Regeneration is initiated by the meter and carried through its various steps by rotation of this valve by the electric motor.

Figure 8 shows an automatic softener similar to the Bamberg unit. The analyses before and after the softener treatment are given in Table IV.

TABLE IV. EFFECT OF SOFTENER TREATMENT

	(In parts per million)	
	RAW WATER	EFFLUENT OF SOFTENER
Hardness as CaCO <sub>3</sub>	123	0
Methyl orange alkalinity as CaCO <sub>3</sub>	110	115
Free CO <sub>2</sub>	10	8
Chlorides as Cl	18	18
Sulfates as SO <sub>3</sub>	15	15
Iron as Fe	1-3	0.1

**IRON REMOVAL PLANT AT BUFFALO ELECTROCHEMICAL COMPANY.** This company manufactures hydrogen peroxide. Condensers constitute an important step in the process, and consequently large amounts of cold water are essential. A well supply was developed of 600 gallons per minute capacity, the wells being 200 feet deep; some were close to a river and others were some distance away. A typical analysis of this well water is as follows:



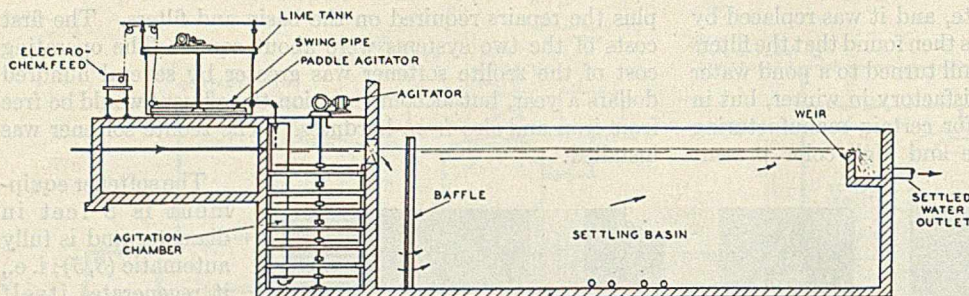


FIGURE 9. LIME FEED, AGITATOR, AND SETTLING BASIN AHEAD OF IRON REMOVAL FILTERS OF THE BUFFALO ELECTROCHEMICAL COMPANY

Hardness as CaCO <sub>3</sub>	P. p. m.
Methyl orange alkalinity as CaCO <sub>3</sub>	1514
Free CO <sub>2</sub>	240
Cl	25
SO <sub>4</sub>	85
Fe	900
	2.5

It was soon found that the iron present deposited on the lead spiral cooling coils, affected the vacuum, and reduced the capacity of the factory. It was therefore decided to install an iron removal plant. By laboratory test it was found that the iron might be oxidized by hydrogen peroxide, and therefore arrangements were made to add this hydrogen peroxide at the entrance of a basin of 30 minutes' detention period. Three horizontal pressure sand filters, 8 feet in diameter and 14 feet 3 inches long, were installed in 1929. In 1930 an additional unit was installed. This filter plant satisfactorily removed the iron and kept the cooling coils clean.

Towards the end of 1930 the wells that were nearer the river began to show increasing amounts of iron. Some of the wells increased in iron content up to 40 p. p. m. This increasing load of iron soon caused excessive amounts of iron hydroxide to accumulate in the sand beds so that the filters had to be backwashed much more frequently than originally when the iron content was 2 to 3 p. p. m. This frequent backwashing wasted valuable cold water of which there was a limited supply.

A field experimental study was then made of the conditions for the most favorable settling out of iron. The 30-minute basin in use settled out about 20 per cent of the iron. Experiments showed that, by increasing the amount of peroxide employed to react with all of the iron and allowing the water, after dosage, to settle for about 2 hours, 70 per cent of the iron settled out. Also when sufficient lime was added to raise the pH value to about 8, 80 per cent settled out in 2 hours.

In 1932 a 120,000-gallon settling basin was constructed, providing a detention period of over 3 hours. The basin has a concrete cover over which sod was placed so that the water is kept cool inside. In this basin a tile sludge spider was installed, with openings at regular intervals for the removal of sludge. A mixing chamber was provided with a paddle agitator to accelerate the formation of the precipitates. The lime feed installed consists of a tank, 9 feet in diameter, with motor-driven agitator to maintain uniform suspension of lime hydrate. A swing joint pipe in this tank is lowered at a steady rate by a small motor and gears, thus feeding lime suspension out at a steady rate. The water is pumped into the basin at a constant rate so that the correct dosage of chemical is always obtained. When the basin is full, a float switch stops the well pumps and at the same time stops the chemical feed. Figure 9 shows in elevation the design of this lime feed and basin.

Operation of the lime feed and settling basin was started in June, 1932. It was soon found that the filters could be backwashed once every 24 hours instead of every 12 hours as had been the case previously. Also the loss of head through

the filters had formerly risen to 10 to 12 pounds, whereas now the filters were washed when the loss of head was only 6 pounds. At the start about 400 pounds of lime hydrate were fed daily, together with some peroxide or chlorine. The pH was maintained at slightly over 7, and the iron was satisfactorily removed by the filters.

In February, 1933, the water table in the wells dropped to a very low point and the iron content increased still farther. One of the wells showed as much as 76 p. p. m. of iron. This additional load on the iron removal plant called for the greatest possible efficiency in the settling basin. At that time about 450 pounds of lime were being used daily plus 36 pounds of chlorine, and the settling basin efficiency was about 54 per cent in its iron removal. To improve this efficiency, the lime was increased to 900 to 1000 pounds and the pH was maintained well over 8. It was then found that the chlorine was unnecessary and yet the basin efficiency was 85 to 90 per cent.

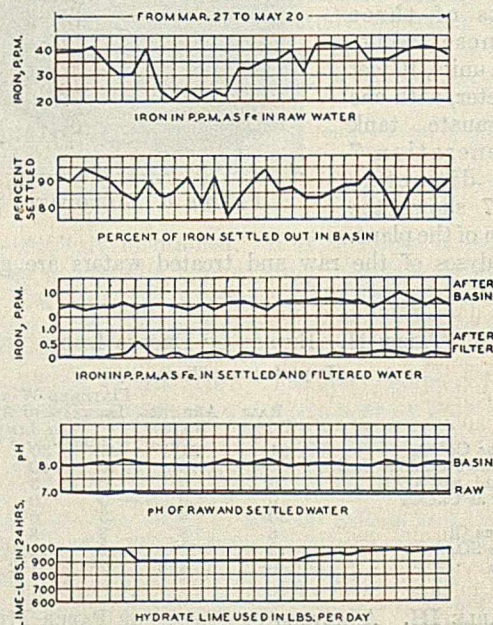


FIGURE 10. CHEMICAL RESULTS OBTAINED IN 1933 IN IRON REMOVAL PLANT OF BUFFALO ELECTROCHEMICAL COMPANY

Apparently the flow through the basin resulted in the pick-up of sufficient oxygen for the oxidation reaction. Figure 10 shows the typical chemical results that were obtained in 1933 as a result of these adjustments. Preaeration, however, would be helpful in removing free carbon dioxide and thereby saving lime. Plans are being considered to blow air through the raw water to accomplish this result.

#### ACKNOWLEDGMENT

Figure 3 was drawn and Table I calculated by Eric Pick of The Permutit Company.

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## Selection and Use of Age Resistors in Rubber Compounds

RICHARD A. CRAWFORD, The B. F. Goodrich Company, Akron, Ohio

THE early development of the rubber industry was handicapped by two serious defects in rubber articles. They were not stable to temperature changes, and they deteriorated rapidly with age. Although the process of vulcanization corrected the first difficulty, rapid deterioration with age was common until the discovery of certain organic accelerators, such as *p*-aminodimethylaniline, the aldehyde-amines, and mercaptobenzothiazole. Prior to these discoveries a number of materials had been patented for the purpose of improving the age-resisting properties of rubber, but many of them were of little merit and most of the others possessed some accelerating value, a fact which was not appreciated at the time. Typical of the more useful early patents for age-resisting materials are American patents by Murphy in 1870 (15), Moore in 1901 (14), and Martin in 1922 (12), and the German and English patents of the Ostwalds in 1908 and 1910 (19, 20). Murphy patented phenol, cresol, and cresylic acid, either added to the uncured stock or as dipping solutions for vulcanized articles for the purpose of improving their resistance to aging. Moore used reducing agents, including hydroquinone, pyrogallol, and *p*-aminophenol hydrochloride, to preserve the adhesive properties of rubber cements. Martin suggested aniline and other organic bases as a surface treatment for vulcanized articles. The Ostwalds also recognized the beneficial effects of aniline on rubber and stated that it could be added at any convenient stage of manufacture. (It is interesting to note that these inventors considered that addition of aniline to uncured stock or dipping the cured article in aniline were equivalent, and they, therefore, evidently did not recognize the accelerating effect of aniline.)

The beneficial effect of certain organic accelerators on aging has also been recognized and has been the basis of a number of patents. For example, *p*-aminodimethylaniline was used commercially as early as 1912, although never patented.

*Although the discovery and use of certain organic accelerators resulted in the manufacture of rubber articles with good aging properties, control of aging by choice of accelerator was not a satisfactory solution to the aging problem, because independent control of curing and aging properties was not possible. Such a control, however, was provided by the invention of non-accelerating age resistors. Although tensile strength is the property most used to measure aging effects, in recent years other factors have become recognized as important in influencing the choice of an age resistor. Among these are the effects of age resistors on processing, bloom, and various physical properties of unaged and aged vulcanized rubber. These effects are presented in detail. Superaging compounds are discussed, and advantages resulting from the use of age resistors in such compounds are shown. A guide is given for the choice of age resistors for specific purposes, and reasons are shown for their use in a large number of commercial rubber articles.*

Later a large number of compounds were patented as accelerators which gave to rubber age-resisting properties. Among these appeared patents for nitro compounds and aromatic amines in 1917-19 (2, 13, 18); for reducing agents such as hydroquinone for diminishing tackiness of light colored, dry-heat-cured articles in 1921 (10); for aldehyde-amines in 1922 (5); and a series of patents covering mercaptobenzothiazole and its derivatives.

Until ten years ago the recognized method of producing good-aging rubber lay in the choice of the proper accelerator. Since not all accelerators produce this effect, the choice was decidedly limited. Some accelerators which imparted good aging conferred on rubber other properties, such as undesirable rate of cure, toxicity, etc., which had to be accepted along with superior aging properties. This method was not

an ideal solution of the aging problem, and it was left to later investigators to find means of controlling aging and curing properties independently.

In 1924 Winkelmann and Gray (23) secured a patent on nonaccelerating aldehyde-amine condensation products as age resistors. This was followed in 1927 by a patent to Cadwell (6) covering the aldehyde-amine condensation products made in the presence of acids. With the introduction of these materials, independent control of age-resisting and curing properties became possible. For the first time accelerators could be chosen to produce the desired rate of cure and physical properties without regard to their possible effect on the aging of rubber articles. This resulted almost immediately in great improvement in the quality of rubber goods because the deficiencies of accelerator-sulfur combinations which produced high quality but were known to produce poor aging could now be corrected by the addition of age resistors. During the past ten years a great many materials which will retard the deterioration of vulcanized rubber on aging have been placed on the market; the principal ones are included in the classes of: (a) phenols, (b) aminophenols, (c) mono-



and diprimary aromatic amines, (d) mono- and dissecondary aromatic amines, (e) aldehyde reaction products of aromatic amines, and (f) ketone reaction products of aromatic amines. It should not be assumed, however, that all chemical compounds in these classes are age resistors.

The beneficial effects of age resistors can be demonstrated by aging under normal storage or service conditions. However, the rapid development of the rubber industry in general

pounds which would be missed entirely if consideration were given only to a few quantitative experiments in a narrow field. In order that rubber compounders may have for their selection and use of age resistors the benefit of this broader experience, conclusions based on numerous qualitative comparisons are included with others for which detailed data are presented.

#### EFFECT ON PROCESSING PROPERTIES

The addition of any material to a rubber compound may affect its properties in both the cured and uncured states. One of the most important factors in influencing the ready acceptance of a rubber compounding ingredient is the manner in which it affects processing properties. Tack, plasticity, scorching tendency, and bloom are factors which must be given consideration if useful articles are to be made from a rubber compound. Of these, plasticity and scorching tendency are perhaps the most important from the processing standpoint. It is proposed, therefore, to discuss in some detail the effect on these properties of several representative age resistors.

**PLASTICITY.** The desired plasticity characteristics of rubber compounds are usually secured by addition of the proper kind and amount of one or more softening agents. A number of claims have been made for the valuable softening action of various age resistors. While it is true that they are in some cases softeners for rubber, it is equally true that some are rubber stiffeners. Age resistors, in general, are not

outstanding in softening value, and in the concentrations generally recommended for rubber compounds (about one per cent) the resultant change in plasticity is frequently negligible. Certainly, equal softness can be obtained at lower cost by using any one of a number of common rubber softeners. Table I shows the net change in plasticity of smoked sheet rubber produced by the addition of various percentages of several commercial softeners and age resistors.

TABLE I. INCREASE IN PLASTICITY<sup>a</sup> OF SMOKED SHEET RUBBER PRODUCED BY ADDITION OF VARIOUS MATERIALS

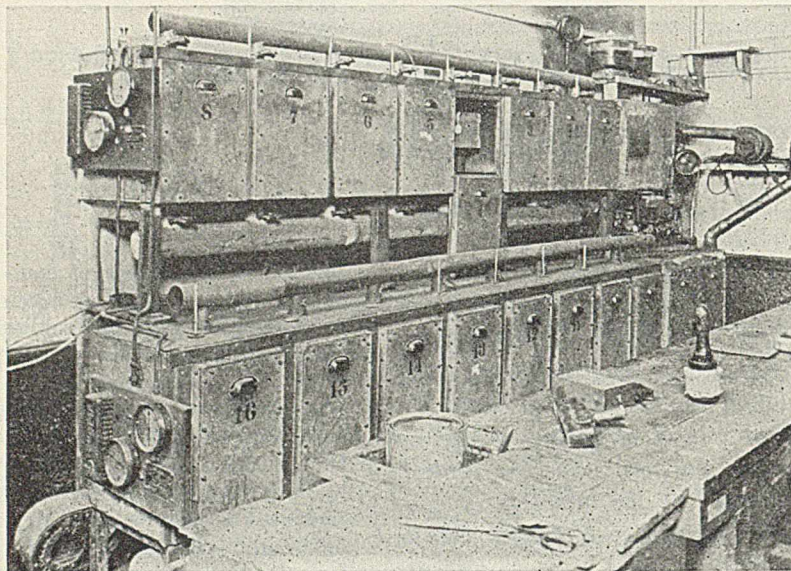
MATERIAL ADDED	PLASTICITY CHANGES PRODUCED BY:		
	1%	2%	3%
Aldol- $\alpha$ -naphthylamine	0.2	2.3	4.6
Mixed ditolylamines	-0.5 <sup>b</sup>	0.5	1.4
Phenyl- $\beta$ -naphthylamine	-0.7	0.0	1.1
Di- $\beta$ -naphthyl- <i>p</i> -phenylenediamine	2.4	1.8	1.2
Synthetic product A <sup>c</sup>	4.6	6.2	10.0
Crude corn oil	6.6	9.5	12.3
Pine tar oil	7.5	10.6	13.7
Crude lauric acid	2.8	13.0	14.2
Natural rosin oil	1.9	6.3	10.7
Liquid jet rosin	3.7	7.7	11.2
Rosin (K gum)	5.7	12.0	18.1
Zinc stearate	0.5	12.2	24.2
Zinc laurate	10.6	15.3	26.5
Oleic acid	15.5	19.7	19.5

<sup>a</sup> Plasticity measurements were all made on the Goodrich plastometer at 100° C.; highest figures denote greatest increase in plasticity.

<sup>b</sup> Minus sign preceding a figure indicates stiffening; the average plasticity for smoked sheet rubber without softener is about 10 units.

<sup>c</sup> A mixture of diarylamino compounds, largely diphenylamine.

The net plasticizing effect of a softener in a rubber compound depends not only upon its softening action on the rubber but also upon its effect upon the subsequent rate of breakdown during further processing. Table II shows that if one per cent of age resistor is added to smoked sheet on a roll mill, the increase in plasticity of the rubber at the end of the mixing is less than when rubber is masticated an equal length of time without the addition of age resistor. Such a result might be expected, since recent data published by Cotton (7) and by Busse (3) indicate that breakdown of rubber on a mill



BATTERY OF GEER AGING OVENS

and of age resistors in particular has made imperative more rapid testing than is possible by natural aging alone. For this reason accelerated aging tests have been employed to an increasing extent for the comparison of resistance to aging of rubber compounds. Of these tests the Geer and Evans oven (8, 9) and the Bierer and Davis oxygen bomb (1) are the most widely used.

In the attempt to obtain quantitative information, measurements have been made of specific physical properties of rubber stocks before and after aging. Change of tensile strength was the first criterion to be utilized and is still used more extensively than any other in measuring the effects of aging. That an age resistor actually does improve resistance to aging, as judged by tensile tests, under both natural and artificial aging conditions is well known (4).

In recent years it has become recognized that the effect in improving the tensile strength of aged cured rubber is only one of the factors to be considered in selecting an age resistor. Some other factors governing the choice are: (a) its effect on processing properties, (b) its tendency to bloom, (c) its effect on properties other than tensile strength of unaged cured rubber, and (d) its effect on properties other than tensile strength of aged cured rubber.

It is the purpose of this paper to present information concerning the proper choice and use of age resistors by the rubber compounder. Data are presented to illustrate effects to be gained by the use of age resistors rather than to serve as a critical comparison of specific materials. The age resistors mentioned in the tables should be considered as representative of the chemical types to which they belong. However, members of any given class vary among themselves in activity, and it should not be assumed that they are all of equal value for any given purpose.

In studying the behavior of age resistors, reliable and valuable generalizations can frequently be drawn from a large number of qualitative observations of a wide variety of com-



is due to the effect of oxygen, and age resistors protect rubber from attack by oxygen. Obviously, this effect of age resistors on the rate of breakdown of rubber tends to neutralize their softening action, so that the net effect of small amounts of most of them is slight. The effect on aging properties, rather than on processing, should be considered in choosing these materials. An ideal age resistor, from the compounder's standpoint, would be one which has no effect on processing properties because no other changes in compound would be necessitated by its use.

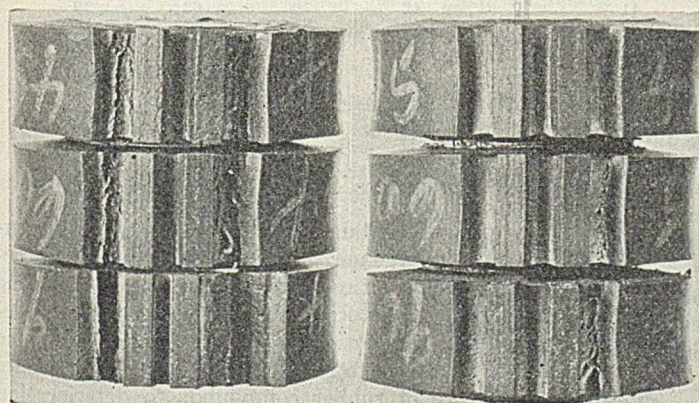
TABLE II. EFFECT OF AGE RESISTORS ON RATE OF BREAKDOWN OF SMOKED SHEET RUBBER

(2 kg. rubber milled 3 minutes on a 30.48 × 60.96 cm. mill, 1 per cent age resistor added, milling continued another 15 minutes; samples taken after 3 and 8 minutes; difference between these figures represents effect of 5-minute milling with or without age resistor.)

AGE RESISTOR	RELATIVE PLASTICITIES <sup>a</sup> AT 100° C.		
	3 min.	8 min.	Difference
None	16.9	51.8	34.9
Aldol- $\alpha$ -naphthylamine	10.4	41.0	30.6
Phenyl- $\beta$ -naphthylamine	13.6	42.0	28.4
Acetaldehyde-aniline reaction product	10.0	23.9	13.9
Phenyl- $\alpha$ -naphthylamine	11.1	40.7	29.6
Phenyl- $\alpha$ -naphthylamine + <i>m</i> -toluylene-diamine and stearic acid	9.7	25.5	15.8

<sup>a</sup> All plasticities measured on Goodrich plastometer; highest figures represent greatest plasticity.

ACTIVATION OF ACCELERATORS. Of the other factors governing the acceptability of rubber compounding ingredients, their effect on scorching and on bloom are, perhaps, next in importance to their effect on plasticity. Since scorching is, in fact, vulcanization, anything which tends to increase the rate of cure of a compound generally increases its scorching tendency at processing temperatures. Acid accelerators are activated by bases, and, since most age resistors are basic, they activate acid accelerators, as is to be expected. The degree of activation depends upon the kind and amounts of accelerator and age resistor used. Primary aromatic amines, and more particularly primary aromatic diamines, such as 2,4-diaminodiphenylamine and *p,p'*-diaminodiphenylmethane, are powerful activators for such accelerators as mercaptobenzothiazole, whereas diaryl amines, in general, are less active.



EFFECT OF CURE ON FLEX CRACKING OF PULLMAN TREADS, WITH AND WITHOUT AGE RESISTOR

Left: without age resistor; right: containing 0.75 per cent phenyl- $\beta$ -naphthylamine. Both samples were cured, aged, and flexed on a Scott machine under the same conditions. The optimum cure was 45 minutes.

With the exception of the primary aromatic diamines, most age resistors do not have much accelerating value in their own right. Moreover, since they are usually bases, their effect on acceleration with basic accelerators is probably merely additive, and they are therefore not likely either to give increased trouble with scorching or upset the rate of cure of the compound.

In Table III are presented data which show the activating

effect of representative age resistors on typical acid accelerators and a typical basic accelerator. Age resistors are not to be recommended for use primarily as activators for accelerators, however, because cheaper and more efficient materials are available for that purpose. An ideal age resistor for general use would have no activating effect, and, the more nearly this ideal is approached, other things being equal, the more readily is the age resistor applied by the compounder.

The base recipe for the compound used in Table III is:

Smoked sheet	100
Zinc oxide	10
Sulfur	3
Age resistor	0.75
	<hr/> 113.75

to which were added accelerators and stearic acid as follows:

ACCELERATOR ADDED	AMOUNT ON RUBBER	AMOUNT OF ACID ON RUBBER
	%	%
Tetramethylthiuram disulfide (Tuads)	0.2	1
Zinc salt of dimethyldithiocarbamic acid (Zimate)	0.2	1
Mercaptobenzothiazole (Captax)	0.5	2
Heptaldehyde-aniline (Heptene base)	0.3	1

BLOOM. Certain age resistors contribute to the blooming of vulcanized rubber compounds. This effect is dependent upon both the specific age resistor and the particular compound in which it is used. The amount of age resistor required to bloom from vulcanized rubber is the resultant of a number of factors, some of which are as follows:

FACTOR	FAVORING BLOOMING	FAVORING NONBLOOMING
Melting point	Medium (30–150° C.)	Low (less than 30° C.) or high (above 200° C.)
Crystallizing tendency	Ability to crystallize in presence of impurities	Low; prevented or retarded by impurities; resinous or sirupy
Solubility in rubber	Medium	High or very low
Solubility in oils	Medium	High or very low

The properties of typical age-resisting materials are listed in Table IV for substances representing a wide variation of physical properties and chemical constitution. The properties listed above are given in Table IV for each age resistor with the notation B or NB in each case, denoting that the particular property is favorable to blooming or to nonblooming, respectively.

CURE  
45 min.  
60 min.  
90 min.

Compounding ingredients other than age resistors may have an important effect on age resistor bloom, if the concentration of the age resistor is near the point above which bloom is to be expected. Other materials—sulfur, some accelerators, fatty acids, soaps, waxes—may increase the tendency of an age resistor to bloom, possibly because of the mutual effect of each material bringing the others to the surface. A smooth film of bloomed material containing age resistor is sometimes desirable, since concentration of age resistor on the surface retards oxidation and the action of light at the point of attack. Oils have a variable effect; usually they decrease tendency to bloom, but, whenever the oil tends to solubilize the age resistor, an increase in blooming may occur. The fact that age resistors bloom when used in high percentages is no more valid argument against their use than the fact that 6 per cent of sulfur on the rubber, for example, will cause bloom is a valid argument against the use of sulfur in nonblooming stocks. In either case knowledge of the material is necessary for its satisfactory application.

Blooming is an elusive effect and must be carefully investigated with reference to specific compounds. Often blooming does not occur until the surface of the stock has been me-



TABLE III. EFFECT OF VARIOUS AGE RESISTORS ON CURING PROPERTIES OF REPRESENTATIVE ACCELERATORS

ACCELERATOR	TEMP. OF CURE ° C.	CURE Min.	No AGE RESISTOR	ALDOL- α- NAPHTHYL- AMINE	PHENYL- β- NAPHTHYL- AMINE	Di-β- NAPHTHYL- p-PHENYLENE- DIAMINE	MIXED DITOLYL- AMINES	2,4-DI- AMINO-DI- PHENYL- AMINE	p,p'-DI- AMINO- DIPHENYL- METHANE	PHENYL- α- NAPHTHYL- AMINE
EFFECT ON TENSILE STRENGTH (KG. PER SQ. CM.)										
Tuads	127	10	7	35	7	7	7	309	232	18
		20	295	320	295	281	281	281	346	301
		30	313	302	302	309	295	285	336	309
		45	295	281	285	301	288	288	295	285
		60	279	295	278	294	285	295	302	288
Zimate	115	10	160	200	188	190	183	232	189	162
		20	253	295	239	288	232	236	225	246
		30	278	292	281	304	211	303	246	275
		45	287	309	315	309	253	309	281	295
		60	315	309	327	296	292	336	267	313
Captax	138	10	158	141	113	153	169	225	232	183
		20	229	218	230	211	232	281	274	232
		30	243	243	225	218	253	282	278	239
		45	241	241	232	246	225	272	260	253
		60	218	229	243	253	253	266	260	253
Heptene base	138	10	98	98	120	102	125	155	172	105
		20	169	171	188	204	185	211	248	182
		30	239	239	229	240	243	268	253	226
		45	268	279	265	268	260	264	309	258
		60	267	267	264	274	255	278	281	253
EFFECT ON ULTIMATE ELONGATION (PER CENT)										
Tuads	127	10	900	788	830	960	853	770	795	840
		20	780	730	753	763	767	683	740	787
		30	730	693	730	730	693	630	707	720
		45	715	690	700	720	697	647	678	703
		60	715	713	712	737	710	653	705	727
Zimate	115	10	895	847	940	855	955	830	770	930
		20	850	823	855	805	835	750	760	840
		30	830	790	840	785	815	775	785	840
		45	813	770	815	760	835	735	775	785
		60	815	755	800	725	780	720	740	785
Captax	138	10	905	870	905	870	853	775	823	873
		20	803	805	840	800	800	710	753	800
		30	785	797	770	780	770	703	740	803
		45	770	757	773	760	733	683	723	787
		60	757	723	780	763	743	663	723	770
Heptene base	138	10	920	930	925	895	945	870	885	975
		20	815	850	810	840	815	790	785	853
		30	790	800	790	785	795	790	765	783
		45	760	790	765	750	770	720	770	787
		60	740	750	750	730	730	715	730	747
EFFECT ON STRESS AT 500 PER CENT ELONGATION (KG. PER SQ. CM.)										
Tuads	127	10	..	26	..	..	..	56	42	11
		20	55	71	60	56	53	97	77	53
		30	73	84	72	72	84	120	91	77
		45	77	77	70	70	77	116	93	77
		60	63	69	63	61	70	113	91	65
Zimate	115	10	21	21	20	23	14	29	35	18
		20	28	37	29	42	28	48	54	28
		30	35	43	35	46	32	56	46	33
		45	39	56	46	63	33	69	55	41
		60	42	56	49	67	39	84	63	49
Captax	138	10	19	19	18	19	21	35	20	19
		20	35	29	32	33	35	63	56	39
		30	42	35	41	37	42	70	63	39
		45	49	42	42	42	43	84	63	43
		60	50	49	42	44	52	90	63	43
Heptene base	138	10	15	15	15	18	14	21	21	14
		20	28	26	28	32	27	40	43	27
		30	38	38	35	42	34	49	49	35
		45	49	50	46	56	49	64	60	42
		60	56	57	49	70	53	77	70	49

chanically abraded or until the compound has been exposed to indirect light—as through a glass window—or stored in a warm place. Instances are known where no bloom occurred during the first six months of storage but became quite noticeable at the end of a year. The only way to be sure that objectionable bloom is not encountered is to compound the stock intelligently, store various cures under different conditions, and make periodic examinations for bloom.

If objectionable age-resistor bloom is encountered, there are several methods to combat it:

1. Use less age resistor or a different age resistor. Sometimes a mixture of age resistors can be used to advantage to eliminate bloom, at the same time maintaining or even improving the age-resisting properties of the compound.
2. Change the acidity of the compound. Some age resistors bloom at a lower concentration in a basic stock than in an acid stock.
3. Use another accelerator.
4. Eliminate bloom due to other constituents. Other constituents, even when blooming in only slight amount themselves, will sometimes induce bloom of the age resistor.
5. Change the type or concentration of oils. The type and amount of oils used sometimes change the limiting concentration of an age resistor, possibly because of their solvent action upon it.

#### EFFECT ON PROPERTIES OF UNAGED CURED RUBBER

While the ready acceptance of rubber compounding ingredients depends in large measure upon their effects on processing and curing properties, nevertheless the outstanding reason for using age resistors is that they impart some desirable property or properties to vulcanized rubber. The primary object of using age resistors, of course, is to secure improved resistance of rubber compounds to deterioration on aging. However, research during the past few years has shown that chemicals can be made which will impart other desirable properties. That is, if the proper age resistor is used, properties important in the service life of the rubber are improved even in unaged rubber. These properties are tensile strength (in some cases), quality of overcures, resistance to flex cracking, and resistance to abrasion. As might be expected, the improvement becomes more marked as the age of the cured rubber increases.

**TENSILE STRENGTH AND MODULUS.** Improved tensile strength and increased modulus are probably due to the accelerating power of the age resistors, or to their activating effect on accelerators, as shown in Table III. Although



TABLE IV. PROPERTIES OF COMMERCIAL AGE RESISTORS AFFECTING BLOOM<sup>a</sup>

AGE RESISTORS	MELTING POINT ° C.	CRYSTALLIZING TENDENCY	SOLUBILITY IN RUBBER	SOLUBILITY IN OILS	MAX. PERCENTAGE NONBLOOMING IN PURE GUM STOCK	EFFECT OF OILS IN COMPD. ON BLOOMING TENDENCY
Aldol- $\alpha$ -naphthylamine	Not definite; NB	None, resinous; NB	High; NB	High; NB	Above 5	Increase
Phenyl- $\alpha$ -naphthylamine	62; B	Low; NB	Medium; B	High; NB	3	Decrease
Phenyl- $\beta$ -naphthylamine	108; B	High; B	Medium; B	Medium; B	1	Decrease
Ditolylamine	Low; NB	None, liquid; NB	High; NB	High; NB	Above 5	None
Di- $\beta$ -naphthyl- <i>p</i> -phenylenediamine	235; NB	High; N	Very low; NB	Very low; NB	Above 5	Increase
Synthetic product A	Low; NB	None, sirupy; NB	Medium; B	High; NB	3	Decrease
Synthetic product B <sup>b</sup>	Low; NB	None, sirupy; NB	High; NB	High; NB	Above 5	None
Diaminodiphenylmethane	93; B	Low; NB	Medium; B	Medium; B	1	Decrease
Diaminodiphenylamine	127-134; B	High; B	Low; B	Low; B	1	Decrease

<sup>a</sup> B = favorable to blooming; NB = favorable to nonblooming.

<sup>b</sup> A mixture of trimethyldihydroquinoline and its polymers.

high tensile strength is usually not the most important property of a rubber compound from a service standpoint, it is a useful one because many specifications contain tensile requirements. Increased modulus is sometimes undesirable.

**OVERCURES.** The improvement effected by age resistors in overcured stocks is important from a service standpoint because increased uniformity of cure in thick masses of rubber can be obtained in commercial practice. In other words, bad effects due to overcure at the surface of thick articles can be reduced. It appears obvious that this will result in improved abrasive wear in such articles as tires and conveyor belts, and improved flexing life of belt and tire carcasses.

**FLEXURE CRACKING.** Nellen (17) noticed that certain age resistors improved resistance to flexure cracking of tires. This property of age resistors is now regarded as of the highest commercial importance. The factors which appear to be more or less definitely involved in flex cracking are oxidation, cure, pigment dispersion, inclusion of dirt or other foreign material, and grade of rubber used. Other factors of importance are pigment loading, acceleration, type and concentration of reclaim, and softeners. That oxidation is a factor in flexure cracking has been shown by Neal and Northam (16), and Jones and Craig (11) have shown that certain age resistors reduce this tendency. The effect of cure is shown by the experience of several years with flex cracking tests of tread compounds which indicates that increasing cure beyond the optimum tends to decrease flex cracking resistance. The influence of pigment dispersion on flexure cracking is shown by tests of well-mixed *vs.* poorly mixed batches of the same compound:

The sample, cured in a special mold, is 15.2 × 20.3 × 1.3 cm. and is tapered at the ends. It is backed by a piece of heavy frictioned fabric. There are three crosswise grooves about 0.4 cm. deep and 0.65 cm. apart. Strips 2.54 cm. wide are cut lengthwise which, when bent, resemble a section that might be cut from a tire. These 2.54-cm. strips are flexed on the Henry L. Scott belt flexing machine over a 3.18-cm. pulley. The rate of flexing is 12,600 or 10,000 flexures per hour, depending upon which of two machines is used.

It has been found that this test will give consistent results which generally check road tests on tires within reasonable limits, and will allow fairly accurate estimation of the influence of various factors in flex cracking. Table V shows the results of this investigation.

The presence of dirt and other foreign material affects flex cracking resistance, as indicated by the fact that cracking usually starts, both in road-tested tires and in laboratory samples, at the interface between such materials and rubber (cf. Street, 21).

That the grade of rubber influences flex cracking is shown by Table VI, which gives results of tests on the same compound with different rubbers.

The statement that pigment loading probably affects flex cracking of treads is based on factory experience which has shown flex cracking resistance to vary as carbon black loading is changed. Experience has shown too that, other things

being equal, the resistance to flex cracking of tire treads depends upon the accelerator used.

TABLE V. EFFECT OF PIGMENT DISPERSION ON FLEX CRACKING OF UNAGED TREAD STOCK

(Compound is intermediate-grade tread and contains 0.75 per cent phenyl- $\beta$ -naphthylamine on the rubber; Scott machine test)

COMPOUND	TEMP. TO CAUSE OF FIRST MILL CRACKING ° C.	No. OF FLEXURES TO CAUSE FIRST CRACKING	OPINION OF TEST OPERATOR
(1) Poor mix <sup>a</sup>	60	28,560	Small cracks in grooves; worst of group
(2) Poor mix	Cold	33,750	Small cracks in grooves; better than (1)
(3) Good mix <sup>b</sup>	60	47,444	Very small cracks and pinholes in grooves; better than (2)
(4) Good mix	Cold	63,745	Few pinholes in grooves; best compound of group
(1) Poor mix	60	28,560	Crack across groove; worst compound of group
(2) Poor mix	Cold	39,757	Cracks in grooves; better than (1)
(3) Good mix	60	49,343	Cracks in grooves; better than (2)
(4) Good mix	Cold	76,552	Small cracks in grooves; best compound of group

<sup>a</sup> Mixing designed to give poor pigment dispersion.

<sup>b</sup> Mixing designed to give good pigment dispersion.

TABLE VI. EFFECT OF KIND OF RUBBER ON FLEX CRACKING OF UNAGED TREAD STOCK

(Diphenylguanidine-hexamethylenetetramine used as accelerator; Scott machine test)

KIND OF RUBBER	No. OF FLEXURES TO CAUSE FIRST CRACKING	APPEARANCE AFTER FLEXING
(1) Blend of amber and smoked sheets	417,698	Good
(2) Smoked sheets	319,762	Not as good as (1)
(3) Rolled brown	278,978	Much worse than (1) or (2)

Microscopic examination of reclaim-rubber mixtures has shown that most reclaims do not dissolve in or flux with rubber but disperse in small particles as a pigment does. A lumpy reclaim or one which disperses poorly would, therefore, be expected to act like dirt or poorly dispersed pigment.

In testing for the effect of age resistors on flex cracking it is important to use clean, high-grade rubbers, and to secure good pigment dispersion.

**ABRASION.** Not much information is available on the effect of age resistors on resistance to abrasion of rubber compounds. Claims have been made that certain age resistors have a large effect in improving tread wear. Preliminary tests have failed to show great improvement due to age resistors but have indicated that some improvement can be expected when age resistors are used. Laboratory data have been obtained for phenyl- $\beta$ -naphthylamine on several machines, some of which (notably the Bureau of Standards type) seem to give results agreeing with road test data. Comparison on this machine of a typical high-grade tread accelerated with the aldehyde-amine accelerator Pullman, with and without phenyl- $\beta$ -naphthylamine, at optimum cure are shown below. The time of cure was 60 minutes at 146° C., and 0.75 per cent of age resistor on the rubber was used:



AGE RESISTOR	VOL. LOSS PER 1000 REVOLUTIONS OF ABRASIVE <sup>a</sup> Cc.	RELATIVE MILEAGE INDICATED
None	4.56	100
Phenyl- $\beta$ -naphthylamine	4.32	106

<sup>a</sup> Average of two or more tests.

These data indicate that a slight improvement in abrasive resistance may be expected in the presence of an age resistor even when the tread has not been aged.

#### EFFECT OF AGE RESISTORS ON PROPERTIES OF AGED CURED RUBBER

The beneficial effects of age resistors become more marked as the samples are aged. Properties of aged rubber compounds affected by the presence of age resistors are tensile strength and elongation, modulus, flex cracking resistance, abrasion resistance, and flexing life of tire and belt carcasses.

**TENSILE STRENGTH.** The maintenance of tensile properties of aged rubber was the first observed effect and is now so well known that it is not necessary to discuss it in detail. In general, age resistors are effective with either acid or basic accelerators, and the degree of protection depends upon the chemical nature of the age resistor. Primary diamines (*m*-toluenediamine, *p,p'*-diaminodiphenylmethane, 2,4-diamino diphenylamine) are generally ineffective from the standpoint of preserving tensile strength. Aldehyde-amines are somewhat more effective and in high concentration (3 to 5 per cent) compare favorably with the best age resistors. Secondary amines (di- $\beta$ -naphthyl-*p*-phenylenediamine, mixed ditolylamines, phenyl- $\beta$ -naphthylamine) are very effective preservatives of tensile strength in both the bomb and oven tests.

TABLE VII. EFFECT OF PHENYL- $\beta$ -NAPHTHYLAMINE ON FLEX CRACKING RESISTANCE OF A TREAD COMPOUND UNAGED AND AGED IN THE GEER OVEN

(Diphenylguanidine-hexamethylenetetramine tread; Scott machine test; cure, 55 minutes at 146° C.)

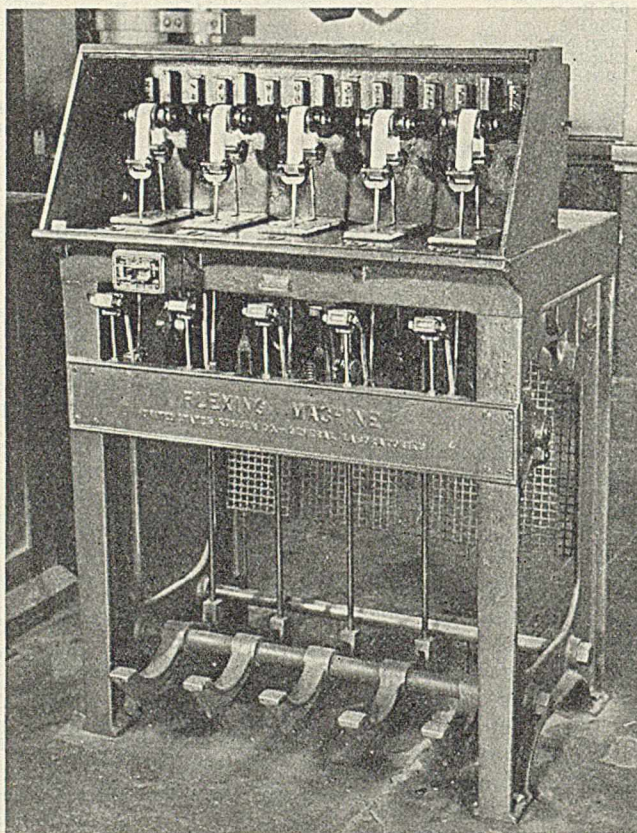
AGE RESISTOR	AGING PERIOD Days	NO. OF FLEXURES TO CAUSE CRACKING	APPEARANCE AFTER FLEXING
None	0	21,669	Fair, cracks in grooves
	2	17,404	Poor, cracks in grooves
	4	11,549	Bad, cracks in grooves
	7	5,963	Very bad, cracks in grooves
Phenyl- $\beta$ -naphthylamine (0.5% on the recipe)	0	27,056	Good, pinholes in grooves
	2	19,188	Good, pinholes in grooves
	4	17,136	Good, pinholes in grooves
	7	16,184	Good, pinholes in grooves

**FLEX CRACKING.** The effect of age resistors on the flex cracking resistance of tread stocks is also more striking after aging. Seven-day Geer-oven aging roughly quadruples the tendency of a diphenylguanidine-hexamethylenetetramine tread stock to crack in the absence of age resistor. If 0.5 per cent phenyl- $\beta$ -naphthylamine is added to the compound, the cracking tendency after 7-day Geer-oven aging is less than

double that of the unaged stock. This comparison is shown in Table VII.

Some chemicals of doubtful value before aging will increase flex resistance after aging. *p,p'*-Diaminodiphenylmethane has some value after aging but none before; and di- $\beta$ -naphthyl-*p*-phenylenediamine has value in aged stock but none in unaged stock.

The comparison of flexing properties of various compounds by means of the Scott belt flexing machine as described above is time-consuming because it is necessary to test a relatively large number of samples, and the number of samples which can be tested at one time is not great. For these reasons some comparisons have been made on the Rubber Service Laboratories (R. S. L.) flexing machine. This machine has four wheels on a single, motor-driven shaft. These wheels are approximately 25.4 cm. in diameter and about 2.54 cm. wide. In each wheel are twelve slots in each of which is fitted a molded sample of special design. The samples project from the wheels 1.9 cm. and, when rotated, strike two smooth idler pulleys and are thereby flexed 1050 times per minute.



[SCOTT FLEXING MACHINE

Experience has shown that stocks containing a high percentage of carbon black are perhaps the most suitable for flex testing with this machine. The failure of the samples extends through a range from tiny pinholes through checks and cracks to complete breaks. It is not unusual for a good tread stock to require as many as 4,000,000 flexures before cracking through. Four samples of each stock are tested at one time. Comparisons of various stocks are based on visual inspection, and good agreement on repeated tests is obtained. This method is made clear by the following examples: Stock A containing no age resistor was flexed with stocks B and C (which contained age resistor) for a total of 1,000,000 flexures. At the end of this time all four samples of A were completely broken or cracked across the face. Such samples are rated 10. Samples with no cracks or pinholes are rated 0, and all others proportionally on a scale between 10 and 0.

In Table VIII are shown the effects of several age resistors on the flex cracking resistance of three tread stocks as measured by the R. S. L. machine. The comparison is on the basis noted above, and the data are therefore roughly quantitative comparisons. Aging was carried out in the Bierer bomb for 48 hours at 70° C. and 21.1 kg. per sq. cm. oxygen pressure. Aged samples did not receive as many flexures as unaged stock. It was found that, if both unaged and aged stocks were flexed the same number of times, no comparisons could be made, because either the aged stocks would all be rated 10 or the unaged stocks would all be rated 0. Table VIII does not show, therefore, an accurate quantitative comparison of the flex resistance of any single com-



TABLE VIII. EFFECT OF AGE RESISTORS ON FLEX CRACKING RESISTANCE OF AGED AND UNAGED TREAD COMPOUNDS

COMPOUND	TEMP. OF CURE ° C.	CURE Min.	1% AGE RESISTOR ON RUBBER	No. of FLEXES		RATING	
				Unaged	Aged	Unaged	Aged
Polybutyraldehyde-aniline (Pullman) tread, 43% black on rubber	146	45	None	1,250,000	350,000	8.50	10.00
			Phenyl- $\beta$ -naphthylamine	1,250,000	350,000	0.33	1.25
			Synthetic product A	1,250,000	350,000	1.30	1.25
			Phenyl- $\beta$ -naphthylamine	1,250,000	350,000	2.00	3.00
			Synthetic product A	1,250,000	350,000	1.25	3.75
Polybutyraldehyde-aniline (Pullman) tread, 45% black on rubber	146	60	None	2,800,000	120,000	10.00	10.00
			Phenyl- $\beta$ -naphthylamine	3,000,000	750,000	0.75	1.50
			Aldol- $\alpha$ -naphthylamine	3,000,000	750,000	9.50	6.25
			Mixed ditolylamines	3,000,000	750,000	2.75	3.25
			Di- <i>p</i> -tolylamine	3,000,000	750,000	1.00	1.50
			Synthetic product A	3,000,000	750,000	3.00	2.25
			Synthetic product B	3,000,000	750,000	3.00	3.50
			1,8-Naphthylenediamine	1,700,000	240,000	10.00	10.00
			Di- $\beta$ -naphthyl- <i>p</i> -phenylenediamine	2,200,000	750,000	10.00	6.50
			2-Mercaptobenzimidazole	3,000,000	350,000	8.50	10.00
Mercaptobenzothiazole tread, 40% black on rubber	138	45	None	4,000,000	1,000,000	5.50	10.00
			Phenyl- $\beta$ -naphthylamine	4,000,000	1,000,000	0.50	2.00
			Synthetic product A	4,000,000	1,000,000	1.00	2.00
			Phenylcumylamine	4,000,000	1,000,000	0.50	2.00
			Di- <i>p</i> -tolylamine	4,000,000	1,000,000	4.25	3.00
			Synthetic product B	4,000,000	1,000,000	2.00	4.50

found before and after aging. It does show, however, the relative value of various age resistors before aging and a similar comparison after aging.

**ABRASION RESISTANCE.** As mentioned above, the resistance to abrasion of even unaged treads may be better in the presence of an age resistor than in its absence. Table IX shows that, when the tread is aged, this improvement becomes greater.

TABLE IX. EFFECT OF AGE RESISTOR ON THE RESISTANCE TO ABRASION OF AN AGED TREAD STOCK<sup>a</sup>

0.75% AGE RESISTOR ON RUBBER	AGING PERIOD Days	VOL. LOSS PER 1000 REVOLUTIONS OF ABRASIVE <sup>c</sup> Cc.	RELATIVE MILEAGE INDICATED
AGED IN GEER OVEN			
None	0	4.56	100
Phenyl- $\beta$ -naphthylamine	0	4.32	106
None	7	4.53	101
Phenyl- $\beta$ -naphthylamine	7	4.00	114
None	14	5.08	90
Phenyl- $\beta$ -naphthylamine	14	4.08	112
None	21	6.43	71
Phenyl- $\beta$ -naphthylamine	21	5.12	89
AGED IN BIERER BOMB			
None	24	11.55	40
Phenyl- $\beta$ -naphthylamine	24	6.46	71
None	48	20.36	22
Phenyl- $\beta$ -naphthylamine	48	8.57	53

<sup>a</sup> Pullman tread stock, optimum cure.

<sup>b</sup> This machine uses a medium-coarse aloxite wheel for the abrasive. The sample is clamped to a lever arm and is abraded against the periphery of the wheel. The load is applied by means of weights on the end of the lever arm. The abrasion loss is measured by volume loss in cc. per 1000 revolutions of the abrasive. The conditions of operation for these tests are: size of wheel, 30 × 7.5 cm.; size of sample, 2.5 × 15.25 × 0.95 cm.; speed of abrasive, 60.55 meters per minute; and total load, 5.54 kg.

<sup>c</sup> Each figure is the average of two or more tests.

**FLEXING LIFE OF TIRE CARCASSES.** Since some air is present in tire cords at the time they are coated with carcass stock, it might be expected that an age resistor would improve the aging properties of tire carcasses and hence the flexing properties of aged tires. An experiment designed to test this effect showed that, although there was no improvement in the unaged stock, 0.25 per cent of phenyl- $\beta$ -naphthylamine on the rubber doubled the flexing life of a tire carcass after 14 days in the Geer oven. In this test, improvement in flexing life due to age resistor became apparent after 5 days of Geer-oven aging.

#### SUPERAGING COMPOUNDS

During the past three years a new compounding technic has been developed relating to "superaging" compounds. The essential features of this technic are the use of relatively large amounts of powerful accelerators (usually thiurams), with or without auxiliary acceleration, and relatively small amounts or no added sulfur. They may also contain selenium

or tellurium. The outstanding property of compounds produced by this method is their extraordinary resistance to aging by accelerated tests such as the Bierer bomb, the Geer oven, and the high-temperature autoclave, even in the absence of age resistors. At first glance this property would seem to render superfluous the addition of age resistors to such compounds. That this is not necessarily so is shown by Table X (from data published by the R. T. Vanderbilt Company, 22) which shows the effect of one per cent phenyl- $\beta$ -naphthylamine on the rubber in a superaging tire friction.

TABLE X. EFFECT OF PHENYL- $\beta$ -NAPHTHYLAMINE ON A SUPERAGING COMPOUND (22)

AGE RESISTOR	CURE <sup>a</sup> Min.	(Tensile strength, kg. per sq. cm.; elongation, per cent)			
		ORIGINAL Tensile strength	ORIGINAL Elongation	14-DAY BIERER BOMB TEST Tensile strength	5-Hr. AIR-BOMB TEST <sup>b</sup> Tensile strength
None	15	269	800	219	750
	30	279	750	191	710
	45	274	730	169	690
	60	270	730	164	680
Phenyl- $\beta$ -naphthylamine (1% on rubber)	15	261	800	234	740
	30	288	750	215	700
	45	271	720	204	700
	60	255	720	183	670

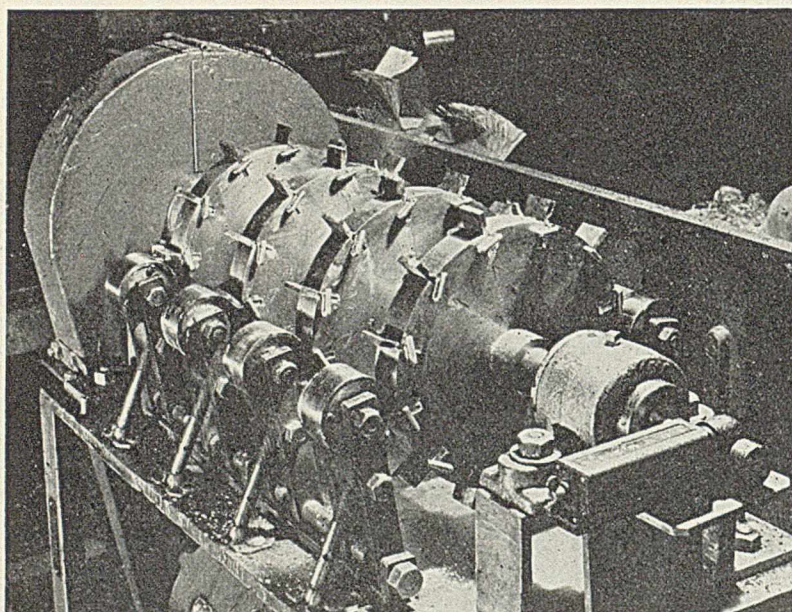
<sup>a</sup> At 138.3° C.

<sup>b</sup> At 127° C. and 5.6 kg. per sq. cm. pressure.

If the other properties of superaging compounds were as superior as their aging properties, standard compounding practice would be obsolete and superaging compounds would find universal acceptance for the production of all kinds of rubber goods. That this has not occurred may be due to too short acquaintance with superaging compounding or to lack of knowledge of the results attainable. It appears more probable, however, that the change in structure which produces the aging properties also produces other fundamental properties differing from those of standard compounds, some of which may not be desirable.

Superaging compounds are not superior in all respects to properly compounded stocks based on standard compounding. They have been found inferior to properly compounded standard type compounds for water resistance, abrasion or flexing under heavy loads, flex cracking, freezing, and resistance to overcure due to sulfur migration in service. They are little or no better than the best standard type compounds for sun checking and oil resistance. Their comparative value for the latter service depends a good deal on the temperature of test. At elevated temperatures they are usually better, at room temperature they may not be. They are superior to standard type compounds in all kinds of accelerated aging tests and in high-temperature service in





RUBBER SERVICE LABORATORIES FLEXING MACHINE

air. In the latter service they are of outstanding value and should find their greatest use there.

The abrasion characteristics of a superaging and a standard type tread compound are shown in Table XI for different loads on a Bureau of Standards type abrasion machine. The treads are identical except for acceleration.

TABLE XI. ABRASION RESISTANCE UNDER VARIOUS LOADS OF A SUPERAGING *vs.* A STANDARD TYPE TREAD<sup>a</sup>

(Bureau of Standards type machine; cure, 70 minutes at 138° C.)

COMPOUND	LOAD ON SAMPLE Kg.	VOLUME LOSS AT GIVEN AGING PERIOD <sup>b</sup> PER 1000 REVOLUTIONS OF ABRASIVE		RELATIVE MILEAGE INDICATED		
		Original Cc.	48 hr. Cc.	Original	48 hr.	96 hr.
Standard	1.81	0.60	0.87	100	68	48
Superaging	1.81	0.59	0.82	102	74	51
Standard	4.31	2.21	2.93	100	75	52
Superaging	4.31	2.97	3.49	74	63	41
Standard	5.56	2.98	4.25	100	70	..
Superaging	5.56	3.81	4.68	78	64	..
Standard	6.92	3.64	5.41	100	67	48
Superaging	6.92	5.50	6.54	66	55	39

<sup>a</sup> Treads used are A2 and B1 in *Vanderbilt News* (22).

<sup>b</sup> Samples aged in Bierer bomb at 70° C. and 21.1 kg. per sq. cm. oxygen pressure.

Although flex cracking properties of superaging stocks have proved inferior, both by laboratory flex cracking tests and by road tests on tires, they can be improved by the addition of a properly chosen age resistor. This is illustrated for a superaging belt cover compound (laboratory test) by Table XII.

TABLE XII. EFFECT OF AGE RESISTORS ON FLEX CRACKING RESISTANCE OF A SUPERAGING BELT COVER COMPOUND

(3% age resistor on rubber; R. S. L. machine test)

AGE RESISTOR	UNAGED AFTER 600,000 FLEXURES <sup>a</sup>	AGED 48 HR. IN BOMB AFTER 450,000 FLEX- URES <sup>a</sup>
None	2.50	7.25
Phenyl- $\beta$ -naphthylamine	1.75	1.00
Synthetic product A	5.00	2.00
Di- <i>p</i> -tolylamine	1.25	1.50
Phenylcumylamine	2.50	1.00

<sup>a</sup> Indices on same basis as Table VIII.

### CHOICE OF AN AGE RESISTOR

Age resistors are as specific in their effects on the service qualities of rubber articles as accelerators, and they must be chosen as carefully if the most desirable results are to be ob-

tained. For example, if age resistors A and B are under consideration, and both are of equal value in bomb and oven aging, A may be of great value in increasing resistance to flex cracking, while B is of little or no value; A may have bad staining properties, while B is relatively nonstaining; A may have little value in protection against deterioration at high temperatures, while B is outstanding in this respect. It is necessary, therefore, to determine which properties are desired for a particular article and choose the age resistor which will best maintain them. The choice of the best age resistor for any specific use must depend upon wide experience and critical knowledge of composition and service factors involved.

In Table XIII are listed some of the reasons for using age resistors in typical rubber stocks. The fact that age resistors improve natural, bomb, and oven aging and also minimize the effect of variation in cure is common to all stocks and is not mentioned in the table.

TABLE XIII. REASONS FOR USING AGE RESISTORS IN TYPICAL RUBBER STOCKS AND OTHER MATERIALS

MATERIAL	OUTSTANDING SPECIFIC REASONS FOR USING AGE RESISTORS
	<b>RUBBER STOCKS</b>
Pneumatic tire tread	To improve flex resistance and increase resistance to abrasion
Carcass stock	To retard ply separation and lengthen flexing life in service
Solid tire tread	To maintain resiliency and retard tendency to blow out
Passenger tube stock	To improve shelf life
Truck tube stock	To resist high temperatures and prevent melting or stiffening
Air bag stock	To retard embrittlement and minimize the effect of migration of sulfur
Water bag stock	To retard surface cracking and to prevent oxidation of interior surface
Side-wall stock	To retard sun checking and flex cracking
Flaps	To maintain resiliency
Repair stocks	To maintain surface tack and stabilize the curing properties
Black shoe upper	To give nonbrittle shelf aging and nontacky dry heat cures, and to retard flex cracking
White shoe upper	To prevent chalking and cracking
Boot upper	To increase tear resistance and retard flex cracking
Soling stocks	To increase flex and abrasive resistance and flatten cure
Heel stocks	To maintain snap and shelf life
Heel lifts	To maintain elongation and permit bending after aging
Rubber flooring	To retard surface erosion and chalking
Tile	To retard surface erosion and chalking
Matting	To allow a cheaper original stock to be used and still maintain sufficient quality in aged material
Running board stocks	To maintain adhesion to metal
General mechanical stocks	To flatten cure and permit higher curing temperatures
Motor support stocks	To prevent the action of brass on the rubber, maintain resiliency, and maintain adhesion
Belt cover stocks	To retard flex cracking, improve resistance to abrasion, and improve the heat and corrosion resistance of the surface
Belt frictions	To prevent ply separation from building or operating causes
Gum tubing	To prevent softening and cracking
Colored garden hose	To retard chalking and reduce marking
Black hose	To prevent hardening and cracking
Gasoline hose	To maintain flexibility of tightly cured or over-cured stock
Fire hose	To prevent development of acid in the tube
Water bottles	To prevent melting or hardening
Bath caps	To prevent melting or hardening
Jar rings	To maintain elongation
Auto topping	To prevent cracking from sunlight
Leatherette	To prevent hardening
Rubber-covered rolls	To maintain original hardness
Tank linings	To make them more corrosion resistant and prevent deterioration by materials such as copper or iron salts
Sheetings	To prevent development of offensive odor
Rubber cements	To maintain tack
Dipped goods	To maintain tensile and resistance to tear
Thread rubber	To maintain elongation and shelf life
Rubber bands	To maintain elongation
Transparent rubber	To insure good aging
Dental dam	To maintain tear resistance
Latex goods	To protect against impurities, to permit dry heat cures, to withstand sterilization



TABLE XIII. (Continued)

MATERIAL	OUTSTANDING SPECIFIC REASONS FOR USING AGE RESISTORS	MATERIAL	OUTSTANDING SPECIFIC REASONS FOR USING AGE RESISTORS
Sponge rubber	Very essential to insure good aging	Rosin-base adhesives	To maintain adhesive properties
Wire	To prevent stiffening and shortness of cover	Fly stickies	To prevent drying out of the film
Hard rubber	To minimize discoloration on aging	Asphalt	To prevent checking, chalking, and cracking
Sulfur-free stocks	To improve flex resistance and heat resistance	Asphalt paint	To improve weather exposure test
Low-sulfur stocks	To improve flex resistance and heat resistance	Tire paint	To prevent deterioration of surface to which applied
Latex-fiber combinations	To prevent resinification and maintain flexibility	Top dressing	To prevent deterioration of surface to which applied
Rubber base adhesives	To maintain adhesive properties	Linseed oil	To retard drying
		Oil-base adhesives	To maintain adhesive properties
Balata	OTHER MATERIALS	Nitrocellulose and lacquers	To stabilize and prevent embrittlement
Chicle, Pontianak, etc.	To prevent resinification	Paper	To prevent embrittlement
Rosin	To prevent oxidation which catalyzes deterioration of rubber goods		

TABLE XIV. CAUSES AND REMEDIES FOR VARIOUS TYPES<sup>a</sup> OF DETERIORATION OF RUBBER COMPOUNDS

TYPE OF DETERIORATION	CAUSE	REMEDY	COMMENT
1. Loss of tensile strength at ordinary temperatures	Oxidation	Diaryl amines, aldehyde-amines, or ketone-amines	Use any highly active age resistor
2. Decrease in elongation	Oxidation of rubber, oxidation of free or combined sulfur, or continued cure	Same as 1	Low-melting diaryl amines are especially good
3. General hardening			
4. Tendency of highly compounded aged stocks to smudge	Surface oxidation destroying the bonding action of the rubber for the pigments	Same as 1	Waxes, petrolatum, or paraffin also help
5. Chalking			
6. Development of odor	Oxidation, giving rise to volatile, terpene-like materials	Same as 1	Leave out rosin oil or other readily oxidizable materials
7. Oxidation catalyzed by resinous ingredients, drying oils, deteriorated rubber in compound, deteriorated rubber in contact, metal salts or soaps in compound, or contact with certain metals		Same as 1	In contact with easily oxidizable materials, use of age resistor is essential
8. Effect of under- and overcures	.....	Same as 1	Age resistors flatten curing curves and impart better aging to poorly cured articles
9. Effect of curing above optimum temp.	.....	Same as 1	Same as 1
10. Brittle skin formation	High-temp. service, surface oxidation, or surface overcure due to sulfur migration	Aldehyde-amines and certain diaryl-amines	Aldol- $\alpha$ -naphthylamine is recommended
11. Softening by water or steam	Water penetration and reversion	Aldehyde-amines, polyprimary amines	Improvement notable in water bags and steam hose; aldol- $\alpha$ -naphthylamine is recommended
12. Heat deterioration	Oxidation and reversion	Same as 11	.....
13. Oxidation of solvent-swollen rubber	Swelling often affords easier access to oxygen	Same as 11	Effect is seen in gaskets and gasoline hose
14. Oxidation of free or combined sulfur	High free or combined sulfur; overcures	Polyprimary amines	.....
15. Acid formation on oxidized surface	Moist, oxidized sulfur products retained on surface	Polyprimary amines, diaryl amines	Acid deterioration of fire hose cover
16. Effect of inorganic acid materials	Acid hardening of surface	Same as 15	Noted in tank linings
17. Melting or sticky perishing	Oxidation and reversion	Same as 15	Often seen in water bottles and pure gum articles
18. Loss of adhesive bond to metal (brass-copper plate)	Softening at interface	Diaryl amines	.....
19. Copper poisoning of rubber stocks	Accelerated oxidation	Same as 18	.....
20. Flexure cracking	.....	Diaryl amines	Low-melting diaryl amines are especially good
21. Growth of cracks on flexing	.....	Same as 20	.....
22. Cracking originating from dirt nuclei in stock	.....	Diaryl amines	Eliminate dirt from stock
23. Ply separation in service	.....	Same as 22	.....
24. Internal heating by flexure	.....	Diaryl amines + a polyprimary amine	.....
25. Development of tack in dry heat cures	Oxidation	Aldehyde-amines, polyprimary amines	.....

<sup>a</sup> Commercial age resistors which belong to the classifications given in this table are:

Diaryl amines:  
Phenyl- $\alpha$ -naphthylamine  
Phenyl- $\beta$ -naphthylamine  
Di- $\beta$ -naphthyl-*p*-phenylenediamine  
Mixed ditolylamines  
Synthetic product A

Aldehyde-amine condensation products:

Aldol- $\alpha$ -naphthylamine  
Acetaldehyde-aniline  
Butyraldehyde-aniline  
Polyprimary amines:  
Benzidine  
2,4-Diaminodiphenylamine  
4,4-Diaminodiphenylmethane  
2,4-Diaminotoluene

The ways in which rubber may deteriorate are manifold. It is often not possible to correct completely a given difficulty merely by adding an age resistor. It may be necessary to change the accelerator, the accelerator-sulfur ratio, the pigmentation, or the cure. However, the use of an age resistor is always an additional improvement or factor of safety. Types of deterioration which may be remedied by the use of certain classes of age resistors are shown, together with their causes, in Table XIV. It should be understood that not all members of any given group will remedy the type of deterioration given. Age resistors are often specific in their effects, and Table XIV is intended merely as a guide in the selection of classes of age resistors suitable for the purpose in question.

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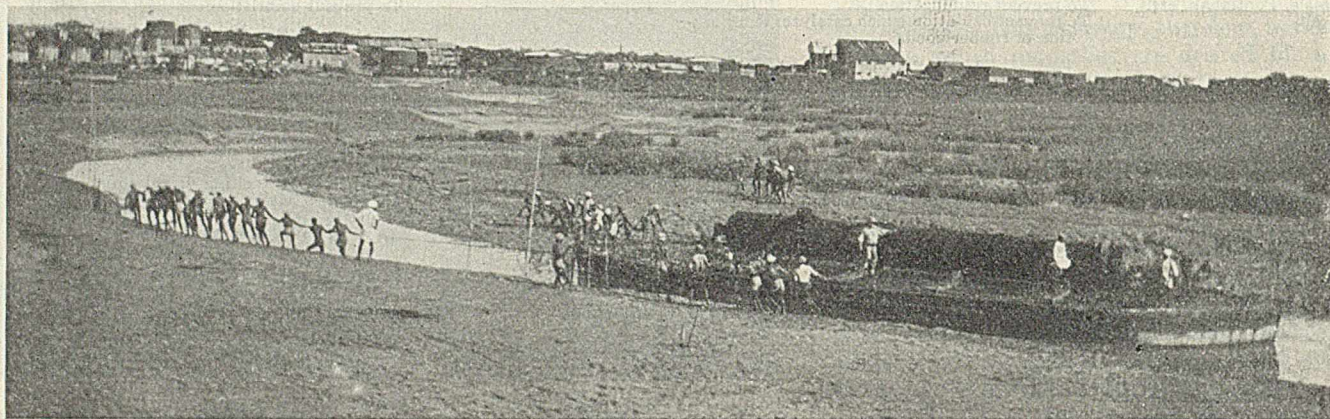
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HAULING A DEPHLEGMATOR TO THE REFINERY SITE FOR A DUBBS UNIT IN UPPER ASSAM, INDIA

## Gases from Cracking Hydrocarbon Oils

GUSTAV EGLOFF AND J. C. MORRELL, Universal Oil Products Company, Chicago, Ill.

THE oil industry is developing more and more along the line of synthesis because of the enormous quantities of unsaturated hydrocarbons which it is producing from the cracking of gasolines, naphthas, kerosene, gas oils, fuel oils, and crude petroleum. These unsaturated hydrocarbons are present not only in the cracked products comprising gasoline, kerosene, and tractor, stove, furnace, Diesel, and fuel oils, and asphalt, but also in the gas produced. The volume of cracked gas now available yearly is over 300 billion cubic feet (8.4 billion cubic meters) averaging over 20 per cent of unsaturated hydrocarbons with some exceeding 50 per cent. The volume of cracked gasoline per year is 7.6 billion gallons (28.85 billion liters), which contains an average of about 20 per cent of unsaturated hydrocarbons.

The potential significance of processes by which olefinic or unsaturated hydrocarbons may be converted into organic chemicals, gasoline of high knock rating, lubricating oils, solvents, and resins is apparent when one considers the enormous quantities available in cracked gases and producible from hydrocarbon oils.

Among the products obtained from cracking oil under conditions of elevated temperatures and pressures is hydrocarbon gas having high heating value which is at present largely used as a fuel. This gas can be fractionated to obtain ethylene, propylene, butylenes, butadiene, acetylene, and other unsaturated hydrocarbons which makes it a source of enormous quantities of pure hydrocarbons to be used in synthetic chemistry.

The amount of gas produced in the cracking process is governed by several factors, notably the composition of the charging stock and the operating conditions of time, temperature, and pressure used during the processing of the oil. The problem of utilization of 300 billion cubic feet of cracked gas is simplified by a knowledge of the chemical composition of the gases.

The object of the present work is to study the cracking of various oils, particularly from the viewpoint of gas formation and its composition, especially when producing commercial yields of gasoline.

### CRACKING EXPERIMENTS

Cracking tests were made on various stocks including gasoline, naphtha, and kerosene from Midcontinent crude oils; kerosene distillate, a mixture of heavy naphtha and light gas oil, and gas oils from California crude oils; topped crude oils from Midcontinent and Somerset crudes and Mt. Pleasant and Refugio (Texas) crude oils. The operating pressures of these runs varied from 250 to 750 pounds per square inch (17.57 to 52.73 kg. per sq. cm.) and the temperature from 875° to 975° F. (468° to 524° C.).

The products from the cracking tests were: gasoline, representing from 52 to 76.8 per cent of the charge; flashed liquid residue in various amounts up to 47.1 per cent; and the gas representing from 164 to 1182 cubic feet per barrel.

The calorific values of the gas, where determined, ranged from 1280 to 1590 B. t. u. per cubic foot (11.37 to 14.11 Calories per liter).

The Somerset topped crude was cracked to produce gasoline, gas, and coke. Gasoline, gas, and liquid residue were produced in all other runs.

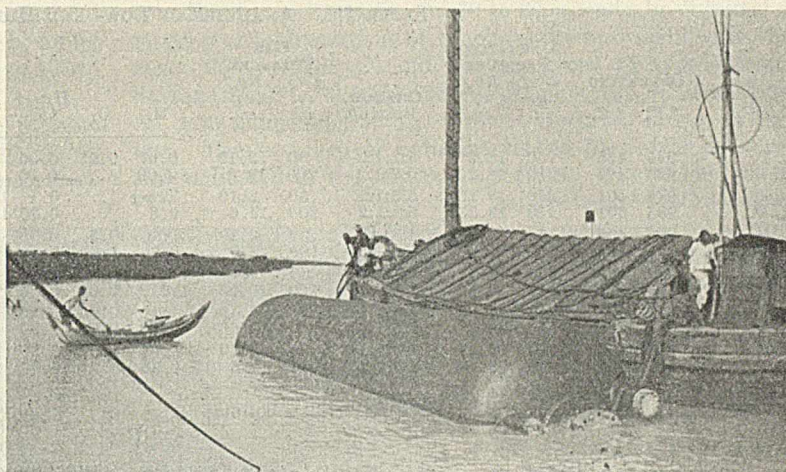
The apparatus employed in carrying out the tests was a continuous cracking unit varying in charging capacity or throughput from approximately 1 to 35 gallons (3.8 to 132.6 liters) per hour, depending upon the types of charging stock, the operating conditions, and the results desired. The apparatus comprised a continuous tubular heating coil, a reaction chamber, an evaporating or flash chamber, a fractionator, a condenser and receiver, and a stabilizer for the cracked gasoline. The full operating pressure was maintained upon the heating coil and reaction chamber. The evaporating or flash chamber and the remainder of the system were under a reduced pressure relative to these ele-



ments. In the runs wherein liquid residue was produced, the hydrocarbon oil leaving the heating coil under the cracking conditions of temperature and pressure was introduced into the reaction chamber, the vapor and nonvaporous residue being withdrawn therefrom and introduced into the evaporating chamber under reduced pressure. The nonvaporous liquid residue was withdrawn continuously from the flash chamber. The reflux condensate from the fractionator, comprising hydrocarbons in general of higher boiling range than the gasoline, was returned to the heating coil for further conversion. The operating conditions and yields of products from the various runs are summarized in Table I.

The gas from the above cracking runs was analyzed by the Podbielniak method for the individual hydrocarbon constituents. Methane and other uncondensable gases formed the greater part of the gas in each case. Next in order of amounts produced were ethane, propylene, propane, and ethylene. Acetylene, where determined, was found to be present in the smallest amount. Complete analyses of the gases from each of the cracking operations are shown in Table II.

Analyses were made of the gases produced in the commercial operation of a cracking unit producing 9000 barrels of gasoline per day. The charge was a West Texas gasoline with an octane number of 53 and an end point of 400° F. (204° C.). Eighty-two per cent of a 72 octane number gasoline (C. F. R. motor method) having a Reid vapor pressure of 10 pounds per square inch (0.7 kg. per sq. cm.) was produced in this operation. This unit produces at the rate of 3.5 million cubic feet (98 thousand cubic meters) of gas per day. The cracked gas is obtained from the gasoline receiver of the cracking unit and



FLOATING A REACTION CHAMBER TO THE REFINERY SITE FOR A DUBBS UNIT IN BURMA

from the stabilization unit. The cracked gas is produced at the rate of about 400 cubic feet per barrel of gasoline processed, 280 cubic feet of which comes from the receiver and 120 from the stabilizer. The components in the gas are as follows:

	RECEIVER Gas	STABILIZER Gas
	Per cent by volume	
Methane	42.0	7.1
Ethane and ethylene	25.1	30.3
Propane	11.0	28.5
Propylene	9.5	19.8
Isobutane	2.8	4.3
Butylenes	1.0	2.5
Butane	4.8	7.5
Pentane	3.9	..

TABLE I. OPERATING CONDITIONS AND YIELDS OF PRODUCTS

	MIDCONTINENT		KEROSENE DISTILLATE		HEAVY NAPHTHA AND LIGHT GAS OIL (CALIF.)	GAS OILS			TOPPED CRUDE OILS		CRUDE OILS		
	Gasoline	Naphtha	Mid-continent	California		Calif.	Coastal	East Texas	Mid-continent	Somerset	Mt. Pleasant	Refugio	
Pressure:													
Kg./sq. cm.	29.2	54.75	29.2	36.5	29.2	25.5	29.2	25.5	18.2	18.2	25.5	25.5	
Lb./sq. in.	400	750	400	500	400	350	400	350	250	250	350	350	
Temperature:													
° C.	510	523	510	510	510	510	487	510	510	495	501	498	
° F.	950	975	950	950	950	950	910	950	950	925	935	930	
Yields, % of charge:													
Gasoline	76.8	52.0	70.6	72.3	61.5	70.7	63.2	60.4	63.4	69.4	69.5	60.1	
Octane No. of gasoline <sup>a</sup>	88	104	82	80	83	78	79	89	74	72	73	62	89
Residue (liquid)	6.8	6.0	14.6	9.7	14.7	15.5	28.2	21.6	26.2	23.5	0.0	20.0	31.3
Gas and loss, %	16.4	43.0	14.8	18.0	23.8	13.8	8.6	18.0	13.4	13.1	30.6	10.5	8.6
Gas:													
Cu. ft./bbl. charge	483	1182	694	636	625	570	495	460	489	531	794	307	382
B. t. u./cu. ft. gas	..	..	..	..	..	1462	1590	..	1280	..	1486	..	..
Kg. Cal./liter	..	..	..	..	..	12.97	14.3	..	11.36	..	13.2	..	..

<sup>a</sup> All octane values were determined by the C. F. R. research method.

TABLE II. GAS ANALYSES

(Per cent by volume)

	MIDCONTINENT		KEROSENE DISTILLATE		CALIFORNIA		HEAVY NAPHTHA AND LIGHT GAS OIL (CALIF.)	GAS OILS			TOPPED CRUDE OILS		CRUDE OILS	
	GASOLINE	NAPHTHA	Low-pressure receiver gas	Stabilizer gas	1	2		CALIF.	COASTAL	EAST TEXAS	MID-CONTINENT	SOMERSET	MT. PLEASANT	REFUGIO
Methane. + uncondensables	56.0	60.2	53.0	11.3	50.4	73.0	46.8	44.8	52.1	39.2	39.4	41.3	26.0	60.4
Ethylene	3.6	4.0	4.4	2.2	3.4	2.7	3.4	4.0	3.1	3.9	4.7	4.3	4.8	6.2
Ethane	18.6	8.2	20.6	18.6	11.1	11.5	18.0	16.2	15.8	21.0	19.7	21.6	16.8	13.4
Propylene	9.5	5.2	7.0	14.5	17.8	5.6	13.5	14.2	8.7	7.4	11.6	15.4	23.3	7.1
Propane	5.1	10.5	8.7	19.5	6.6	3.2	5.7	7.4	9.5	16.2	12.0	6.2	5.4	6.2
Butylene	1.2	5.1	1.9	7.6	7.6	2.6	{2.2	..	..	{2.6	3.0	4.1	..	..
Butanes	2.4	3.4	3.1	10.3	..	..	{4.1	6.0	8.0	{2.3	4.1	3.1	17.8	2.4
Butadiene	1.2	..	..	6.9	..	..	1.6	4.0	..	4.2	1.9	1.7	..	..
Pentane and higher	2.4	3.3	9.1	..	1.8	0.5	4.7	3.4	2.8	3.2	3.6	2.3	5.4	3.3
Acetylene	..	..	..	..	1.3	0.9	..	..	..	..	..	..	0.5	0.9
Unsaturated hydrocarbons, total per cent	15.5	14.3	13.3	31.2	..	..	20.5	22.2	..	24.9	21.2	25.5	..	..



TABLE III. ANALYSES OF LOW- AND HIGH-PRESSURE GASES

GAS <sup>a</sup>	OPERATING TEMP.		OPERATING PRESSURE		CHARGE BLEND <sup>b</sup>	GAS PRESSURE		H <sub>2</sub>	O <sub>2</sub>	H <sub>2</sub> S + CO <sub>2</sub>	CO	CH <sub>4</sub> + N <sub>2</sub>	Per cent							
	° F.	° C.	Lb./sq. in.	Kg./sq. cm.		Lb./sq. in.	Kg./sq. cm.						C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>4</sub> H <sub>8</sub>	C <sub>4</sub> H <sub>6</sub>	C <sub>4</sub> H <sub>10</sub>	C <sub>4</sub> H <sub>12</sub>
L. P.	925	495	250	18.23	5:2:1:2	30	2.19	0.67	0.25	0.35	0.1	9.4	2.18	24.77	15.24	30.68	3.85	7.7	4.81	
H. P.	925	495	250	18.23	5:2:1:2	200	14.6	2.00	..	0.25	..	64.48	2.75	16.06	1.90	6.75	1.25	2.93	Trace	
L. P.	935	501	250	18.23	5:2:1:2	30	2.19	Trace	..	0.1	11.90	29.10	0.6	8.30	11.7	18.40	4.70	9.00	6.13	
H. P.	935	501	250	18.23	5:2:1:2	200	14.6	9.8	..	0.25	16.90	39.58	4.40	15.60	3.0	5.68	1.20	2.44	1.10	
L. P.	925	495	150	10.95	4:3:1:2	30	2.19	Trace	0.5	0.30	5.00	32.33	2.90	25.80	7.80	13.90	3.40	5.00	3.03	
H. P.	925	495	150	10.95	4:3:1:2	100	7.3	0.7	1.70	0.12	5.10	56.94	2.00	17.80	3.10	5.92	1.60	2.95	2.07	
L. P.	925	495	200	14.6	4:3:1:2	30	2.19	0.0	0.0	0.60	4.60	31.00	3.90	28.00	7.60	17.40	0.50	2.80	3.57	
H. P.	925	495	200	14.6	4:3:1:2	150	10.95	12.10	0.0	0.20	4.90	50.27	2.30	15.70	3.60	6.40	0.80	2.20	1.45	
L. P.	925	495	250	18.23	4:3:1:2	30	2.19	1.50	0.75	0.80	1.7	30.85	2.45	25.70	8.1	15.77	3.15	5.00	3.63	
H. P.	925	495	250	18.23	4:3:1:2	200	14.6	7.80	0.50	0.30	4.20	65.75	0.60	12.10	1.50	3.00	..	3.88	0.37	
L. P.	945	506	250	18.23	4:3:1:2	30	2.19	1.56	0.60	0.50	2.82	29.60	2.2	24.00	8.88	17.80	3.8	5.34	3.90	
H. P.	945	506	250	18.23	4:3:1:2	200	14.6	9.50	0.7	0.07	9.20	52.65	0.25	14.00	3.2	7.08	1.0	2.20	1.14	

<sup>a</sup> L. P. = low pressure; H. P. = high pressure.

<sup>b</sup> Fuel oil: heavy gas oil: wax distillate: pressure distillate bottoms.

TABLE IV. ANALYSES OF GASES FROM CRACKING OPERATIONS ABOVE 1000° F. (537° C.)

	(In per cent by volume)								
	GAS OIL (5)		GAS OIL (3)	PA. GAS OIL (17)	MIDCONTINENT CRUDE (11) Gas from absorption oil	Stabilizer gas	CORNING CRUDE DRY GAS (11)	GULF COAST DRY GAS	CRUDE (11) Stabilizer gas
CO <sub>2</sub> + H <sub>2</sub> S	0.89	0.28	...	0.25	...	...	...	...	...
CH <sub>4</sub> + H <sub>2</sub>	29.6	28.5	35.4	46.6	44.4	4.20	37.95	38.81	11.37
C <sub>2</sub> H <sub>4</sub>	23.1	23.1	22.9	27.0	30.35	1.60	25.52	20.31	15.56
C <sub>2</sub> H <sub>6</sub>	12.8	11.1	13.3	...	10.30	...	13.80	13.15	12.35
C <sub>3</sub> H <sub>6</sub>	13.3	15.7	18.1	16.0	12.0	27.10	15.84	13.15	44.87
C <sub>3</sub> H <sub>8</sub>	4.9	4.4	0.0	...	2.95	...	3.10	3.68	...
C <sub>4</sub> H <sub>6</sub>	...	...	...	9.0	...	...	...	...	...
C <sub>4</sub> H <sub>8</sub>	...	...	...	1.0	...	...	...	...	...
C <sub>4</sub> H <sub>8</sub> + C <sub>4</sub> H <sub>6</sub>	...	...	55.	...	...	...	...	...	...
C <sub>4</sub> H <sub>8</sub> + C <sub>4</sub> H <sub>10</sub>	8.3	10.1	..	...	...	66.45	2.76	6.43	13.86
C <sub>5</sub> H <sub>10</sub> + C <sub>5</sub> H <sub>12</sub>	4.1	4.0	..	...	...	0.64	1.03	2.47	1.99
Above C <sub>5</sub> H <sub>10</sub> + C <sub>5</sub> H <sub>12</sub>	3.9	3.1	3.4	...	...	...	...	...	...
Olefins, total	47.2	48.4	46.5	53.0	42.35	...	...	...	...

A series of gas analyses made on low-pressure and high-pressure receiver gas from commercial cracking operations shows an interesting comparison. The operating pressure in all cases was 250 pounds per square inch (17.57 kg. per sq. cm.). The charging stocks varied, however, and operating temperatures ranged from 925° to 945° F. (496° to 507° C.). The charging stocks were blends, in different proportions, of fuel oil, heavy gas oil, wax distillate, and pressure distillate bottoms. The low-pressure gas was taken off at 30 pounds per square inch (2.1 kg. per sq. cm.), the high-pressure gas at 100 to 200 pounds per square inch (7 to 14.1 kg. per sq. cm.). In every case the hydrogen content was much greater for the high-pressure gas than for the low-pressure gas from the same run. The percentage of methane and nitrogen was also considerably higher in the gas from the high-pressure receiver whereas there were more ethane and propylene in the low-pressure gas. Propane, propylene, butane, butylene, and pentane were contained to a great extent in the low-pressure product, as would be expected.

Analyses of both low-pressure and high-pressure gases from the cracking operation, produced as described above, are summarized in detail in Table III.

Cracking at temperatures of 1000° F. (537° C.) and higher, primarily to produce high-antiknock gasoline, increases gas yield and lowers the gasoline percentage when compared to milder temperature conditions. When cracking gas oils under these conditions, the gas produced is upward of 1000 cubic feet per barrel of charge.

The gases produced in these so-called vapor-phase processes are richer in olefins than those obtained in liquid-phase processes.

#### DATA OF OTHER INVESTIGATORS

Typical analyses (3, 4, 9, 12) of gases from cracking operations with various types of oils employing temperatures above 1000° F. are shown in Table IV.

In operations primarily to make gas by cracking hydro-

carbon oils, the yield of gas may be more than 3000 cubic feet per barrel of oil. Some typical results in such gas-making operations at temperatures of 650° to 850° C. are shown in Table V. The yields of gas in cubic feet per barrel varied from approximately 2500 to 3400. The olefin content of the gases varied from approximately 27 to 46 per cent, which is approximately 900 to 1400 cubic feet of olefins per barrel of gas oil charged.

TABLE V. YIELDS OF GAS PER BARREL OF GAS OIL

REFER- ENCE	TEMPERATURE		YIELD	OLEFINS (AND DI- OLEFINS)	OLEFINS
	° C.	° F.	Cu. ft./bbl.	Vol. %	Cu. ft./bbl.
(10)	743-785	1352-1455	2800-3365	27.3-36.6	906-1094
(15)	682-760	1261-1400	2490-2963	30.1-35.8	891-930
(12)	700	1292	2520	36.5	919
(16)	800-850	1472-1562	2370-3255	43.1-46.2	1325-1402
(19)	650-750	1202-1382	1887-2884	43.6-30.6	822-882

Brooks (4) reports the following analyses of Pintsch gas from the cracking of various hydrocarbon oil gases:

TEMPERATURE <sup>a</sup>		ETHYL- ENE	PROPYL- ENE	HIGHER OLEFINS	TOTAL OLEFINS
° C.	° F.	%	%	%	%
805-850	1481-1202	16.3	18.6	1.4	36.3
660-635	1220-1175	18.3	19.0	1.6	38.9
635-535	1175-995	12.5	22.4	2.4	37.3
625-535	1157-995	13.7	22.6	2.6	38.5
615-425	1139-797	12.0	25.7	3.8	41.5

<sup>a</sup> The temperatures given are those at the beginning and end of the gas-making period.

The amount of unsaturated hydrocarbons that can be produced by cracking is enormous, being limited only by the production of crude oil. There is also a potential supply of billions of cubic feet of olefins from the cracking of natural gas.

Under the influence of heat and pressure and also in the presence of catalysts, olefins can be converted into higher hydrocarbons that are suitable for use as gasoline and lubricating oil. Gasoline has been obtained by polymerizing a



cracked gas containing ethylene, propylene, butylenes, and butadiene with an octane number of over 100 on a blending basis, an A. P. I. gravity of 63, and a boiling range of 90° to 400° F. (32.2° to 204° C.).

The conversion of olefins to higher hydrocarbons may be effected by the use of heat and pressure alone. By increasing the pressure, it is possible to reduce the temperature necessary to effect polymerization. The operating temperature may be reduced further when suitable catalysts are used. Many catalysts have been proposed for use in the polymerization of olefins.

Dunstan, Hague, and Wheeler (6) have obtained 92 per cent yields of liquid hydrocarbons from ethylene by heating the gas at 380° to 400° C. (716° to 752° F.) under pressures of about 1500 pounds per square inch (105.4 kg. per sq. cm.) in the absence of catalysts. Eighty-six per cent of their product boiled below 200° C. (392° F.) and had an antiknock value five-sixths that of benzene. They reported the presence of "considerable quantities" of hexenes and higher olefins in the product.

By passing ethylene through a steel tube at 430° C. (806° F.) under 70 atmospheres (73 kg. per sq. cm.) pressure, Egloff and Schaad (7) obtained a mixture of liquid hydrocarbons which represented 78 per cent of the ethylene. The product was separated into the following fractions:

FRACTION	BOILING RANGE		YIELD Vol. %
	° C.	° F.	
Gasoline	35-210	95-410	78.5
Kerosene	210-292	410-558	13.5
Lubricating oil	145-257 (7 mm.)	293-495	6.7
Residue and loss	.....	.....	1.3

The gasoline fraction had an octane number of 76 and contained 44.5 per cent of olefins, 9.6 of aromatics, and 45.9 of paraffins and naphthenes. There were discontinuities in the distillation curve at temperatures corresponding to the boiling ranges of paraffins and olefins having from 5 to 9 carbon atoms per molecule.

Frey (8) states that, by subjecting ethylene to a pressure of 1000 pounds per square inch (70.3 kg. per sq. cm.) for 5 minutes at 840° F. (449° C.) followed by a similar treatment for 10 minutes after removal of the intermediate products formed in the first stage of the process, there is obtained a 70 per cent yield of hydrocarbons boiling in the range of gasoline, together with a small amount of hydrocarbons boiling above this range.

Wagner (18) produced gasoline by treating mixtures of ethylene, propylene, and butylenes at a temperature of 350° to 700° F. (177° to 371° C.) under pressures of 600 to 1500 pounds per square inch (42.2 to 105.4 kg. per sq. cm.) in the presence of chlorides of aluminum, nickel, iron, and titanium, or in the presence of activated charcoal, silica gel, or fuller's earth.

Gayer (9) has published an interesting paper on the polymerization of propylene in the presence of floridin earth. By passing propylene over floridin at 350° C. at a rate corre-

sponding to a contact time of 70 to 80 seconds, he obtained a mixture of hydrocarbons of which 96 per cent distilled in the range 25° to 220° C. and was composed of hydrocarbons having from 5 to 12 carbon atoms per molecule. His analytical data indicated that the product consisted largely of olefins. The presence of paraffins rather than cycloparaffins was indicated in the saturated portion. The yields, which ranged from 6 to 32 per cent, were determined to a large extent by the method of preparation of the catalyst. The crude product had an octane number of 91 and a gum content of 24 mg. per 100 cc., while the fraction obtained by steam-distilling 90 per cent of the product had a gum content of 0.2 mg. per 100 cc. Catalysts of synthetic aluminum silicate and alumina deposited on silica were also shown to be effective.

Aluminum chloride and boron fluoride have been used by Stanley (14) in the conversion of olefins to synthetic lubricating oils. When operating under pressure and in the presence of these catalysts, it is possible to convert olefins to lubricating oils at temperatures below 100° C. High temperatures are usually avoided when polymerizing with aluminum chloride, as this material has a tendency

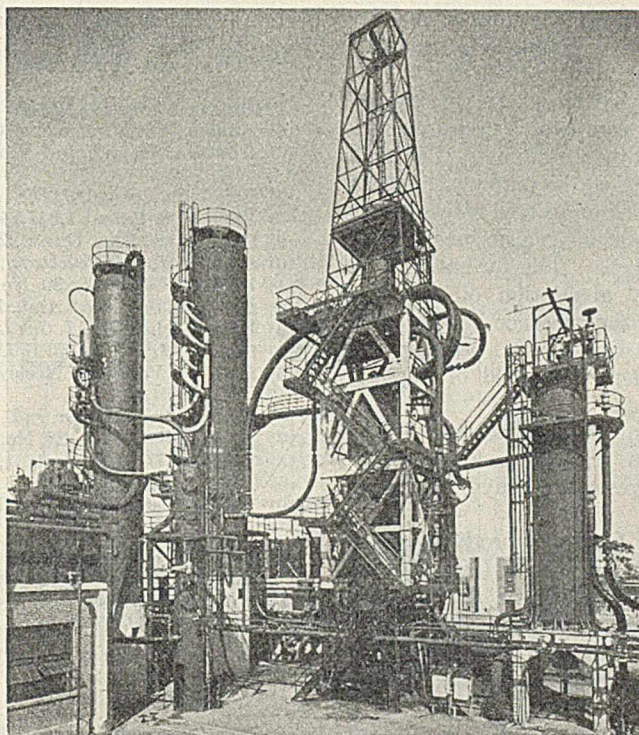
to promote decomposition at moderately high temperatures. Stanley has suggested that the formation of the numerous products by the action of aluminum chloride can be explained on the basis of three types of reactions—namely, (1) polymerization of the reactants to higher olefins, (2) isomerization of olefins to produce the corresponding cycloparaffins, and (3) cracking of the latter under the influence of aluminum chloride to produce light paraffin hydrocarbons and heavy oils less rich in hydrogen.

Sullivan, Voorhees, Neeley, and Shankland (15) have converted olefins to synthetic lubricating oils by polymerization in the presence of aluminum chloride. They have demonstrated the following relationships between the constitution of the olefin polymerized and the properties of the polymerized product:

The longer the straight chain of the olefin treated, the lower will be the temperature-viscosity coefficient of the resulting oil. "In the case of isomeric olefins, the change of viscosity with temperature increases with the degree of branching of the starting material. This cannot be expressed quantitatively, and there are exceptions, as in the case of normal butylene compared with isobutylene."

The synthetic oils contain no paraffin wax. An oil prepared by polymerizing a cracked paraffin wax distillate was shown to be equal, if not superior, to highly refined natural lubricating oils with regard to oxidation stability, temperature coefficient of viscosity, color stability, and comparative lubricating properties.

Synthetic resins have been prepared from olefins and diolefins obtained from cracked petroleum distillates. Varnishes made with this resin dry exceedingly fast and are highly resistant to water, alkali, and acid. The resin is thermoplastic and can be molded when mixed with suitable fillers (1).



PORTION OF A 5000-BARREL-PER-DAY DUBBS COMBINATION TOPPING AND CRACKING UNIT



A mixture of, essentially, polymerized olefins and diolefins is obtained as a by-product in the refining of highly cracked gasoline distillates. It is used as a substitute for linseed and other drying oils. The properties are as follows: specific gravity, 0.956; viscosity (Saybolt Universal at 100° F., or 37.8° C.), 200 seconds; and iodine number, 173 (2).

#### USES FOR CRACKED GASES

Cracked gases now form the basis of a synthetic chemical industry wherein a large number of compounds, having a wide variety of uses, are produced.

Chemically, the unsaturated hydrocarbons in cracked gases react readily to form many compounds useful as such, or as intermediates for making other products. The chlorides, such as ethylene dichloride, may be made without difficulty by simple addition. Hypochlorous acid reacts readily with olefins to form chlorohydrins which can be subsequently converted into glycols by hydrolysis. The formation of alcohols may be accomplished by absorption of olefins in cracked gases by sulfuric acid in the presence or absence of a catalyst followed by subsequent hydrolysis. Starting with the simple addition reactions, the whole field of aliphatic chemistry may be developed.

The following groups of compounds have been synthesized and produced commercially from cracked gases: alcohols, amines, chlorides, glycols, nitroglycols, chlorohydrins, ethers, ketones, acids, and esters.

Some of the outstanding uses for these products are as antifreeze agents (ethylene glycol), explosives (nitroglycols), agents to remove hydrogen sulfide or carbon dioxide from gases (triethanolamine), solvents for lubricating oil treatment

(dichloroethyl ether), medicinals (acetoacetanilide), fumigants (ethylene oxide), solvents for plastics and lacquers (alcohols, esters, ketones), resins, synthetic rubber, and others. It is reported that two hundred thousand tires were produced in Russia during 1933 from the polymerization of butadiene from cracked gases.

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## Rate of Heat Transfer from a Steam Coil to Water

F. H. RHODES, Cornell University, Ithaca, N. Y.

**D**ESPITE the very common use of steam coils in heating liquids in tanks, there is but little information available as to the rate of transfer of heat from the surface of a steam coil to a surrounding liquid. In this article some data are given as to the rate of heat transfer from a steam-heated coil to water. In some of the experiments the water was stirred mechanically; in others the stirring was by natural convection only.

The apparatus used consisted of a cone-bottomed vertical cylindrical agitator of steel with a capacity of about 45 gallons, and was provided with a heating coil of standard 3/4-inch wrought iron pipe in the form of a vertical helix and with a single-bladed propeller agitator and a draft tube to prevent swirling (Figure 1). The heating coil had a total length of 17.3 feet, and was 1.05 inches in external diameter and 0.824 inch in internal diameter. The steam entering the coil was passed through a separator to remove entrained water. The pressure of the steam within the coil was controlled by an automatic pressure regulator and was registered on a calibrated gage. The condensate from the coil was discharged through a steam trap of the expansion type. The stirrer was driven at 250 r. p. m., the direction of rotation of the propeller blade being such that the water was lifted upward through the draft tube and discharged over its top into the space between the draft tube and the shell of the agitator. The temperature of the water was indicated by a thermometer, calibrated to 0.1° C. (0.18° F.) inserted through an opening in the side of the tank. The agitator was insulated with 1.5 inches of 85 per cent magnesia and was provided with a hinged steel cover.

The heat capacity of the agitator, as determined directly by experiment, was equivalent to that of 40 pounds of water.

The heat generated by stirring was found experimentally to be 8.1 B. t. u. per minute. In a series of experiments made to determine the rate of loss of heat by radiation and convection from the outer surface of the agitator, the following results were obtained:

$t_a$  = temp. of air, ° F.  
 $t_w$  = temp. of water in agitator, ° F.  
 $dQ_r/dT$  = rate of loss of heat by "radiation," B. t. u. per min.

$t_w - t_a$ ° F.	$dQ_r/dT$ B. t. u. per min.
0	0
33.3	17.9
51.6	29.4
53.2	30.2
104	63.1

These results were plotted as a smooth curve from which it was possible to determine the rate of loss of heat by radiation at any known difference in temperature between the water and the air.

#### HEAT TRANSFER WITH LIQUID STIRRED

In determining the rates of transfer of heat when the liquid was stirred continuously, a known quantity (approximately 40 gallons) of cold water was placed in the agitator and stirring was started. Then steam at the desired temperature was admitted to the coil. When the water was heating regularly and had attained a temperature of about 65° F., the collection of data was begun. Readings of the temperature of the water in the agitator were taken at 3-minute in-



tervals until a final temperature of about 185° F. was attained.

From the experimental data were computed:

$Q_c/\text{hr.}/1^\circ\text{F.}$  = amount of heat transferred through the coil in one hour under a temperature differential of 1° F. between the steam and the water.

$U_{it.}$  = amount of heat, in B. t. u., transferred through one linear foot of  $3/4$ -inch pipe in one hour under a temperature gradient of 1° F. between the steam and the water.

$C_1$  = thermal conductance between the outer surface of the coil and the water, in B. t. u. per hour per square foot of outer surface of the coil per 1° F. difference between the temperature of the outer surface of the coil and the average temperature of the surrounding liquid. In computing  $C_1$  the thermal conductance of the film between the condensing steam and the inner surface of the pipe was taken as 1800 B. t. u. per 1° F. per hour per square foot, and the thermal conductivity of the metal of the pipe was assumed to be 26 B. t. u. per hour per square foot per 1° F. per foot.

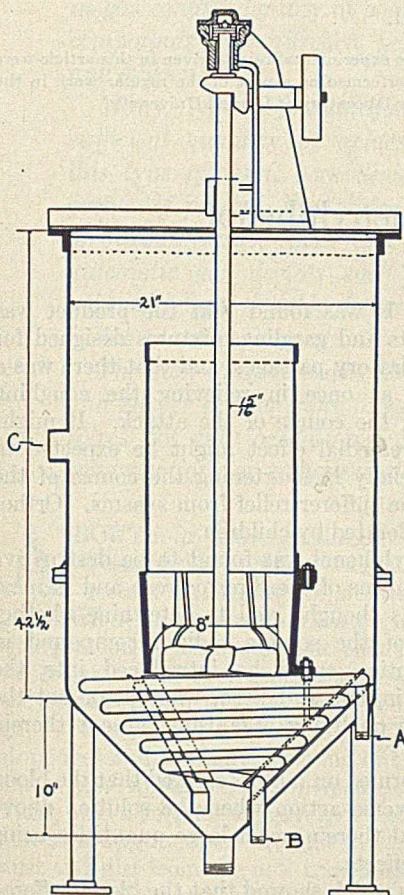


FIGURE 1. AGITATOR WITH HEATING COIL AND STIRRER

- A. Steam inlet  
B. Outlet for condensed steam  
C. Opening for thermometer

The total amount of heat transferred through the coil in the entire period of heating was also determined, and from this value and the logarithmic average difference between the temperature of the steam and the temperature of the water an average value for  $Q_c/\text{hour}/1^\circ\text{F.}$  was computed. From this,

average values of  $U_{it.}$  and  $C_1$  were calculated. The results are shown in Table I.

#### HEAT TRANSFER WITH LIQUID UNSTIRRED

In a second pair of experiments the water was not stirred while it was being heated. The agitator was charged with cold water, agitation was started, and steam at the desired pressure was admitted to the coil. When the water reached a temperature of about 75° F., the steam was shut off and the water was stirred for one minute. At the end of this time the temperature of the water was noted, the stirring was discontinued, and steam at the desired pressure was again admitted to the coil. The water was heated for 5 minutes without stirring, at the end of which time the steam was shut off and the water was stirred for one minute. After noting the temperature, the agitation was discontinued and the water was again heated for 5 minutes without stirring. This cycle of alternate heating and stirring was repeated until a final

temperature of about 185° F. was attained. The results are shown in Table II.

TABLE I. RATES OF HEAT TRANSFER FROM STEAM COILS TO WATER WITH THE WATER STIRRED CONTINUOUSLY

RUN 1: HEATING STEAM AT 5 LB. GAGE PRESSURE = 226.1° F.; WEIGHT OF WATER IN AGITATOR = 330 LB.; TEMP. OF AIR = 73.6° F.					RUN 2: HEATING STEAM AT 12 LB. GAGE PRESSURE = 243° F.; WEIGHT OF WATER IN AGITATOR = 327 LB.; TEMP. OF AIR = 73.2° F.									
Time Min.	Temp. of water ° F.	$Q_c/\text{hr.}/1^\circ\text{F.}$	$U_{it.}$	$C_1$	Time Min.	Temp. of water ° F.	$Q_c/\text{hr.}/1^\circ\text{F.}$	$U_{it.}$	$C_1$					
0	70.5	1070	61.9	300	0	66.6	972	56.2	264					
3	91.4	1175	68	343	3	88.5	1125	65	320					
6	111.2	1170	67.6	340	6	110.5	1195	69.1	352					
9	127.9	1005	58	278	9	130.3	1220	70.5	359					
12	140.2	1175	68	343	12	147.4	1265	73.1	378					
15	152.6	1000	57.8	274	15	162.3	1000	57.8	274					
18	161.6	870	50.3	230	18	172.2	810	46.9	210					
21	168.4	945	54.6	255	21	179.2	846	48.9	222					
24	174.9	890	51.4	236	24	185.7	1067	61.6	295					
27	180.3	920	53.1	246										
30	185.2	1022	59.1	283										
Average														
Total heat lost by radiation, B. t. u.					RUN 1					RUN 2				
Total heat utilized in heating water and agitator, B. t. u.					42,439					43,709.7				
Total heat supplied by stirring, B. t. u.					243					194.4				
Total heat transferred through coil, B. t. u.					43,437					44,447.4				
Log. av. difference in temp., ° F.					85.8					106				
$Q_c/\text{hr.}/1^\circ\text{F.}$ (av.), B. t. u./hr./1° F.					1,010					1,050				
$U_{it.}$ (av.), B. t. u./hr./ft./1° F.					58					60.7				
$C_1$ (av.), B. t. u./hr./sq. ft./1° F.					278					292				

TABLE II. RATES OF HEAT TRANSFER FROM STEAM COIL TO WATER WITH WATER NOT STIRRED

RUN 3: HEATING STEAM AT 5 LB. GAGE PRESSURE = 226.2° F.; WEIGHT OF WATER IN AGITATOR = 323 LB.; TEMP. OF AIR = 80.6° F.					RUN 4: HEATING STEAM AT 12 LB. GAGE PRESSURE = 243.1° F.; WEIGHT OF WATER IN AGITATOR = 327 LB.; TEMP. OF AIR = 81.3° F.									
Time Min.	Temp. of water ° F.	$Q_c/\text{hr.}/1^\circ\text{F.}$	$U_{it.}$	$C_1$	Time Min.	Temp. of water ° F.	$Q_c/\text{hr.}/1^\circ\text{F.}$	$U_{it.}$	$C_1$					
0	88.6	723	41.8	182.5	0	79.7	780	45	199.5					
6	109.6	700	40.5	176.5	6	106.3	780	45	199.5					
12	126.7	613	35.4	150	12	128.3	618	35.6	150.5					
18	139.4	593	34.4	145	18	142.9	656	37.9	162.5					
24	149.9	583	33.8	142.5	24	156.2	677	39.1	168.5					
30	158.8	650	36.4	155.5	30	167.9	666	38.5	165.5					
42	174.5	565	32.7	137	36	177.6	703	40.5	175.5					
48	179.9	577	33.4	140	42	186.4	697	40.2	174.5					
54	184.7	626	36.6	156										
Average														
Total heat lost by radiation, B. t. u.					RUN 3					RUN 4				
Total heat utilized in heating water and agitator, B. t. u.					34,884					39,159				
Total heat supplied by stirring, B. t. u.					73					57				
Total heat transferred through coil, B. t. u.					36,965					40,623				
Log. av. temp. difference, ° F.					80					101				
$Q_c/\text{hr.}/1^\circ\text{F.}$ (av.), B. t. u./hr./1° F.					616.1					690				
$U_{it.}$ (av.), B. t. u./hr./ft./1° F.					35.7					39.8				
$C_1$ (av.), B. t. u./hr./sq. ft./1° F.					152					172.3				

#### RESULTS

The results for the individual sections of each of the experiments made with constant stirring vary considerably among themselves. The variation is due to the fact that complete mixing and equalization of the temperature throughout the mass of the water are not reached instantaneously, so that the



temperatures as read are not the exact average temperatures of the charge. The error in any one reading is small, but, since the rise in temperature in each interval is also small, the relative error in determining the coefficient of heat transfer for a single interval is sometimes appreciable. The agreement between the average value for the coefficient of heat transfer, as calculated from the results for the individual intervals, and the average value as calculated from the total heat input and the logarithmic temperature difference is satisfactory.

These experiments show that the over-all rate of heat transfer between steam condensing in a coil of standard  $\frac{3}{4}$ -inch iron pipe and mechanically stirred water surrounding the coil is approximately 60 B. t. u. per hour per ° F. difference in temperature between the water and the steam per linear foot of pipe, and that the coefficient of heat transfer at the outer

surface of the coil, under the conditions specified above, is approximately 285 B. t. u. per square foot per hour per ° F. difference in temperature. The rate of heat transfer increases slightly with increase in the temperature of the steam. When the water surrounding the coil is stirred by natural convection only, the over-all rate of heat transfer is from 36 to 40 B. t. u. per ° F. per hour per foot of coil, and the film conductance varies from 152 to 172 B. t. u. per square foot per hour per ° F. When the water is not stirred mechanically, the rate of heat transfer increases rather rapidly with an increase in the temperature of the steam. This is to be expected, since with higher steam temperatures there is more convection in the liquid.

RECEIVED June 7, 1934. The experimental results given in this article were obtained in an experiment performed as a part of the regular work in the course in chemical engineering laboratory at Cornell University.

## Communication to the Editor on Orthophenylphenol as an Antiseptic

STR: In the course of experiments conducted during the past year or more with diphenyl compounds which have recently come into the market in commercial quantities, it was noted that the orthohydroxy compound, and certain derivatives thereof, have possessed interesting possibilities as antiseptic and disinfectant agents for therapeutic employment.

A series of tests has been performed on orthophenylphenol and its derivatives in which it appears that these products have a high antiseptic value and are relatively nontoxic to the animal economy. It also appears that the phenol possesses definite penetrating properties and can be used not only for its own effect, but to bring about penetration of other chemicals that ordinarily do not exert their effects beyond the surface of the skin.

The ability of orthophenylphenol to penetrate the intact skin and become effective beyond the site of administration was first tested in agar plate media, and the killing effect on bacteria was noted. Then well-known substances such as menthol, camphor, thymol, and methyl salicylate were mixed therewith, and it was found that they, too, had gone into the medium beyond the point of contact. This led to the belief that beneficial effects in local congestion might be enhanced by combining the remedial agents with orthophenylphenol in salves, ointments, sprays, and the like, commonly used for treating colds and so-called rheumatic conditions and muscular aches and pains. In an extended series of tests whereby the combination in the form of an ointment was applied to the surface of the skin and allowed to remain in contact therewith, it was definitely proved that the substances were absorbed, and sufficient material reached the blood stream to give evidence in the eliminations—that is, the urine. These tests were checked by running another series in which menthol, camphor, methyl salicylate, and the like were used alone in the salve, and no evidence of their presence was found in the urine; when orthophenylphenol occurred in the mixture, it was immediately demonstrated that absorption on penetration had occurred. Inasmuch as the organic compounds above mentioned have a wide use in the treatment of local congestion, it would appear that their effects can be materially enhanced by combining them with certain of the diphenyl compounds.

The nontoxic feature of the orthophenylphenol suggested that it might be useful in combination with other remedies used for combating conditions of the throat accompanied by cough and irritation, which might be accelerated by the

presence of bacteria. It was found that the product was well tolerated in tablets and gargling mixtures designed for application to the respiratory passages, and that there was a soothing effect noted at once in relieving the coughing spasms and shortening the course of the attack. It might be hoped that some remedial effect might be expected in whooping cough, especially in shortening the course of the difficulty and giving the sufferer relief from spasms. Orthophenylphenol is well tolerated by children.

Since the orthophenylphenol was found to be destructive to the pathogenic organisms of the *Streptococcus* and *Staphylococcus* groups, it was thought well to determine whether or not combinations of the soluble sodium compound in physiological salt solution could be introduced into the blood stream without injury, and if so, whether or not the effect of the antiseptic on living organisms present therein would be noticeable.

A series of tests performed on rabbits showed that the blood supply suffered no adverse action when the solution above mentioned was injected therein, even large quantities being tolerated with no aftereffects.

Following these tests which showed that the blood suffered no ill effects from the administration, a series of tests was performed on some rabbits in whose blood living cultures of *Staphylococcus aureus* had been demonstrated. After considerable experimentation in order to control the dosage, the organisms were killed, and the animals survived; in those instances where no injections were made, the creatures succumbed.

Two interesting cases of *Streptococcus* and *Staphylococcus* infections of the blood stream in human individuals were successfully treated with injections of sodium orthophenylphenol in physiological salt solution accompanied by transfusion. Definite improvement followed the early administrations, the subjects experiencing a reduction in temperature and a general improvement in condition. On recovery, the blood gave negative evidence of infection.

These tests lead to the hope that there is a possibility of working out a satisfactory remedy for treating septicemia by the use of an antiseptic which is not harmful to the blood supply.

The research is being continued and the results will be published in detail.

H. C. FULLER

COLUMBIA MEDICAL BLDG.,  
WASHINGTON, D. C.  
July 1, 1934



# Gum Deposits in Gas Distribution Systems

## Vapor-Phase Gum<sup>1</sup>

C. W. JORDAN, A. L. WARD, AND W. H. FULWEILER

The United Gas Improvement Company, Philadelphia, Pa.

*Gum particles are formed and remain dispersed in gas containing any of a large number of organic compounds and nitrogen peroxide or nitric oxide and oxygen.*

*Many types of manufactured gas contain a sufficient quantity of oxides of nitrogen to form this type of gum, here designated as vapor-phase gum. If present, this material will cause stoppage of ordinary pilot lights and the malfunctioning of automatic gas devices such as water heaters. It may also give trouble in gas-handling apparatus in the plant.*

*The gum itself contains about 5 per cent nitrogen and 20 per cent or more oxygen. Its formation involves not only oxidation but probably adsorption, condensation, or polymerization in addition to the*

*primary reaction between the carbon compound and the oxide of nitrogen.*

*About 80 per cent of the gum particles are electrically charged. When first formed they are probably of molecular size. They coalesce until, at a size of approximately 0.1  $\mu$ , they become visible in the ultra-microscope with arc lamp illumination. The coalescence continues until a size of 1 to 1.5  $\mu$  is reached, after which they can no longer remain dispersed in the gas. In manufactured gas which always contains oxygen, the presence of nitric oxide to the extent of a few tenths of a milligram per cubic meter, or a concentration by volume of a few parts in ten million, will cause the formation of particles the number of which reaches the order of  $10^{12}$  per cubic meter.*

**A**BOUT four years ago the Department of Research and Tests of this company was called upon to diagnose and correct a troublesome situation that had arisen in a gas distribution system embracing a number of cities. Sometime previously this system had changed over from carbureted water gas to coke-oven gas. Soon after the change was made, the system began to experience trouble with a new type of gum. The worst effect of the gum was evident in gas pilot stoppages and in malfunctioning of the thermostats of automatic gas appliances, principally storage water heaters. There was also gum on governor valves, compressor valves, and in rotary meters. At first the troubles were ascribed to dust and dirt from the new transmission mains and from the drying up of the deposits in the old gas mains. Shortly after these troubles began, oil fogging in the gas distribution mains was undertaken, but this did not alleviate the troubles and in some cases increased them.

The situation grew rapidly worse until in several cities the number of stoppages became a serious distribution problem. At one time the number of complaints in some districts was running at a rate equivalent to one yearly for each three meters in the district.

The investigation begun in 1930 on coke-oven gas was later broadened to include other systems producing different types of manufactured gas and reporting similar trouble. Although there are a number of stray ends to be traced out and some unfinished identification work which will be of great scientific interest when successfully completed, the

problem has been solved for all practical purposes. The work of this laboratory has led to the discovery of a new type of gum, the discovery of its causes, the discovery of the mechanism of its formation, an analysis of the factors and conditions which promote or retard its formation, and finally the discovery of an inexpensive and effective method of controlling or preventing its formation. The method of preventing gum formation is available for the purification of gases other than town gas—for example, hydrogen or nitrogen.

The essential facts have been available for some time. Certain of them were indicated by one of the authors (6) in discussing a paper on gum at the 1931 Technical Session of the American Gas Association. When a number of publications in American and foreign technical journals showed either a complete misconception of this new type of gum or a confusion of it with the older type, the authors obtained permission from The United Gas Improvement Company to publish their findings.

In the initial paper of the series (13) it was pointed out for the first time that two types of gum are encountered in the distribution of manufactured gas. The fundamental differences in their source, method of formation, and properties were emphasized. The term "vapor-phase gum" was used to describe gum formed in the gas phase by one or more oxides of nitrogen, principally on the unsaturated hydrocarbons in gas. The term "liquid-phase gum" was used to describe a type of gum formed by the polymerization and oxidation of previously condensed styrene and indene. The distinc-

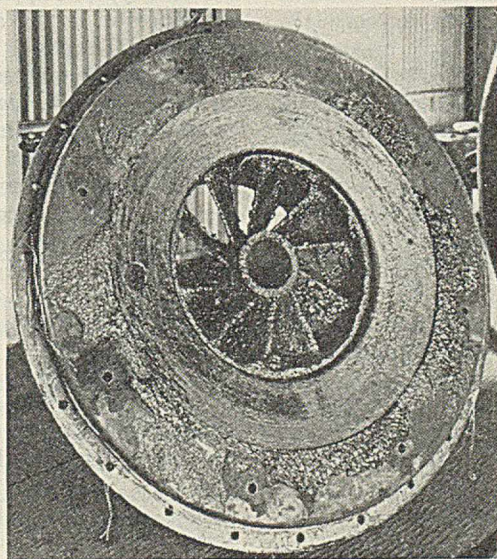


FIGURE 1. GUM DEPOSIT IN COMPRESSOR

<sup>1</sup> For previous articles in this series, see literature citation 13.



tion between the two types of gum and even the names applied to them have since been generally accepted in this country and abroad (3, 4).

In the first and two subsequent papers (13) the mode of formation and methods of control of liquid-phase gum have been described. In this and subsequent papers, it is planned to treat the subject of vapor-phase gum in a similar manner.

#### CHARACTERISTICS OF VAPOR-PHASE GUM

From a preliminary survey it was evident that the conditions previously determined as prerequisite to the formation of liquid-phase gum were not necessary to the formation of the new material. The quantity of condensate and the concentration of styrene and indene of the system were low [see plants H and I, Table V in the first paper (13) of this series] and, although the oxygen content was moderately high, other conditions indicated that there should be no gum trouble.

It was obvious also that the quantities of the material involved were very much smaller. It has since been shown that a quantity as small as 0.02 mg. will extinguish the type of pilot light commonly used on gas ranges.

The first sample of the material now known as vapor-phase gum, as removed from a rotary-type station meter, proved to be a dark brown, amorphous powder aggregated into lumps of various sizes. It was sufficiently dry and hard to permit easy grinding to a powder. Most subsequent samples have resembled the first. One sample was a sticky material of a molasses-like consistency, which hardened quickly on exposure to the air.

Vapor-phase gum is somewhat soluble in many organic solvents, particularly those containing oxygen, such as acetone, acetic acid, and acetic anhydride, and less so in solvents of the hydrocarbon type. When fresh, the material appears to be completely soluble in caustic alkalies and in alkali carbonates, and somewhat soluble in alkali bicarbonates. Acids precipitate the gum from alkaline solutions in the form of a gelatinous mass closely resembling freshly precipitated ferric hydroxide in color and other physical appearance.

Although a diluted alkaline solution can be readily filtered, actually only a portion of the material is in true solution, the remainder being a colloidal suspension. It was impossible to determine the acidity of the material accurately because of its strong tendency to adsorb dilute alkalies. The ultimate analyses of four samples as received from two systems are given in Table I. The two most striking characteristics are the high nitrogen and oxygen contents.

TABLE I. ANALYSES OF VAPOR-PHASE GUM AS RECEIVED

Sample	(In per cent)			
	1	2	3	4
Carbon	55.75	63.36	63.44	64.46
Hydrogen	6.05	6.71	6.35	5.94
Nitrogen	5.05	3.81	7.26	5.15
Oxygen	31.47	23.51	21.98	22.17
Sulfur	0.14	0.82	0.65	0.53
Ash	1.54	1.79	0.32	1.75
CALCD. ON ASH- AND SULFUR-FREE BASIS				
Carbon	56.70	65.06	64.06	65.96
Hydrogen	6.15	6.89	6.41	6.08
Nitrogen	5.14	3.91	7.33	5.27
Oxygen	32.01	24.14	22.20	22.69
Simplest formula	$C_{13}H_{17}NO_2$	$C_{19}H_{24}NO_2$	$C_{15}H_{12}NO_2$	$C_{13}H_{16}NO_2$
Calcd. mol. wt.	283	346	194	274
Obsvd. mol. wt. (in nitrobenzene)	343	381	...	...

The gum is unstable to heat. When heated alone, its decomposition becomes violent around 175° C. Large quantities of gases are formed. These include nitric oxide, the presence of which in the decomposition products is a characteristic test for vapor-phase gum.

#### TROUBLE FROM VAPOR-PHASE GUM

In aggravated cases the quantity of vapor-phase gum in coke-oven gas is so large that it may give serious trouble in

station meters, compressors, and other handling apparatus. The effect of gum in such cases is given in Figure 1 which shows a gas compressor taken apart for cleaning. The compressor was one of a pair in use at the outlet of a coke-oven gas holder. The gas from the two boosters was metered in a Venturi meter. As much as 15 pounds (33 kg.) of gum was taken from the throat of this meter at a single cleaning. At the peak of the trouble, gum was depositing in the meter at the rate of 1 pound per 50 million cubic feet (0.34 mg.<sup>2</sup> per cubic meter) and the meter was reading as much as 35 per cent fast.

In general, however, the quantities of vapor-phase gum are small. Under reasonable operating conditions, the total mass of the gum particles carried by gas is of the order of 0.022 to 1.1 pounds per million cubic feet (0.38 to 19 mg. per cubic meter). These quantities are so small that the presence of vapor-phase gum is normally not troublesome in plant apparatus but rather in devices used in connection with customers' appliances. The three principal places on which the gum is encountered are the pilot lights used largely on cooking ranges, the pilots and the thermostatic control disks used on many water heaters, and the control devices used on gas refrigerators. The details of the mechanism by which the gum stops up these and other control devices will be discussed below.

The ratio of the number of stoppages per meter that occurred at the peak of the trouble in one district of the first system investigated has not been exceeded in any other situation, but the number of stoppages in some other cities has been serious. In one large city the peak reached was fourteen per ten thousand meters over a 14-day period. If such a condition were allowed to continue, it would be equivalent to 2640 stoppages per year in a city with a hundred thousand meters. An analysis of the number of stoppages by appliances in two cities is shown in Table II.

TABLE II. ANALYSIS OF VAPOR-PHASE GUM STOPPAGES BY APPLIANCES

TYPE OF APPLIANCE	PLANT A	PLANT B
	%	%
Automatic water heaters	49.2	56.0
Ranges	27.9	34.5
Refrigerators	21.2	0.7
House heaters	0.7	Not reported
Miscellaneous	1.0	8.8
Total	100.0	100.0

The complaints from gum stoppages in the system served by plant A are further analyzed in Table III which was obtained by dividing the number of stoppages reported for the different types of appliances by the estimated number of such appliances in service and then calculating the ratio between the different types.

In considering these figures, it should be emphasized that on ranges the pilot light is the only place in which gum can cause a stoppage. On water heaters stoppages may occur in two places—the pilot and the thermostatic disks. In refrigerators there are three possible places—the needle by-pass, the thermostatic control, and the burner orifice.

TABLE III. FREQUENCY OF COMPLAINTS BY APPLIANCES (PLANT A)

APPLIANCE	COMPLAINT PER YEAR PER APPLIANCE	RATIO
Ranges	0.016	1.0
House heaters	0.026	1.6
Water heaters	0.085	5.3
Refrigerators	0.270	16.9

The rapid introduction of safety pilots in recent years is responsible for some distortion of the figures given in Tables

<sup>2</sup> The units in which gas volumes are reported in this paper are those in common use in the American gas industry, the unit being 1 cubic foot measured at 60° F. and 30 inches of mercury, and saturated with water vapor. They are also given here in the metric system at standard conditions, 0° C., 760 mm., and dry.



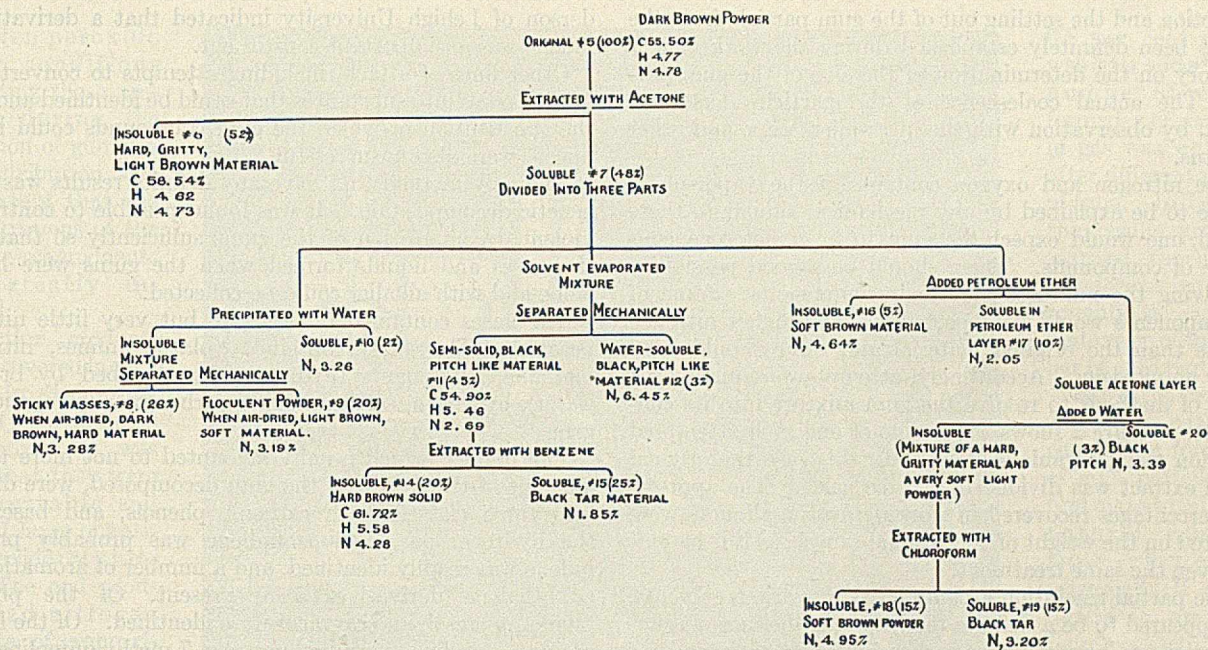


FIGURE 2. RESOLUTION OF GUM MIXTURE WITH ORGANIC SOLVENTS

II and III because these safety pilots put the apparatus completely out of commission if the light goes out. As a result all of the stoppages are translated into complaints to the service department. In the case of range lighters, the customer can correct the trouble easily or can use matches until it has been corrected by the service department. Consequently, the percentage of stoppages of manually operated range lighters reported as complaints is smaller than with the various automatically operated appliances.

However, the nuisance value of a stoppage is approximately the same whether the customer reports it or fixes it. The gas companies troubled with the gum problem have always considered this nuisance value to be even more serious than the cost of servicing the appliances.

If a company delivers gas with which the customer's appliance will not function perfectly, the customer is not getting the service to which he is entitled. The present series of papers is a review of the effort of one large company to give the customer satisfactory service, regardless of the time and money required to correct a situation that was interfering with such service.

#### COMPOUNDS FORMED FROM OXIDES OF NITROGEN

Vapor-phase gum is formed by the action of oxides of nitrogen on different carbon-hydrogen compounds in gas. This was first suspected when nitric oxide was discovered in the decomposition products of the gum. It was proved by removing the oxides of nitrogen from gas in which gum particles had been observed with an ultra-microscope. The formation of particles practically ceased. Oxides of nitrogen were again added to the gas, and large numbers of particles were formed. The action of the oxides of nitrogen produces particles of gum which are so small that they tend to remain dispersed in the gas and to be carried throughout the distribution system.

The source of the oxides of nitrogen in gas will be discussed later. Here it is sufficient to state that these oxides occur in quantities varying from practically zero to several grains per 100 cubic feet (up to 50 mg. per cubic meter) in all types of manufactured gas. It will be shown later that the oxides of importance to this problem are nitric oxide (NO) and nitrogen peroxide (NO<sub>2</sub>).

The formation of various nitrogen-oxygen compounds is

a standard method of identification of unsaturated hydrocarbons. Several such derivatives of the unsaturated hydrocarbons in gas are well known. However, no known compounds having nitrogen and oxygen contents similar to those of the natural gums have been prepared directly. As shown in Table I, the nitrogen and oxygen contents of the crude natural gums varied from 3.9 to 7.3 and from 22 to 32 per cent, respectively. A sample purified by repeated solution in dilute alkali and reprecipitation with dilute acid gave the following ultimate analysis (in per cent): carbon, 65.94; hydrogen, 5.34; nitrogen, 4.40; oxygen (difference), 24.32. It is impossible to write an equation for the direct formation of compounds having such analyses. Dicyclopentadiene would give compounds with the lowest nitrogen content. Starting with nitrogen peroxide, nitrogen trioxide, or nitrous acid, the nitrogen content would be 12.5, 13.5, and 8.7 per cent, respectively. In the latter case the oxygen content would be 9.9 per cent.

One known compound formed indirectly has a nitrogen and oxygen content of 8.7 and 19.9 per cent, respectively. This is nitroindene formed by the action of steam on the  $\alpha$ -nitrosite. The molecular weights and physical properties of the natural gums are quite different from such a compound.

However, there are several methods, each involving a series of steps, that could account for the formation of mixtures having nitrogen and oxygen contents of the order that are observed for vapor-phase gums.

The gums as removed may be the decomposition products of compounds which have lost a portion of their nitrogen.

It is also easy to postulate a series of steps involving condensation, polymerization, and oxidation, either before or after the combination of the hydrocarbon and the oxide of nitrogen. The nitrogen compounds could easily catalyze the polymerization and oxidation of the highly reactive hydrocarbons in gas.

Another theory for which there is considerable support is that, after the vapor-phase gum has formed, it adsorbs other material. The highly dispersed physical state in which the vapor-phase gum is formed should make it an excellent adsorption agent. The additional material could be adsorbed either before or after its oxidation.

That some such process, whether it be called condensation, polymerization, or adsorption, takes place between the origi-



nal reaction and the settling out of the gum particle from the gas, has been definitely established during the work of this laboratory on the determination of the size of the gum particles. The actual coalescence of the particles has been followed by observation with the ultra-microscope and other apparatus.

If the nitrogen and oxygen contents of the vapor-phase gum are to be explained by any mechanism similar to these outlined, one would expect the gum to be a heterogeneous mixture of compounds. There should be a good possibility of resolving the mixtures into their components. Some of the components would be expected to have higher nitrogen contents than the original material and some should have little or no nitrogen. Accordingly, attempts were made by a variety of methods to resolve the gum mixture into its constituents. Figure 2 shows the results of one such attempted separation using organic solvents. In this case the original acetone extract was divided into three parts. The approximate percentages recovered in working up the aliquots were calculated on the weight of the original sample as if it had all been given the same treatment.

In the partial resolution accomplished by various solvents, there appeared to be a definite tendency for the more insoluble fractions to have a higher carbon-hydrogen ratio and for the more soluble fractions to have a lower ratio than the original mixture, the higher ratios approaching indene and the lower being close to that of cyclopentadiene. The following analyses of some of the samples, the separation of which was outlined in Figure 2, illustrate this tendency:

SAMPLE	C %	H %	RATIO
5 (original)	55.5	4.7	11.8
6	58.5	4.6	12.7
9	71.9	5.8	12.4
14	61.7	5.6	11.0
11	54.9	5.5	10.0
19	65.6	6.6	9.94

It is unsafe to put too much reliance on these ratios, however, because, if the gum-forming reaction involved the loss of water, there would be a sharp increase in the carbon-hydrogen ratio of the product in comparison with the parent hydrocarbon.

None of the methods tried for the resolution of the gum mixture resulted in the isolation of any important quantity of any product having a nitrogen content significantly higher than the original. In general, the net result of all the treatments was a loss in the total nitrogen of the products as compared to the original.

The known chemistry of the products formed by the reaction of oxides of nitrogen and unsaturated hydrocarbons indicated that this could occur if the products have a nitrogen atom linked to carbon through an oxygen atom (C—O—N=O). Such compounds are easily broken, for example, by boiling water, alcohol, or aniline, whereas the C—N=O

or  $\text{C}=\text{N} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{O} \end{array}$  linkages are relatively stable.

This suggests, of course, that the low nitrogen contents of the gums removed from the distribution system are partially accounted for by decomposition during the period between the time they are formed and the time when a sufficient quantity has collected to permit their removal. Subsequent observations indicated a marked difference in the stability of the different portions of the nitrogen. A portion of it appears to be loosely bound, while the remainder is firmly held to the rest of the gum molecule.

The work failed to establish any definite facts except that the gums could not be resolved into pure compounds by the methods employed. X-ray diffraction patterns of some of the products of the separation photographed by H. V. An-

derson of Lehigh University indicated that a derivative of indene was an important constituent.

Other lines of attack, including attempts to convert some of the bodies into substances that could be identified and from the constitution of which the gum compounds could be deduced, were also unsuccessful.

The only method that gave any definite results was pyrogenetic decomposition. It was found possible to control the violent decomposition of the gums sufficiently so that both the gases and liquids formed when the gums were heated alone and with alkalis could be collected.

The gases contained nitric oxide but very little nitrogen peroxide. They also contained volatile amines, nitrogen, methane, illuminants (hydrocarbons absorbed by bromine water), hydrogen, carbon dioxide, carbon monoxide, and oxygen.

The liquids, which usually amounted to not more than 1 per cent of the weight of the gum decomposed, were divided into three classes—hydrocarbons, phenols, and bases. Of the hydrocarbons, cyclopentadiene was probably present, indene was readily identified, and a number of aromatics and naphthalene derivatives were present. Of the phenols, phenol, *p*-cresol, and carvacol were identified. Of the liquids amines, pyridine, isoquinoline, and 7-methylquinoline were identified. At least two chain diamines were believed to have been present, but only their picrates were successfully prepared and their identification was accordingly incomplete.

The basic nitrogen makes the inexplicably low nitrogen content of the natural gums a still greater obstacle to the postulation of a plausible reaction to explain their direct formation from oxides of nitrogen.

The form in which the isolated hydrocarbons and phenols were present in the gum was not established. The ring nitrogen compounds were present as substituted polycarboxylic acids. It is a characteristic of these acids that they give carbon dioxide and the base when heated with lime. However, the compounds in the natural gums must have been heavily substituted since the simple acids should have been easily isolated if present. No attempt to isolate an acid either free, as a salt, or as an ester or other derivative was successful. The presence of several carboxyl groups helps to explain the high oxygen content of the gums.

Nevertheless, the ease with which the gums break up to give carbon dioxide and an amine with a strong pyridine-like odor makes an excellent confirmatory test for vapor-phase gums. The test has failed on but one sample on which it was tried.

The known reactivity of unsaturated hydrocarbons, particularly the dienes, had led to the natural assumption that the gums were the end products of some reaction or chain of reactions starting with a diene and an oxide of nitrogen. It is possible for a ring nitrogen compound to be formed by the loss of water from an unsaturated oxime, but the probabilities are that the ring nitrogen compounds in the gums represent such compounds originally present in the gas. It will be shown that such compounds form gum particles at a rate comparable to very reactive dienes.

The problem of the composition of the natural gums was also attacked from the synthetic side. As a preliminary to the preparation of compounds in the vapor phase, a number of bodies were prepared by treating the different fractions of gas condensate in alcohol solution with ethyl nitrite and sodium. From each fraction at least one body was isolated which was similar in physical appearance to the natural gums after solution in alkali and precipitation with acid. The nitrogen contents were of the expected order, varying from 8.5 to 15.2.

Next, cyclopentadiene, styrene, and indene fractions of condensate were vaporized with nitrogen and treated with



nitrogen peroxide under conditions simulating those prevailing during the formation of gums in the distribution system, except that the concentrations of the reactive components were greatly increased.

Reaction products were recovered in each case. In attempting to purify the products for analysis, it was found that they were very unstable and gave off large quantities of oxides of nitrogen. The end products had nitrogen contents of approximately 5 per cent.

In view of the difficulties involved in this work and of the pressing necessity for developing a method for the practical control of the gum problem, it was decided to postpone further work on the identification of the natural gums.

Summing up the information gained from the work outlined above and from other observations, it seems fair to conclude that the natural gums are the products of the reaction between oxides of nitrogen and reactive unsaturated hydrocarbons such as cyclopentadiene and indene, and probably also to a lesser extent of phenols and some ring nitrogen bases such as pyridine. The reaction with the oxides of nitrogen is but one step in the formation of the gum as it is found in the distribution system. Subsequent steps involve polymerization and oxidation and probably adsorption, as well as the loss of a portion of the originally combined nitrogen. At least a portion of the oxidation involves the formation of polycarboxylic acids.

Since this work was done, Thoma (12) has referred briefly to somewhat similar work in Germany. He prepared gum by adding nitrogen oxides to gas. The prepared product was similar to the natural gums with the "single difference from the formerly found bodies that it contained about twice as much nitrogen as the others." It is interesting to note that the gum compounds found in Germany are also low in nitrogen.

#### FORMATION OF GUM PARTICLES IN THE VAPOR PHASE

Even before attempting to prepare a sufficient quantity of synthetic vapor-phase gum for microanalysis, the formation of gum particles under different conditions was followed by observing their diffraction images with the ultra-microscope.

The equipment used was a Ziegmondy-Siedentopf ultra-microscope. A number of these instruments were purchased, and one was mounted on a truck so that the formation of gum particles could be observed not only in the laboratory but anywhere in the distribution system of Philadelphia and of other cities within a reasonable distance. Figure 3 shows one of the portable ultra-microscopes.

Fractions of gas condensate were vaporized with nitrogen or hydrogen, and nitric oxide, nitrogen peroxide and nitrous oxide, or oxygen was added. Where nitric oxide was used,

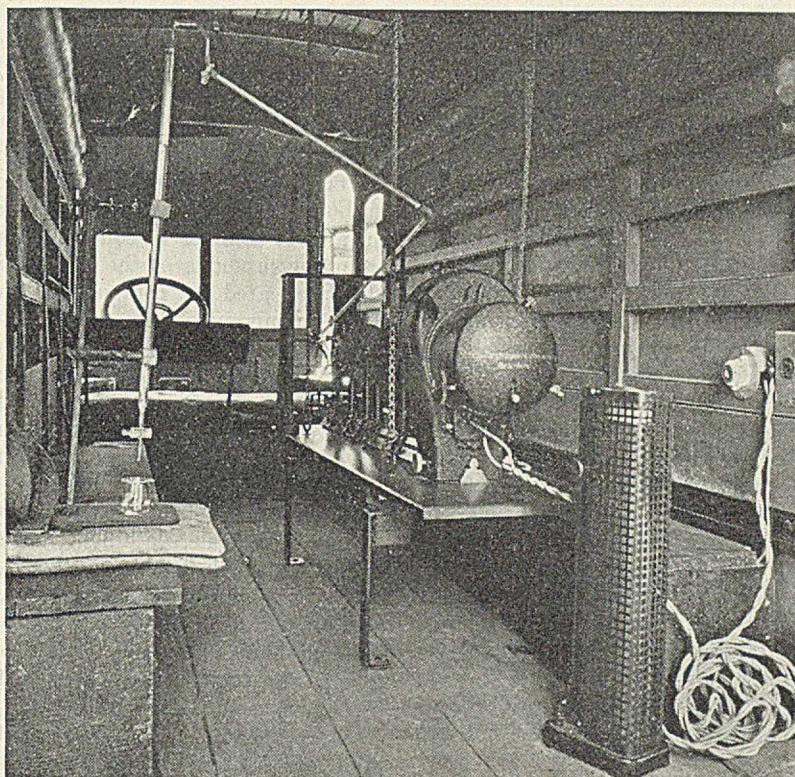


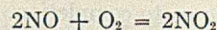
FIGURE 3. PORTABLE MOUNTING OF ULTRA-MICROSCOPE IN TRUCK

tion of nitric oxide by the oxygen in the gas; it can result from the action of nitric oxide itself; or it can be caused by the action of both nitric oxide and nitrogen peroxide. These four possibilities may be condensed to the question—will nitric oxide react of itself or is the presence of nitrogen peroxide or oxygen necessary?

TABLE IV. FORMATION OF GUM PARTICLES IN THE VAPOR PHASE

BOILING RANGE OF FRACTION OF GAS CONDENSATE ° C.	DISPERSING MEDIUM	PARTICLE FORMATION				
		NO alone	NO + O <sub>2</sub>	NO <sub>2</sub>	N <sub>2</sub> O + O <sub>2</sub>	O <sub>2</sub> alone
Below 75	Nitrogen	*	**	*****	0	0
75-120	Nitrogen	0	**	*****	0	0
75-120	Hydrogen	*	**	*****	0	0
120-160	Nitrogen	0	*	*****	0	0
120-160	Hydrogen	0	*	*****	0	0
160-200	Nitrogen	**	**	*****	0	0
Whole condensate	Nitrogen	***	****	*****	0	0

In Germany where an extensive study of a similar problem is now under way, it seems to be assumed, a priori, that only nitrogen peroxide will form gum. This laboratory was unwilling to make such an assumption. In fact, there is a seemingly sound argument against it. Gas free from nitrogen peroxide was known to form gum. The constants for the reaction velocity of the reaction



are well known at higher concentrations of nitric oxide and can be extended with reasonable accuracy to the low concentrations involved in this work. Calculations showed that the rate of nitrogen peroxide formation was theoretically too slow to account for the rate of gum formation in gas containing small quantities of nitric oxide and oxygen, but substantially free from nitrogen peroxide. For example, assuming 0.092 grain of nitric oxide per 100 cubic feet (2.3 mg. per cubic meter) and 0.7 per cent oxygen, calculations show that it would require 9 hours to oxidize even one per cent of the nitric oxide. It would require nearly an hour to oxidize 0.1 per cent.

0.8 per cent oxygen was later added. The number of particles formed per milliliter of gas was counted after different periods of time. In Table IV the results are summarized, the number of asterisks indicating roughly the approximate ratio of the number of gum particles.

When the fact that oxides of nitrogen caused the formation of gum particles was first established, a natural question arose—which oxide of nitrogen? If nitrous oxide is omitted, four possibilities are open. The trouble can be caused by nitrogen peroxide already present; it can result from nitrogen peroxide not originally present but formed by the oxida-



The nitric oxide used in the experiments summarized above and in many others was as free from nitrogen peroxide as it was possible to make it. Before use it was thoroughly scrubbed with strong caustic potash solution in Freidrich wash bottles. Every effort was made to provide nitrogen and hydrogen as free as possible from oxygen.

The results indicate that nitric oxide did form gum particles. Nevertheless, it could still be argued that the results were not caused by the nitric oxide itself, but by traces of nitrogen peroxide formed from it and extremely small traces of oxygen which persisted through all attempts to remove it. In answer to the known rate of nitrogen peroxide formation, the possibility that the reaction is catalyzed by something in the gas or by gum particles after they are formed, or that the removal of nitrogen peroxide as rapidly as it is formed constantly upsets the equilibrium can always be advanced. Later results have proved the catalytic theory. There are substances in gas which catalyze the oxidation of nitric oxide to nitrogen peroxide. These have been identified and will be discussed in connection with their effect on the method of analysis used by this laboratory. In some cases substances are also present which catalyze the gum-forming reaction. Time curves for the formation of gum particles to be shown later also indicate an autocatalytic effect.

The question is of great theoretical interest and of some practical importance. It is obvious that if nitric oxide itself does not react, one method of curing the gum problem would be to remove the oxygen in commercial gas.

Gas treated for oxygen removal by available processes and reported free from oxygen by available analytical methods may still contain oxygen in excess of that required for the oxidation of the small quantity of nitric oxide present. In view of this and of other experimental difficulties involved, the following statement seems all that is warranted: In gas from which nitrogen peroxide and oxygen have previously been substantially removed, nitric oxide will form gum particles provided the other necessary reactive compounds are present. The rate of formation will be much slower than would be observed if appreciable quantities of oxygen were present. The particles formed will be smaller and will tend to remain dispersed in gas for a longer time than particles formed either when relatively large quantities of oxygen are present or from nitrogen peroxide added to gas as such. It has not been proved definitely whether the nitric oxide reacts itself or only after oxidation to nitrogen peroxide by minute traces of oxygen. Any statement in this paper regarding the reaction of nitric oxide should be read in the light of this paragraph.

Further facts are that nitrous oxide does not form particles from any fraction of gas condensate and that nitrogen peroxide forms particles rapidly and in large numbers from all fractions.

Normally, the quantity of oxygen present in manufactured gas is many times greater than that necessary to oxidize all of the nitric oxide present, if other conditions are such as to permit the reaction to go to completion.

In view of these and other considerations, there is eminent justification for the conclusion that the bulk of the vapor-phase gum formed naturally in manufactured gas is the result of the reaction of nitrogen peroxide previously formed by the oxidation of nitric oxide.

There is also justification for the statement that in all probability vapor-phase gum would not be formed in sufficient quantities to cause trouble in the distribution of manufactured gas were it not for the fact that the reaction  $2\text{NO} + \text{O}_2 = 2\text{NO}_2$  is strongly catalyzed by certain conjugated diolefins, such as butadiene and cyclopentadiene, which are normally present in manufactured gas. The mechanism of the reactions involved in the catalytic oxidation of nitric oxide to

nitrogen peroxide, and the subsequent reaction of the nitrogen peroxide to form gum particles is extremely important. This phase of the investigation is being actively prosecuted, and it is hoped that the results may be described at a later date.

In order to determine whether the reaction with oxides of nitrogen was confined to the reactive unsaturated hydrocarbons in gas, the effect of nitrogen peroxide was observed on a large number of compounds which have been isolated from the products of the carbonization of coal or are very closely related to compounds which have been isolated. These compounds were vaporized in nitrogen. The mixtures were examined for particles, nitrogen peroxide was added, and the number of particles formed was counted after different intervals of time. In no case were particles observed before the addition of the nitrogen peroxide. In all cases in which organic compounds were used, particles were formed in varying numbers. The compounds used included: ethane, butane, decane, ethylene, amylene, butylene, decene, butadiene, decadiene, benzene, mesitylene, toluene, xylene, acenaphthene, anthracene, naphthalene, cyclohexane, cyclohexene, cyclohexadiene, tetrahydronaphthalene, acetonitrile, benzonitrile, aniline, pyrrole, pyridine, picoline, carbon disulfide, phenyl mercaptan, thiophene, phenol, cresol, naphthol, benzoic acid, anthranilic acid, butyraldehyde, and methyl ethyl ketone.

In a number of cases the gas mixtures were passed through pilot lights to determine if the particles formed would stop up the lighters in a way similar to that observed with natural gums. The particles formed from amylene, pyrrole, pyridine, picoline, and carbon disulfide stopped the pilots in less than 17 hours. Those formed from benzene, toluene, and xylene caused outages in 30 to 45 hours. The quantity of gum on the needles varied from 0.002 to 0.05 mg.

The proof that such a large number of compounds found in varying quantities in the products of the carbonization of coal will form gum particles when exposed to nitrogen peroxide showed one reason for the difficulties encountered in the task of identifying the components of natural vapor-phase gum.

From a scientific standpoint, it is to be regretted that the identification work has not been completed. From a practical point of view it is not of such great moment because the formation of gum deposits in the gas distribution system can be prevented, and this was the primary object of the investigation. The publication of the results of this laboratory's investigation and a description of the method for removing nitric oxide have been delayed in the hope that the identification work could be included in the logical order of presenting the facts of the problem. It has now been decided to report the completed phases and to leave for a later date the publication of further identification work and certain other subjects such as analytical methods.

#### SUSPENSION OF PARTICLES FORMED BY OXIDES OF NITROGEN

The nature of the particles formed under different conditions is of importance not only because of the theoretical interest but from a practical standpoint. One of the earliest of the attempts made by this laboratory to remove gum particles from gas was by the use of various filters. It was found that the particles that put out pilot lights would pass through most filters. Although certain filters such as the denser types of alundum and some of the newer types of filters remove many of the particles, the use of filters for the control of the gum problem has too many limitations to be of general value.

Later it was found that if the particles were below a certain size they would pass through the pilot lights, and that if they



were above a certain size they would not remain dispersed in the gas long enough to reach the pilots. This is obviously of the utmost importance.

The results of some experiments on the suspension of particles are given in Table V. The different fractions of gas condensate were vaporized into nitrogen in the approximate concentrations in which they occur in town gas (mixture of coke-oven and carbureted water gas). The nitric oxide and nitrogen peroxide were added at the rate of 10 grains per 100 cubic feet (246 mg. per cubic meter).

TABLE V. SUSPENSION OF PARTICLES FORMED FROM OXIDES OF NITROGEN

Fraction, °C.:	(In thousands of particles per ml.)					NO Mixture
	Below 75	75-120	120-160	160-200	Mixture	
TIME Min.						
10	30	80	70	130	225	10
15	120	140	80	180	350	23
30	285	190	100	220	450	33
45	365	190	80	210	420	48
60	400	145	30	180	340	33
90	390	...	...	10	70	29
120	330	...	...	...	...	25
19 hours	12	...	...	...	...	..

From a practical standpoint the results mean that, in general, the most dangerous oxide of nitrogen, as far as gum troubles in the distribution system (as contrasted with the formation of gum before the gas leaves the plant) are concerned, is nitric oxide. The slow reaction and long suspension are ideal for the formation of particles that will stop pilot lights.

It would also appear that, if a town gas contains sufficient indene, the oxides of nitrogen should react rapidly and produce particles tending to drop out before the gas reaches the customer's appliance. Other variables have so far prevented a satisfactory confirmation of this prediction in observations made on different types of gas.

#### FORMATION OF VAPOR-PHASE GUM IN CITY GAS

The concentration of oxides of nitrogen in the three common types of manufactured gas varies over very wide limits. Concentrations of 0.15, 0.25, and 0.75 grain per 100 cubic feet (3.7, 6.1, and 18 mg. per cubic meter) are considered high for carbureted water gas, coal gas, and coke-oven gas, respectively. Although both the oxides of nitrogen and the organic compounds necessary to the formation of vapor-phase gum are normally present in all types of manufactured gas, serious trouble from vapor-phase gum occurs most frequently in coke-oven gas.

There are two reasons for this fact. In the first place the quantity of oxides of nitrogen formed in the proper operation of a water gas set is small. Secondly, the removal of nitric oxide from water gas is much easier than from coke-oven gas. Water gas plants are not entirely immune to vapor-phase gum trouble, however, and in one situation studied the authors observed crude carbureted water gas with a nitric oxide content higher than that normally found in crude coke-oven gas.

Examples have been given of the results obtained in the laboratory experiments in which oxides of nitrogen were added to various gas mixtures prepared for the purpose. The result of this type of experiment, and of others in which the formation of particles in city gas was studied, explained many of the observations made in plant surveys. For example, the fact that nitrogen peroxide is normally not found in appreciable quantities in manufactured gas is due to its tendency to react rapidly with organic compounds to form relatively large gum particles. The fact that gum particles are still found dispersed in the gas by the time it reaches the cus-

tomers' appliance is due to the fact that the particles formed from nitric oxide are sufficiently small to be able to remain dispersed in the gas for relatively long periods of time and also to the fact that the steps involved in their formation from nitric oxide are so slow that the reactions may not even be complete before the gas reaches the restricted orifices of the appliances.

The laboratory results also explained such apparently unreasonable observations as that sometimes no particles were found in gas before it entered a holder and large numbers were found when it left the holder, and that sometimes larger numbers were found in the inlet gas than in the gas at the outlet of the holder. The question of time, or rather the age of the gas, is the most important factor in such observations, although temperature, oxygen content, type of gas, and other variables play a part. If gas containing nitric oxide and no particles is stored for a long enough time, it will eventually contain no nitric oxide and few particles. In the intervening period the gas will have passed through a definite cycle. Nitric oxide will have been oxidized to nitrogen peroxide, and the nitrogen peroxide will have reacted so that both will have disappeared. Particles will have formed, their number will have increased, their size will have increased, and they will have settled out of the gas. What is observed in an examination of the gas will depend entirely on the particular phase of the cycle at which the observation is made. It is assumed that, if gas were stored for a sufficiently long time, the number of suspended particles would approach zero. The time required, however, would be quite long. This laboratory has kept gas under observation for 3 weeks, and particles were still observed at the end of that time.

#### SUSPENSION OF PARTICLES IN CITY GAS

The formation and suspension of gum particles in manufactured gas are illustrated in typical observations made with the ultra-microscope on three types of town gas shown in Figure 4. Each gas contained the normal quantity of oxygen and the quantity of natural nitric oxide in purified gas, nothing having been added to the gas as it would normally enter the holders. The concentrations of nitric oxide were 0.0086, 0.0092, and 0.013 grain per 100 cubic feet (0.21, 0.23, and 0.32 mg. per cubic meter) for the carbureted water, coke-

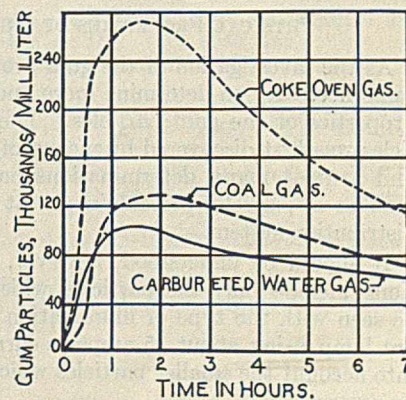


FIGURE 4. FORMATION AND SUSPENSION OF GUM PARTICLES IN CITY GAS

oven, and horizontal coal gases, respectively. The curves for all three types of gas are somewhat similar.

The rate of formation of gum particles is at first slow. An apparently autocatalytic effect is then observed. As a result the particle count increases very rapidly, reaching a well-defined maximum after a period of 80 to 120 minutes, depending upon the concentration of the oxides of nitrogen and the type of gas. The number then begins to fall off rapidly. Later the rate of formation and number of particles remaining in suspension taper off. Probably the formation of some small particles would continue as long as a finite quantity of nitric oxide remained, and it has been demonstrated that some particles will remain suspended in gas for a long time.



The shape of three curves shown is typical, although the time required for the number of particles to reach a peak is sometimes shorter or longer.

The rapid acceleration in the rate of particle formation in the first 2 hours seems to point to an autocatalytic effect, but the study of the rate of formation of gum particles is complicated by the fact that in certain types of gas, substances which catalyze the gum-forming reaction are present.

The mass of gum particles formed in a given time from nitric oxide can also be explained only on the basis of catalysis. Both the known rate of formation of particles from nitric oxide in the absence of appreciable quantities of oxygen, and the known rate of the oxidation of nitric oxide to nitrogen peroxide are too slow to account for the observed facts. Consequently, it was early assumed that oxidation of nitric oxide was catalyzed either by the gum particles themselves or by some constituent of the gas. The fact that the nitrogen peroxide starts to react almost instantly on its formation and is thus constantly being removed from the sphere of the oxidation reaction, resulting in a continuous change in the equilibrium of this reaction, is not sufficient to account for the rate of particle formation.

#### EFFECT OF NITRIC OXIDE CONCENTRATION ON PARTICLE FORMATION

It is obvious that the rate of formation of gum particles must be some function of the nitric oxide concentration. There are so many other variables, however, that, unless a thorough knowledge of each were at hand, it would be of little value to attempt to discuss the effect of concentration in anything but the most general terms. To give a rough idea of the effect, it may be stated that with a nitric oxide concentration of more than 0.03 grain per 100 cubic feet (0.74 mg. per cubic meter) the peak of the particle formation will be reached in from 20 minutes to 2 hours, while with a concentration of 0.003 grain or less, 18 to 20 hours are required.

#### PHYSICAL PROPERTIES OF GUM PARTICLES

As the investigation of the gum problem proceeded, it became necessary to determine more and more of the physical properties of the gum particles. The existence of the particles was first discovered by means of the ultra-microscope, and a great many determinations have been made of the number of particles present in gas at different parts of the distribution system.

It should be understood, however, that these determinations include only the particles which are large enough to be seen with the type of illumination available—that is, an arc lamp using about 15 amperes current—and do not take into account the smaller particles which were later shown to be present.

A great deal of time was spent in attempting to determine the size of the particles, the number of neutral and charged particles, and the size and sign of the electric charge. In view of the large amount of detailed work that had been done on this problem and the fact that it is essentially physical in nature, it is planned to describe this in some other publication. Here an attempt will be made merely to outline enough of the work to explain why the particles appear to have some of the characteristics which have already been described and which will be further discussed in connection with the stoppage of pilots.

An attempt was made to correlate the counts made with the ultra-microscope with the results obtained with an Aiken nuclei counter (1). Although there is evidently some correlation, more work will have to be done before definite conclusions can be reached.

Four methods were used for determining the approximate size of the particles:

(a) The determination of the velocity in an oscillating electric field as described by Ehrenhaft (5) and de Broglie (2). This is the most convenient method for a routine determination.

(b) The Millikan method (9) which involves the determination of the velocity of the particle with and against gravity in a known electrostatic field. This method is exceedingly tedious to operate, and the apparatus required is complicated. Both of the above methods require a knowledge of a number of electric charges carried by the particles, and the correction term to Stokes law. Methods *a* and *b* involve the determination of the velocity of the particles as well as their charge.

(c) Collection of the particles in water by the use of the Greenburg-Smith impinger (7). The dispersion thus obtained was examined in accordance with Perrin's method (11), the size being calculated from the distribution of particles at equilibrium at different levels. In this method it was not necessary to know the magnitude of the charge.

(d) A modification of the Owens jet method (10), as described by the English Air Pollution Committee, which seemed to be the most direct method. By enlarging the size of the sample taken, it was possible to deposit the gum on a cover slip and actually weigh the mass of gum thus collected on a microbalance. The cover slip was then photographed, using dark-field illumination, and the photographs were projected so that it was possible to make an accurate count of the number of particles.

Assuming a reasonable efficiency in the collection of particles, the fourth method seemed to give the most direct determination of the number, mass, and therefore the average size of the particles, but the labor involved was very great. One determination required several weeks' work.

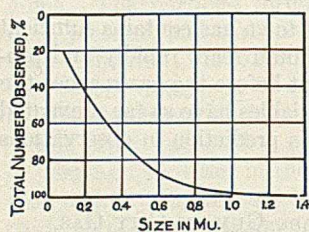


FIGURE 5. OGIVE CURVE SHOWING APPROXIMATE DISTRIBUTION IN SIZE OF PARTICLES VISIBLE UNDER ULTRA-MICROSCOPE

The approximate distribution in size of particles visible in the ultra-microscope is shown in an ogive curve in Figure 5. The particles when first formed are believed to be—or at least to approach—molecular in size. They are formed in enormous numbers, are highly mobile, and carry either positive or negative electric charges. As a result of the large number and high mobility of the particles, collisions are frequent and the particles coalesce. This continues until the particles which were individual molecules or aggregates of not more than a few molecules are of a size sufficiently large to be visible in the ultra-microscope.

The ultra-microscope was used with arc lamp illumination. When first observed under these conditions, the particles are about  $0.1 \mu$  in their largest dimension (apparent diameter). The movement and coalescence of the particles continue until they reach a size of about  $1 \mu$ . As their size approaches this value, they begin to drop out of the gas with great rapidity. Few particles above  $1.5 \mu$  remain dispersed in the gas.

As the number of particles falling out of the gas increases, the opportunities for collision between particles remaining dispersed continually decrease. This fact, together with a progressively slower rate of formation as the quantity of available oxides of nitrogen approaches zero, presumably accounts for the persistence with which some small particles remain in suspension after weeks of storage.

Wherever visible particles are referred to and whenever figures for the numbers of particles are given in this paper, they are of the size observed with arc lamp illumination in the ultra-microscope,  $0.1$  to  $1.5 \mu$ .

The number of visible particles in gas that contains or has contained a few thousandths of a grain of nitric oxide per 100 cubic feet is very large. The figure of 270,000 per milliliter



shown for coke-oven gas in Figure 4 is equivalent to  $7.1 \times 10^9$  per cubic foot ( $2.7 \times 10^{10}$  per cubic meter). The maximum number observed in gas to which no oxides of nitrogen had been artificially added was  $10^{11}$  per cubic foot. In experimental work, in which nitrogen peroxide was added to gas, the count sometimes reached  $10^{14}$  per cubic foot ( $3.8 \times 10^{16}$  per cubic meter).

Various observations had indicated the probability that the particles when first formed were far too small to be observed in the ultra-microscope. The ratio between the number of invisible and visible particles is of considerable interest as indicating to some extent the probable tendency of the gas to cause stoppages.

This subject was investigated with apparatus of the type developed by McClelland (8) and used in studying the large and small ions in the air. Essentially, the method consists in passing a known volume of gas between two concentric brass tubes suitably insulated and charged to a definite difference of potential and measuring the current carried by the particles. Two sets of tubes are used in series. A short tube with a relatively weak field is first used to throw out the small charged particles and then a longer tube with a high voltage designed to throw out all of the particles. The field can be imposed on either tube separately or simultaneously.

The currents involved are of the order of 2 to  $170 \times 10^{-13}$  ampere. The first apparatus involved the classical electrometer set-up, using a Dolazeniak electrometer. This equipment requires delicate adjustments and a firm foundation to eliminate vibrations. The results were sufficiently interesting to justify designing a rugged and portable apparatus set-up. This has been so successfully accomplished that the whole apparatus, together with the necessary ultra-microscope, batteries to supply the necessary currents, and auxiliary equipment, have all been mounted on a 2.5-ton truck. The equipment used for measuring the very small currents involved consists of an interesting application of a pliatron tube. The set-up permits measurements to be made with a robust type of microammeter. The equipment has permitted observations to be made not only in the laboratory but throughout the Philadelphia distribution system and even at a point 125 miles from the laboratory.

It is hoped to be able to present a clearer picture of the distribution of the electric charges at a later date. Certain significant facts have already been established. It has been found that, when gas leaves the plant still containing nitric oxide—for example, of the order of 0.008 to 0.025 grain per 100 cubic feet (0.2 to 0.61 mg. per cubic meter)—the number of particles continues to increase for a distance of 4 or 5 miles (6.4 or 8 km.) and then falls off. During the interval when the particle count is still increasing, the ratio between the currents set up by the small particles and by the large particles is high. Two determinations gave a ratio of 5.5 and 6.6.

This confirms results of the laboratory investigation to the effect that the gum when first formed is produced in the form of a very large number of highly mobile charged particles too small to be seen with the ultra-microscope.

On the contrary, observations made on gas from which all the nitric oxide had been removed before it left the plant showed that the number of particles gradually decreased throughout its passage through the distribution system. The ratio between the currents is very much lower, being of the order of 1.6 compared to 6 for the gas containing nitric oxide as it leaves the plant, showing the smaller number of invisible particles under these conditions. This type of work is being continued. It has many interesting possibilities. It is believed that it will ultimately be possible to present a complete picture of the changes involved from the moment of formation of a gum particle to the ultimate deposition of a large particle aggregate.

#### ACKNOWLEDGMENT

Credit should be extended to E. H. Smoker of this laboratory for work on certain phases of the effect of catalysts on the oxidation of nitric oxide and to J. R. Sken of this laboratory and W. E. Stackhouse of the United Gas Improvement Company's physical laboratory for carrying out some of the work summarized in this paper, particularly in connection with the determination of the physical properties of the gum particles.

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## MANY NATIONS SEEK SELF-SUFFICIENCY IN MOTOR FUEL

The determination of many nations to become as self-sufficient as possible with regard to motor fuel is evidenced by the numerous plans in operation throughout the world to obtain this essential commodity synthetically from domestic sources, according to the Chemical Division of the Department of Commerce.

While many products for admixture with gasoline have been tried, alcohol, benzene, and menthanol appear to have been the most successful. In Germany progress has been made in producing gasoline from coal. Recent reports state that, after three years' experimental research, a British company capitalized at £1,000,000 will establish 20 plants at different points, which are expected when completed to produce 6,000,000 gallons per annum.

In practically every instance it has been necessary to support the production of synthetic motor fuel either through govern-

ment subsidy or by legislation requiring certain percentages to be mixed with gasoline. In some countries plans have been promoted and discontinued as impractical, but in many, notably Germany, laws regarding the uses of substitutes stand, and in at least one legislation is pending.

Several reasons are put forth for the encouragement of substitute motor fuels, chief of which are national defense and the utilization of surplus products and by-products. In England the purpose is to utilize surplus coal; in Germany, potatoes, coal, and lignite; in cane-producing countries, molasses, a by-product of the sugar industry; and in others, corn and other surplus agricultural products.

In Germany from 70 to 80 per cent of the alcohol produced comes from potatoes and by law all motor fuel must contain 10 per cent alcohol.



# Four-Year Exposure Test on White Lead Paints

W. J. CLAPSON AND JOHN A. SCHAEFFER, The Eagle-Picher Lead Company, Joplin, Mo.

**I**N 1929 The Eagle-Picher Lead Company erected a test fence for paints at Flossmoor, Ill., near Chicago, to study the two-coat painting of wood exposed out of doors. Many paint formulas were used. Most of the paints were white and of the white lead-in-oil type; a few "mixed" paints were included. There were also several gray paints derived from the white paints by tinting them with lampblack. In addition to these formula variations, other conditions varied simultaneously were: kind of wood, direction of grain, angle of exposure, direction of exposure. In all, 1232 panels were exposed. The exposure period was approximately four years, during which time six major inspections of the panels were made. The inspections and reports thereon were made by various persons. This paper presents a partial analysis covering largely statistical studies on the data obtained from this exposure test. At a later date the authors propose to report on other conclusions covering certain other variables which were present in this exposure.

## CONSTRUCTION OF FENCE

The fence consisted originally of two main sections 96 feet long and 80 feet apart running east and west, and a short section 12 feet long running north and south between the two main sections. These two main sections will be spoken of as

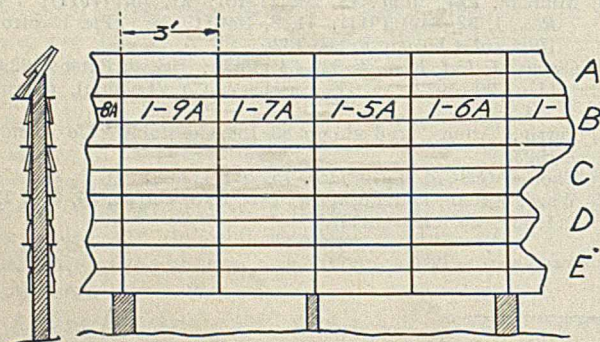


FIGURE 1. DIAGRAM OF PORTION OF NORTH FENCE

- |                            |                         |
|----------------------------|-------------------------|
| A. 45° Northern white pine | C. Northern white pine  |
| B. Redwood                 | D. Southern yellow pine |
| E. Douglas fir             |                         |

Northern white pine and redwood are bevel siding; southern yellow pine and Douglas fir are drop siding.

the north fence and south fence, respectively. The fences consisted of house siding nailed to both sides of suitable supports (Figure 1). On top of the two main sections running east and west were two boards of white-pine bevel siding set at 45° to the vertical, facing south. On the sides of these fences the two upper boards were of redwood, the next two below of northern white pine, the next two of southern yellow pine, and the two bottom boards of Douglas fir, making eight vertical boards from top to bottom. Above each two boards

*The analysis pertains to a four-year outdoor exposure test on paints, mostly of white lead base, used in two-coat work on new lumber involving four kinds of wood. Statistical studies on the effect of kind of wood, direction of exposure, angle of exposure, and pigment concentration on the appearance and integrity of the paints are presented. The optimum range of pigment concentration of second coats and of the average of first and second coats for these paints is deduced. Formulas for three white lead paints that were satisfactory for four years on the majority of the woods are cited.*

of each kind was a drip cap to prevent water from running behind the boards, and there was also a 2-inch board running along the top of the fence to prevent water from running down between the two sides of the fence.

On the north fence the wood was put on without reference to grain, but on the south the boards were placed with reference to the grain of the wood. Flat grain and edge grain were compared in the case of redwood and Douglas fir; pith side and bark side<sup>1</sup> grains were compared in the case of southern

yellow pine. On the short fence running north and south, only northern white pine with the grain at random was used. This fence was 10 panels high and 12 feet long.

There were seventeen different first-coat paints and twenty-three different second-coat paints, but out of the total possible 391 combinations, only 64 different combinations of first-coat and second-coat were used on the north and south fences. Each paint combination was used to paint a strip 3 feet wide from the top to the bottom of the north and south fences. Since on the southern exposure of either fence there were 10 (4 × 2 + 2) panels and on the northern exposure 8 (4 × 2) panels in a tier, there were in all 1152 (18 × 64) panels on the main fences.

On the short fence running north and south, four gray paints were used, the first and second coats being identical in composition. On this fence there were 80 (4 × 10 × 2) panels. This fence was removed before May 1, 1932; hence there were fewer inspections on it. The inspection data on this fence are not considered in the present analysis.

## FORMULAS

Formulas of the white lead paints were originally based on 100 pounds of soft-paste white lead which, as made at that time, consisted of 85 pounds of white lead mixed with 15 pounds of raw linseed oil. The formulas of the white lead paints converted to a common basis (85 pounds of white lead) are shown in detail in Table I. Table I also shows the pigment concentration by volume in the wet and in the dry paints. A few gray white-lead paints, and a few "mixed" paints (in which white lead was more or less replaced by other white pigments) were used; these, however, are not considered except statistically in this present analysis.

An ingredient of many paints was "flattening oil," a mixture of heavy bodied oils, drier, and thinner, the flattening oil being added so as to obtain resultant paint of proper flow and brushing consistency.

The brushing property of the various paints has been recorded in the tables with the formulas. There was considerable experimental error in the classification of the paints as to their brushing property. Part of this error may possibly be

<sup>1</sup> Pith side is the side of the board towards the center of the log, bark side is the side nearest the bark.



TABLE I. FORMULAS FOR WHITE PAINTS HAVING NO PIGMENT EXCEPT WHITE LEAD

FORMULA No.	WHITE LEAD	RAW LINSEED OIL	BOILED LINSEED OIL	FLATTING OIL BASE	(On a weight basis)				PIGMENT CONC'N BY VOL. <sup>b</sup>		BRUSHING PROPERTY	
					P. & L. <sup>a</sup> MANGANESE DRIER	COBALT LINOLEATE DRIER	TURPENTINE	NAPHTHA	Dry paint	Wet paint		
FIRST-COAT FORMULAS												
1	85	15	..	..	..	..	..	17.1	..	43.7	25.9	OK
2	85	15	..	2.0	..	0.007	..	..	11.5	40.7	28.8	Very good
3	85	36.3	..	..	0.24	..	..	..	..	24.2	24.2	OK
4	85	15	20.6	..	..	..	..	..	..	24.7	24.7	OK
5	85	23.7	..	..	0.24	..	..	8.1	..	32.6	26.3	OK
6	85	20.4	..	..	..	..	..	10.2	..	36.4	27.1	OK
7	85	26.2	..	..	0.24	..	..	5.3	..	30.7	26.0	OK
8	85	23.2	..	1.0	0.24	0.003	..	..	5.8	32.4	27.7	Stiff
9	85	20.2	..	1.3	..	0.004	..	..	7.7	35.2	28.4	OK
10	85	26.6	..	0.76	0.24	0.002	..	..	4.3	29.6	26.0	OK
11	85	15.0	11.4	..	..	..	..	5.2	..	30.7	26.8	OK
12	Formulated but not used											
13	85	15	11.8	0.76	..	0.002	..	..	4.3	29.8	26.8	OK
SECOND-COAT FORMULAS												
1A	85	15	..	..	..	..	18	..	..	43.7	25.3	Good
2A	85	15	..	1.8	..	0.006	..	..	10.1	41.0	30.0	Good
3A	85	35.4	..	..	0.24	..	..	..	..	24.6	24.6	Stiff, slow dry
4A	85	15	21.6	..	..	..	..	..	..	24.3	24.3	Stiff
5A	85	24.2	..	..	0.24	..	..	8.6	..	32.2	25.7	OK
6A	85	20.6	..	..	0.20	..	..	10.5	..	35.9	26.7	Good
7A	85	26.3	..	..	0.20	..	..	5.3	..	30.6	26.6	OK, slow dry
8A	85	22.7	..	1.02	0.24	0.003	..	..	5.76	32.6	28.0	?
9A	85	20.5	..	1.44	..	0.005	..	..	8.2	34.7	27.7	OK
10A	85	27.3	..	0.81	0.24	0.002	..	..	4.6	29.2	26.0	OK
11A	85	15.0	9.3	..	..	..	..	8.6	..	32.5	25.8	OK
12A	85	15.0	11.5	..	..	..	..	5.3	..	30.6	26.7	OK
13A	85	15.0	5.7	..	..	..	..	10.5	..	36.0	26.5	Good
14A	85	15.0	5.6	1.44	..	0.055	..	..	4.2	34.6	27.7	Good
15A	85	15.0	7.8	1.02	..	0.003	..	..	5.8	32.9	28.2	Good
16A	85	23.7	..	..	0.24	..	..	2.7	..	32.7	30.3	OK
17A	85	15.0	12.4	0.82	..	0.002	..	..	4.6	29.3	26.2	OK

<sup>a</sup> Pratt and Lambert's Patent Manganese Drier, concentrated.  
<sup>b</sup> Expressed as per cent by volume of pigment, drier considered as oil.

accounted for by the rather large variations in temperature which occurred at the time the paints were applied, but this does not seem to account for all the experimental error. In general, the total quantity of vehicle (nonvolatile plus volatile) that was required to yield proper painting consistency with white lead as pigment was 70 to 76 per cent by volume.

EFFECT OF DIFFERENT KINDS OF WOOD

APPEARANCE OF DRY NEW PAINTS. Each paint combination (first coat and second coat) was applied to all four kinds of wood on the same day; hence, although some paints were older than others when inspected on December 26, 1929 (though none was older than two and a half months), all panels involving different kinds of wood, but painted with any one combination of paints, were of the same age when inspected. Moreover, although the grain of the wood varied in some cases, grain had no effect on the appearance of the newly applied paint. Hence, we can study the effect of varying the kind of wood in the panel on the gloss of the overlying paint. At the first examination (December 26, 1929) the inspector classified panels as: glossy, little glossy, flat, nonuniform in gloss, dirty. Table II shows the relation of the appearance of the new paint to the kind of wood in the panel.

TABLE II. EFFECT OF KIND OF WOOD IN PANEL ON APPEARANCE OF NEW PAINTS

DIRECTION OF EXPOSURE	KIND OF WOOD	NUMBER OF CASES WHERE SURFACE WAS:					
		Glossy	Little glossy	Flat	Total	Non-uniform in gloss	More or less dirty
North	Redwood	12	25	18	55	9	10
	White pine	17	23	12	52	13	8
	Southern yellow pine	20	22	10	52	14	6
	Douglas fir	26	24	8	58	6	6
		75	94	48	217	42	30
South	Redwood	1	20	40	61	4	5
	White pine	3	25	34	62	9	6
	Southern yellow pine	6	35	22	63	7	5
	Douglas fir	13	33	17	63	3	1
		23	113	113	249	23	17

The effect of kind of wood on gloss is given in Figure 2. The change in flatness or glossiness is shown by the slope of the

lines. It is evident that gloss increased in the order: redwood, white pine, southern yellow pine, Douglas fir; flatness decreased in the same order. Figure 2 also shows that paints tended to be more glossy on the northern than on the southern exposure.

LIFE OF PAINTS. The last inspection made of the paints was in October, 1933, after approximately four years of exposure. At that time they were graded as to appearance, integrity, protection to the wood, and type of failure. The ratings were 1 (good) to 5 (failed). Table III shows how the various ratings of integrity were distributed with respect to the kind of wood in the panel. It is evident from Table III that southern yellow pine was the least desirable wood, while redwood and white pine rated about equally and best. Douglas fir rated about midway.

EFFECT OF DIRECTION OF EXPOSURE

APPEARANCE OF DRY NEW PAINTS. Attention has already

been drawn to the difference in effect of northern as against southern exposure on gloss. Table II shows that paints on the northern exposure had more nonuniformity of gloss and a greater tendency to collect dirt than those on the southern exposure. No doubt the lesser tendency of the paints on the southern exposure to collect dirt is connected with their greater tendency to flatness, a flat paint having less tendency to collect dirt than a glossy one.

APPEARANCE OF AGED PAINTS. Although at the time of the various examinations the inspectors used various designations to classify the paints, in general they employed five orders to indicate different degrees of excellence of appearance.

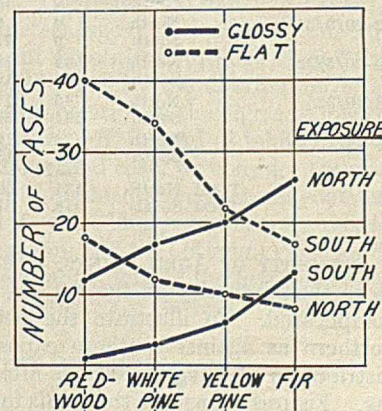


FIGURE 2. EFFECT OF KIND OF WOOD ON GLOSS OF NEW PAINTS



TABLE III. EFFECT OF KIND OF WOOD IN PANEL ON INTEGRITY OF PAINT FILM

DIRECTION OF EXPOSURE	KIND OF WOOD	NO. OF PANELS HAVING INTEGRITY RATING OF:					TOTAL
		1 (good)	2	3	4	5 (failed)	
South	Redwood	29	54	25	14	6	128
	White pine	27	57	17	24	3	128
	Southern yellow pine	1	0	12	7	108	128
	Douglas fir	5	29	27	45	22	128
North	Redwood	111	7	4	2	0	124
	White pine	117	7	6	2	0	132
	Southern yellow pine	91	20	12	5	0	128
	Douglas fir	115	7	4	2	0	128

If, therefore, we determine the distribution of panels with respect to the classification as to appearance, grouping together all panels on the north regardless of the kind of wood and all on the south regardless of the kind of wood, we find statistically the relation between appearance on the northern as against the southern exposure. Such a relation is shown in Table IV, where in the case of the northern exposure the dominant classification was towards the low end of the scale of appearance, and in the case of the southern exposure it was towards the high end. This means that the general tendency was towards better appearance on the southern exposure than on the northern. Inasmuch as the difference in appearance was due to a difference in amounts of chalking on the two exposures, it is obvious that sooner or later the paints on the southern exposure would wear down to a point where the northern exposure would have the better appearance.

TABLE IV. EFFECT OF DIRECTION OF EXPOSURE ON APPEARANCE OF AGED PAINTS

DATE INSPECTED	APPROX. AGE OF PAINT Years	DIRECTION OF EXPOSURE	TOTAL PANELS (ALL FOUR WOODS) WHERE APPEARANCE RATING WAS OF THE ORDER OF:				
			1 (best)	2	3	4	5 (poorest)
5/11/30	1	North	0	76	166	208	52
		South	0	165	232	101	14
22-29/9/31	2	North	0	95	175	240	0
		South	0	179	225	90	0
10-20/5/32	2 1/2	North	64	121	79	221	19
		South	59	199	139	79	18
28/10/32	3	North	46	178	194	94	0
		South	141	201	119	47	4
23-24/10/33	4	North	24	164	173	111	40
		South	118	133	88	75	98
Total		North	134	634	787	874	111
Total		South	318	877	803	392	134

INTEGRITY OF AGED PAINTS. The classification of paints as to their integrity on the various inspections is somewhat complicated. To illustrate the net effect on integrity of northern as against southern exposure, Table V gives the distribution of integrity ratings after four years of weathering. Figures shown are the totals for the four kinds of wood. It is evident that the dominant classification of integrity on the northern exposure was 1—that is, the highest integrity rating used.

In the case of the southern exposure, however, there were many panels in the lower ratings of integrity. Table V confirms the well-known tendency for paints to fail earlier on southern exposures than on northern.

EFFECT OF ANGLE OF EXPOSURE

APPEARANCE OF DRY NEW PLANTS. Table VI shows the effect on the appearance of the dry new paints of vertical as compared with 45° exposure, both being on the same kind of wood (white pine). In the short period of exposure (less than two and a half months) before the first inspection, 45° exposure produced less gloss, more flatness, less nonuniformity of gloss, and more dirt than vertical exposure.

TABLE V. EFFECT OF DIRECTION OF EXPOSURE ON INTEGRITY OF AGED PAINTS

(Inspection of October, 1933, only; four-year exposure)

DIRECTION OF EXPOSURE	TOTAL CASES WHERE INTEGRITY RATING WAS:				
	1 (good)	2	3	4	5 (failed)
North	434	41	26	11	0
South	62	140	81	90	139

TABLE VI. EFFECT OF ANGLE OF EXPOSURE ON APPEARANCE OF NEW PAINTS

ANGLE OF EXPOSURE	NUMBER OF CASES WHERE SURFACE WAS:				
	Glossy	Little glossy	Flat	Total	Non-uniform in gloss or less dirty
Vertical	3	25	34	62	9
45°	1	8	53	62	1
				124	47

Why the 45° exposures resulted in greater flatness in those freshly applied paints is not known; but the speculations offered above for the northern and southern exposures hold here also. The fact that, in spite of the flatter character of the 45° paints, those paints were dirtier, is independent of their flatness or gloss and is rather a consequence of the greater settling area exposed by a 45° surface to dirt as compared with a vertical surface.

APPEARANCE OF AGED PAINTS. The relation between appearance of the 45° and vertical panels (white pine) at various inspections is shown in Table VII. It is evident that in the case of any given inspection the vertical panels had, on the average, much better appearance than the 45° panels. The vertical panels tended to improve in appearance with age, as shown by (a) the tendency of the dominant rating to improve with age, and (b) the tendency towards a greater number of panels in the higher gradings as the age of the paint increased. In the case of the 45° exposures, however, there was little tendency towards improvement in appearance with age.

TABLE VII. EFFECT OF ANGLE OF EXPOSURE ON APPEARANCE OF AGED PAINTS

DATE INSPECTED	AGE WHEN INSPECTED Years	ANGLE OF EXPOSURE	NO. OF CASES WHERE RATING WAS:				WAS: Very poor
			Very good	Good	Fair	Poor	
5/11/30	1	Vertical	0	41	56	26	5
		45°	0	7	46	45	30
22-29/9/31	2	Vertical	0	41	59	24	0
		45°	0	10	47	56	8
10-20/5/32	2.5	Vertical	12	62	36	14	0
		45°	0	0	32	70	22
			1 (best)	2	3	4	5 (worst)
28/10/32	3	Vertical	47	60	20	1	0
		45°	0	16	52	58	0
			1 (good)	2	3	4	5 (failed)
23-24/10/33	4	Vertical	54	35	29	9	1
		45°	0	0	32	20	76
Total			113	239	200	74	6
			0	33	209	249	136

INTEGRITY OF AGED PAINTS. The effect of the angle of exposure on the integrity of the paint films of 45° as against vertical exposures is shown in Table VIII for white pine panels.

TABLE VIII. EFFECT OF ANGLE OF EXPOSURE ON INTEGRITY OF AGED PAINTS

DATE INSPECTED	APPROX. AGE OF PAINTS Years	ANGLE OF EXPOSURE	NO. OF PANELS FOR WHICH THE INTEGRITY RATING WAS:				
			1 (highest)	2	3	4	5 (lowest)
5/11/30	1	Vertical	22	97	9	0	0
		45°	6	97	19	5	1
23-24/10/33	4	Vertical	27	57	17	24	3
		45°	0	0	0	6	122



It is evident that in the case of these two inspections, which are representative of the others, paints on vertical panels had a much greater tendency on the average to rate high than had those on 45° panels. At the end of four years (October, 1933) most of the paints on the 45° panels had failed, while many of those on the vertical panels were still in good condition. The 45° panels, of course, were subjected to a more severe test than the vertical panels because of the greater amount of radiant energy, as well as of rain, which they received.

#### EFFECT OF PIGMENT CONCENTRATION

**GLOSS OF DRY NEW PAINTS.** It has been pointed out that in the wet paints the quantity of total vehicle which was required to yield proper painting consistency with white lead as pigment was 70 to 76 per cent by volume; expressing it another way, the pigment concentration in the wet paints ranged from 30 to 24 per cent by volume, respectively. The pigment concentration in the dry white lead paints, however, ranged from 24.2 to 43.7 per cent by volume. Let us study the effect of pigment concentration in the dry paint on the gloss of the newly applied paints (less than two and a half months old). Second coat 1A, pigment concentration 43.7 per cent, gave flat paints regardless of the first coat. However, with a constant first coat, second coats other than 1A showed no relation between gloss and pigment concentration, although possibly this may have been largely due to the varying difference in time interval between the time of application of the paints and the time of the first inspection; hence, no conclusions relative to gloss and pigment concentration of the second coat, as between varying second coats and a constant first coat, can be drawn. Similarly, with the second coat held constant, no relation between gloss of the second coat and the pigment concentration of the first coats was found.

However, a relation was found when a statistical study of second coats, regardless of first coats, was made with respect to their pigment concentration. In making this statistical study, the entire range of pigment concentration was divided into arbitrary intervals, and the pigment concentrations of second coats which had been listed as ranging from glossy to flat were rearranged to show the distribution of gloss in these intervals. The result of that statistical study is shown in Figure 3. The association of glossy paints with low pigment concentration and of flat paints with high pigment concentration is evident. This general relationship has been well known for some time. Figure 3 also shows a greater tendency towards glossy paints on the northern as compared with the southern exposure. This tendency has been mentioned above and confirms the general opinion which has been held in this matter.

this, the data to be discussed pertain only to second-coat white lead paints, to the inspection made when the panels had had two and a half years of exposure, to the southern vertical exposures, and to redwood, white pine, and southern yellow pine. The study was made along the same lines as in the statistical study of the relation of gloss to pigment concentration discussed above. In the present case there were eleven classifications of integrity—namely, 0 (failed) to 10 (excellent), inclusive. With kind of wood and direction and angle of exposure held constant, the pigment concentrations of the second coats of the paint combinations were classified according to the integrity rating given that paint combination by the inspector. The range of pigment concentration of all the

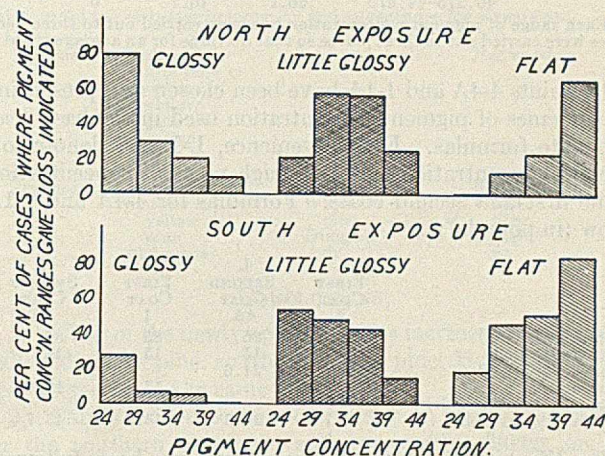


FIGURE 3. RELATION BETWEEN GLOSS AND PIGMENT CONCENTRATION

paints was divided into four arbitrary intervals. The number of cases of second-coat pigment concentrations that occurred in each of the four ranges was then noted for each classification of integrity. The results are shown in Table IX, calculated in terms of percentages. For each of the three kinds of wood, the pigment concentration range 29 to 34 per cent by volume was best, judged by the distribution of the four ranges of pigment concentration in the high and low ratings of integrity classification. If, instead of taking the pigment concentration of the second coat, we consider the average pigment concentrations of the first and second coats and employ the same data along these lines, we obtain the relation shown in Table X. It appears that the optimum value for the average of the pigment concentrations of the first and second coats lies in the range 28.275 to 32.275 per cent by volume. It

TABLE IX. RELATION OF PIGMENT CONCENTRATION OF SECOND COATS TO INTEGRITY  
(Inspected May 10 to 20, 1932)

KIND OF WOOD	RANGE OF PIGMENT CONC'N. % by vol.	PERCENTAGE OF CASES WHERE PIGMENT CONC'N. RANGE OCCURRED WHEN INTEGRITY RATING WAS:										
		0	1	2	3	4	5	6	7	8	9	10
Redwood	24-29	0	0	0	11.1	33.3	27.8	16.7	11.1	0	0	0
	29-34	4	0	10	2	0	24	32	18	8	2	0
	34-39	0	3.6	7.2	3.6	3.6	25	32.1	17.9	7.2	0	0
	39-44	16.7	8.3	8.3	16.7	16.7	16.7	8.3	8.3	0	0	0
White pine	24-29	0	11.1	11.1	22.2	22.2	22.2	11.1	0	0	0	0
	29-34	0	4	8	14	20	28	20	4	2	0	0
	34-39	0	0	17.9	14.3	17.9	8.6	17.9	7.1	0	0	0
	39-44	25.0	8.3	25.0	25.0	8.3	8.3	0	0	0	0	0
Southern yellow pine	24-29	33.3	11.1	27.8	22.2	5.6	0	0	0	0	0	0
	29-34	22	18	24	22	8	6	0	0	0	0	0
	34-39	32.2	14.3	35.7	17.9	0	0	0	0	0	0	0
	39-44	66.7	8.3	8.3	8.3	8.3	0	0	0	0	0	0

**INTEGRITY OF AGED PAINTS.** A statistical study of the relation between integrity and pigment concentration could be made large and complicated, inasmuch as separate studies would have to be made for variables such as each kind of wood, each direction of exposure, and each inspection. To simplify

is interesting to note that the range so obtained is roughly the optimum range found for second coats—namely, 29 to 34.

**LOW vs. HIGH PIGMENT CONCENTRATION IN FIRST AND SECOND COATS.** As an example of the effect of using low as against high pigment concentration in the first and second



TABLE X. RELATION OF AVERAGE PIGMENT CONCENTRATION OF FIRST AND SECOND COATS TO INTEGRITY CLASSIFICATION  
(Inspected May 10 to 20, 1932)

KIND OF WOOD	RANGE OF AV. PIGMENT CONC. <sup>a</sup> % by vol.	PERCENTAGE OF CASES WHERE PIGMENT CONC. RANGE OCCURRED WHEN INTEGRITY RATING WAS:										
		0	1	2	3	4	5	6	7	8	9	10
Redwood	24.275-28.275	0	0	0	0	16.7	50	33.3	0	0	0	0
	28.275-32.275	0	0	4.5	0	4.5	22.7	31.8	22.7	11.4	2.3	0
	32.275-36.275	0	0	2.6	10.5	13.2	26.3	29.0	15.8	2.6	0	0
	36.275-40.275	21.4	0	28.6	14.3	0	21.4	7.1	7.1	0	0	0
	40.275-44.275	33.3	16.7	16.7	0	16.7	16.7	0	0	0	0	0
White pine	24.275-28.275	0	0	16.7	0	33.3	50	0	0	0	0	0
	28.275-32.275	0	0	2.3	15.9	22.7	29.6	22.7	4.6	2.3	0	0
	32.275-36.275	0	5.2	7.9	21.1	21.1	31.6	13.2	0	0	0	0
	36.275-40.275	0	14.3	57.2	14.3	7.1	0	7.1	0	0	0	0
	40.275-44.275	50	16.7	16.7	16.7	0	0	0	0	0	0	0
Southern yellow pine	24.275-28.275	66.7	0	0	16.7	16.7	0	0	0	0	0	0
	28.275-32.275	15.9	18.2	28.5	25.0	4.6	6.8	0	0	0	0	0
	32.275-36.275	21.1	13.2	36.8	23.7	5.3	0	0	0	0	0	0
	36.275-40.275	78.6	14.3	7.1	0	0	0	0	0	0	0	0
	40.275-44.275	66.7	16.7	0	0	16.7	0	0	0	0	0	0

<sup>a</sup> Each range of pigment concentration has been carried out to three decimal places. Many of the averages had two decimal places; consequently the ranges were carried out to three places so that no value for an average could fall on the border line between two ranges.

coats, paints 4-4A and 1-1A have been chosen as representing the extremes of pigment concentration used in the basic lead carbonate formulas. For convenience, L-L will denote low pigment concentration and H-H high pigment concentration in the first and second coats. Formulas for 4-4A and 1-1A follow (in pounds):

	L FIRST COAT 4	L SECOND COAT 4A	H FIRST COAT 1	H SECOND COAT 1A
White lead	85	85	85	85
Raw linseed oil	15	15	15	15
Boiled linseed oil	20.6	21.6	..	..
Turpentine	..	..	17.1	18.0
Pigment concn. in dry paint, % by vol.	24.7	24.3	43.7	43.7

The life history of these two paints has been followed. When new, both were a good white in color. L-L tended to be glossy and H-H flat. On exposure on the 45° white pine panels facing south, L-L gave better protection than H-H, though the latter had the better appearance. On the vertical southern exposure, L-L was much better in integrity and appearance than H-H. H-H failed by chalking freely at first, then by checking, and finally by cracking and scaling; L-L failed by chalking slowly at first and then freely, checking, and finally cracking and scaling. On the northern exposure L-L gave the better protection, but H-H the better appearance. As might be expected, chalking was less free on the northern than on the southern exposure. On the whole, 4-4A was more desirable than 1-1A.

EFFECT OF REVERSING PIGMENT CONCENTRATION IN FIRST AND SECOND COATS. Several of the paints were so formulated and applied that in the case of a given pair of paint combinations substantially the only difference between them was in the relative pigment concentrations of the first and second coats; for example, we may compare the effect of applying a paint of low pigment concentration over one of high pigment concentration (H-L), with the effect of applying a paint of high pigment concentration over one of low pigment concentration (L-H), the differences in formulation being substantially in the percentage of pigment in the dry paint film. Two examples will be discussed, their life history having been followed.

As the first example of L-H as against H-L, paints 3-6A and 6-3A were chosen. The formulas for these follow (in pounds):

	L FIRST COAT 3	H SECOND COAT 6A	H FIRST COAT 6	L SECOND COAT 3A
White lead	85	85	85	85
Raw linseed oil	36.3	20.6	20.4	35.4
Turpentine	..	10.5	10.2	..
P. & L. Drier	0.24	0.20	..	0.24
Pigment concn. in dry paint, % by vol.	24.2	35.9	36.4	24.6

On the vertical exposures when freshly applied, L-H was flat to little glossy, depending on the woods, while H-L was

little glossy to glossy. The greatest difference in the weathering properties appeared in the case of the southern exposures. Here L-H had the better appearance at early inspections, H-L at later inspections. On the 45° exposures L-H had the longer life; on the vertical exposures they were about equal, except on Douglas fir where H-L was the better. On the northern exposure L-H was much the better in appearance, while H-L tended to have the better integrity. The poor appearance of H-L on the northern exposure was largely due to wrinkles.

As a second example of L-H vs. H-L, paints 4-1A and 1-4A were chosen; formulas are as follows (in pounds):

	L FIRST COAT 4	H SECOND COAT 1A	H FIRST COAT 1	L SECOND COAT 4A
White lead	85	85	85	85
Raw linseed oil	15	15	15	15
Boiled linseed oil	20.6	..	..	21.6
Turpentine	..	18	17.1	..
Pigment concn. in dry paint, % by vol.	24.7	43.7	43.7	24.3

When freshly applied, L-H had a good white color and was flat. H-L tended to be yellowish in color and nonuniform in gloss. The greatest difference in the aged paints was found on the southern exposures, where L-H was better in appearance and integrity than H-L. L-H chalked freely at first, then checked, and finally cracked and scaled; H-L chalked less than L-H, but checked, cracked, and scaled earlier than L-H. On the northern exposure there was not much difference in the two: L-H had the better appearance; there was little difference in integrity, H-L being slightly the better on Douglas fir, L-H on southern yellow pine.

So far as these two examples show, L-H paints similar to those chosen generally are preferable to H-L paints similar to those chosen; on Douglas fir, however, H-L tended to be more desirable than L-H.

#### SELECTION OF BEST WHITE LEAD PAINTS

After four years of exposure many of the white lead paints were still giving good service, being rated by the inspectors as "good" in integrity, appearance, and protection to the wood. However, the records show that, when freshly applied or after an exposure of a year or two, many of these paints were poor in appearance. By selecting only paints which were fair or better in appearance and integrity over the entire four years of exposure, many of the paint formulas are eliminated. The formulas of the paints classified as fair or better in appearance and integrity over the entire four years of exposure for each kind of wood and for each direction of exposure are shown in Table XI (45° exposures were not considered in this classification). It will be observed that the paints which conformed to the above classification differed for the different kinds of wood, as well as for the direction of exposure, but the method



by which the list of formulas was obtained is quite arbitrary and Table XI does not prove that variation in paint mixtures is required to suit the needs of the different woods. A few paints, however, gave reasonably good service on more than one kind of wood—for example, paints 3-8A, 4-15A, and 4-14A. Formulas for these paints together with the kind of wood and exposure on which they gave satisfactory service are shown in Table XII.

TABLE XI. PAINTS WHICH WERE FAIR OR BETTER IN APPEARANCE AND INTEGRITY DURING FOUR-YEAR EXPOSURE

KIND OF WOOD	DIRECTION OF EXPOSURE	FIRST COAT		SECOND COAT		
		Formula No.	Pigment concn. in dry paint % by vol.	Formula No.	Pigment concn. in dry paint % by vol.	
Redwood	South	3	24.2	5A	32.2	
		4	24.7	8A	32.6	
				4A	24.3	
				15A	32.9	
				14A	34.6	
				13A	36.0	
				1A	43.7	
			7	29.6		
			8	30.7		
			9	35.2		
			6	36.4		
			2	40.7		
					10A	29.2
					8A	32.6
				9A	34.7	
				8A	32.6	
				6A	35.9	
				14A	34.6	
				1A	43.7	
				8A	32.6	
				9A	34.7	
				2A	41.0	
White pine	South	3	24.2	5A	32.2	
		4	24.7	15A	32.9	
				14A	34.6	
				13A	36.0	
				1A	43.7	
			13	20.8		
			11	30.7		
			9	35.2		
			4A	24.3		
			3A	24.6		
		9A	34.7			
		3	24.2	8A	32.6	
		2	40.7	9A	34.7	
		1	43.7	2A	41.0	
Douglas fir	South	4	24.7	15A	32.0	
				14A	34.6	
				10A	29.2	
			11	30.7		
			3	24.2	8A	32.6
			1	43.7	10A	29.2
Southern yellow pine	South	3	24.2 <sup>a</sup>	5A	32.2	
				9A	34.7	
				8A	32.6	
				8A	32.6	
	North	3	24.2 <sup>b</sup>	6A	35.9	
		2	40.7 <sup>b</sup>	10A	29.2	
				9A	34.7	
		1	43.7 <sup>b</sup>	7A	30.6	
				6A	35.9	

<sup>a</sup> At 2.5 years; none at 4 years.

<sup>b</sup> Up to 2.5 years.

The first coats were low in pigment concentration and contained either raw oil and P. & L. Drier, or some boiled oil with the raw oil. The second coats all contained flattening oil and ranged from 32.6 to 34.6 in pigment concentration. In this connection it is interesting to compare these pigment concentrations with those derived from the statistical study on pigment concentrations, as related to integrity classified after two and one-half years of exposure (by the inspection of May 10 to 20, 1932). That study indicated the optimum range of pigment concentration for the second coats to be 29 to 34 per cent by volume. The second coats in the above three paints fall in or close to that range. Moreover, the statistical study on the relation between the average of the pigment concentrations of first and second coats as related to integrity and pertaining to the inspection of May 10 to 20, 1932, indicated the optimum range of this average to be about 28.3 to 32.3. The averages of the pigment concentrations of the first and second coats of paints 3-8A, 4-15A, and 4-14A are, respectively, 28.4, 28.8, 29.7, falling within the range 28.3 to 32.3. This

range also would include the generally recommended pigment concentration for white lead paints to be used on new lumber.

TABLE XII. THREE SELECTED PAINT COMBINATIONS (In pounds)

	FIRST COAT 3	SECOND COAT 8A	FIRST COAT 4	SECOND COAT 15A	FIRST COAT 4	SECOND COAT 14A
White lead	85	85	85	85	85	85
Raw linseed oil	36.3	22.7	15	15	15	15
Boiled linseed oil	..	...	20.6	7.8	20.6	5.6
Flattening oil base	..	1.02	..	1.02	..	1.44
Naphtha	..	5.76	..	5.8	..	8.2
Cobalt linoleate drier	..	0.003	..	0.003	..	0.005
P. & L. Drier	0.24	0.24	..	..	..	..
Pigment concn. in dry paint, % by vol.	24.2	32.6	24.7	32.9	24.7	34.6

Paints rated fair or better in integrity and appearance for 4 years on:

Northern exposure	Southern exposure	Redwood	White pine	Southern yellow pine	Douglas fir
Redwood	Redwood	Redwood	White pine	White pine	Douglas fir
White pine	Southern yellow pine	White pine	Douglas fir	Douglas fir	Redwood
Southern yellow pine	Douglas fir	Douglas fir	Redwood	White pine	Douglas fir
Douglas fir	Redwood	White pine	Douglas fir	Redwood	White pine
	Southern yellow pine	Douglas fir	Redwood	White pine	Douglas fir
	(2.5 years)				

### CONCLUSIONS

1. Gloss of the newly applied paints increased in the order: redwood, white pine, southern yellow pine, Douglas fir; flatness decreased in the same order.

2. Paints tended to be more glossy on the northern than on the southern exposure, and conversely, flatter on the southern than on the northern exposure.

3. The paints failed to the greatest extent on southern yellow pine; least, and about equally, on redwood and white pine. Douglas fir rated about midway.

4. During the four years of weathering, the general tendency was towards better appearance on the southern than on the northern exposure. In integrity, however, the paint films failed earlier on the southern than on the northern exposure.

5. Newly applied paints on the 45° southern exposure had less gloss, more flatness, less nonuniformity of gloss, and more dirt than the vertical southern exposure.

6. Paints on the 45° southern exposure showed little tendency to improve in appearance with age, as contrasted with the tendency on the vertical southern exposure.

7. Paints failed much sooner on the 45° than on the vertical southern exposure.

8. Gloss of newly applied paints was found to be associated with low pigment concentration and flatness with high pigment concentration of the second coat. No relation between gloss of the second coat and the pigment concentration of the first coat was found.

9. The optimum loading of white lead for second coats, based on a statistical study of pigment concentration and integrity rating after two and one-half years of exposure, was found to lie in the range 29 to 34 per cent by volume in the dry paint. Similarly, the optimum range for the average pigment concentration of the first and second coats was found to lie in the range 28.3 to 32.3 per cent by volume.

### ACKNOWLEDGMENT

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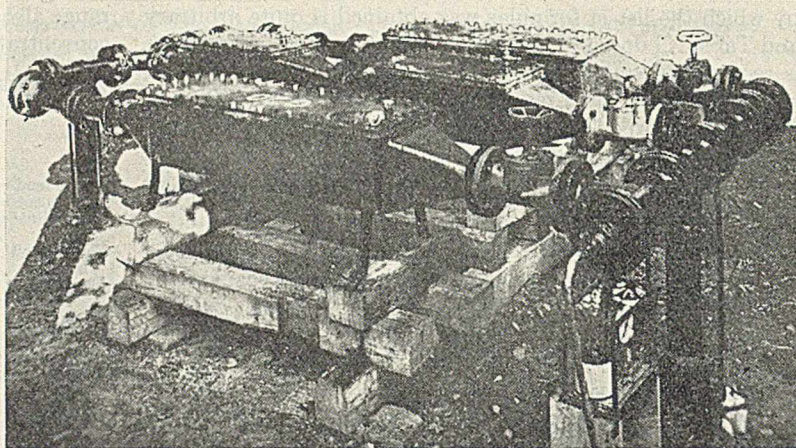


# Ionic Silver Sterilization

## Industrial Sterilization by Minute Dosages of Silver

C. H. BRANDES

405 Lexington Ave., New York, N. Y.



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TREATER FOR WATER IN AN OUTDOOR SWIMMING POOL

**M**ETALLIC silver, in concentrations so minute as to be practically undetectable by the usual methods of analysis, exercises remarkable bactericidal power but is quite without effect on human beings and the higher organisms. The concentrations required for destroying most forms of microorganisms is of the order of a few hundredths of a milligram per liter of water, for instance, and can be reached by utilizing the solution pressure of metallic silver surfaces exposed to clear water. This phenomenon, discovered by Naegeli in 1893, has been called the "oligodynamic" effect of metals.

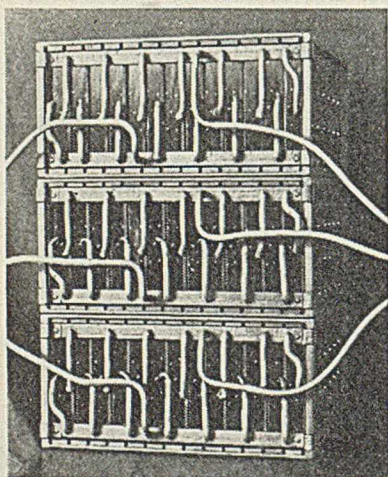
Silver, copper, and some other metals are particularly potent in this respect. The fact that silver goes thus into solution in water to a very limited extent and that this minute concentration behaves in extraordinary ways has only recently been used to produce practical results. Its industrial application has been largely the result of the efforts of Krause and his co-workers who have

surfaces be provided in contact with the water, but under these conditions at ordinary temperatures enough silver will dissolve in water in the course of a few hours at most to render it sterile and bactericidal. Not only can the exposed water destroy germs introduced into it, but it is also able to impart this property to a limited quantity of other water added to it. In other words, having once attained a bactericidal concentration of silver ions in the water, it is possible to dilute even this tiny concentration and to transfer its properties on a corresponding scale to untreated water.

Necessarily the ability to dilute the original solution without destroying its usefulness depends upon the initial concentration of silver ions in it. For the disinfection of drinking water the required concentration of silver ions is of the order of 0.050 mg. of silver per liter, or 5 parts per hundred million of water. Concentrations of this magnitude after standing for a shorter or longer period (10 minutes to several hours, depending on conditions) yield completely germ-free water. The dosage may be increased to 0.600 mg. or more of silver per liter if more prompt action is required. Such solutions of ionic silver are active germicides and may be used for cleansing and sterilizing infected utensils with safety.

For commercial purposes the natural solution pressure of

silver in water requires such an enormous amount of surface exposure of the metal or such a long time of contact that it is now the practice to promote ionic solution of the metal by inducing an electric potential between the silver plate and the liquid. For this purpose plates of relatively large surface spaced 15 mm. apart are immersed in the liquid being treated, and a direct current voltage is induced across them. The effect of the current is to

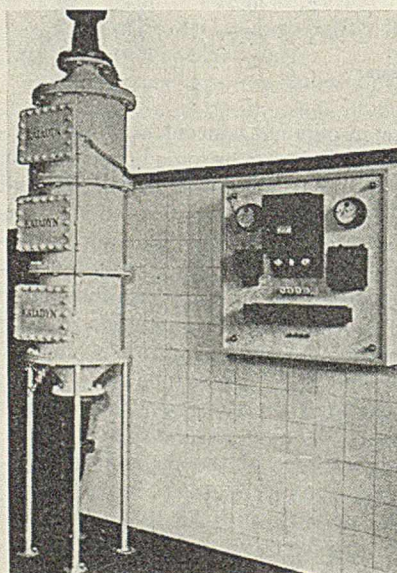


SILVER ELECTRODES FOR CHARGING  
WATER WITH SILVER IONS

made numerous installations of the equipment for this oligodynamic treatment of water and other fluids in Europe, particularly in Germany, Switzerland, and England. More recently the idea has been brought to this country, and the initial stages of its application here have attracted wide attention. The first American installation was recently made in the form of a continuous treatment for the water in the swimming pool of the Congressional Country Club in Washington, D. C.

### THE OLIGODYNAMIC EFFECT

The fundamental principles of the oligodynamic effect (so-called from the Greek words meaning force of trifles or traces) are relatively simple. The normal solution pressure of silver in water is infinitesimal, but it has a definite positive value. Its use to secure the solution of even correspondingly minute amounts of silver requires that relatively large silver



TREATMENT OF WATER FOR ICE MANUFACTURE



augment the apparent solution pressure of the metallic silver and to shorten materially the time necessary to reach the desired concentration. It is, of course, necessary to reverse the direction of the current at suitable short intervals to insure against the formation of anodic coatings of high resistance. It is also essential that the voltage drop between the two plates be kept below the decomposition potential of water (1.6 volts) to prevent waste of current.

#### LIMITING FACTORS

It has been quite definitely shown that silver under such conditions goes into solution in the ionic form and that these charged atoms of silver are the effective agents in destroying the life of microorganisms. It is necessary, therefore, that the water or other liquid be as free as possible from turbidity before treatment, since suspended particles act as nuclei

for the adsorption of the silver particles and render them incapable of functioning. If suspended particles are unavoidably present in the liquid, the quantity of silver dissolved to give any desired degree of potency must be increased to allow for this loss of ions.

Both the conductivity of the water and its pH value affect the ease of solution of the requisite amount of silver and its effectiveness in solution. It is, of course, obvious that solution of metal from the surface of silver is an electrochemical phenomenon and that its speed depends upon the concentration of dissolved solids which controls the conductivity of the water. The effect of hydrogen-ion concentration is also important but less well understood. If the pH value of the water is above 7.0 (slightly alkaline), the potency of the silver used is increased.

Even with such minute amounts of silver as are required for this treatment, there is a tendency to plate out of solution very slowly. The nature of the surface of the confining vessel apparently influences the deposition of metallic silver. Treated water kept in tightly stoppered bottles for as long as a year has been shown to retain a large part of its original germicidal potency. Some diminution in effectiveness has been noted in the samples so stored, but the loss occurs very slowly and is scarcely detectable except after a period of many months.

#### EQUIPMENT

The equipment by which this solution of silver ions is accomplished is extremely simple, since it is necessary only to bring the liquid to be sterilized into contact with the active silver surface for a sufficient length of time.

In its simplest form this requires only that water shall remain in contact with a plate of metallic silver for a short time. This may be accomplished by merely allowing a silver plate to stand in the water for 10 to 24 hours. The time required depends upon the ratio of the silver surface to the

volume of water, the conductivity and pH value of the water, and the concentration of silver ions required. However, this process is tediously long, and to improve the situation in this respect the smallest commercial electrical unit consists of two plates of silver mounted close together on a synthetic plastic handle containing a tiny dry cell. This unit is usable anywhere and is of such a size that the two

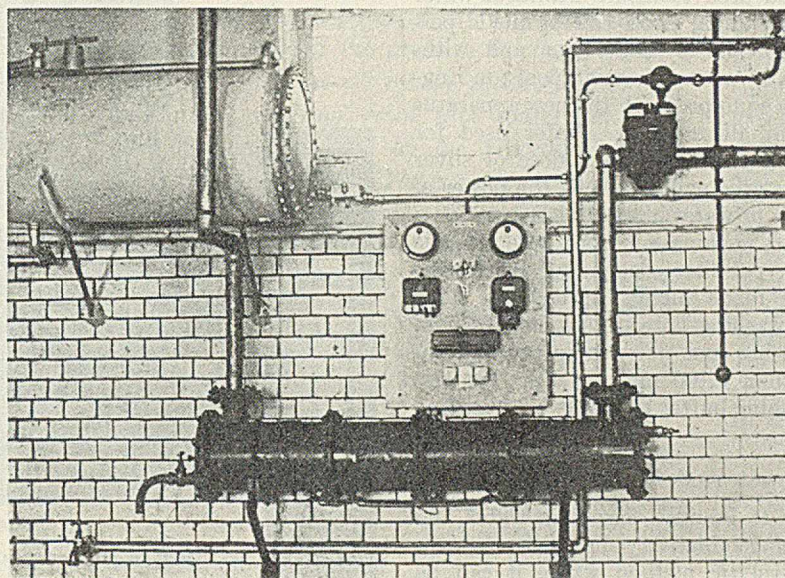
electrodes can be placed in an ordinary pitcher of clear water and is so efficient that 60 to 80 seconds are required to build up a concentration of silver ions in a liter of ordinary water great enough to sterilize it within an hour. Similarly, higher concentrations for active sterilization by washing can be reached by longer exposure.

For commercial sterilization, where larger quantities of water are to be treated, a battery of plates arranged in a chamber with

a clearance of 15 mm. is placed in the line containing the flowing water. The size of the chamber, number and area of plates, and other factors are so adjusted as to produce the desired concentration of silver ions during the passage of the water between the plates. The direct current voltage between the plates is adjusted with regard to the conductivity of the water to give maximum efficiency without reaching the decomposition point of water (1.6 volts). The amount of silver taken into solution is proportional to the current flowing according to Faraday's law, but the current efficiency is only about 50 per cent. Having installed the treating cell in the line, its performance is controlled by the rate of flow of liquid and the current passed (1 mg. of silver is dissolved per 0.5 milliampere-hour of current).

After treatment, sterilization is accomplished by allowing the treated water to stand for an appropriate period. The concentration of silver ions required depends upon the purpose of the sterilization. For clear drinking water having a pH value above 7.0, 0.05 mg. per liter is sufficient to kill all bacteria within an hour. If the water is slightly turbid or if its composition is such as to interfere with the action of the silver, somewhat higher dosages may be necessary. The water in a swimming pool can be kept permanently sterile by producing a concentration of 0.150 mg. of silver ions per liter in the make-up water added daily. To produce an actively disinfecting solution for sterilizing by washing, the concentration may range from 0.100 to as high as 0.900 mg. of silver per liter. This solution provides an effective germicide for all kinds of disinfection which is entirely noncorrosive and harmless.

The equipment for producing these effects requires practically no personal supervision. For continuous operation it is necessary merely to adjust the voltage at appropriate intervals, since the periodic reversal of current is controlled automatically, and to renew the silver electrodes not oftener than once a year.



WATER-STERILIZING INSTALLATION IN A SLAUGHTER HOUSE



## APPLICATIONS TO WATER

The usefulness of this treatment is important in a number of varied fields. Water supplies can be completely sterilized without affecting healthfulness or flavor, and once properly dosed with silver they remain sterile. The water supply of Heidelberg, Germany, is treated by this method. In contrast to such large plants, the smallest apparatus can be carried in one's pocket and used to insure healthful water wherever one may be. Swimming pools can be made permanently sterile and germicidal without odor and without toxicity for bathers. Numerous swimming pools, in England particularly, have been equipped with the new apparatus which gives satisfaction in all respects. Water used for making ice from raw water can be given a dose of silver before freezing to make it sterile and to give it the power of disinfecting fish cooled by it or water in which it is melted.

By giving water used for washing a proper dose of ionic silver (0.400 to 0.900 mg. per liter, depending on specific requirements), it may be made highly germicidal. Such treated water is used for washing hose, filters, bottles, and other utensils in the brewing and dairy industries. Concentrations of not more than 0.100 mg. per liter are also used largely abroad for washing butter to improve its keeping qualities.

## LIQUIDS OTHER THAN WATER

In applying this technic to liquids other than water and water solutions, their lower conductivity materially reduces the efficiency of the electrolytic method where it can be applied at all. Thus it is necessary to provide a large surface of silver for contact with such liquids. This may take the form of silver dispersed on an inert medium, such as silica sand or diatomaceous earth, silver foil, or silver-plated vessels, or a special form of silver dispersion (Katadyn silver) may be used. Katadyn silver is so dispersed as to have approximately 1.6 square meters of surface per gram of silver and is of a spongy structure well adapted for maximum contact with liquid. In use the silver mass is held in a suitable glass chamber, and the liquid to be treated is run through at such a rate as to produce the required effect.

In addition to its germicidal activity, ionic silver in concentrations as low as 0.015 mg. per liter has a definite effect on the acid-ester ratio of alcoholic liquids. This presumably catalytic action improves the odor and flavor of raw alcohol materially and is important to both the perfumery and the beverage trades.

## APPLICATIONS TO ALCOHOLIC AND OTHER LIQUIDS

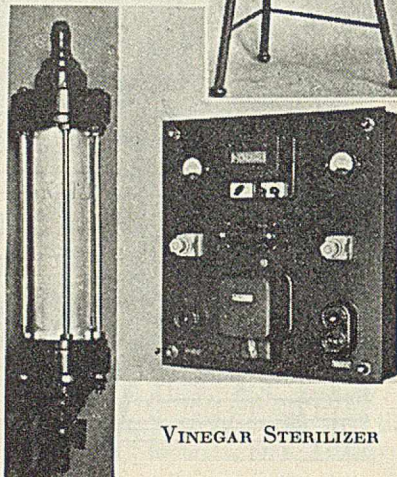
Numerous liquids produced by fermentation have a tendency to cloud by continued growth of microorganisms on standing. By introducing proper concentrations of ionic silver into them, this can be permanently prevented. In Europe some 60,000 liters of vinegar per hour are so treated to yield a product free from living microorganisms and permanently bright after filtering. Wine can be similarly freed from bacterial cloudiness. Experiments are under way to apply a similar technic to fruit juices and beer.

Alcohol solutions undergo a change when charged with

**PROJECTED ARTIFICIAL WOOL MANUFACTURE IN GERMANY.** The government policy of restricting imports of textile raw materials into Germany is causing manufacturers to search for native raw materials such as used in producing textiles during the war.

The Leipzig press reports that experiments have been conducted by a large local wool-spinning plant in the use of a domestic material as a wool substitute. This material, called "Vistra," is also known as German beech tree wool and consists of beech tree fiber. The material is spun with natural raw wool into yarn,

RIGHT: UNIT FOR TREATING ALCOHOL WITH SILVER (OXY-ESTERATOR)



VINEGAR STERILIZER

ionic silver which is somewhat similar to aging. This technic has been successfully applied to the alcohol used in perfumes where the alcoholic odor is lessened by the treatment, and to the alcohol used in liqueurs. Its applications to the improvement of the taste and odor of gin, whisky, and brandy is the subject of experiments now in progress.

The process is not expensive as compared with other methods. In the treatment of water supplies the initial cost may be somewhat greater than that of the chlorine treatment but the advantages of this method (absence of

added taste or odor) practically balance this. The treatment is much cheaper than sterilization by ultraviolet light.

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RECEIVED July 28, 1934.

in the proportion of 1 : 1. The firm states that it would be possible to produce 30 million kilograms annually of this fiber in Germany.

Suiting material spun from the yarn is claimed to have exceptionally good wearing qualities. If conditions on the wool market remain as at present, the German textile industry will thus be basically independent of foreign wool imports, not only for domestic production but also for exports of finished textiles made in part of Vistra.



# Disposal of Refinery Waste Waters

W. B. HART, The Atlantic Refining Company, Philadelphia, Pa.

LITTLE attention was paid to the disposal of industrial wastes until comparatively recent years. With mills and factories scattered, waste disposal was a comparatively simple process and no harm or annoyance resulted.

Then there came the intensely rapid growth of industry and the concentration of industrial establishments in and around population centers. In some instances the industry was the nucleus around which the population settled. The ultimate result was that industrial and residential sections were brought together and there came into existence the waste disposal problem as we know it today.

## PETROLEUM-REFINING WASTES

Petroleum refining has developed rapidly during the past thirty years. The first oil well was drilled in 1859, and the crude oil produced that year amounted to 2 thousand barrels. In 1900 production had reached 64 million barrels and in 1929 over 1 billion barrels of oil were brought to the surface. Practically all of this oil was run through the various refineries.

This marked increase in refinery operation is directly traceable to the development of the motor car, the internal combustion engine, and the use of fuel oil. Prior to 1900 gasoline was a waste. It is now a major product. One disposal problem was solved, but many others were created. Originally all crude petroleum produced was what is known as Pennsylvania grade, a very high-grade crude. Further, specifications for petroleum products were comparatively simple, and simple refining processes would make this required quality.

Then the Midcontinent, Texas, and California crude oils appeared and created new problems in refining. New processes were developed, not only because of the new crudes but also because product specifications were more difficult to meet. All these changes combined to produce waste materials that presented real problems in disposal, and in many cases the development was rather sudden. In the desire to enter attractive markets, little thought was given to anything but the quality of the product, the design of the process, equipment to produce it, and the starting of operations. Not infrequently, as soon as the operation was well under way, waste products were found to be causing water or air pollution.

Such conditions were not confined to the petroleum-refining industry alone or to industry as a whole. Cities and towns had increased in size, and the sewage load had become proportionately greater. Whereas dilution had been a satisfactory method of disposal, the increased amount of sewage created an overload. These conditions, involving both industry and population, resulted in many instances of serious water pollution.

## NATURE OF PETROLEUM REFINERY WASTES

Wastes that are gases, liquids, and solids occur in present-day oil refining. They may occur unaccompanied by other substance or may be in suspension or solution in water. Gases or vapors are produced by distillation processes, acid-treating

*This paper describes the development of the problem of the disposal of refinery waste water, the recognition of the problem by the industry, the machinery set up by the industry to combat pollution resulting from this source, and the results being obtained by the procedures which have been instituted. The various types of waste waters are described on the basis of the characteristics of the public waters which they effect, and brief reference is made to methods developed for the prevention of the pollution which would be caused by the polluting constituents of these various types of waste waters.*

operations, sludge separation, acid concentration, etc. These gases or vapors are mainly hydrocarbons of low boiling point, or sulfur dioxide or trioxide. Such gases will quickly diffuse to an unnoticeable concentration, but there are produced with them small concentrations of mercaptans and other more complex organic sulfur compounds of intense and disagreeable odor. It is these substances that are frequently the cause of atmospheric pollution complaints, particularly when diffusion is hindered by smoke, dust,

or weather conditions.

A major refinery waste is oil. It may originate anywhere in the plant from leakage or be discarded for various reasons, such as being emulsified or contaminated. It may vary in quality from gasoline to heavy lubricants.

Many refineries use large quantities of water which is discarded as waste. Most of it is for cooling purposes only and never contacts oil. This water is unimpaired. Water used in processes where it contacts oil, although constituting only a small percentage, dissolves various compounds. These compounds may be simple acids or alkalies or very complex organic sulfur compounds. Phenols may also be present. All these give the water a disagreeable taste and odor, due in most cases to the organic sulfur compounds present, although in some instances they are due to phenols.

Discarded waxes, asphalts, sludges, clays, and general rubbish make up the solid wastes.

## DEVELOPMENT OF METHODS FOR WASTE DISPOSAL

Some thought was given to the disposal of refinery wastes prior to 1919 when the American Petroleum Institute was organized. Further attention was given the subject by the Pollution Committee of the institute. Following the passage of the Federal Pollution Act of 1924 and the meeting of the International Oil Pollution Conference in 1926, the institute authorized an investigation of oil pollution in the United States. This was carried out in 1927 and revealed that pollution did occur in certain localities and that some progress was being made in its prevention. The most important finding, however, was that little was known about how to dispose of the various waste materials properly. This led to the formation of a committee of technical men from various companies, known as the Committee on Disposal of Refinery Wastes. Its duty was to develop methods which would permit disposal of waste substances without causing damage to others or causing nuisance. This committee began its work in 1929, taking up first the disposal of waste water containing oil. The literature was scanned for information but the result was not encouraging. It was evident that the matter was a pioneering one.

The information gathered in the 1927 investigation was taken as a starting point. Equipment for separating oil from waste water, called "separators" or "oil traps," was known to vary greatly in design. Also, certain designs were effective and others not. To determine how much oil was really



present in the effluent of the separators that were considered acceptable, required a testing method. After considerable study a method using solvents was devised. Using this test, the most effective separators were definitely identified and their design studied, together with conditions of the water into which they discharged, as to oil films, oil markings, etc. Velocities, eddy currents, and general conditions within the separators were also studied. It was found that in all cases, low velocity and particularly freedom from eddy currents were essential to high effectiveness.

But all separators discharged some oil with the effluent water, whereas laws covering the situation all specify "no oil." It is practically impossible to meet this specification unless it is construed to mean no visible oil film such as is usually recognized as oil pollution. Based on the information obtained during the separator studies, a limit of 30 parts of oil per million parts of effluent was set. This concentration was found not to cause visible film and is probably quickly eliminated by oxidation.

A separator design specification was then developed and laboratory-size equipment with glass sides constructed so that the effectiveness could be studied. Certain modifications were found necessary, and final design data were assembled.

Actual applications of these data were made at the Philadelphia Refinery of The Atlantic Refining Company. Three large separators were modified to meet the recommendations. The results were highly satisfactory.

Oil separators of this type function on the specific gravity differential between the water they are to discharge and the oil they are to retain. Obviously, emulsions of oil and water pass on through. The committee, therefore, started work on methods for "breaking" the various types of emulsions that occur in refinery practice. Much of this research was conducted by the Research Laboratories of The Atlantic Refining Company, and the methods developed were tested at the Philadelphia Refinery. The methods vary with the type of emulsion. In some cases heat alone is all that is required, while in others a change in pH followed by a floc clarification of the water is necessary. In any event the separated oil is retained, and only water discharged to the separator or a mixture of water and oil in "free" form is discharged so that the separator can properly function.

In 1931 the American Petroleum Institute published the work of its Committee on Disposal of Refinery Wastes as Section I of what is to be a complete manual (1). This section gives in detail the various methods for proper disposal. This publication is available from the institute.

While preparing the publication on waste waters containing oil, the matter of atmospheric pollution had been gaining prominence. Attention of the committee was turned to this subject immediately, and from the literature and from the experience of refineries that individually had been confronted with and had solved the problem, details of methods were accumulated. It was found that few intricate methods were involved; closed systems, scrubbing towers, and similar means had proved effective. Again the recommended procedures were tested under actual practice conditions and found to be satisfactory, and in 1932 Section II of the manual was published by the institute (2).

The most difficult problem of all, however, still remained. This concerned tastes and odors in public water supplies, oxygen depletion in streams affecting aquatic life, injury to pleasure craft from dissolved sulfides, and other similar conditions; all were said to be traceable to dissolved substances in refinery waste waters.

It was at first thought that either these conditions would be impossible to prevent or would at least cost almost prohibitive amounts of money. In fact, the proposal was once made to drop the whole idea on the basis that any activity would

only further emphasize the problem. Fortunately this was not done, and work was started to determine if refinery waste waters were causing the conditions described and if so to what extent. There was practically nothing in the literature that would help answer these questions, and it was soon realized that to try to identify definite compounds and eliminate them was a waste of time. No testing methods were known for the purpose.

There was but one thing to do and that was to go directly to the people who were investigating the complaints and learn from them how they went to work and what they could offer. This proved to be the most valuable decision the committee ever made. It started contacts with such groups as the engineers of the Pennsylvania State Sanitary Water Board, engineers in charge of various public water supply plants, fish and game commissions, and similar groups. In conversations with these men the work and problems of the Committee on Disposal of Refinery Wastes were outlined, and they, in turn, placed before the committee sources of information, both data and experience, that were not known before.

From these conversations, together with other information at hand, it was evident that the basis of any plan should be the protection of the general characteristics of the public waters. The compounds effecting the characteristics would then assume secondary importance as tests for the characteristics themselves were already available for running down pollution sources. A practical and flexible plan was then evolved to cover acidity and alkalinity, dissolved sulfides, dissolved oxygen, tastes and odors, and total solids.

The next phase of the problem involved the point at which the waste water control should become effective, whether at the point of entering the public waters or after admixture with such waters. Considering this proposition, it was evident that, if the waste water had to be made of practically potable quality, the refinery would either have to find another location or go out of business. Further, if the water coming to the refinery were polluted, it would obviously be unfair to expect the refinery to correct this pollution. All effort, therefore, was directed toward devising control methods that would be applied within the refinery and so correct the effluent waste waters that, after the latter were mixed with the public waters and influenced by purifying processes encountered, they would not cause undue difficulty or expense in the use of the public waters by others. This makes possible waste correction without prohibitive cost and serves the best interests of the community, for it is a community problem wherein both industry and population are concerned, and neither industry nor population stands alone under the circumstances.

There is ample precedent for this idea. When industry slows up, the population suffers as is well evidenced by the past several years. That coöperative effort is successful has been demonstrated over the entire country. Examples may be had in the procedures of the Pennsylvania State Sanitary Water Board as described by its chief engineer (3); in the Willamette Valley Sanitary Program in Oregon; in Wisconsin, Ohio, Connecticut, and other states where modifications of this same general plan are followed.

The methods recommended for correcting refinery waste water before discharge vary with the condition to be controlled. One recommendation is general and that is a thorough survey of the entire plant drainage system so that individual operation wastes may be located and segregated since the waste water from a single operation may render the entire plant effluent unfit for discharge. Further, segregation means economy, for the operation may be changed or the small amount of waste water recirculated or a corrective treatment applied at a cost much lower than that for correcting the entire plant discharge.



Excessive acidity or alkalinity is best corrected by neutralization with a suitable plant waste of opposite reaction and then, if further neutralization is required, by using the cheapest desirable agent. This may be soda ash, lime, limestone, or dilute sulfuric acid. In all cases laboratory trial of any proposed method should be made to assure that, in correcting one condition, another objectionable one does not result.

In controlling the reaction of waste water, the plant should see that high "total solids" do not occur. Recirculation of the waste water with elimination of such a portion that will increase only slightly the total solids of the public waters will take care of such a condition. In no case should the effluent water contain more than 1000 parts per million.

Refinery waste waters do not place a very great load upon the oxygen reserve of the water they enter. The waste contains little or no oxygen when discharged, owing to the high temperatures encountered in coolers. By so arranging the discharge as to permit a path of oxygen-containing water around it, admixture with the public waters and reaeration will soon occur. There will be only negligible quantities of oxygen-consuming materials, such as fats, fatty oils, greases, soaps, etc., present and very little of any reduced inorganic material.

The matter of taste and odor is probably the most important characteristic of all and is closest to public health. Tastes and odors can be traced almost entirely to two general classes of compounds—organic sulfur compounds and phenols. As a rule both of these classes come from one source—waste caustic solutions. At times they occur in wastes from other operations. The segregation and treatment of the waste caustic will greatly reduce the taste and odor characteristics of the effluent. In one instance, the threshold point of samples taken from a stream at a distance 500 yards below the plant outlet was reduced from 50,000 to less than 75 by eliminating the waste caustic. Further, tests of the waste water with fish showed no effect in 2 per cent concentration of waste in spring water and very low mortality undiluted. The fish used were brook trout, sunfish, yellow perch, and catfish. The testing tanks were aerated, and analyses over the test period averaged as follows:

	2% TEST	UNDILUTED TEST
Dissolved oxygen, p. p. m.	5.8	5.9
Alkalinity to methyl orange, p. p. m.	24.0	49.0
Total acidity, p. p. m.	13.2	6.5
CO <sub>2</sub> , p. p. m.	9.2	5.3
pH	6.5	7.1
Temperature, ° C.	17.0	18.0

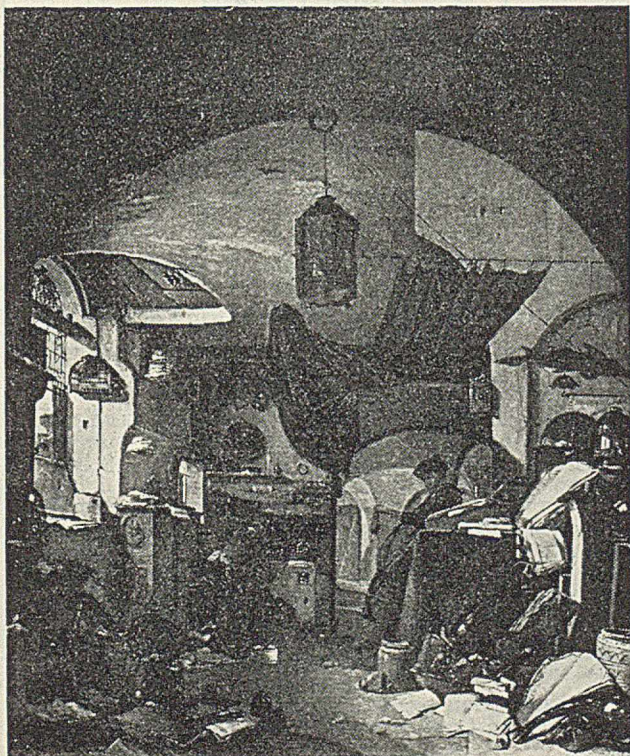
Various chemical methods have been developed for treating waste caustic solutions. Some return valuable products. These methods, together with procedures for treating wastes which cause taste and odor due to phenols, will form an important part of Section III of the manual on Disposal of Refinery Wastes which will probably be published about January 1935. It is felt that this section will do away with many ideas that have been serious obstacles to progress in industrial pollution abatement. One of these is that intricate and very expensive processes would be necessary. The procedures recommended are simple and not excessively costly, and in some cases offer a return on the money invested. Tolerances for water characteristics at points of consumption are given as a guide to control required. These tolerances are thought to be fair but are entirely a pioneering effort, and constructive criticism will be welcomed.

In this manner one industry is taking great strides toward the solution of a vast problem in an entirely coöperative way. There is much yet to be done, but a great deal has been accomplished. Each step has been tried and tested. Very nearly all of the recommended procedures have been applied at the Philadelphia Refinery of The Atlantic Refining Company at an expense, during the past four years, of approximately half a million dollars. In all cases the results have been satisfactory.

#### LITERATURE CITED

- (1) Am. Petroleum Inst., "Disposal of Refinery Wastes, Section I, Waste Water Containing Oil," 1931.
- (2) *Ibid.*, "Section II, Waste Gases and Vapors," 1932.
- (3) Stevenson, W. L., paper presented before meeting of Am. Inst. of Chem. Engrs., Atlantic City, N. J., Dec., 1931.

RECEIVED May 21, 1934. Presented before the Division of Water, Sewage, and Sanitation Chemistry at the 87th Meeting of the American Chemical Society, St. Petersburg, Fla., March 25 to 30, 1934.



## LABORATORIUM DES ALCHYMISTEN

By Thomas Wyck

This, the 45th in the Berolzheimer Series of Alchemical and Historical Reproductions, is the fourth we have brought by that Dutch artist with the somber style, Thomas Wyck (Wijck) (1617-1677).

The original painting is in the Gemäldegalerie in Dresden, Germany. It shows Wyck's usual stained glass window, draperies, and apprentice in the background, attending the furnace.

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A detailed list of the first thirty-six reproductions in the series, together with the particulars for obtaining photographic copies of the originals, will be found in our issue for January 1934, page 112. A supplementary list of Nos. 37 to 42, together with Reproduction No. 43, appears in our July 1934 issue, page 802. No. 44 is in our August 1934 issue, page 884. An additional reproduction will appear each month.



# Shortening Value of Plastic Fats

JENNIE FISHER CAWOOD

Institute of American Meat Packers, Chicago, Ill.

*Shortening equivalence by weight of fats in pie crust formulas cannot be directly calculated from the relative shortening values determined at one level of fat by means of the shortometer. The amounts of fats which show equal shortening results must be determined by cut-and-try methods, but in general they bear a close relationship to the relative shortening values. The relative shortening values of the fats used, as determined by the Bailey shortometer for pie crust, were found to be of the same order for the general-purpose flour and the pastry flour used.*

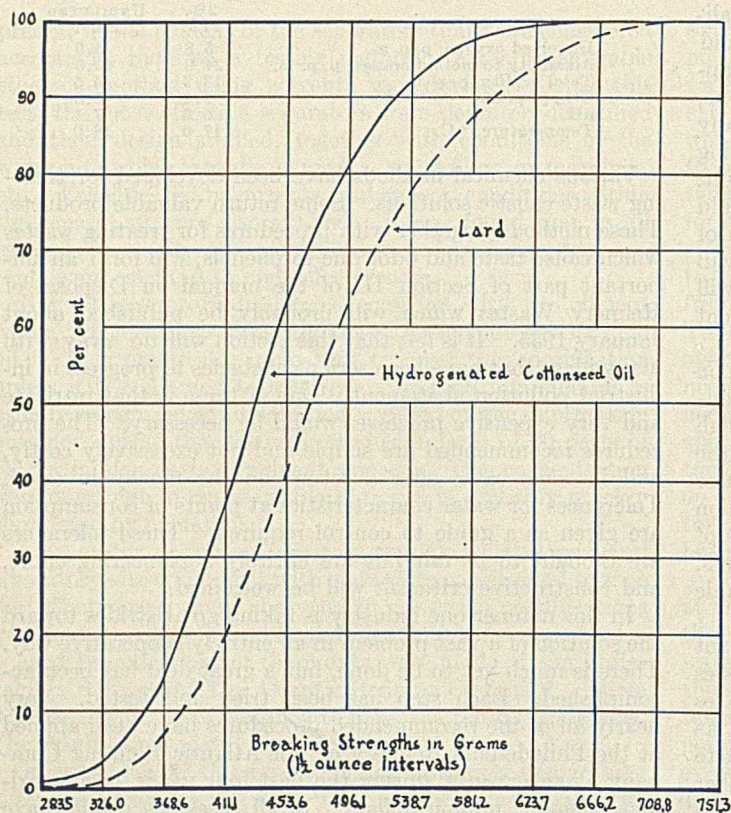


FIGURE 1. DISTRIBUTION OF BREAKING STRENGTHS IN PIE CRUST MADE WITH 70 PER CENT LARD, 100 PER CENT HYDROGENATED COTTONSEED OIL

THE first paper in this series<sup>1</sup> gave a standard procedure for determining the shortening value of fats by means of the shortometer, such that the resulting data meet the requirements of statistical measurements as to scope and validity of the average figure. In that study it was shown that, using pie crust wafers and 41 to 44 per cent of fat, five lards, two hydrogenated oils, a hydrogenated lard, an animal stearin-vegetable oil compound, and an all vegetable oil compound gave shortening values by the Bailey shortometer which coordinated closely with their congealing points.

The present paper gives the results of further studies designed to determine: (1) whether the comparative shortening values observed index the relative amounts of the several fats that can be used to produce pie crust of equal tenderness; and (2) whether the comparative shortening values of the different types of fats are affected by the type of flour used.

The method used in these experiments was that reported in the former paper. The statistical analysis of the data showed that in each instance the frequency distributions (one thousand breaking strength determinations for each fat tested) approached closely the normal or ideal distribution. In every case the mean was characteristic and representative of its series.

In the earlier studies it was found that refined steam lard was from 17 to 30 per cent higher in shortening power than the other fats tested. The ratio of 100 to 70 for the relative shortening power of lard and hydrogenated cottonseed oil raised the question of the equivalence of 100 per cent of hydrogenated cottonseed oil and 70 per cent of lard in

pie crust formulas. Would the resulting pie crusts possess the same shortness? Accordingly, the same prime steam lard was used with the same hydrogenated cottonseed oil, the

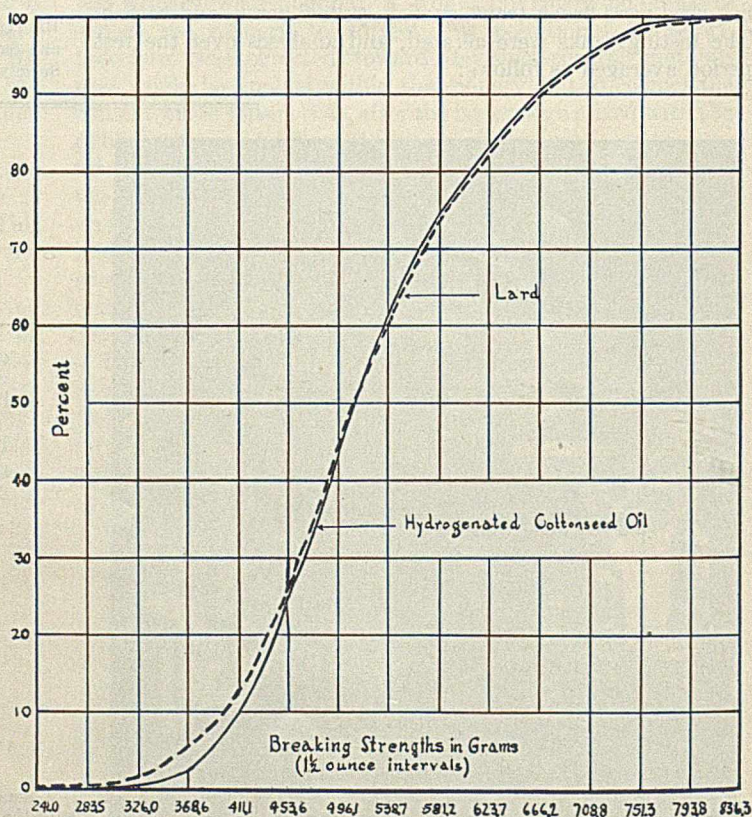


FIGURE 2. DISTRIBUTION OF BREAKING STRENGTHS IN PIE CRUST MADE WITH 75.4 PER CENT LARD, 100 PER CENT HYDROGENATED COTTONSEED OIL

<sup>1</sup> Fisher, J. D., IND. ENG. CHEM., 25, 1171 (1933).



tests being conducted entirely as heretofore except that the amount of lard used (44 to 100 grams pastry flour) was reduced by 30 per cent. The results of this study (experiment IV) are as follows:

KIND OF FAT	AV. BREAK- ING STRENGTH Grams	STANDARD DEVI- ATION	COEFFI- CIENT OF VARIATION	COMPARA- TIVE SHORTEN- ING VALUE %
Refined steam lard	470.9	78.5	16.6	100
Hydrogenated cottonseed oil	435.2	66.0	15.1	108

A comparison of the distribution of breaking strengths for pie crust made with the two fats is given in Figure 1. The class intervals in grams are expressed on the abscissa and the percentage of breaking strengths falling below the top level of each succeeding class interval on the ordinate.

It is apparent that shortening equivalence by weight cannot be directly calculated from the relative shortening values determined at one level of fat. Therefore, another experiment was carried out in which the amount of lard used in experiment IV was increased in proportion to the difference in shortness—i. e., 100:108. In other words, 75.4 per cent (33.2 grams) as much lard as hydrogenated cottonseed oil, 100 per cent (44 grams), was used. The results of this study (experiment V) are as follows:

KIND OF FAT	AV. BREAK- ING STRENGTH Grams	STAND- ARD DEVI- ATION	COEFFI- CIENT OF VARI- ATION	COMPARA- TIVE SHORTEN- ING VALUE %
Refined steam lard	516.5	106.9	20.5	100
Hydrogenated cottonseed oil 6	517.4	95.2	18.4	99.82

The average breaking strengths for the wafers made from 75.4 per cent as much lard as hydrogenated cottonseed oil were practically identical. A comparison of the distribution of breaking strengths is given in Figure 2.

General-purpose flour (protein content 10.4 per cent) was used for experiment VI where the pie crust was made with 200 grams general-purpose flour, 118 grams fat, 45 cc. water, and 6 grams salt. The procedure was identical with that previously employed. The results of this experiment are as follows:

KIND OF FAT	AV. BREAK- ING STRENGTH Grams	STANDARD DEVI- ATION	COEFFICIENT OF VARIATION	COMPARATIVE SHORTENING VALUES %
Refined steam lard	317.8	77.4	24.3	100
Vegetable oil com- pound	356.4	63.8	17.9	89.2
Hydrogenated lard	395.2	76.5	19.3	80.4
Hydrogenated cot- tonseed oil 4	412.5	69.5	16.8	77.0
Animal stearin-vege- table oil compound	428.7	69.9	16.3	74.1
Hydrogenated cot- tonseed oil 6	435.7	77.1	17.6	72.9

A comparison of the distribution of breaking strengths for the wafers made from the six fats is given in Figure 3. While the figures for comparative shortening value are not identical

U. S. A LEADING MARKET FOR CRUDE DRUGS. Overseas trade in crude drugs of vegetable origin has notably increased, both in value and quantity since the beginning of the year, indicating more activity in the production of medicinals, according to the Department of Commerce.

The United States leads all other countries in the manufacture of medicines, producing approximately one-third the total world output, and more than double that of Germany, the second largest producer. Despite outstanding advances made with synthetic medicinals in recent years, drugs of vegetable origin continue to maintain a dominant position, not only in the manufacture of proprietary medicines and on the prescription counter, but as the basis of home-made remedies.

Almost every state in the union and every foreign country contributes raw materials for the botanical drug grinder. In 1931 twenty-three establishments were engaged solely in grinding

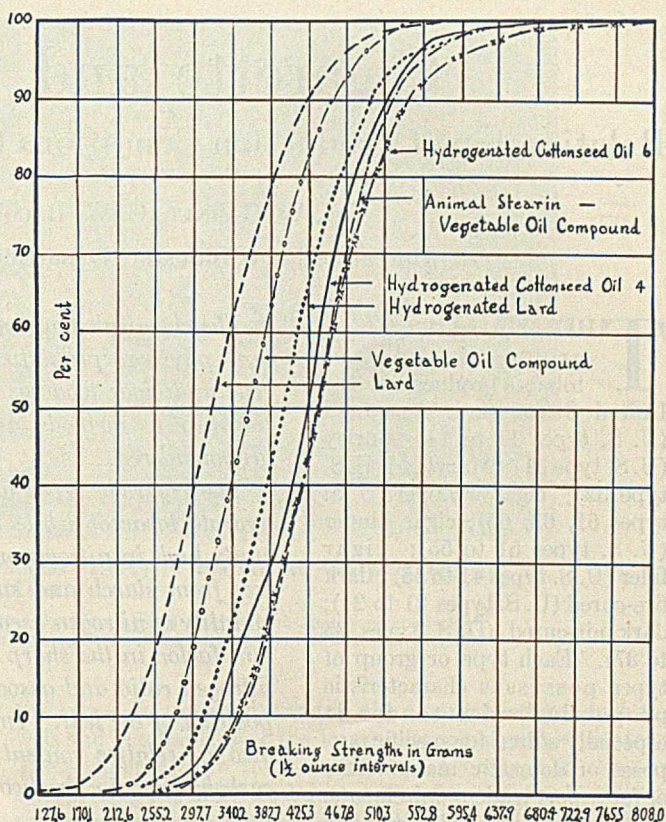


FIGURE 3. DISTRIBUTION OF BREAKING STRENGTHS IN PIE CRUST MADE WITH GENERAL-PURPOSE FLOUR

with those in studies made using pastry flour, they are of about the same magnitude and in the same order.

Some investigators have used a sweetened cookie as the test product for determining shortening value. Preliminary tests in this laboratory indicate that there may be more than one variable which affects the breaking strength of the sugar cookie wafers made from different types of fats even when the method of procedure is the same for each fat. When equal amounts of different types of fats and sugar are stirred or creamed together in a mechanical mixer for the same length of time under identical conditions, the volume of the creamed mass is not the same for each fat. Thus the amount of air incorporated varies. This probably affects the structure of the wafer and introduces a breaking factor other than that of the inherent shortening power of the fat. In other words, preliminary results indicate that, in order to use sweetened cookies to test the relative shortening power of fats, it is necessary to separate the factor of intrinsic shortening value of the fat from the shortening effects of varying creaming power, varying mixing, and other possible factors.

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drugs of vegetable origin, and during that year the output was valued at \$9,160,000.

Imports into the United States of crude vegetable drugs during the first four months of the year were valued at \$2,057,000, a figure double that of the corresponding period of last year. Licorice root ranked first and totaled 27,670,000 pounds, valued at \$428,000, compared with 10,230,000 pounds, valued at \$220,000, for the 1933 period.

While licorice is classed as a crude drug and is used extensively in medicinals, approximately 90 per cent goes into the manufacture of chewing tobacco, and considerable quantities serve as flavoring for candies and gums.

The United States is also an exporter of drugs of vegetable origin. Exports during the first four months of the year were valued at \$273,000, an increase of almost 60 per cent over the 1933 period.



# Cigarette and Cigar Tobaccos

## Relationship of Production Conditions to Chemical and Physical Characteristics

W. W. GARNER, C. W. BACON, AND JOHN D. BOWLING, JR.

Bureau of Plant Industry, Department of Agriculture, Washington, D. C.

THE principal types or groups of types of tobacco produced in the United States are: flue-cured (U. S. types 11 to 14); Burley (U. S. type 31); Maryland (U. S. type 32); cigar wrapper (U. S. types 61, 62, 65); cigar binder (U. S. types 51 to 55); cigar filler (U. S. types 41 to 45); dark fire-cured (U. S. types 21 to 24); dark air-cured (U. S. types 35 to 37). Each type or group of types possesses characteristic properties which render it especially suited for specific purposes of domestic manufacture or for export trade requirements. In general, the distinctive properties of each type are due primarily to the variety of seed used, the kind of soil on which it is grown, the climatic conditions, and the methods of fertilizing, growing, curing, and handling employed by the grower. In view of present trends in the consumption of manufactured tobacco products, special interest attaches to those types of leaf chiefly used in the manufacture of cigarettes and cigars.

In the domestic manufacture of cigarettes the flue-cured, Burley, and Maryland types are chiefly used. In the production of blended cigarettes varying proportions of imported

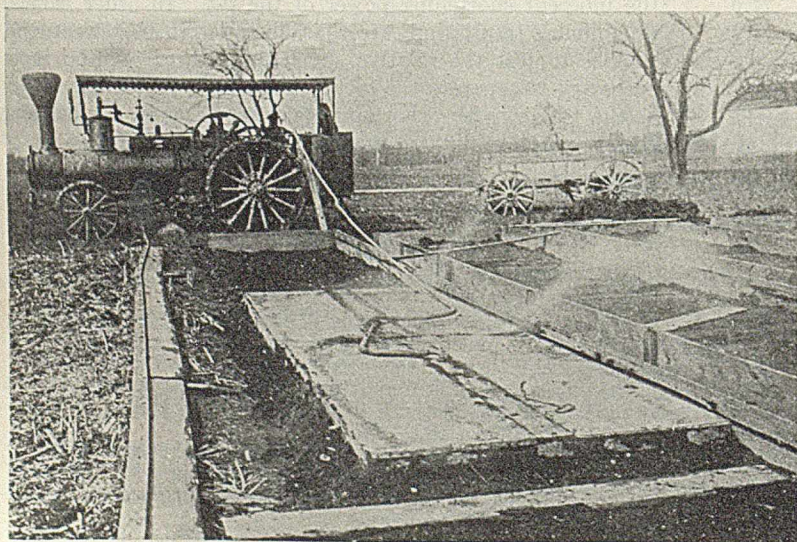
*The chemical composition and the more important physical properties of representative cigarette and cigar tobaccos are given, and their relationship to methods and conditions of culture are considered.*

*The cigarette types are essentially high-carbohydrate tobaccos while the cigar types are especially high in nitrogenous compounds and almost free from starch and sugars. The difference in quantity of nitrogen used as fertilizer is an important factor in the sharp contrast in carbohydrate-nitrogen ratio and associated differences in composition of the leaf. Important differences occur also in relative content of the various forms of carbohydrate in the two cigarette tobaccos examined.*

*Distinctive properties of the two classes of leaf that are of importance in the tobacco trade, such as weight per unit area, color, elasticity, grain development, aroma, "burn," and physiological strength, can be partially correlated with the differences in chemical composition and in some instances with special methods of culture employed.*

cigar tobaccos are extensively used for the manufacture of both cigars and cigarettes. However, not all leaf of a given type is adapted to a particular form of manufacture. For example, only a portion of the flue-cured crop is suitable for production of cigarettes, other portions being utilized for the manufacture of chewing and smoking tobaccos.

The purpose of the present paper is to direct attention to certain differences existing between cigarette and cigar tobaccos as such, as well as between certain individual types of these two classes, with respect to their chemical and physical properties, and to point out the relationship of methods and conditions of production to some of these contrasts in properties. Only the contrasts existing between classes and types are considered, no attempt being made to establish characteristic differences in chemical or physical properties between the numerous commercial grades of leaf into which each type is subdivided for marketing purposes. However, the discussion throughout relates primarily to the grades of each type of leaf adapted to production of cigarettes or cigars, as the case may be. Four types were selected for detailed study, the cigarette tobaccos being represented by the flue-cured and Maryland, and the cigar tobaccos



STEAMING TOBACCO SEED BEDS IN THE LANCASTER, PA., CIGAR-FILLER DISTRICT TO DESTROY WEED SEEDS, DISEASES, AND INSECTS

The seedlings are reared in cold frames which are covered with either glass or cheesecloth.





EFFECT OF 40 POUNDS PER ACRE OF FERTILIZER NITROGEN (LEFT) IN PROMOTING GROWTH OF CROP IN SOUTHERN MARYLAND

Considerably less than this quantity of nitrogen commonly gives a good yield of high-quality cigarette leaf; for cigar tobaccos, however, much larger quantities are employed resulting in important changes in chemical and physical properties of the cured leaf.

by the Connecticut broadleaf binder and the Pennsylvania seedleaf filler tobaccos. No data are available for Burley or for the other cigar tobacco types. The leaf samples are from crops grown and cured according to the methods customarily applied to their respective types except that methods of fertilization in the Connecticut Valley have changed slightly since the cigar binder leaf sample was taken.

#### DIFFERENCES IN PRODUCTION METHODS

The numerous differences in methods and conditions of production applicable to these four types cannot be considered in detail, and it will suffice perhaps to indicate briefly some of the principal contrasts. The variety of seed used is of considerable importance but on the whole is not a decisive factor in the type of leaf produced. The Pennsylvania (and Ohio) cigar filler leaf is grown mainly on heavy clay or silt loam soils while the cigar binder and wrapper as well as the two cigarette types are grown chiefly on relatively infertile, light sandy and sandy loam soils. As regards differences in fertilization, which constitute a highly important factor, the quantity of nitrogen per acre required for best results under average conditions seems to be about 200 pounds for the Connecticut Valley binder and wrapper, 100 pounds for Pennsylvania filler, 30 pounds for Maryland leaf, and 25 pounds for flue-cured tobacco; the corresponding quantities of phosphoric acid ( $P_2O_5$ ) are about 100 pounds for the two cigar types and 60 to 80 pounds for the two cigarette types; the quantities of potash are approximately 200 pounds for cigar wrapper and binder, 125 pounds for cigar filler, 100 pounds for Maryland leaf, and 40 pounds or more for flue-cured. For cigar filler a large proportion of the indicated plant food is derived from barnyard manure, but commercial fertilizer alone is generally used for the other types. On the light soils the fertilizer frequently is made to include 10 to 20 pounds of magnesia per acre, and calcium also may be required though the quantities actually used as yet have not been definitely brought under control. As indicated by the name, a special method of rapid curing at elevated temperature is applied to the flue-cured type while the other types ordinarily are cured much more slowly without use of artificial heat.

In the flue-cured and Maryland samples the midribs of the leaves were not removed in preparing the material for analysis; in the Pennsylvania sample only the lamina or web of

the leaves was utilized; and in the Connecticut product the web and the midribs of the leaves were analyzed separately. These differences in the samples have been kept in mind in interpreting the analytical data. The flue-cured tobacco was grown in Granville County, N. C.; the cigar filler leaf in Lancaster County, Pa.; the cigar binder leaf in Hartford County, Conn. This material which represents only a limited sampling in each case possibly does not reflect the mean composition of the respective types in all particulars. Each of the types considered is subject to rather wide variation in chemical composition, chiefly because of both local and regional differences in soil and weather conditions and various modifications of procedure employed in growing and curing the crop. This is especially true, perhaps, of the flue-cured type of leaf which is produced over a very large area and with a wide range in conditions. However, it is believed that with respect to most constituents the material used for study is adequate for developing the outstanding contrasts in composition of the leaf types represented.

#### DIFFERENCES IN COMPOSITION OF TOBACCOS

In the chemical analyses, citric, malic, and oxalic acids were determined in accordance with the procedure developed by Vickery and Pucher (?). The methods employed for all other constituents have been described or cited in a previous publication (4). The residual nitrogen after determination of protein, nitrate, ammonia, and nicotine nitrogen was multiplied by 4.7, the conversion factor for asparagine, to obtain values for the nitrogen complex which is arbitrarily designated as "amides and amino acids." These values have significance only for comparative purposes. The results of the analyses are shown in Table I.

The cigarette types thus have a very high content of total carbohydrate and a relatively low content of organic acids, various nitrogen compounds, and total ash. The content of total carbohydrate approaches 40 per cent as against less than 25 per cent in the cigar types. The cigarette types are essentially high-carbohydrate tobaccos. With respect to ash content, the flue-cured sample was grown in the Piedmont region and its content of total ash is fairly representative of the flue-cured type of that locality, but unpublished data indicate that the flue-cured crop of the Coastal Plain region contains considerably lower percentages of ash, perhaps averaging only 8 to 10 per cent. The cigar types are especially high in ni-



trogenous compounds, including ammonia and nitrates, and in total ash, but they are almost free of starch and sugars. Also, as is true generally in tobacco, a high percentage of non-volatile organic acids is associated with the high nitrogen content of the cigar types. Data recently reported by Vickery and Pucher (8) in connection with an extensive study made by them of the chemical changes taking place in Connecticut shade-grown cigar wrapper leaf during the curing process indicate that this type contains even a somewhat higher total nitrogen fraction than the binder and filler types. In view of their high content of nitrogen compounds, the cigar types as a whole may well be classed as high-nitrogen tobaccos.

TABLE I. PERCENTAGE COMPOSITION OF REPRESENTATIVE CIGARETTE AND CIGAR TYPES OF LEAF TOBACCO ON A WATER-FREE BASIS

CONSTITUENTS	TYPE OF LEAF					
	FLUE-CURED, CIGARETTE (ENTIRE LEAF)	MD. CIGARETTE (ENTIRE LEAF)	PA. CIGAR FILLER (LEAF WEB ONLY)	CONN. BROADLEAF CIGAR BINDER (LEAF WEB)	BROADLEAF CIGAR BINDER (LEAF MIDRIB)	Whole leaf
Starch	3.02	3.34	0.0	0.0	0.0	0.0
Reducing sugars (as dextrose)	9.40	1.40	0.12	0.25	0.06	0.21
Invert sugars by acid hydrolysis (as sucrose)	1.08	0.20	0.0	..	..	..
Pectic acid (as calcium pectate)	10.81	16.01	9.15	7.71	14.99	9.14
Protopectin (as calcium pectate)	1.40	0.70	0.10	0.55	0.05	0.45
Pectin (as calcium pectate)	0.0	0.0	0.20	0.16	0.27	0.18
Cellulose (crude fiber)	10.80	17.20	8.72	12.09	18.18	13.28
Citric acid	1.84	1.46	5.02	7.27	2.41	6.31
Malic acid	3.27	2.77	5.52	3.63	1.46	3.20
Oxalic acid	2.11	1.73	2.75	2.80	1.55	2.55
Protein	6.38	9.06	11.75	9.08	4.75	8.23
Amides and amino acids	2.91	2.49	5.73	10.53	1.27	8.71
Ammonia	0.01	0.06	0.27	0.61	0.23	0.55
Nicotine	2.25	0.73	4.49	3.43	0.82	2.92
Nitric acid (NO <sub>2</sub> )	0.03	0.11	0.80	1.74	9.07	3.19
Total resins	7.12	5.60	8.16	6.14	1.44	5.20
Plant wax	0.29	0.20	0.25	0.27	0.04	0.22
Total ash	16.00	12.88	19.41	17.83	28.96	20.01
Total nitrogen	2.04	2.18	4.28	5.19	3.41	4.84

On the whole the two cigarette types are somewhat similar in composition but there are two important exceptions—namely, differences in the form of the carbohydrate contained in the leaf and in the nicotine content. In the flue-cured tobacco analyzed in this study, the content of total sugars is about 12 per cent; in the lower leaves of the plant it has been found to run as high as 20 per cent. On the other hand, in the Maryland type nearly 90 per cent of the total carbohydrate, amounting to 39 per cent of the total dry weight, appears as the cell-wall-forming materials, cellulose and pectin. Patterson (6) also found a high content of cellulose in southern Maryland tobacco grown on light soils. The Maryland type has a very low content of nicotine while the cigarette grades of flue-cured leaf usually contain somewhat more than was found in the present sample. There are no outstanding differences in organic constituents between the cigar filler and binder types. Comparing the web and the midrib of the Connecticut leaf, it is apparent that the latter has a high content of carbohydrate of the types found mainly in the cell wall and also of nitrates and ash. In several respects the midrib of the cigar binder leaf is strikingly similar in composition to the entire leaf of the Maryland type, further emphasizing the peculiarities of the latter in chemical composition.

There are important differences, also, in the relative content of the different tobaccos in potash, lime, and magnesia, the principal basic constituents of the ash. As has been shown by Ames and Boltz (1) and by Haley and associates (5), potash applied to the cigar filler soils, which are heavy

loams, is not readily absorbed by the plant; and despite liberal potash fertilization, the content of potash in the leaf averages only 2 to 4 per cent, while the content of lime usually ranges from 5 to 8 per cent, and that of magnesia varies from 0.75 to 3 per cent. On the other hand, the plant freely absorbs potash applied to the light soils on which the cigar binder and wrapper of the Connecticut Valley and the cigarette types are chiefly grown. Hence, as found by Anderson, Swanback, and Street (2) and by Bailey and Anderson (3), the binder and wrapper types, which are heavily fertilized, have a high content of potash (5 to 8 per cent). In these types the leaf was found to contain about 5 to 8 per cent lime and 0.75 to 1.5 per cent magnesia. Unpublished data indicate that the cigarette types of leaf, which are only moderately fertilized, usually contain 2.5 to 3.5 per cent potash, 3 to 5 per cent lime, and less than 1 per cent magnesia. Data from various sources show that the phosphorus content is always low (0.4 to 1.0 per cent P<sub>2</sub>O<sub>5</sub>). The chlorine content is less than 1 per cent unless chlorides are added in the fertilizer, in which case it may exceed 5 per cent. The sulfur content expressed as SO<sub>2</sub> ranges from less than 1 to more than 2.5 per cent, depending largely on the quantity of sulfates included in the fertilizer.

#### COMMERCIALY IMPORTANT PROPERTIES

The relative value of cured leaf of a given type for specific manufacturing purposes is arrived at by the buyer through inspection of the product, the chief elements of quality taken into account being the so-called body and texture, the grain, elasticity, and color, and in some cases the size and shape of the leaf. Moreover, consciously or unconsciously the experienced buyer largely utilizes variations in these characteristics in judging the strength (mainly the nicotine content), aroma, and burning qualities of the leaf. The terms "body" and "texture" are not easily defined or clearly separated, and their meaning varies somewhat when applied to different types of leaf. The leaf contains varying quantities of so-called gum or oil, the chemical nature of which is not known although apparently no true oil is involved. The content of gum or oil as judged by inspection, together with the apparent thickness and density of structure of the leaf, constitutes the principal measure of its body. The texture relates largely to the relative prominence of the fine veins on the leaf surface and the density of structure of the tissue.

Unfortunately, no method for measurement of content of oil or gum has been developed, and, because of the unevenness of the leaf surface and variation in the compressibility of the tissues with change in moisture content and other factors, absolute values for leaf thickness are not easily obtained. Under a given set of conditions, however, relative values for thickness suitable for comparative purposes can be secured by direct measurement with calipers. The weight per unit area is more readily determined. The "grain" consists of multitudinous small protuberances on the leaf surface caused by internal crystalline aggregates or particles of mineral salts of the organic acids. The identity of the chemical constituents which govern the elasticity has not been determined although plant wax and the so-called oil or gum may be factors of some importance. The hygroscopic properties greatly affect the elasticity, all tobacco leaf being quite brittle in the dry state. Burning qualities include the relative capacity of a leaf to continue to glow when ignited, and the color and firmness or cohesiveness of the ash. Factors especially favorable to good burning qualities are: a thin leaf; open structure of the leaf tissue; a high content of cellulose and related carbohydrates; well-defined aggregation of the grain-forming material; a high content of potash, especially when combined with organic acids; a liberal but not excessive con-



TABLE II. COMMERCIALY IMPORTANT PROPERTIES OF REPRESENTATIVE CIGARETTE AND CIGAR TYPES OF LEAF TOBACCO

TYPE	WEIGHT PER SQ. FT. <i>Grams (ounces)</i>	THICKNESS <i>Mm. (in.)</i>	GRAIN DEVELOPMENT	ELASTICITY	MOISTURE CONTENT <sup>a</sup> %	COLOR	BURNING QUALITIES	AROMA	PHYSIOLOGICAL STRENGTH
Flue-cured (cigarette grade)	7-9 (0.25-0.32)	0.12-0.14 (0.0047-0.0055)	Lacking	Moderately elastic	17-20	Clear lemon to orange	Rather poor	Pronounced	Rather strong
Maryland (cigarette grade)	4-6 (0.14-0.21)	0.11-0.13 (0.0043-0.0051)	Not abundant	Deficient	11-14	Light brownish red	Excellent	Not pronounced	Mild
Cigar binder and wrapper	2.75-4 (0.10-0.14)	0.09-0.11 (0.0035-0.0043)	Abundant	Very elastic	12-15	Clear light brown, high luster	Excellent	Not pronounced	Moderately strong
Cigar filler	5-7 (0.18-0.25)	0.12-0.14 (0.0047-0.0055)	Moderate	Elastic	12-15	Medium to dark brown	Fair	Pronounced	Strong

<sup>a</sup> At 72% relative humidity.

tent of magnesia and lime; and a low content of mineral salts, especially chlorides. Nicotine content largely determines the physiological strength of the leaf, and the total content of resins probably affords a rough measure of the amount but not the quality of the aroma. Comparison of properties affecting commercial value in one or more of the cigarette and cigar types is made in Table II.

Where numerical values are employed in Table II, it is to be understood that these are only approximate averages and do not represent the full range in variation within the leaf type. Measurements made on Connecticut shade-grown cigar wrapper leaf did not differ materially from those obtained with the binder leaf. The values for weight per square foot are on a water-free basis and with the midrib of the leaf excluded. The measurements of thickness were made on the moist leaf and are not directly comparable with measurements based on dry material. It should be emphasized that relative weakness or deficiency of a given type of tobacco with respect to one or more of the properties listed in Table II does not necessarily detract from the value of the product but, on the contrary, may materially add to its usefulness. In general, the degree to which each of these characteristics needs to be developed for best results varies with the type, approximately as indicated in Table II.

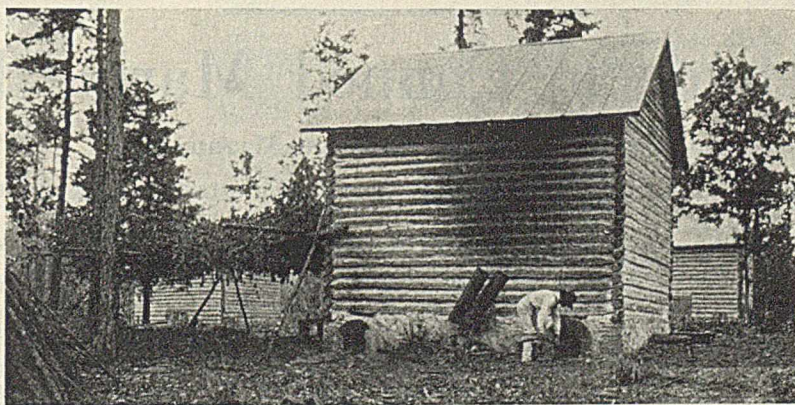
The very light weight of the cigar binder and wrapper types is due primarily to their thinness and relatively open structure, while the much heavier weight of the cigar filler appears to be due in part to its greater thickness and in part to greater density. The cigarette grades of Maryland leaf are relatively thin and also have a very low density. Flue-

cured leaf is quite heavy, owing partly to its thickness but especially to its density. The large quantity of nitrogen assimilated by the cigar binder and wrapper tobaccos as a result of heavy fertilization is an important factor in the thin leaf which is produced and its color characteristics and high elasticity (4). The abundant grain development taking place in these types during the slow process of air-curing results primarily from the high content of salts of organic acids, which also is associated with the high nitrogen content. In the filler types the tendency of the high nitrogen content to produce a thin leaf is more than offset by the effects of the heavy type of soil on which the crop is grown and by certain cultural

practices (relatively wide spacing and low topping of the plants), both of which also tend to darken the color.

Although the cigarette grade of Maryland leaf is relatively thin, its outstanding physical property is its very light, dry, chaffy character which undoubtedly is due largely to its exceptionally high content of cell-wall-forming material and a correspondingly low content of nitrogenous constituents, plastic carbohydrate (starch and sugar), organic acids, and mineral matter. To these chemical characteristics are due in large part also the sparse development of grain, the lack of elasticity, and the relatively light color. Flue-cured leaf is heavy and fairly thick, partly because of the small quantity of nitrogen assimilated by the plant and the fact that the resultant high content of carbohydrate chiefly assumes the form of sugar. The low rate of nitrogen assimilation and the rapid flue method of curing are mainly responsible for the lack of grain development and the characteristic yellow color. The high sugar content apparently explains the highly hygroscopic character of the leaf which is rather outstanding when compared with other types. This high content of sugar probably is the immediate result of the quick method of drying and curing employed whereby starch is largely converted into sugar.

With respect to burning qualities, the property of continuing to glow freely when ignited and yielding a satisfactory ash apparently is due to somewhat different causes in the Maryland tobacco and the cigar binder and wrapper tobaccos. In the former the major factor is the high content of cellulose and pectin, which are easily combustible, and the limited cell content of more difficultly combustible substances. In



BARN EMPLOYED IN THE FLUE-CURING PROCESS

The barn is provided with furnaces and metal pipes for distributing the heat; this rapid method of curing is an important factor in the distinctive properties of the flue-cured type of cigarette leaf.

the cigar binder and wrapper the tendency of the high content of organic nitrogen to injure the burning qualities may be completely overcome by the thinness of the leaf, effective aggregation of the grain material which increases the porosity of the leaf tissues, the exceptionally high content of potash combined with organic acids which functions as a catalyst, and a sufficient content of magnesia and lime to produce a white, firm ash. In the cigar filler and the flue-cured types the increased thickness and density of the leaf, its low content of potash, the high-nitrogen fraction in the former, and the high content of sugar and lack of grain development in the latter tend to reduce the combustibility. It should be



added that, when present in the leaf to the extent of 1 per cent or more, chlorine tends to impair the combustibility.

Although heredity plays a part, aroma in tobacco apparently is governed chiefly by soil and climate, but the specific factors involved and their mode of action are not known. However, the heavy fertilization of cigar tobaccos with nitrogen appears to be partly responsible for the decided difference between these and the cigarette tobaccos in the character of the aroma produced when the leaf is smoked. The differences in resin content shown in Table I are hardly sufficient to indicate definite correlation with the aromatic properties of the different types of leaf, although the two most aromatic types, cigar filler and flue-cured, also have the highest content of resins. The sugar content of the flue-cured type is a factor of importance in the distinctive character of its aroma. The physiological strength of tobacco is largely measured by its nicotine content, and available information indicates that increased production of nicotine is favored by use of heavy soil types, heavy nitrogen fertilization, wide spacing and low topping of plants, dry seasons, and advanced maturity at time of harvest. In this connection it should be stated that, in the heavy fermentation to which cigar filler leaf is commonly subjected, a half or more of the nicotine may disappear, so that, while the leaf must be classed as strong when in the freshly cured state, it is to be regarded as comparatively mild when ready for manufacture.

#### CONCLUSIONS

From the data presented it may be concluded that the marked difference in quantity of fertilizer nitrogen applied to the cigarette and the cigar types constitutes a highly significant factor in the sharp contrast which exists between these two classes of tobacco with respect to the nitrogen carbohydrate ratio and associated differences in composition of the leaf. Certain commercially important distinctions in properties or qualities in the two classes of leaf, including color,

elasticity, grain development, aroma, and, in part, combustibility, are correlated with these differences in chemical composition. Difference in soil types and details of culture employed in growing the crop are important factors in the less pronounced contrasts in properties existing between the cigar binder and the cigar filler types, both of which are high-nitrogen products. In this instance the contrasts in properties are not so clearly reflected in the organic constituents of the leaf although there are significant differences in composition of the ash. As between the two cigarette tobaccos, both of which have a high content of total carbohydrate, the reason why the Maryland type possesses an especially high content of pectin and cellulose instead of the high content of sugar and starch found in the flue-cured type has not been determined, although apparently a soil factor is involved. The distinctive method of curing commonly employed materially influences the chemical and physical characteristics of the flue-cured type.

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## Formaldehyde in Canned Marine Products

GULBRAND LUNDE AND ERLING MATHIESEN

Research Laboratory of the Norwegian Canning Industry, Stavanger, Norway

THE problem of the natural occurrence of formaldehyde in fish and canned marine products is of considerable interest to those engaged in food analysis. Kawahata and Namba (6) have shown that smoked meats contain formaldehyde. Ishio and Aoki (5) found formaldehyde in twenty samples of smoked meat in concentrations varying from 1 part of formaldehyde to 10,000 to 50,000 parts of meat. Dill and Clark (3) obtained positive tests for formaldehyde in a commercial pack of canned herring (*Clupea palorsii*) and in canned rock cod (*Sebastes* species). They failed to find formaldehyde in an experimental pack of smoked sardines (*Sardinia caerulea*). Ishida (4) found that fresh crab meat gave a weakly positive result when tested for formaldehyde. After canning and storage for 8 months, the crab meat gave a distinctly positive test. The results of Ishida were confirmed by Dill and Clark who obtained formaldehyde from canned *Crustacea* in amounts of 1 in 30,000 to 1 in 200,000.

Tankard and Bagnall (8) report positive results for formaldehyde in fresh fish when using phenylhydrazine hydrochloride with potassium ferricyanide according to the method of Schryver (7). They conclude that the results are probably due to the natural occurrence of trimethylamine in the flesh of the fish.

Shipments of kippered herring have been condemned in the United States on the claim that formaldehyde was used as a preservative. The use of any preservative was strenuously denied by the Norwegian packer, and it is certain that no Norwegian canning factory is using formaldehyde or any other preservative in any of its sterilized canned products. The present work was begun with the object of investigating the extent of the natural occurrence of formaldehyde in canned marine products.

#### METHODS OF ANALYSIS

In determining formaldehyde, the general procedure and tests of the Association of Official Agricultural Chemists (1) were followed:

Two hundred grams of the sample were ground with water in a mortar and transferred to a distillation flask, and water was added until the mixture weighed about 450 grams. Seventy-five grams of phosphoric acid were added; the flask was connected with a condenser, and 50 ml. of distillate were collected. The distillate was tested for formaldehyde by the phloroglucinol and the Hehner tests. In certain cases the gallic acid test of Barbier and Jandrier (2), the phenylhydrazine hydrochloride test, and the test using phenylhydrazine hydrochloride with sodium nitroprusside were also employed. The amount of formaldehyde



present was estimated by comparison with standardized solutions of formaldehyde in water.

Only a portion of the formaldehyde actually present is recovered in the first 50 ml. of distillate. When additional 20-ml. fractions were examined, the first gave a positive and the second a trace of the reaction for formaldehyde. Dill and Clark have shown that even with a 6-hour distillation only one-third to one-fifth of the formaldehyde which they added to salmon was recovered. Further experiments have shown that the figures given here should be at least three times as high to show the actual amount of formaldehyde present in the food.

### RESULTS

When the fish flesh of herring was examined as described above, the distillate was negative to the phloroglucinol test and only slightly positive to the gallic acid and the Hehner tests. When this flesh was canned and examined after being stored for 3 days, all the tests were distinctly positive.

Fresh kippered (smoked) herring was examined and gave positive results, the amount of formaldehyde being less than 1 in 200,000. The quantity of formaldehyde in the kippered herring was not as high as in the canned kippered products. Smoked haddock gave a much stronger reaction, corresponding to a concentration of about 1 part of formaldehyde in 20,000 parts of distillate.

EXAMINATION OF AN EXPERIMENTAL AND COMMERCIAL PACK OF CANNED KIPPERED HERRING. Kippered herring were packed in enameled cans and sterilized. After 12 months of storage, eleven samples were examined. All of the samples were positive. The concentration of formaldehyde found in the first distillate was 1 in 200,000 or less. Samples from ten commercial packs of different factories were examined after 21 months of storage. All of the samples were positive and the amount of formaldehyde present in the distillate varied from 1 part in 75,000 to 1 in 150,000.

TABLE I. EXAMINATION OF SMOKED AND CANNED HERRING AND BRISLING

NO. OF SAMPLES	DESCRIPTION	AGE Years	HCHO IN FIRST DISTILLATE Parts
1	Smoked small herring before canning	..	Positive
2	Smoked brisling before canning	..	Positive
1	Canned unsmoked herring in oil	2	1 in 200,000
1	Canned smoked herring in oil	5	Negative
1	Canned smoked herring in oil	5	1 in 200,000
1	Canned smoked herring in oil	..	Positive
1	Canned smoked herring in oil in aluminum container	..	Negative
11	Exptl. pack of smoked herring	1	1 in 200,000
10	Commercial pack of smoked herring	1.75	1 in 75,000 to 1 in 150,000

EFFECT OF CONTAINER. As it was thought that the formaldehyde might be formed by a reaction between the container and the fish, several samples were canned in tin plate and aluminum, and after various periods of storage these were compared. The results shown in Table II indicate that there is little or no difference in the amount of formaldehyde formed when packed in aluminum or tin.

TABLE II. FORMALDEHYDE IN HERRING CANNED IN METAL CONTAINERS

HERRING	CONTAINER	AGE Months	HCHO IN FIRST DISTILLATE Parts
Fresh	Tin plate	14	1 in 50,000
Fresh	Aluminum	14	1 in 100,000
Kippered	Tin plate	9	1 in 50,000
Kippered	Aluminum	9	1 in 100,000
Kippered	Tin plate	20	1 in 100,000
Kippered	Aluminum	20	1 in 75,000

EFFECT OF STORAGE. It was thought that aging of the product might result in an increase in the amount of formaldehyde. In order to solve this problem, the case samples of kippered herring which had been in storage for various lengths of time were tested. The results shown in Table III indicate that the amount of formaldehyde present is not dependent on the age of the product.

\*TABLE III. FORMALDEHYDE IN STORED KIPPERED HERRING

AGE OF KIPPERED HERRING Years	HCHO IN FIRST DISTILLATE Parts	AGE OF KIPPERED HERRING Years	HCHO IN FIRST DISTILLATE Parts
1.5	1 in 75,000	2.5	1 in 50,000
1.5	1 in 100,000	4.5	1 in 50,000
2.5	1 in 25,000	10.5	1 in 200,000

FORMALDEHYDE IN COMMERCIAL PRODUCTS. As analysis showed that formaldehyde occurred naturally in Norwegian kippered herring, the experiment was extended to determine to what extent it was present in commercially canned products of the *Clupea* and similar families produced in other countries. The results shown in Table IV indicate that it is of common occurrence. Analyses of several cans of crab and lobster are also included.

TABLE IV. FORMALDEHYDE IN CANNED HERRING, SARDINES, TUNA, AND Crustacea FROM VARIOUS COUNTRIES

PRODUCT	ORIGIN	HCHO IN FIRST DISTILLATE Parts
Sardines in cottonseed oil ( <i>Clupea harengus</i> )	Maine, U. S.	Positive
Sardines in olive oil ( <i>Clupea harengus</i> )	Maine, U. S.	Negative
Sardines in oil ( <i>Clupea harengus</i> )	Maine, U. S.	Doubtful
Sardines in olive oil ( <i>Sardinia caerulea</i> )	California, U. S.	Negative
Smoked pilchards in tomato sauce ( <i>Sardinia caerulea</i> )	California, U. S.	Negative
Sardines in olive oil ( <i>Clupea pilchardus</i> )	Portugal	Positive
Sardines in oil ( <i>Clupea pilchardus</i> )	Portugal	Positive
Sardines in oil ( <i>Clupea pilchardus</i> )	France	Negative
Sardines in olive oil ( <i>Clupea sprattus</i> )	Great Britain	Positive
Sardines in olive oil ( <i>Clupea sprattus</i> )	Finland	Positive
Sardines in olive oil ( <i>Clupea sprattus</i> )	Spain	Positive
Sardines in sesame, soy-bean, and mustard oils	Latvia	Positive
Herring in tomato sauce	Germany	Positive
Herring in tomato sauce	Great Britain	Positive
Tuna in oil	France	Positive
Crab ( <i>Cancer magister</i> )	Norway	1 in 200,000
Crab	Japan	1 in 75,000
Lobster ( <i>Homarus Americanus</i> )	Canada	1 in 100,000

### DISCUSSION OF RESULTS

After having found that many canned marine products contain small amounts of formaldehyde when tested by the usual methods, an effort was made to determine the nature of its origin.

Since all of the cans examined were sterile, it was evident that the formaldehyde was not formed as a result of bacterial activity. In order to determine whether it was possible that the formaldehyde was formed by oxidation during distillation, a sample of canned herring was steam-distilled, and, during the distillation, air was passed through the flask. The color reaction of the distillate from this sample was found to be the same as that from an equal portion of canned herring which was distilled in an atmosphere of carbon dioxide. This indicated that the formaldehyde was not formed by oxidation during the distillation process.

Tests were then made to determine the presence of formaldehyde without distillation. Portions of the canned fish were mixed with distilled water, vigorously shaken in a glass-stoppered bottle, and centrifugalized, and the milky liquid was used for the tests. Tankard and Bagnall have shown that Schryver's test gives positive results in the presence of trimethylamine. It was found that all of the tests using phenylhydrazine as a reagent were positive to trimethylamine and therefore could not be applied directly to an aqueous extract of the fish. Of the remaining methods, only the Hehner test proved to be specific and sensitive enough for use. By means of this test the amount of formaldehyde present in the aqueous extracts was estimated, by comparison with known formaldehyde solutions, to be 1 in 100,000 to 1 in 200,000.

Yanagisawa, Horii, and Nishiura (9) are of the opinion that



the formaldehyde found in the distillate from crab meat is formed during distillation with phosphoric acid by decomposition of histidine. As formaldehyde is found in the aqueous extract of canned fish without distillation, it is the authors' opinion that the amount found in the distillate is really present in the canned fish.

Since formaldehyde, added as a preservative, is prohibited in most countries, the fact that it may occur naturally in canned marine products is of considerable importance. Formaldehyde must be present in quantities of at least 1 in 25,000 (possibly even more in smoked products), before it can be stated with certainty that it has been artificially added.

#### SUMMARY

Canned marine products frequently give a positive reaction when tested for formaldehyde by the official tests of the Association of Official Agricultural Chemists. The official tests where phenylhydrazine hydrochloride is used as a reagent cannot be applied directly to liquid foods or aqueous extracts of foods which may possibly contain trimethylamine. The trimethylamine naturally present in fish foods causes a positive reaction with these tests. Of the other tests used, only the Hehner test could be satisfactorily applied directly to an

aqueous extract of the fish. All the tests can be used upon the distillate from an acid distillation.

Formaldehyde has been detected in the distillate from fresh and canned herring, crab, and other marine products. The amount found in the canned food is somewhat higher than in the fresh fish. The formation of formaldehyde in canned fish appears to be independent of the nature of the container and does not increase during long storage.

The formaldehyde is not formed during the distillation process, as it can be detected in an aqueous extract of the fish by means of the Hehner test.

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## Hydrocarbon Oils

### Molecular Weights by the Cryoscopic Method and from Thermal Data

M. R. FENSKE, W. B. McCLUER, AND M. R. CANNON

Pennsylvania State College, State College, Pa.

THE cryoscopic method for determining molecular weights is based on the equation:

$$\frac{dT}{dx} = \frac{RT^2}{\Delta H}$$

where  $\Delta H$  = heat of fusion of the pure solvent at temperature  $T$   
 $x$  = mole fraction of the solute

Integrated forms of this equation have been used to measure molecular weights of hydrocarbon oils, but there seems to be considerable disagreement among the various investigations as to the accuracy of the results obtained. In particular it has been shown (4) that, when different solvents are used in determining the molecular weight of definite chemical compounds, the results obtained differ considerably from the true molecular weight. Specifically, it was found (4) that, when benzene was used as the reference solvent, ethylene dichloride gave results 5 per cent too high, stearic acid gave results 15 per cent too low, and carbon tetrachloride gave results 5 per cent too low. In general, the opinion appears to prevail that molecular weights of extremely complex high-boiling hydrocarbon mixtures cannot be determined by the cryoscopic method with an accuracy exceeding approximately 5 per cent, even though the solvent

*Average molecular weights of complex high-boiling hydrocarbon mixtures have been obtained by a method based on heats of vaporization. This permits an independent check on the cryoscopic method of molecular weight determinations. Using six different oils, the greatest difference between the two methods was found to be 7 per cent. The average molecular weights of fourteen different hydrocarbon oil fractions have been determined satisfactorily by the method involving heats of vaporization. These data have been correlated on the basis of viscosity index and 37.8° C. (100° F.) Saybolt viscosity by the following equation:*

$$\text{Mol. wt.} = 240 + \frac{32,310 \log_{10} \frac{100^\circ \text{F. viscosity}}{28.0}}{305 - \text{viscosity index}}$$

may have a high value for its molal freezing point lowering and satisfactory solution characteristics. Table I summarizes the differences of opinion that exist in the literature.

In this paper are given the results obtained by carefully measuring the molecular weights of six pure compounds and six hydrocarbon oils with cyclohexane as the solvent. Molecular weights of these six oils, as well as those of eight other oils, were also obtained from measurements of their heats of vaporization. This permits an independent check on the molecular weights of the oils. Cyclohexane was chosen as the solvent because of its large freezing point constant.

#### EXPERIMENTAL RESULTS BY CRYOSCOPIC METHODS

The cyclohexane as well as all the solutes listed in Table II were of a very high purity. The cyclohexane had a freezing point of  $5.68 \pm 0.05^\circ \text{C}$ .; and, using a value of its heat of fusion of  $7.41 \pm 0.01$  calories per gram as measured by Parks, Huffman, and Thomas (10), the purity was calculated to be 99.8 per cent. In Figure 1 the apparent molecular weights of the substances are plotted against the freezing point lowering,  $\Delta T$ , in order to give the basis used to extrapolate to



TABLE I. LITERATURE SURVEY OF CRYOSCOPIC MOLECULAR WEIGHT DETERMINATIONS ON HYDROCARBON OILS

SOLVENT	TYPE OF SOLUTE	REMARKS	REFERENCE
Benzene	Oil	Claim accuracy of 3-4% for oils of mol. weight below 400; unsatisfactory for higher mol. weights. Agrees with (5), (4); conflicts with (8), (12).	(18)
Benzene	Oil	Claim accuracy of 1% for oils of mol. weight 360 to 800. No other investigator claims such high accuracy.	(5)
Benzene	Oil	Claims accuracy of 2-3% for oils of mol. weight above 250. Agrees with (17), (5); conflicts with (8), (12).	(6)
Benzene	Oil	Finds benzene unsatisfactory for mol. weights above 400. Agrees with (17), (12); conflicts with (6), (5).	(8)
Benzene	Oil	Find benzene unsatisfactory for oils of high mol. weight. Agrees with (8), (17); conflicts with (6), (5).	(12)
Nitrobenzene	Oil	Satisfactory results obtained for oils of low mol. weights. Agrees with (5); conflicts with (6), (12).	(14)
Nitrobenzene	Oil	Claim high accuracy for oils of mol. weight 360 to 800. Conflicts with (6), (12).	(5)
Nitrobenzene	Oil	Very unsatisfactory for oils of mol. weight above 250. Illustrates conflicting results with many curves and experimental data. Agrees with (12); conflicts with (5).	(6)
Nitrobenzene	Oil	Find nitrobenzene unsatisfactory for oils of high mol. weight. Agrees with (6); conflicts with (5).	(12)
Stearic acid	Oil	Stearic acid satisfactory for oils. Agrees with (8); conflicts with (4).	(12)
Stearic acid	Oil	Stearic acid satisfactory for oils of high mol. weights. Agrees with (12); conflicts with (4).	(8)
Stearic acid	Oil	Stearic acid gives values for mol. weight decidedly low. Conflicts with (8), (12).	(4)
Ethylene bromide	Oil	Claim accuracy of 1% for oils investigated.	(5)
Naphthalene	Oil	Give no indication of accuracy and no data other than values of mol. weights obtained.	(11)
Cyclohexane	Oil	Give no indication of accuracy and no data other than values of mol. weights obtained.	(21)
Cyclohexane	Oil	Checks mol. weights as determined by thermal measurements within 7% for all cases investigated (Table IV).	This report
Cyclohexane	Six pure compounds	See Table II.	This report

zero concentration. The vertical lines attached to the circles show the limits of error possible. The data on benzene indicate that a perfect solution was not formed.

TABLE II. APPARENT MOLECULAR WEIGHTS OF PURE COMPOUNDS IN CYCLOHEXANE

COMPOUND	CYCLO-HEXANE Grams	SOLUTE Gram	ΔT ° C.	EXPTL. TRUE		ER-ROR %
				MOL. WT.	MOL. WT.	
Diphenylmethane	10.326	0.0381	0.477	172	168	1.8
	10.700	0.1813	2.120	166		
	10.386	0.2405	2.69	178		
				Extrapolated = 171		
Naphthalene	11.460	0.0327	0.462	129.5	128	0
	10.286	0.1314	2.00	133		
	10.707	0.1800	2.65	131		
				Extrapolated = 128		
n-Heptane	10.490	0.0180	0.30	112	100	12
	10.619	0.0787	1.437	108		
	11.307	0.1602	2.780	107		
				Extrapolated = 112		
Benzene	11.242	0.0415	0.643	120	78	?
	14.744	0.0937	1.18	113		
	15.190	0.1071	1.44	102		
	14.720	0.1848	2.30	114		
	10.384	0.1530	2.76	112		
				Extrapolated = ?		
Dibutyl phthalate	10.748	0.0623	0.436	278	278	2.9
	11.708	0.3113	1.800	307		
	10.773	0.4807	2.86	323		
				Extrapolated = 270		
Diphenyl	14.492	0.0222	0.22	146	154	6.5
	11.296	0.2881	3.27	164		
					Extrapolated = 144	

TABLE III. PHYSICAL PROPERTIES OF HYDROCARBON OILS INVESTIGATED

OIL No.	SP. GR. AT 15.6° C. (60° F.)	50% B. P. AT 10 MM. ° C.	VISCOSITY				VIS-COSITY INDEX
			98.9° C. K.V. <sup>a</sup> S.S.		37.8° C. K.V. S.S.		
1	0.867	219	0.0320	37.3	0.1502	77.6	95
2	0.867	240	0.0420	40.1	0.2375	113.4	95
3	0.869	251	0.0484	42.0	0.2977	139.7	96
4	0.870	265	0.0551	44.0	0.3585	166.6	102
5	0.871	271	0.0613	45.9	0.4259	196.7	102
6	0.932	200	0.0342	37.9	0.2118	102.3	15
7	0.933	219	0.0477	41.8	0.4076	188.5	10
8	0.934	237	0.0619	46.1	0.6822	312	8
9	0.938	250	0.0829	53.0	1.258	573	-22
10	0.934	271	0.1187	65.7	2.245	1021	-4
11	0.888	214	0.0327	37.5	0.1742	87.0	57
12	0.888	244	0.0477	41.8	0.3233	151	73
13	0.896	263	0.0654	47.2	0.5625	258	73
14	0.900	271	0.0770	51.0	0.7662	350	58

<sup>a</sup> K.V. = kinematic viscosity in Stokes; S.S. = viscosity in Saybolt seconds.

The properties of the hydrocarbon oils are given in Table III. The oils were closely cut fractions obtained by vacuum fractionation of three different types of lubricating oils in an efficient fractionating column. These oil fractions had boiling ranges of 10° to 14° C. (18° to 25° F.) from initial to the 90 per cent distilled point as determined in a vacuum-Engler

distillation apparatus operating at 10 mm. pressure. This distillation is essentially a simple distillation at 10 mm. of mercury absolute pressure. The specific gravity of the oil was determined in calibrated pycnometers at 20° C., and converted to degrees A. P. I. by the usual tables (16). The viscosities at 37.8° and 98.9° C. (100° and 210° F.) were determined in accurately calibrated pipets similar to the usual Ostwald viscosity pipets; the bath temperatures were maintained constant to ±0.05° C. (±0.1° F.). The resultant kinematic viscosities, in Stokes, were converted to Saybolt Universal seconds by the equations recently adopted by the A. S. T. M. committee on viscosity-temperature chart. The viscosity index of the various oil fractions was calculated from the original tables of Dean and Davis (3), when the 98.9° C. (210° F.) viscosity was greater than 50 Saybolt seconds, while special tables were used to calculate the viscosity index of the oil fractions when the 210° F. viscosity was less than 50 Saybolt seconds.

TABLE IV. APPARENT MOLECULAR WEIGHTS OF OILS IN CYCLO-HEXANE

SOLUTE OIL NO.	CYCLO-HEXANE Grams	SOLUTE Gram	ΔT ° C.	CRY-SCOPIC MOL. WT.	THER-MAL MOL. WT.	DIFFER-ENCE %
5	11.294	0.0855	0.392	404	374	7.0
	10.567	0.1591	0.760	416		
	10.864	0.2638	1.244	408		
				Extrapolated = 400		
3	10.227	0.1437	0.782	374	350	4.6
	10.523	0.2579	1.340	380		
	10.649	0.4497	2.299	382		
				Extrapolated = 368		
7	10.645	0.0621	0.380	322	328	1.8
	11.029	0.1294	0.810	304		
	10.875	0.1336	0.830	311		
	10.641	0.2413	1.540	309		
					Extrapolated = 322	
8	11.091	0.1223	0.662	349	356	0.6
	10.079	0.2807	1.738	334		
	10.817	0.4243	2.438	334		
				Extrapolated = 355		
11	10.888	0.0964	0.605	307	304	1.0
	10.539	0.2268	1.490	304		
	10.239	0.3806	2.490	209		
				Extrapolated = 307		
12	10.164	0.1287	0.740	357	349	2.3
	10.306	0.2633	1.495	356		
	10.542	0.4708	2.595	357		
				Extrapolated = 357		

Table IV gives the results obtained in determining the molecular weight of six of these oil fractions by the cryoscopic method. The column marked "thermal molecular weight" is the result obtained from heat of vaporization measurements described below. Figure 2 shows the extrapolation to zero concentration. In the case of two of the oils the slope of the molecular weight-freezing point depression curve



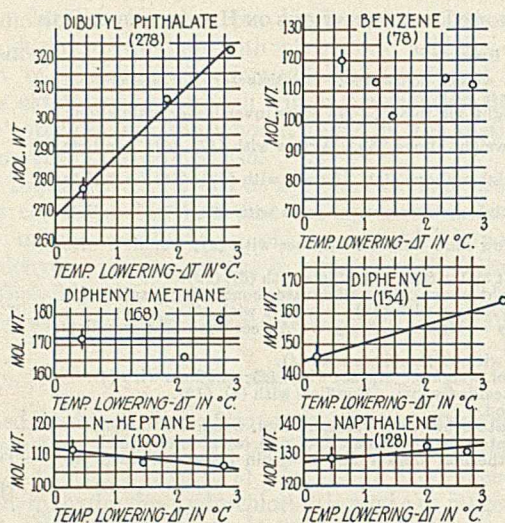


FIGURE 1. PLOT OF MOLECULAR WEIGHT *vs.*  $\Delta T$  FOR PURE COMPOUNDS

Numbers in parentheses are correct molecular weights.

has a negative value. This has been observed before (4, 12) in working with hydrocarbon oils.

#### MOLECULAR WEIGHTS FROM THERMAL DATA

The determination of molecular weights of high-boiling petroleum oils by means of vapor density measurements was not considered practical, since the materials are quite non-volatile and tend to decompose if heated above 300° C. (572° F.) for any appreciable period of time. Also the problem of insuring complete vaporization without any adsorption or condensation of the material would have to be solved. However, the following method permitted molecular weights to be obtained conveniently and apparently quite accurately, and also afforded an independent means of checking the cryoscopic method for these high-boiling substances of large molecular weight. The method developed used the specific heat of vaporization of the material and a vapor pressure at a suitable temperature. That is, the molal heat of vaporization was calculated from the vapor pressure-temperature data, and this value divided by the specific heat of vaporization resulted in a value for the average molecular weight of the material vaporized.

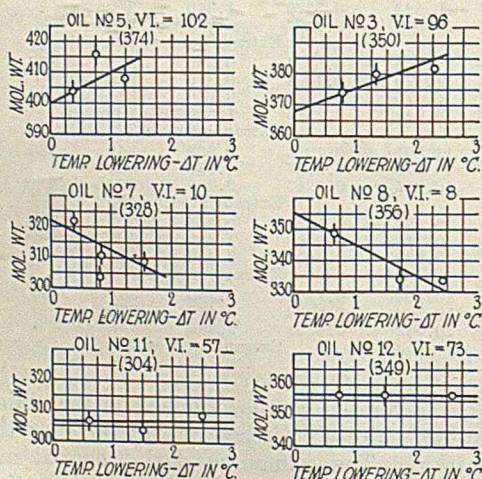


FIGURE 2. PLOT OF MOLECULAR WEIGHT *vs.*  $\Delta T$  FOR OILS

Numbers in parentheses are molecular weights from thermal data; V.I. = viscosity index.

Wilson and Bahlke (17) have investigated several of the more feasible methods of obtaining the molal heat of vaporization from vapor pressure data in order to ascertain the method most applicable to petroleum fractions. The results of their work indicate that the greatest precision was realized when the Hildebrand method (7) was employed. The underlying theory of this method is expressed in Hildebrand's postulation: "The molal entropy of vaporization of all normal liquids is the same at equal vapor concentrations." In order to use this method, it is necessary to have accurate vapor pressure data as well as the corresponding molal heats of vaporization of some definite reference material. Fortunately for this work, considerable data were available on diphenyl.

A convenient diagram from which the molal heats of vaporization can be quickly and accurately determined may be constructed from diphenyl data<sup>1</sup> by plotting the vapor pressure *vs.* the absolute temperature on logarithmic coordinates and then drawing a series of lines of unit slope through the curve. These lines of unit slope represent constant vapor concentration and, on the basis of the above postulation, constant entropy. The upper portion of Figure 3 represents a diagram of this type while the lower portion of the figure has been constructed to obtain conveniently the molal heat of vaporization of the oil fractions at 254° C. (489° F.). A value of 75.8 calories per gram (136.5 B. t. u. per pound) was used as the heat of vaporization of diphenyl at its normal boiling point, 254° C.

The method of using this plot was as follows: The vapor pressure of the material at 254° C. was located on the upper portion of Figure 3. A line was drawn through this point parallel to the nearest line of constant entropy until it intersected the line marked "diphenyl." Then a vertical line was followed downward until it intersected the line marked 527° K., when the heat of vaporization in B. t. u. per pound mole at 254° C. (527° K.) was read off the ordinate at the left. Hence when the vapor pressure of any oil fraction was known at 254° C., its molal heat of vaporization was obtained directly from Figure 3. Lines for other temperatures than 527° K. could be drawn in from diphenyl data if heats of vaporization at other temperatures were needed.

The probable accuracy with which molal heats of vaporization could be evaluated in this manner was determined from physical data in the literature on benzene, toluene, bromobenzene, and carbon tetrachloride. The maximum deviation was found to be approximately 1.5 per cent while the average deviation was 1.0 per cent from the true values. It was concluded that molal heats of vaporization could be obtained through the Hildebrand method with sufficient accuracy for the present purpose. Other correlations of heat of vaporization data are given by Watson and Nelson (15).

#### APPARATUS

Having accepted Hildebrand's method for determining the molal heat of vaporization, it was necessary to construct a piece of equipment for determining the specific heat of vaporization. The apparatus selected is shown in Figure 4 and consisted of a large Pyrex glass constant-temperature vapor calorimeter which employed diphenyl vapor as the heating medium:

Diphenyl vapor was generated in *A* by a 600-watt immersion heater. A portion of this vapor condensed on flask *B* and was collected in flask *C* while the remainder of the vapor was condensed in air condenser *D*, and drained back into *A*. Any part of the diphenyl vapor which may have condensed on tubes *E*

<sup>1</sup> Diphenyl data obtained from the Swann Chemical Company, Birmingham, Ala.



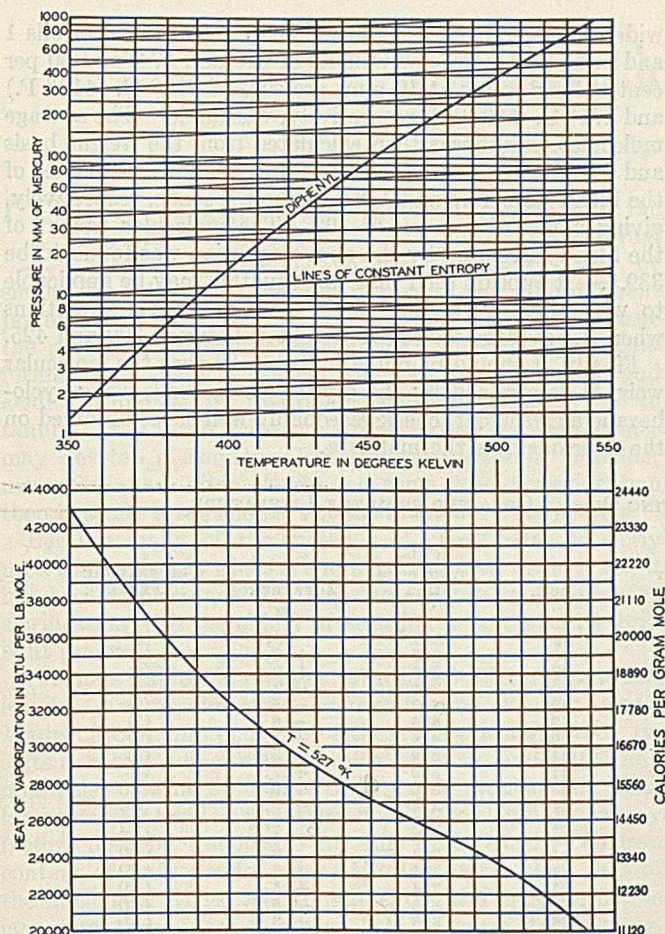


FIGURE 3. DIAGRAM FOR OBTAINING MOLAL HEATS OF VAPORIZATION AT 254° C.

and *I* drained back into *A* since flasks *B* and *C* were protected from this drainage by the inverted beaker, *J*, which was sealed onto tube *E*. Hence, the only portion of the diphenyl vapor that was collected in flask *C* was that part which gave up its heat of vaporization to the oil contained in flask *B*. The bulb of flask *C* was designed so that it would be filled with condensed diphenyl when the oil in *B* had been heated to the boiling point of diphenyl (254° C.). The steam above *C* was graduated in 0.20 cc. so that the diphenyl used in vaporizing the oil at 254° C. (489° F.) could be measured accurately.

When the oil in flask *B* reached a temperature of 254° C., the pressure on the system containing the oil was reduced until the oil boiled at a slow rate. The oil vapor then passed up tube *E*, the upper part of which was heated electrically to prevent condensation, and passed into *F* where it was condensed. The oil then drained into buret *H* where the amount of oil which had been vaporized was measured.

Therefore, the apparatus consisted essentially of a large calorimeter in which the heat required to vaporize a definite quantity of oil at a definite pressure could be determined. Thus, the specific heat of vaporization of the various oil fractions was evaluated. At the same time that the oil was distilled, the vapor pressure of the oil at 254° C. (489° F.) was obtained by means of a mercury manometer attached to the system. From the latter value and Figure 3, the molal heat of vaporization of the oil was determined. The molecular weight of the oil fraction was then obtained by dividing the molal heat of vaporization by the specific heat of vaporization.

#### RESULTS AND DISCUSSION

Prior to determining the molecular weights of the oil fractions, the apparatus was tested with *n*-dibutyl phthalate and diethyl phthalate. A very slight heat loss from the system, amounting to 0.0168 cc. of diphenyl condensed per minute or approximately 2 per cent, was found and all determinations were corrected by this amount. The results on the phthalates are given in Table V. The determined molecular weight

for *n*-butyl phthalate had a maximum deviation of -1.08 per cent from the true value while the maximum deviation for ethyl phthalate was +0.90 per cent.

TABLE V. RESULTS OF CHECKING THERMAL METHOD USING PHTHALATES

SUBSTANCE	VAPOR PRESSURE AT 254° C. Mm.	SUBSTANCE VAPORIZED PER GRAM OF DIPHENYL CONDENSED Grams	HEATS OF VAPORIZATION		MOL. WT. Exptl.	MOL. WT. True	ERROR %
			Molal Cal./g. mole	Specific Cal./g.			
<i>n</i> -Dibutyl phthalate	65	1.339	15,900	56.6	280	278	+0.72
		1.315	15,900	57.6	275	278	-1.08
		1.326	15,900	57.2	278	278	0
		1.315	15,900	57.6	275	278	-1.08
Diethyl phthalate	220	1.210	14,050	62.6	224	222	+0.90
		1.210	14,050	62.6	224	222	+0.90

In Table VI are the heat of vaporization data and the molecular weight determinations on the fourteen oils whose properties are given in Table III. The average time for each determination was approximately 45 minutes. The oil fractions had specific heats of vaporization which varied between 51.6 and 55.5 calories per gram (92.9 and 100.0 B. t. u. per pound) but were practically constant for each of the three different types of oils investigated. For instance, the specific heats of vaporization of the oils of high viscosity index were 55.1 ± 0.4 calories per gram (99.2 ± 0.8 B. t. u. per pound), while they were

53.4 ± 0.3 calories per gram (96.0 ± 0.6 B. t. u. per pound) for the oils of intermediate viscosity index and 52.2 ± 0.9 calories per gram (94.0 ± 0.9 B. t. u. per pound) for the oils of low viscosity index. A publication of the U. S. Bureau of Standards (*1*) states that the heat of vaporization per cubic foot is approximately the same at any definite temperature for a variety of oils. When the values from Table VI were converted to B. t. u. per cubic foot, it was found that the deviation was about ± 3 per cent from the average value of 48 calories per cc. (5400 B. t. u. per cubic foot) as the heat of vaporization.

It has been pointed out that viscosity index relates to the type or base of an oil and to its molecular structure (*2*). From a study of the data obtained in this work, it was found possible to correlate the molecular weights with the viscosity at 37.8° C. (100° F.) in Saybolt seconds and with the viscosity index by the following empirical equation:

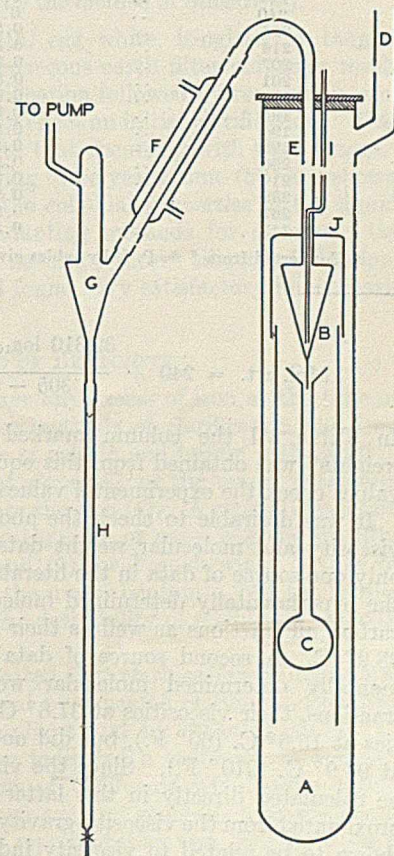


FIGURE 4. VAPOR CALORIMETER FOR DETERMINING SPECIFIC HEATS OF VAPORIZATION



TABLE VI. MOLECULAR WEIGHTS OF OIL FRACTIONS FROM THERMAL DATA

OIL No.	OIL VAPORIZED PER GRAM OF DIPHENYL CONDENSED	SP. HEAT OF VAPORIZATION	VAPOR PRESSURE OF OIL AT 254° C.	MOLAL HEAT OF VAPORIZATION	MOL. WT.	
	Grams	Cal./g.	Mm. Hg	Cal./g. mole	Exptl.	Calcd. from equation
1	1.370	55.4	30.0	17,270	310	308
2	1.366	55.5	14.0	18,800	338	334
3	1.385	54.8	11.0	19,150	350	349
4	1.374	55.2	7.5	19,950	362	363
5	1.388	54.6	6.0	20,400	374	374
6	1.438	52.7	50.0	16,100	305	320
7	1.427	53.1	29.0	17,450	328	329
8	1.469	51.6	16.0	18,400	356	353
9	1.460	52.0	12.0	19,150	369	370
10	1.470	51.6	5.5	20,800	404	404
11	1.420	53.4	51.0	16,100	304	306
12	1.417	53.5	15.0	18,650	349	344
13	1.432	53.0	8.0	19,800	374	373
14	1.423	53.3	5.5	20,800	390	383

wider boiling ranges, a 50-50 weight per cent blend of oils 1 and 5, having molecular weights of 310 and 374, and 50 per cent boiling points at 10 mm. pressure of 210° C. (410° F.) and 271° C. (520° F.), respectively, was made. The average molecular weight was then calculated from the weight basis and found to be 339. The 98.9° and 37.8° C. viscosities of the blend were 40.7 and 118.2 Saybolt seconds, respectively, giving a viscosity index of 102. The molecular weight of the blend calculated by the above equation was found to be 339.5. It appears then that this equation may be applicable to wider boiling fractions as well as to close-cut fractions when the average molecular weight is between 300 and 425.

Finally, it should be noted in Table IV that the molecular weights determined by the cryoscopic method, using cyclohexane as a solvent, check reasonably well those obtained on the same oils from thermal data.

TABLE VII. MOLECULAR WEIGHTS OF LUBRICATING OILS AS OBTAINED FROM THE LITERATURE

Viscosity 37.8° C.	Viscosity 98.9° C.	SP. GR. AT 15.6° C. <sup>a</sup>	VISCOSITY INDEX	GRAVITY INDEX	MOL. WT.		DIFFERENCE %	LITERATURE REFERENCE
					Exptl.	Calcd. from equation		
213	47.4	...	108	...	398	385	- 3.2	(2)
440	54.6	...	57	...	365	395	+ 8.2	(2)
207	47.4	...	112	...	384	386	+ 0.5	(2)
175	46.4	...	126	...	395	384	- 2.8	(2)
224	51.0	...	126	...	425	403	- 5.2	(2)
269	51.0	...	101	...	425	396	- 6.8	(2)
558	60.0	...	63	...	395	414	+ 4.8	(2)
267	51.7	...	109	...	413	399	- 3.4	(2)
249	..	0.904	...	67	315	369	+17.1	(13)
240	..	0.899	...	74	335	370	+10.4	(13)
226	..	0.891	...	83	340	372	+ 9.4	(13)
214	..	0.885	...	90	340	372	+ 9.4	(13)
207	..	0.881	...	94	335	373	+11.3	(13)
201	..	0.877	...	97	345	373	+ 8.1	(13)
197	..	0.874	...	100	350	374	+ 6.9	(13)
195	..	0.872	...	102	355	374	+ 5.4	(13)
196	..	0.870	...	103	355	375	+ 5.6	(13)
199	..	0.868	...	106	365	378	+ 3.6	(13)
206	..	0.867	...	107	370	381	+ 3.0	(13)
219	..	0.866	...	108	385	386	+ 0.3	(13)
238	..	0.866	...	109	385	393	+ 2.1	(13)
267	..	0.866	...	111	405	403	- 0.5	(13)
313	..	0.866	...	113	415	416	+ 0.3	(13)

<sup>a</sup> Converted from ° A. P. I. by tables given in reference 16.

$$\text{Mol. wt.} = 240 + \frac{32,310 \log_{10} \frac{100^\circ \text{ F. viscosity}}{28.0}}{305 - \text{viscosity index}}$$

In Table VI the column marked "calculated molecular weights" was obtained from this equation; these calculated values check the experimental values to within 2 per cent.

It was desirable to check the above equation with other viscosity and molecular weight data. However, there was only one source of data in the literature (2) which contained the experimentally determined molecular weights of hydrocarbon oil fractions as well as their viscosities at 37.8° and 98.9° C. A second source of data (13) contained experimentally determined molecular weights of extracted oil fractions, their viscosities at 37.8° C. (100° F.), their gravities at 15.6° C. (60° F.), but did not include their viscosity at 98.9° C. (210° F.). Since the viscosity index could not be calculated directly in this latter set of data, it was approximated from the viscosity-gravity relation which has been shown to be related to viscosity index (9). The molecular weights of these various oil fractions were calculated by the above equation and appear in Table VII with the physical data on the oils and their experimentally determined molecular weights. Only those oil fractions which had molecular weights between 300 and 425 were considered, since this was the range covered in the present investigation. The agreement is reasonably good but not as close as with the oils in this present investigation.

In order to test the validity of the developed molecular weight equation when applied to hydrocarbon oils having

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# Clarification of Wine

L. G. SAYWELL, University of California, Berkeley, Calif.

THE clouding of wine is a problem important to the wine industries of Europe, Australia, and the United States. In general, the causative factors may be similar, but the composition of the wines from the different production areas may vary considerably and thus change the nature of occurrence of clouding. In relation to California wines, many European wines are high in tannin and acidity, while certain Australian wines are markedly low in tannin. As a result, wine types that may be stable in France may develop a cloud in California or Australia. Further, newer wines are often cloudy and some type of clarification then becomes a routine part of the manufacturing process.

Because many of the methods of clarification formerly used for California wines are now being found inadequate, it has become necessary to study the general process of wine clarification with the object of securing a permanently brilliant product.

Previous California practice (2) utilized gelatin, egg white, isinglass, and tannin as the chief clarification or fining agents. Inadequate or improper use of these materials generally results in a reclouding of the clarified product, and often tank quantities of wine from juice of the same pressing and same later treatment will vary in their stability to clouding. Many factors may be responsible for this occurrence. The iron content of such clouded wines is often higher than that of the unclouded wines, and consequently, the presence of the larger amount of iron has been held to cause the clouding. This may be confirmed by adding iron to a clear sample and thereby inducing clouding, a control remaining clear.

For clearing with gelatin a high grade of product is used, about one part of gelatin being added to 9000 or 10,000 parts of wine. (Rapid approximation of quantities may be secured by taking the weight of one gallon of wine to be 8.3 pounds, 130 ounces, or 3.7 kg.) The gelatin is dissolved in warm water, mixed with a few gallons of the wine to be treated, and added with thorough stirring to the larger volume being clarified.

For clearing with egg white, the material (free of yolk) is mixed with warm water and then beaten to a fluffy foam. One quart of water may be used for the whites from 4 eggs, and the whites from 4 to 8 eggs are required for each 100 gallons of wine. This original aqueous solution of egg white should be diluted with about 10 volumes of wine before adding to the tank quantity. Mixing should be thorough.

The amount of isinglass required may vary considerably, one part of isinglass in 7000 to 25,000 parts of wine being used. The optimum concentration should be determined on smaller quantities of wine at the time of application. The estimated quantity of isinglass is placed in a small volume of cold water for several hours, or until much of the swelling has occurred. The mixture is thoroughly stirred, heated nearly to boiling, passed through a sieve (or heavy cloth), and cooled. Small quantities of wine are then added, with constant stirring, until a light fluid consistency is obtained. This solution may be 1 to 2 gallons in volume.

Tannin, used with gelatin for clarifying white wine, may be added one to two days before the gelatin. One part of tannin is added to 5000 or 10,000 parts of wine. A pure tannin is recommended in order to avoid the introduction of impurities that may tend to produce later reclouding. Several tannins analyzed by the official method (1) showed on the basis of a pure tannic acid (Eastman Kodak Company), the following quantities of tannin: U. S. P. grade, 90 per cent; oak tannin, 94 per cent; California grape tannin, 75 per cent; and Australian grape-seed tannin, 65 per cent. Tests in this laboratory (unpublished data) do not indicate complete verification of the broad claims made for the Australian product.

The use of a filter aid in the filtration is common. From less than 0.1 per cent to 5 per cent is added, depending upon the condition of the wine and the type of filter used. Its

use increases the rate of flow and the brilliancy of the filtrate, but results with different wines vary widely. In general, 0.1 or 0.2 per cent of filter aid has been found most satisfactory. An important criticism of the use of filter aids has been that the iron content of the wine was increased thereby. This condition apparently depends upon the filter aid used.

A certain diatomaceous earth of grayish color had been used in a plant with very unsatisfactory results, added iron being suspected as a possible factor. Analysis of the untreated wine indicated an iron content of 17.3 parts per million, while the treated wine contained 51.5 p. p. m. Evidently, where the only difference in treatment had been the use of the earth, the earth had increased the iron content.

With a better quality of diatomaceous earth, repeated experiments indicate a relatively small or even negligible increase of iron content. Two samples were filtered, using 5 per cent of a 50-50 mixture of Super-Cel and Hi-Flo. The original untreated samples contained 14.3 and 17.5 p. p. m. of iron, while the samples treated with filter aid contained 12.8 and 16.4 p. p. m. of iron, respectively. Portions of another wine containing originally 18.7 p. p. m. of iron were treated with 0.1 per cent Super-Cel and with 0.1 per cent of a 50-50 mixture of Super-Cel and Hi-Flo. These portions were found to contain a final iron content of 18.2 and 17.6 p. p. m. of iron, respectively. All iron analyses reported in this paper are by the method of Stugart (9).

Treatment with gelatin, egg white, isinglass, or tannin, with or without a diatomaceous earth filter aid, may result in only a temporary clarification followed by reclouding, and occasionally may not even effect an initial clarification. This situation is comparable to that occurring with wine vinegar, where experiments covering three years' time (8) have shown that a consideration of the colloidal properties of the liquid considerably aided in adapting methods for clearing. On this basis the use of the natural hydrous silicate of alumina, bentonite, was tried and found very satisfactory in comparison to other methods.

## USE OF BENTONITE

It is desirable to remove any excess of iron at the time of clarification. The earlier methods of clarification and iron removal involved the use of gelatin and tannin with aëration (4), an oxygen treatment alone (5), or the use of potassium ferrocyanide to precipitate the iron (6). A general discussion of the relation of iron to clouding or casse is given by Ribereau-Gayon and Peynaud (7) for French wines. None of these methods involved the use of bentonite, but the results with vinegar suggested the desirability of testing its use with wine.

Preliminary tests indicated that clarification by bentonite was satisfactory, as judged by repeated chilling and heating tests for exposure to sunlight and by standing at 30° C. Qualitative tests for iron indicated a reduction in content. The normal iron content of California wine varies rather widely with wines and their age, but generally averages about 10 p. p. m. Analyses of representative two- and three-year-old wines that have remained brilliantly clear show 15.7, 15.6, 6.7, 11.9, 9.1, 11.5, and 3.0 p. p. m. of iron. In general, the role of iron in causing cloudiness is dependent upon its state of oxidation (3, 7), the ferric iron being associated with the clouding. The oxidation of ferrous iron to ferric iron may be relatively slow, but if the total iron content is low, clouding from this cause is largely prevented.

Several series of tests with bentonite have been completed on different wines with varying iron contents. A wine with an original iron content of 16.7 p. p. m. was treated with 1 part



of bentonite to 2000 parts of wine, and with the same quantity of bentonite to which a peptizing agent had been added. The cleared samples contained 7.4 and 7.2 p. p. m. of iron. With a similar sample containing 17.5 p. p. m. of iron, treatment with bentonite at 1 to 2000 reduced the iron content to 6.3 p. p. m., while treatment with casein at 1 to 2000 for purposes of comparison resulted in an iron content of 13.1 p. p. m. The protein content of the original sample was 0.19 per cent, while the clarified portions contained 0.18 per cent each. A 2 per cent solution of casein in a 1.5 per cent aqueous solution of potassium carbonate was used for adding the casein to the wine. Thorough mixing is essential.

A report that material sold as bentonite left an earthy flavor was investigated, as this had not been observed in tests with the Clay Spur, Wyo., bentonite used exclusively. It was found that the material represented as bentonite was probably fuller's earth. Treatment of another lot of the same wine with Clay Spur bentonite did not impart an earthy taste.

A survey of the bentonites available on the California market resulted in the collection of samples from several sources. The bentonite was prepared for use by making a 5 per cent suspension of the material. An estimated quantity of water (or previously clarified wine) was placed in an appropriate container equipped with a stirring device, and the bentonite powder was gradually sifted in with vigorous stirring. Agitation was continued for several minutes, after which small clumps of bentonite were worked into suspension by hand. This method of preparation has been found the most satisfactory if the addition of the powder is not too rapid. Appropriate volumes of this suspension were added to the wine to give 1 part of bentonite to 2000 parts of wine.

After treatment the filtrates were tasted for alteration of flavor by four persons not familiar with the samples or their treatment. No off flavors were noted. These portions were also analyzed for their iron, total acid, and protein content. It appeared that the decrease in protein (1) content (N  $\times$  6.25) also might be related to the general clearing ability of the bentonite.

TABLE I. EFFECT OF VARIOUS BENTONITES ON WINE COMPOSITION

(1 part of bentonite in 2000 parts of wine)				
SAMPLE	BENTONITE USED	PROTEIN	IRON	TOTAL ACID
		G./100 cc.	P. p. m.	G./100 cc.
Control A	None	0.21	6.7	0.53
A1	Clay Spur, Wyo.	0.19	6.2	0.53
A2	Volclay, Wyo.	0.19	6.6	0.53
A3	Western talc A, Calif.	0.19	6.8	0.53
A4	Baroid A, Calif.	0.20	6.8	0.53
A5	Baroid B, Calif.	0.20	8.4	0.50
A6	Baroid A-5, Calif.	0.20	6.8	0.51
A7	Clay Spur + peptonizing agent	0.19	6.2	0.50

The data presented in Table I indicate a slight decrease in protein content, a marked decrease in iron content with one sample, and a slight (if significant) decrease with another. With the last three bentonites there was also a reduction in total acidity of the wine, which would be of value with wines of high acidity. Clay Spur bentonite would appear the most desirable of the various samples tested. The wine used for the test had an originally low iron content, the experiment being designed to test primarily the effect on flavor and protein removal.

In a subsequent experiment wines of higher iron content were used, adding bentonites used in samples A1, A2, A6, and A7 to the wine at 1 to 2000. A clarification with casein is given for comparison. The filtrates were analyzed for protein and iron content.

The data given in Table II indicate a considerable removal of iron, the Wyoming bentonites probably being more efficient in this respect. About 50 per cent of the iron in the original wine is removed by these clays. Several phases of this investigation are being continued.

TABLE II. REMOVAL OF IRON FROM WINE BY BENTONITE AND CASEIN

SAMPLE	BENTONITE USED	(1 part of bentonite in 2000 parts of wine)	
		PROTEIN G./100 cc.	IRON G./100 cc.
Control B	None	0.18	28.5
B1	Clay Spur, Wyo.	0.17	15.5
B2	Volclay, Wyo.	0.17	16.1
B3	Baroid A-5, Calif.	0.16	19.3
B4	Clay Spur + peptonizing agent	0.16	19.7
B5	Casein (1 to 2000)	0.16	18.2
Control C	None	0.25	25.7
C1	Clay Spur, Wyo.	0.24	11.4
C2	Clay Spur + peptonizing agent	0.23	11.4

In general, the appropriate use of bentonite, particularly that from Wyoming, results in a brilliantly clear wine which is stable to higher and lower changes in temperature, to sunlight, and to storage at average room temperature. There is a rapid rate of flocculation and settling after addition of the bentonite to the wine, and the supernatant liquid may be very rapidly filtered a short time thereafter. This results in a considerable saving of time in comparison to clarification by gelatin or isinglass, for which 10 to 14 days or more may be required for sedimentation. The bentonite method has resulted in positive clarification rather than uncertainty and frequent nonclarification with other agents. The use of added tannin is not necessary in order to maintain the original wine color, since bentonite does not decolorize or appreciably reduce the color. This is of considerable importance in the treatment of delicately colored wine.

In all cases observed the facility of clarification and brilliance obtained is enhanced by adding the bentonite to wine heated to a temperature of 120° to 180° F. (82° C.) (8). Heating and cooling should be continuous and in a closed system.

Plant practice has suggested the use of a filter aid with the bentonite, the resulting precipitate being firmer. Accordingly, 0.1 per cent of Super-Cel and 0.1 per cent of a mixture of equal parts of Super-Cel and Hi-Flo were added with Clay Spur bentonite (1 to 2000) to a portion of the wine, control B in Table II. After flocculation and filtration the original iron content of 28.5 p. p. m. was reduced to 19.1 and 18.5 p. p. m., respectively. The filtering velocity and firmness of cake were increased.

For a final polishing filtration just before bottling the wine, Seitz E. K. type asbestos filters and Berkefeld candle filters have been found very satisfactory. Small plate and frame and also pulp filters have been used, adding a mixture of 10 parts of filter aid and 1 part of asbestos to the wine to be filtered. The individual conditions of filtration and the resulting velocities vary with the wine being treated. In general small quantities of filter aid are required with the plate and frame filter.

#### ACKNOWLEDGMENT

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# The Rate of Reduction of Iron Ores with Carbon Monoxide

## Effect of Particle Size, Gas Velocity, and Gas Composition

W. H. WETHERILL AND C. C. FURNAS, Yale University, New Haven, Conn.

*Two new methods of calculating the rate of metallization from gas analysis data are developed. The probable mechanism of the reaction is indicated. New data on the effect of gas velocity, gas composition, and particle size upon the rate of metallization are obtained. The relative rate of reduction and metallization is shown to increase as density decreases. This confirms the work of others. The hypothesis that the metallization zone advances into the ore particle at a constant linear rate is well substantiated. The rate of advance of the metallization zone is shown to be roughly proportional to the square root of the gas velocity. The effect of gas composition upon the rate of metallization is shown for two ores. The rate of metallization decreases as the*

*carbon dioxide concentration increases. Increasing the percentage of carbon dioxide has a very different effect upon different ores. The effect of particle size is shown for three ores. The rates vary with size so that the time for complete metallization is practically independent of particle size over the range studied. All three sizes were below 1 cm. in diameter. The time required to reach the composition ferrous oxide is given for the various ores, particle sizes, and gas velocities. The data are not extensive enough to make any prediction as to the mechanism of the first two steps of the reaction. In general, the same factors which cause rapid metallization cause a rapid reduction to ferrous oxide.*

THE reduction of iron ore is probably second only to the combustion of carbon in importance to industry. Naturally such a reaction has received a great deal of attention from many investigators in the past. Almost all of the work upon iron ore reduction has, however, taken the form of a study of various aspects of the blast furnace and its operation. Because of the great complexity of the processes which a blast furnace carries out, it is difficult to obtain specific data upon the rates of a single reaction from the study of blast furnace data. Moreover, the greater part of such data has been concerned with the fuel requirements under various conditions or with the effect of operating variables upon the quality of the pig iron produced. Thus the rates of the reactions have received little attention.

More recently, considerable attention has been given to the low-temperature reduction or "sponge iron" process. In such low-temperature reduction processes, the reactions of slag formation and melting are absent, so the results might be used in calculating the rate of the reduction reactions. As a matter of fact, however, most of the available data on sponge iron processes are not sufficiently complete to give fundamental information on actual rates of reduction.

Most of the laboratory investigations on the rate of reduction of iron ores have been carried out under conditions that have little relation to practice, and thus the data obtained are not applicable to the design or operation of commercial equipment.

### KINETICS OF HETEROGENEOUS REACTIONS

In a single-phase, or homogeneous, reaction the reaction velocity is approximately proportional to the "concentration distance" from equilibrium of the reactants. The actual chemical reaction is the only process involved.

In a heterogeneous reaction, such as is encountered in the reduction of iron oxide, the conditions are quite different. Besides the chemical reaction, there is also the transfer of materials across a phase boundary and diffusion of one phase

through another. Thus, in the reduction of iron oxide the over-all reactions consist of five processes in series: diffusion of the reacting gas through the gas film and through the solid, the chemical reaction, and diffusion of the gaseous products out through the solid and the gas film. Under a given set of conditions there will be a definite concentration gradient across each of these "resistances." There is no simple relation between the over-all rate of reaction and the concentration gradient.

As in the case of heat transfer where there are several resistances in series, one resistance may be large relative to the others and will thus be the controlling factor. The effect of changing some one condition upon the over-all rate will depend upon which of the processes is the controlling one. Thus, if gas film diffusion were the controlling factor, increase in gas velocity would have a great effect upon the over-all rate, whereas if the chemical reaction or solid diffusion were the controlling factor, increase in gas velocity would have almost no effect upon the over-all rate. In the same way, if gas film or solid diffusion were controlling, a change in temperature would cause only a relatively small change in the rate because diffusional coefficients change only slightly with temperature. If, however, chemical reaction were controlling, change in temperature would have a very great effect upon the rate of the reaction.

Thus in heterogeneous reactions, while the equilibrium conditions naturally set the limits, they are not necessarily the chief factor in the control of the reaction velocity as they are in the case of homogeneous reactions. The mechanism of the reaction within the solid ore particle can be fairly well predicted. Langmuir (9) has shown that in a gas-solid reaction which involves two solid phases, giving a gaseous product, the gas evolution takes place at the phase boundary. If it can be assumed that, at the time metallization starts, the ore particles have the uniform composition ferrous oxide, then the reaction will occur at the phase boundary between iron and ferrous oxide. In the case of iron and iron oxide,



solid solutions are formed so that the phase boundary, and thus the reaction zone, will be a narrow band of finite thickness instead of a sharp line. This reaction band will appear first at the surface and advance radially inward toward the center of the particle. Work on other reactions, particularly the

at temperatures around 500° to 600° C. and the rate increases rapidly as the temperature is increased. Above 1000° C. the temperature has less effect.

The chemical composition of the ore has a marked effect at low temperature, the ores high in slag-forming constituents showing low rates of reduction. At the higher temperatures, chemical character of the ore has almost no effect upon the reaction rate.

All investigators have shown that the physical character of the ore has a great deal of influence on the reduction rate. Several properties have been used as a means of correlating relative rates of reduction for different ores. In general the dense, impervious ores are reduced slowly while the light porous ores show rapid rates of reduction. There is no such complete agreement in the matter of the effect of gas composition upon the rate of reduction. It is generally recognized that the rate of reduction decreases as the concentration of carbon dioxide in the reducing gas increases. Concerning the quantitative relation, however, the different authors disagree. The work of Bone, Reeve, and Saunders (2) would indicate that the rate of reduction is inversely proportional to the carbon dioxide concentration. Isibi and Hirano (6) indicate in their work that the rate decreases much more rapidly as the carbon dioxide content increases. Stalhane and Malmberg (18) give an equation relating reduction rate and percentage of carbon dioxide. The equation is rather complex and, while it fits their data very well, requires several constants that would be difficult to evaluate and would have little significance for general application.

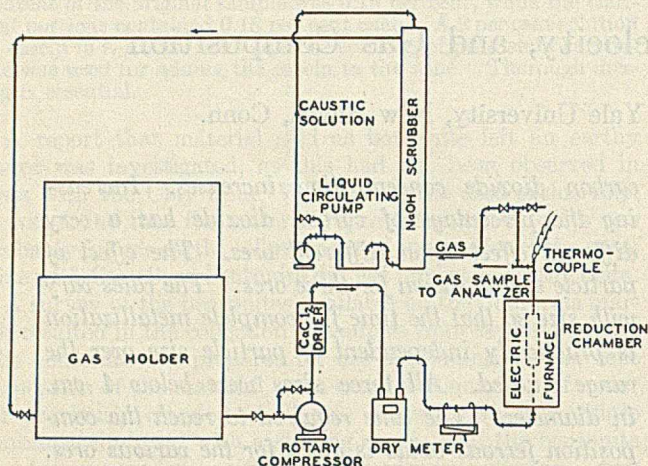


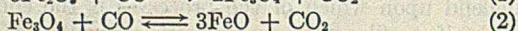
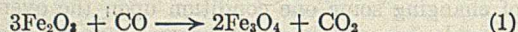
FIGURE 1. APPARATUS FOR STUDY OF RATE OF REDUCTION OF IRON ORES

calcination of limestone and the roasting of sulfide ores, also shows this same reaction mechanism. It is thus seen to be rather general for gas-solid reactions.

#### REVIEW OF PREVIOUS WORK

This paper is confined entirely to a consideration of the reactions between iron oxides and carbon monoxide. The equilibrium conditions in the reaction of carbon monoxide with iron oxides have been investigated by many authors among whom may be mentioned Bauer and Glassner (1), Matsubara (11), Eastman (4), Schenck (17), and Bone, Reeve, and Saunders (2). Ralston (14) gives an excellent summary of the work done up to 1929.

Although slight differences occur in the values of the equilibrium constants obtained by the different investigators, the general conditions are well established. The reduction of iron oxide by carbon monoxide is shown to proceed in three steps:



Reaction 1 is almost irreversible and will proceed in the direction indicated in the presence of small traces of carbon monoxide. Reactions 2 and 3 are definitely reversible. The equilibrium value of carbon dioxide concentration is considerably higher for reaction 2 than for 3. There are no sharp breaks between the three steps, for the solid phases show distinct solid solubility in each other. In this paper the first two steps (1 and 2) are treated together as "reduction to ferrous oxide." The last step (Equation 3) is referred to as "metallization."

Among the investigators who have studied the rate of the reduction of iron ores and sinters may be mentioned Bone, Reeve, and Saunders (2), Meyer (12), Diepschlag and Zillgen (3), Isibi and Hirano (6), Stalhane and Malmberg (18), Kamura (8), Joseph, Barrett, and Wood (7), Eastman (5), Weinert (19), and Royster, Joseph, and Kinney (15).

From the results of the work done with carbon monoxide, the effect of temperature and physical character of the ore on the rate of the reduction reaction has been qualitatively established. The reaction rate is shown to increase considerably as the temperature rises. The reduction is very slow

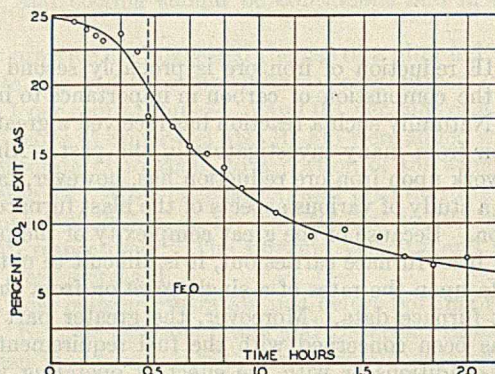


FIGURE 2. TYPICAL RUN IN STUDY OF RATE OF REDUCTION OF IRON ORE

Material, Port Henry sinter through 6 on 10 mesh; depth of bed, 10 cm.; rate of gas flow, 18.0 standard liters per sq. cm. per hour; average temperature, 823° C.

The effect of gas velocity upon the rate of reduction has received very little attention. As far as could be determined, no quantitative results have been described, and only a few writers have even mentioned the fact that the rate did increase with increasing gas velocity.

The effect of particle size, again, is a subject upon which there is some uncertainty. The general opinion is that with fine particles, up to 1 cm. in diameter, particle size has no effect upon the time required for complete metallization. With the larger size, the time for complete metallization, particularly with dense ores, does increase as the particle size is increased. Stalhane and Malmberg (18), working with a magnetite ore, show that the time for complete reduction is about proportional to the diameter in the range of sizes from 1 to 4 cm. Kamura (8), working with a hematite ore, shows that the time for complete reduction was doubled when the particle size had been increased about 3.5 fold.

Relative to the assumption that the ore particles had the uniform composition ferrous oxide at the time that iron first appeared, Diepschlag and Zillgen (3) show that for all par-

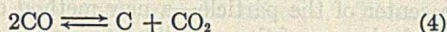


ticles under 1 cm. practically no ferric iron is present in samples which contain metallic iron. This indicates that the supposition that the particle is entirely ferrous oxide before the metallization begins is correct for the small particles. Stalhane and Malmberg (18) state that three zones—iron, ferrous oxide, and ferroferric oxide—were present in all ore particles during the reduction, but their particles were all over 1 cm. in diameter. Thus the hypothesis that the particle is entirely ferrous oxide at the start of the metallization period has a sound basis if the largest particles are below 1 cm.

Concerning the progress of metallization, Stalhane and Malmberg (18) state that, for both hydrogen and carbon monoxide reduction, the iron zone advances radially at a constant rate from the surface towards the center. With all fine-grained ores the distinction between the zones is very sharp.

In the case of very porous ores the distinction becomes less sharp. Weinert (19) states that the metallization starts from several points within the lump and proceeds outward from these points. Most of the evidence, however, supports the Stalhane and Malmberg conclusions (18).

In any study, whether of equilibrium or rates, in which carbon monoxide is involved, the reaction,



must be considered. This reaction is important at all temperatures between 250° and 750° C. It has a maximum rate around 450° C. Iron or iron oxides are excellent catalysts for this reaction. Bone, Reeve, and Saunders (2) have shown that for temperatures below 600° C. carbon deposition limits the extent of reduction which can be reached with any given ore. The carbon deposition increases as the stage of reduction increases until eventually all of the carbon monoxide is being used up in the decomposition reaction. Meyer (12) also shows that carbon deposition increases as the stage of reduction advances. Bone, Reeve, and Saunders (2), Meyer (12), and Diepschlag and Zillgen (3) all show that the carbon deposition increases greatly as the reducibility of the ore decreases.

#### SCOPE OF PRESENT INVESTIGATION

The purpose of the present investigation is to fill in some of the gaps left by the previous experimenters, but it has been practically limited to a study of the reduction of ferrous oxide by carbon monoxide at one temperature only, 825° C.

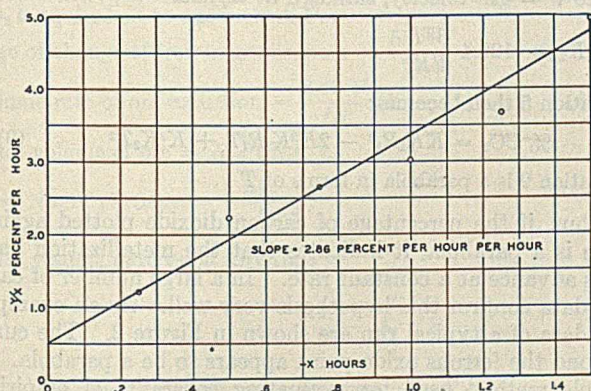


FIGURE 3. EVALUATION OF CONSTANTS FOR PARABOLIC EQUATION OF DATA OF FIGURE 2

The reaction involved is that of Equation 3. At 825° C. the equilibrium conditions are reached when carbon dioxide equals 37 per cent in an atmosphere of carbon dioxide and monoxide. From a practical standpoint this step is by far the most important because it accounts for two-thirds of the total oxygen removal and because its rate is slow, about 90 per

cent of the total reduction time being required for this last step. A few data were also obtained on the length of time required for the first two steps (Equations 1 and 2).

The variables studied were gas velocity, gas composition, particle size, and type of ore. The gas velocity was varied from 1.34 to 200.0 liters per sq. cm. per hour. The reducing

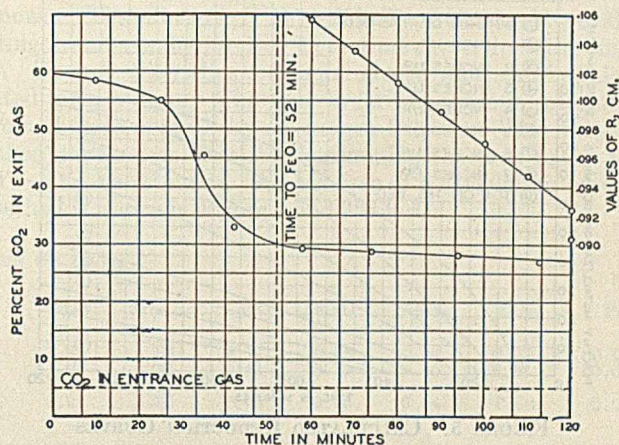


FIGURE 4. TYPICAL CALCULATION BY SECOND METHOD (RUN 51)

Material, Moose Mountain briquet through 6 on 10 mesh; gas velocity, 8.47 standard liters per sq. cm. per hour; average temperature, 824° C.

gases were various mixtures of carbon monoxide and dioxide dried over calcium chloride. Three particle sizes were used: 14 to 20 mesh, 6 to 10 mesh, and 3 to 4 mesh (Tyler screen sizes). The average screen openings were 0.09, 0.216, and 0.575 cm., respectively.

Four ores were used: a natural Mesabi ore, a briquet made from Moose Mountain ore, a sinter made from a concentrate of this same Moose Mountain ore, and a material known as Port Henry sinter. The analysis of the ores is given in Table I.

#### APPARATUS AND EXPERIMENTAL PROCEDURE

The general arrangement of the apparatus is shown in Figure 1:

The electric furnace was 2 feet (61 cm.) long with a uniform nichrome winding. The reduction tube was made from a section of one-inch (2.5-cm.) standard iron pipe. The inlet and outlet tubes were 0.25-inch (0.635-cm.) brass pipe. The length of the one-inch iron section varied according to the depth of bed which was to be used. Most of the runs were made with an 8-inch (20.4-cm.) bed although a few runs were made with 4-inch (10.2-cm.) and 12-inch (30.5-cm.) beds. The section of one-inch pipe was about 3 inches (7.6 cm.) longer than the depth of the bed.

The brass inlet tubes were necessary because in entering and leaving the furnace the gas passed through the 250° to 750° C. temperature range in which there is extensive carbon deposition, as shown by Equation 4. If iron pipes were used, they quickly became clogged with carbon. Carbon deposition reaction did not occur to any detectable extent on the brass surface.

The furnace was hinged along the back to facilitate the insertion of the reduction tube. The reduction tube itself was made with unions on each end. The current to the furnace was regulated by a water-cooled rheostat. Temperatures were measured by a chromel-alumel thermocouple which was inserted to the center of the ore bed inside the reduction tube. The thermocouples had to be renewed quite frequently. All couples were made from a single batch of wire. Samples of these wires were calibrated against a Bureau of Standards platinum couple and found to agree within 5° at 800° C.

By properly placing the one-inch-diameter section of the reduction tube and by inserting refractory plugs around the inlet and outlet tubes above and below this one-inch-diameter section, it was possible to keep the temperature gradients to less than 5° C. in a length of 20 cm. In the case of the 30.6-cm. beds the temperature gradients were about 20° C.



The carbon monoxide was formed by the decomposition of formic acid in the presence of phosphoric acid at about 200° C. The gas was scrubbed with sodium hydroxide and stored in a 50-cubic-foot (1.4-cubic-meter) gas holder. During each run the exit gas from the reduction tube was passed through the sodium hydroxide scrubber to remove the carbon dioxide formed, and the carbon monoxide led back to the holder.

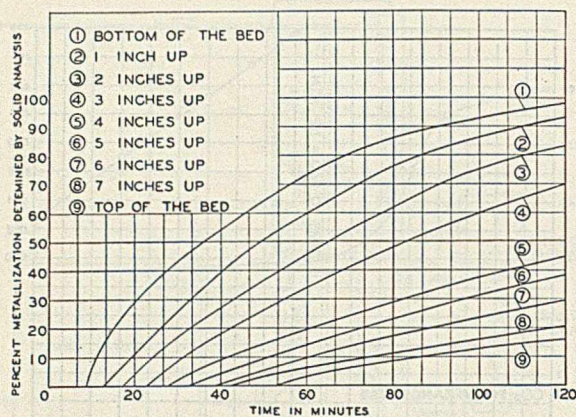


FIGURE 5. CALCULATED REDUCTION CURVES

Material, Moose Mountain briquet; gas velocity, 13.2 standard liters per sq. cm. per hour

The gas was analyzed in a thermal-conductivity gas analyzer similar to that described by Palmer and Weaver (13) for carbon monoxide-dioxide mixtures. The cells were calibrated to read directly in percentage carbon dioxide and were checked by frequent Orsat analysis.

Samples of the ore after the reduction were analyzed for metallic iron by the hydrogen evolution method as described by Martin (10).

In making a run, the general procedure was as follows:

The tube was charged with 2 inches (5 cm.) of crushed fire brick. A copper screen was placed over the brick and the desired depth of ore was added. The thermocouple was inserted from above into the center of the ore bed. The crushed brick distributed the gas stream evenly over the cross section of the bed and heated the incoming gas to the temperature of the bed before it reached the ore.

After charging, the tube was placed in the furnace and connected to the gas line. The temperature of the furnace was regulated by adjusting the current. About 2 hours were required to bring the temperature up to the desired value of 825° C. Because of the large heat capacity of the furnace and reduction tube the starting of the gas stream had very little effect upon the temperature.

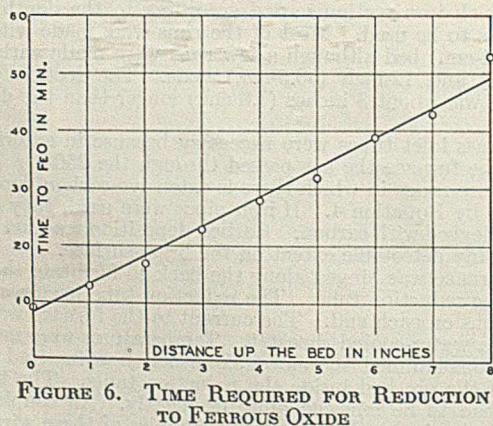


FIGURE 6. TIME REQUIRED FOR REDUCTION TO FERROUS OXIDE

Material, Moose Mountain briquet; gas velocity, 13.2 standard liters per sq. cm. per hour

The gas velocity was regulated by adjusting the by-pass valve on the compressor or by adjusting the valve on the outlet side of the reduction tube. The constancy of gas velocity was noted by watching the slant gage connected around the orifice on the inlet to the reduction tube. The total volume of gas flowing in a given run was read from the dry gas meter.

At the end of the run the sample was allowed to cool in the furnace, but, owing to the small amount of carbon monoxide in the tube at any one time, there was no appreciable reduction after the gas stream had been stopped. Because the reduced material is subject to reoxidation, it was cooled practically to room temperature before it was removed from the tube.

In practically all cases the material had jammed in the tube and had to be dug out with a pointed steel rod. Thus, there was considerable disintegration of the lumps of ore in removing them from the tube.

#### METHODS OF CALCULATION

In working up the data of this investigation, three methods of calculating the rate of metallization were used. Two of these were based on a consideration of the analysis of the entrance and exit gases. The third method was based upon the analysis of the solid material at the end of the reduction period.

**FIRST METHOD.** On the basis of the assumed reaction mechanism—namely, that the particles approximate spheres, that the particle is entirely ferrous oxide when metallization begins, and that the metallization occurs in a narrow band which advances at a constant linear rate from the surface to the center of the particle—a new method of calculating the rate of advance of the metallization zone has been developed:

$$\text{Let } R = \text{radius of the unreduced zone; then } dR/dT = K$$

$$\text{Volume of ore reduced per unit time} = 4\pi R^2 K \quad (5)$$

$$\text{Liters of CO}_2 \text{ formed per unit time} = 4\pi N K (R_1 - KT)^2 SI \frac{22.4}{55.8} \quad (6)$$

$$N = \frac{3}{4} \frac{W}{\pi S R_1^3} \quad (7)$$

where  $N$  = No. of particles in the bed

$W$  = weight of ore in the charge

$S$  = sp. gr. of original charge

$I$  = % total iron in ore

100

$K$  = rate of advance of reduction zone, cm./hour

$R_1$  = initial radius of particle, cm.

$T$  = time, hours

In the experimental data, the percentage and not the total amount of carbon monoxide is known:

$$\% \text{ CO}_2 = (\text{volume of CO}_2 \text{ formed} \times 100) / \text{gas volume flowing}$$

Therefore, from Equations 6 and 7:

$$\% \text{ CO}_2 = 120.4 \frac{W}{V} K \frac{I}{R_1^3} (R_1 - KT)^2 \quad (8)$$

where  $V$  = gas velocity, standard liters/hour

$$\text{Let } K_2 = 120.4 \frac{WI}{VR^3}$$

Equation 8 then becomes:

$$\% \text{ CO}_2 = K K_2 R_1^2 - 2K^2 K_2 R_1 T + K^3 K_2 T^2 \quad (9)$$

Equation 9 is a parabola in terms of  $T$

Thus, if the percentage of carbon dioxide plotted against time is a parabola, it indicates that the metallization band does advance at a constant rate. In a large number of cases the data confirm this hypothesis very well. As an example, the data of a typical run are shown in Figure 2. The curve beyond the ferrous oxide point appears to be a parabola. A simple method used for evaluating constants of empirical equations (16) will show that this is correct.

Let  $\bar{X} = X - X_0$  and  $\bar{Y} = Y - Y_0$ , where  $X_0$  and  $Y_0$  are the coordinates of some arbitrary point on the curve. The plot of  $(\bar{Y}/\bar{X})$  vs.  $\bar{X}$  will be a straight line if the original curve is a parabola. In Figure 3 the  $(\bar{Y}/\bar{X})$  vs.  $\bar{X}$  values for the curve of Figure 2 are given. Although the points spatter somewhat, it is obvious that a straight line fits them better than any other simple curve.



The slope of the  $(\bar{Y}/\bar{X})$  vs.  $\bar{X}$  line is the value of the constant,  $c$ , in the general parabolic equation:

$$Y = a + bX + cX^2$$

In Equation 9, however,  $c$  is equivalent to  $K^3K_2$ . Thus:

$$K = \sqrt[3]{\frac{LV R_1^3}{120.4 WI}} \quad (10)$$

where  $L$  = the slope of the  $(\bar{Y}/\bar{X})$  vs.  $\bar{X}$  line

The fact that, in computing the  $\bar{Y}$  and  $\bar{X}$  values, an arbitrary point  $X_0$  and  $Y_0$  was used is of great advantage in the application of the method. If the values of  $Y$  were shifted, which is equivalent to adding a constant amount to the percentage of carbon dioxide, the calculated rate of advance of

$$R^3 = R_1^3 \left[ 1 - \frac{2.49 V}{IW} \int_0^T (Y - Y_0) dT \right] \quad (16)$$

$$R = R_1 \sqrt[3]{1 - \frac{2.49 V}{IW} \int_0^T (Y - Y_0) dT} \quad (17)$$

From the data of a run the values of  $R_1$ ,  $V$ ,  $W$ , and  $I$  are known. The values of  $\int_0^T (Y - Y_0) dT$  are obtained by evaluating the area under the  $Y - Y_0$  vs. time curve, up to the time,  $T$ . Thus  $R$ , the radius of the unreduced zone, can be calculated for any time. The time to ferrous oxide is calculated from the gas analysis by an oxygen balance. This value is taken as the zero time for determining the area under the  $(Y - Y_0)$  vs.  $T$  curve. An example of a calculation by this method is shown in Figure 4 and Table II.

TABLE I. ANALYSIS OF ORES

MATERIAL	SP. GR.	MOISTURE %	LOSS ON IGNITION %	Fe <sub>2</sub> O <sub>3</sub>	FeO	SiO <sub>2</sub>	Mn <sub>2</sub> O <sub>4</sub>	CaO	MgO	Al <sub>2</sub> O <sub>3</sub>	SO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>
Mesabi	3.25	1.30	5.30	81.0	0.0	7.42	1.05	3.11	0.08	2.51	0.03	0.045
Moose Mt. briquet	4.25	0.0	0.0	81.5	2.58	11.25	3.31	0.44	0.19	1.46	0.02	0.032
Moose Mt. sinter	4.86	0.0	0.0	68.8	30.9	0.10						
Port Henry sinter	4.78	0.0	0.0	68.2	23.4	3.99	3.35	1.76	0.18	2.44	Trace	0.027

the metallization zone would not be affected. Thus, any constant source of carbon dioxide other than iron ore reduction would not affect the calculations. This method depends entirely on the rate of change of the gas composition.

**SECOND METHOD.** In applying the method of calculation just outlined, some of the experimental data gave excellent results. There were a number of runs, however, in which the values of  $(\bar{Y}/\bar{X})$  vs.  $\bar{X}$  spattered so badly that it was difficult to establish the best straight line. In such cases no reasonable accuracy in the calculated rate of advance could be expected.

To meet this situation, a new method of calculation was developed which would not be as sensitive to small variations in the data. This method is based upon an oxygen balance.

Consider the reaction:  $\text{FeO} + \text{CO} \rightleftharpoons \text{Fe} + \text{CO}_2$

Let  $V$  = rate of gas flow, liters/hour

$$Y = \frac{\% \text{CO}_2 \text{ in the exit gas}}{100}$$

$$Y_0 = \frac{\% \text{CO}_2 \text{ due to entrance gas or side reactions}}{100}$$

$$\text{Rate of formation of CO}_2 \text{ in moles/hour} = \frac{V}{22.4} (Y - Y_0) \quad (11)$$

From the equation:  $\text{FeO} + \text{CO} \rightleftharpoons \text{Fe} + \text{CO}_2$ , one mole of  $\text{CO}_2$  is equivalent to one mole of Fe:

$$\text{Rate of change of iron in grams/hour} = \frac{55.8 V}{22.4} (Y - Y_0)$$

$$\text{Volume rate of ore reduction} = \frac{2.49 V}{IS} (Y - Y_0) \quad (12)$$

$$\text{Total volume of ore} = N \frac{4}{3} \pi R_1^3$$

$$N = \text{No. of particles} = \frac{3W}{4\pi R_1^3 S}$$

Total volume reduced at any time =

$$\frac{2.49 V}{IS} \int_0^T (Y - Y_0) dT \quad (13)$$

For a single particle the volume reduced =

$$\frac{4\pi R_1^3 \cdot 2.49 V}{3IW} \int_0^T (Y - Y_0) dT \quad (14)$$

Then at any time,

$$4/3\pi R^3 = 4/3\pi R_1^3 - 4/3\pi R_1^3 \frac{2.49 V}{IW} \int_0^T (Y - Y_0) dT \quad (15)$$

where  $R$  = radius of unreduced zone

$R_1$  = original radius of the particle

Expanding this and collecting terms,

TABLE II. CALCULATION OF RATE OF ADVANCE BY GRAPHICAL INTEGRATION<sup>a</sup>

T FROM GRAPH	$\int_0^T (Y - Y_0) dT$	$1.275 \int_0^T$	$1 - 1.275 \int_0^T$	$\sqrt[3]{1 - 1.275 \int_0^T}$	R
60	0.0557	0.0710	0.929	0.977	0.1055
70	0.0995	0.1263	0.873	0.957	0.1034
80	0.1393	0.1775	0.822	0.937	0.1012
90	0.1780	0.227	0.773	0.918	0.0992
100	0.217	0.277	0.723	0.898	0.0970
110	0.254	0.324	0.676	0.878	0.0948
120	0.291	0.371	0.629	0.857	0.0925

<sup>a</sup> Zero time for the integral limits is 60 minutes.

In this run, gas velocity = 55.2 standard liters per hour,  $W = 182.6$  grams,  $I = 0.59$ , and  $R_1 = 0.108$  cm.  $(2.49 V)/IW = 1.275$ . Since  $W$  refers to the weight of the entire bed, the gas flow is for the entire bed rather than for unit cross-sectional area:

$$R = 0.108 \sqrt[3]{1 - 1.275 \int_0^T (Y - Y_0) dT}$$

The values of  $R$  vs.  $T$  give a very good straight line, from the slope of which the rate of advance of the metallization zone is shown to be equal to 0.0135 cm. per hour.

**COMPARISON OF THE TWO METHODS.** Of the two methods of calculation, the graphical integration method is seen to be more direct. It gives better results in runs in which the data vary slightly from the parabolic form. Also, the graphical integration method makes no assumption as to the mechanism of the reaction but tends to show what the mechanism actually is. It has one disadvantage, however, in that the value of  $Y_0$ , the percentage of carbon dioxide coming from sources other than iron ore reduction, must be known in order to obtain accurate results. The sources of carbon dioxide other than reduction were carbon deposition, carbon dioxide formed by air leaking into the system, and carbon dioxide formed in the reaction  $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ . Since the gas was dried and there was no appreciable amount of hydrogen in the exit gas, this last source of carbon dioxide was of no importance.

**THIRD METHOD.** The parabolic and the graphical integration methods have very definite limitations. They are both based upon the analysis of the exit gas. Since the exit gas shows the summation of all the carbon dioxide formation in the entire bed, any rate of metallization which is calculated from the exit gas analysis must be an average rate for the entire bed. Actually, as the percentage of carbon dioxide increases in going up the bed, the rate of metallization decreases.



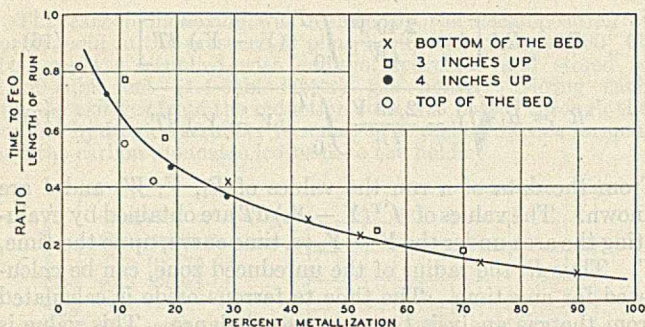


FIGURE 7. RATIO OF (TIME TO FERROUS OXIDE)/(TOTAL TIME) AS A FUNCTION OF PERCENTAGE OF METALLIZATION

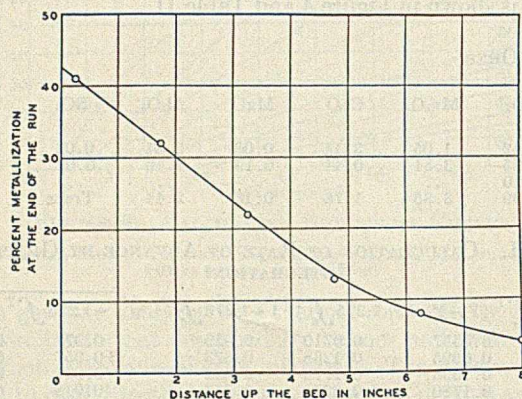


FIGURE 8. SOLID ANALYSIS OF RUN 63

Material, Moose Mountain briquet through 6 on 10 mesh; weight of ore, 176.5 grams; length of run, 17.0 minutes; gas velocity, 52.9 standard liters per sq. cm. per hour

The difficulty of changing gas composition could have been avoided by using very short beds. In such a case, however, the change in composition between the entrance and exit gas would have been so small that the analytical errors would have been greatly magnified.

To eliminate these discrepancies, a third method of calculation was devised, based upon the analysis of the solid material at different levels in the bed. At the end of each run, samples were taken from six different levels. The distance which the metallization zone has advanced at any time is a simple function of the percentage of metallization of the sample, as is shown by the following derivation:

$$\text{Volume reduced} = \frac{4}{3}\pi R_1^3 - \frac{4}{3}\pi R^3 \quad (18)$$

$$\text{Volume reduced} = \frac{4}{3}\pi R_1^3 M \quad (19)$$

$$R_1 = \text{radius of the particle, } R = \text{radius of unreduced ore}$$

$$M = \frac{\% \text{ metallization}}{100}$$

$$\% \text{ metallization} = \frac{\% \text{ metallic iron}}{\% \text{ total iron}} \times 100$$

$$\frac{4}{3}\pi R_1^3 - \frac{4}{3}\pi R^3 = \frac{4}{3}\pi R_1^3 M \quad (20)$$

$$R_1^3 - R^3 = R_1^3 M \quad (21)$$

$$R = R_1 \sqrt[3]{1 - M}$$

$$D = R_1 - R$$

where  $D$  = distance the metallization zone has advanced

$$D = R_1 (1 - \sqrt[3]{1 - M}) \quad (22)$$

Figure 5 shows the experimental results of a number of runs which were made to determine the relation between percentage of metallization and time for various levels in the bed. The original data points are not shown here, as the results had to be corrected to a common gas velocity as will be explained later.

TIME REQUIRED TO REACH THE COMPOSITION FERROUS OXIDE. To obtain the rate of advance, the time during which metallization was taking place must be known. Thus the time required to reach the composition ferrous oxide must be

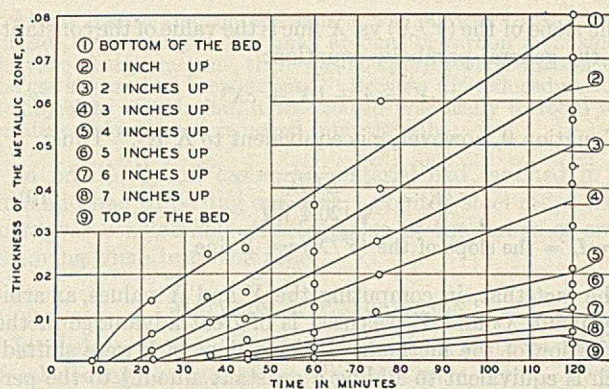


FIGURE 9. THICKNESS OF METALLIC ZONE vs. TIME

All values are corrected to a common basis of 13.2 standard liters per sq. cm. per hour.

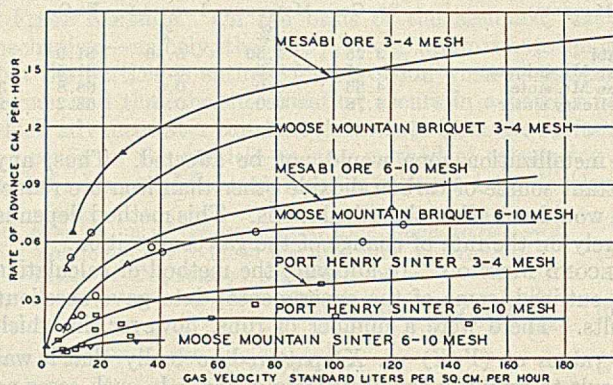


FIGURE 10. RATE OF METALLIZATION vs. GAS VELOCITY

subtracted from the total time of the experiment. In order to compute the time required to reach the composition ferrous oxide, two assumptions were made: (1) the time to reach ferrous oxide vs. the distance up the column is a straight line; (2) the ratio (time to reach ferrous oxide)/(total time) is a function of the percentage of metallization only and is independent of position in the bed, gas velocity, etc. This latter assumption implies that any factor which increases the metallization rate will increase the rate of reduction to ferrous oxide by a proportional amount. Figure 6, which was obtained by taking the time for 0 per cent metal and plotting against distance up the bed as obtained from the extrapolated curves of Figure 5, shows that the first assumption is essentially correct. The curves of Figure 5 were also used to compute the data of Figure 7 which confirms the second assumption. In this figure the ratio (time to reach ferrous oxide)/(total time) is plotted against percentage of metallization for various positions in the bed. Although the data scatter, there is no consistent variation with position in the bed and the points may be best represented by a single curve.

To illustrate the use of this method, consider Figure 8 which gives the solid analysis for run 63. The metallization at the top of the bed is 4 per cent and at the bottom is 42 per cent; the length of the run is 17 minutes. From Figure 7, when percentage metallization = 42 per cent, the ratio (time to reach ferrous oxide)/(total time) = 0.29. Therefore time to reach ferrous oxide at the bottom of the bed = 5.0 minutes. The percentage of metallization at the top of the bed = 4 per cent, from which the ratio (time to reach ferrous oxide)/(total time) = 0.80. Therefore time to reach ferrous oxide at the top of the bed = 13.6 minutes. Since the time to reach ferrous oxide varies linearly up the bed, the average time to reach ferrous oxide would be 9.3 minutes. From an oxygen balance based upon the gas analysis, the average



time to reach ferrous oxide is 9.1 minutes. This is a satisfactory check.

From the total length of the run (17 minutes in the case of run 63) the time to reach ferrous oxide at each level in the bed is subtracted. From the total distance advanced at each level (calculated from the solid analysis by Equation 22) and the time since metallization started, the average rate of advance of the metallization zone can be determined for each position in the bed.

**CALCULATION OF THE GAS COMPOSITION IN THE BED.** From the curves of percentage metallization *vs.* position in the bed, it is possible by an oxygen balance to calculate the values of percentage in carbon dioxide in the gas for all positions in the bed. The bed is divided into equal zones so that a sample is taken from each zone for solid analysis. From the average percentage metallization and the weight of ore in each zone, the total carbon dioxide formed in that zone during the metallization period can be determined. From the gas velocity and the length of the run after ferrous oxide had been reached for each zone, the total amount of gas which passed through each zone during metallization can be determined.

From the carbon dioxide formed and the total gas flowing, the average increase in percentage of carbon dioxide caused by the gas passing through each zone is determined. The average percentage of carbon dioxide at any point in the bed is equal to the percentage of carbon dioxide in the entrance gas plus the summation of the increments of percentage carbon dioxide due to all the zones below the point in question. The resultant curve of percentage carbon dioxide *vs.* position in the bed represents the average conditions for each point during the entire metallization period.

Thus, for each run for which solid analyses are available, both the rate of advance of the metallization zone and the average percentage of carbon dioxide can be determined for each level in the bed.

### EXPERIMENTAL RESULTS

**CONFIRMATION OF THE REACTION MECHANISM.** The parabola method of calculating the rate of advance of the metallization zone was based upon the assumption that this

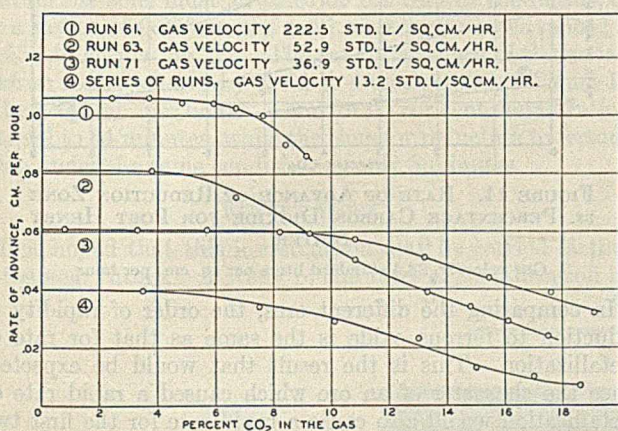


FIGURE 11. RATE OF ADVANCE OF REDUCTION ZONE *vs.* PERCENTAGE CARBON DIOXIDE IN THE GAS FOR MOOSE MOUNTAIN BRIQUET (THROUGH 6 ON 10 MESH)

linear rate of advance was constant. The results of the calculations of the rate of advance by the graphical integration method showed that this rate actually was constant (Figure 4).

In Figure 9 the results of a group of runs in which the calculations were based upon the results of solid analysis are shown. This figure shows distance advanced *vs.* time for

different levels in the bed. Although the points spatter somewhat, it can easily be seen that the lines are for the most part substantially straight. In the series of runs from which Figure 9 was computed, the same material and particle size were used in all cases. All rates of advance were corrected to a common gas velocity by assuming that the rate of advance of the metallization zone is proportional to the square root of the gas velocity. The correctness of this assumption will be shown later in this article.

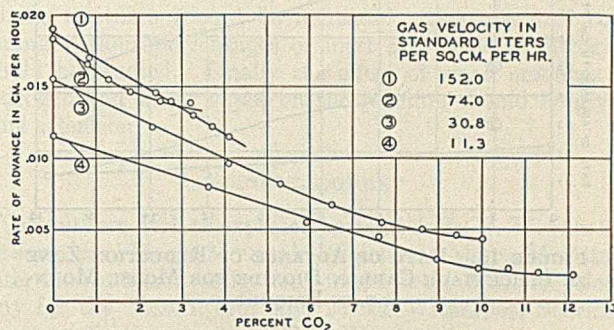


FIGURE 12. RATE OF ADVANCE OF REDUCTION ZONE *vs.* PERCENTAGE CARBON DIOXIDE FOR PORT HENRY SINTER (THROUGH 6 ON 10 MESH)

Thus the constancy of the rate of advance of the metallization zone is shown by the results of calculations both from the gas analysis data and from the solid analysis data.

The curves of Figure 5 were computed from the straight lines of Figure 9 by means of Equation 22. This means of deriving the curves of Figure 5 was used because the data of Figure 9 had been corrected to a common gas velocity so that the percentage metallization *vs.* time curves computed from them would be on a common basis, whereas the original data points were obtained at slightly different gas velocities.

**EFFECT OF GAS VELOCITY.** In Figure 10 the rates of metallization for the different materials and particle sizes are plotted against gas velocity. For the Mesabi ore, the Moose Mountain briquet, and the Moose Mountain sinter the rate of advance of the metallization zone increases approximately as the square root of the gas velocity. In the case of the Port Henry sinter the effect is somewhat different. Over low ranges of gas velocity the rate of advance increases with gas velocity. At about 50 liters per sq. cm. per hour the rate of advance approaches an asymptote, and further increase in gas velocity has no further effect upon the rate of advance of the metallization zone. This change in the effect of gas velocity, in the case of the Port Henry sinter, is probably due to the shift of the controlling process from diffusion through the gas film to diffusion through the solid as described in the section on the kinetics of heterogeneous reactions.

The curves of Figure 10 were computed from the exit gas analysis by the graphical integration method. As mentioned in the discussion of those methods, the rates so computed are average rates for the entire bed. Owing to changing gas velocity, the percentage carbon dioxide in the exit gas and also the average percentage carbon dioxide in the bed will vary from one run to another. As gas composition has a definite effect upon the rate of advance of the metallization zone, this will affect the results of Figure 10, as will be discussed later.

**COMPARISON OF THE DIFFERENT ORES.** The comparative rates of metallization for the different ores are best shown in Figure 10. Considering the 6 to 10 mesh particle size, the Mesabi ore shows the highest rate, the Moose Mountain briquet is slightly less, the Port Henry sinter is considerably lower, and the Moose Mountain sinter is slightly below the



Port Henry sinter. The ores thus follow the usual order of decreasing rate of reduction with increasing density. The relation between rate of metallization and density is not linear. With data on only four materials, no general quantitative relation between metallization rate and density can be made.

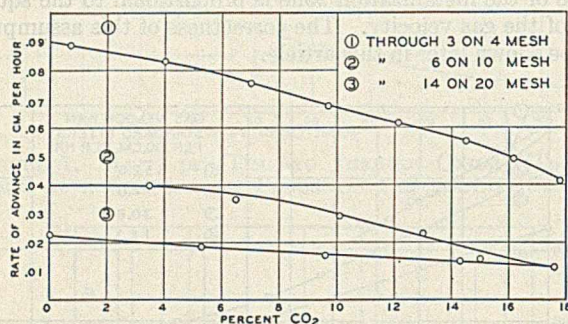


FIGURE 13. RATE OF ADVANCE OF REDUCTION ZONE vs. PERCENTAGE CARBON DIOXIDE FOR MOOSE MOUNTAIN BRIQUET

**EFFECT OF GAS COMPOSITION.** In Figures 11 and 12 the effect of gas composition upon the rate of advance for constant screen size and different gas velocities is shown for Moose Mountain briquet and Port Henry sinter. For both materials the rate decreases as the percentage of carbon dioxide increases, but the shape of the curves is different for the two materials. In neither case is the relation linear.

The data are hardly consistent enough to warrant the development of equations for the curves of rate of advance vs. percentage carbon dioxide. The Port Henry sinter gives slightly more consistent results than does the Moose Mountain briquet.

The data for rate of advance of reduction zone vs. percentage carbon dioxide for different particle sizes but constant gas velocity are plotted in Figures 13 and 14.

**EFFECT OF GAS VELOCITY UPON THE RATE OF ADVANCE OF THE METALLIZATION ZONE AT 0 PER CENT CARBON DIOXIDE.** In Figure 15 the rates of advance of the metallization zone for 0 per cent carbon dioxide are plotted against gas velocity. Data are shown for Moose Mountain briquet and Port Henry sinter. These curves were computed by taking the values at 0 per cent carbon dioxide from Figures 11 and 12. The shapes of the curves are the same as those of Figure 10. The Moose Mountain briquet shows a rate of advance which increases approximately as the square root of the gas velocity. For the Port Henry sinter, the rate first increases with increasing gas velocity and then approaches an asymptote. Further increase in gas velocity has no effect upon the rate.

**COMPARISON OF THE DATA OF FIGURES 10 AND 15.** The data of Figure 10 were computed from the analysis of the entrance and exit gas by the graphical integration method. Thus the rates shown are the average rates for the entire bed. Since the exit gas contained carbon dioxide, these rates are for some average carbon dioxide value and might be expected to be lower than they would be if no carbon dioxide were present. The data of Figure 15 were taken from an extrapolation to 0 per cent carbon dioxide of data from Figures 11 and 12. As would be expected, they show higher rates of advance than does Figure 10.

**EFFECT OF PARTICLE SIZE.** The effect of particle size upon the rate of metallization is shown by Figures 10, 13, and 14. In all cases the rate of advance of the metallization zone, for a given gas velocity, is shown to be approximately proportional to the diameter of the particle. This implies that, over the range studied, the time for complete metallization would be independent of particle size.

This unusual effect is difficult to explain. The rate is

calculated on the basis of the original particle diameter. In the case of Moose Mountain briquet, the apparent increase in rate with larger particles may be due to the fact that these particles disintegrate so that the particles actually being reduced are much smaller than those originally charged. This disintegration is very marked, particularly in the 3 to 4 mesh size. After a run, 70 per cent of the material was below 4 mesh.

In the case of the Port Henry sinter, which shows almost no disintegration, the particles have such large pores that each lump acts as an agglomerate of small particles. Thus, increasing the gross particle size increases the number of particles per lump but has practically no effect upon the surface to volume ratio. There is no obvious explanation for the effect of particle size in the case of the natural ore.

Whatever the explanation may be, the results confirm those of Diepschlag and Zillgen (3) who also show that, for particles up to 1 cm. in diameter, the metallization at the end of a constant reduction treatment was independent of particle size.

**CARBON DEPOSITION.** The results of previous investigations (2, 3, 12) were confirmed in regard to carbon deposition. In all cases, the Port Henry sinter, the most difficultly reducible ore, gave a small amount of carbon deposition. With the other ores carbon deposition occurred only in runs in which the temperature had dropped below 800° C. at some time.

**TIME REQUIRED FOR REDUCTION TO FERROUS OXIDE.** In considering the time required for reduction to ferrous oxide for the various ores and conditions shown in Figure 16, it should be noted that the values of time to reach ferrous oxide were calculated by an oxygen balance obtained from the gas analysis and are therefore average values for the entire bed.

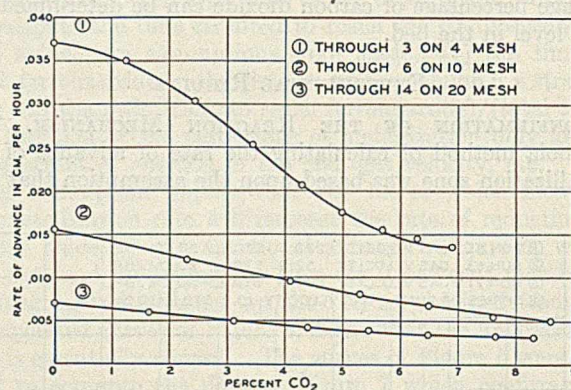


FIGURE 14. RATE OF ADVANCE OF REDUCTION ZONE vs. PERCENTAGE CARBON DIOXIDE FOR PORT HENRY SINTER

Gas velocity, 28.6 standard liters per sq. cm. per hour

In comparing the different ores, the order of rapidity of reduction to ferrous oxide is the same as that for rate of metallization. This is the result that would be expected, since the character of an ore which caused a rapid rate of metallization would also cause a rapid rate for the first two steps of the reduction process.

For the Mesabi ore and the Moose Mountain briquet, the time required for reduction to ferrous oxide for all three particle sizes was the same for a given gas velocity. For the Port Henry sinter this relation did not hold. The time required for reduction to ferrous oxide was about one and one-half times as great for the 3 to 4 mesh size as it was for the 6 to 10 mesh size.

**NUMERICAL EXAMPLE.** The relative importance of the time required to reach the composition ferrous oxide compared to the time for metallization is shown by the following ex-



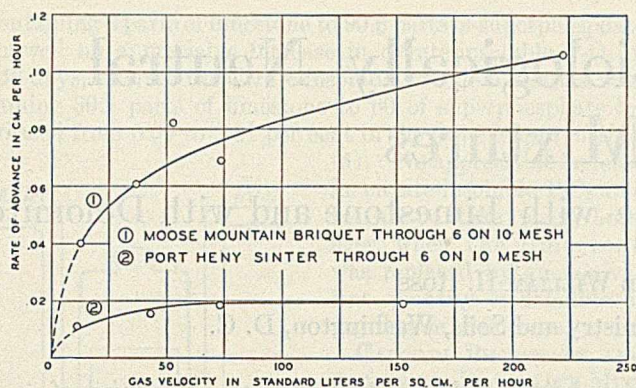


FIGURE 15. RATE OF ADVANCE OF REDUCTION ZONE vs. GAS VELOCITY FOR 0 PER CENT CARBON DIOXIDE

ample: The iron oxide in a lump of Mesabi ore 0.5 cm. in diameter is to be reduced to 95 per cent metal in a gas stream having a low percentage of carbon dioxide and a gas velocity of 100 liters per sq. cm. per hour at a temperature of 825° C. Under these conditions the time to reach ferrous oxide is

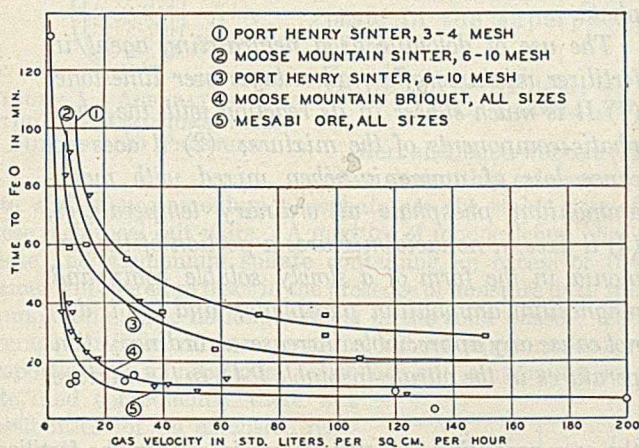


FIGURE 16. TIME TO REACH FERROUS OXIDE vs. GAS VELOCITY

shown by Figure 16 to be 8 minutes. For 95 per cent metallization the zone must advance 62 per cent of the radius, or for a radius of 0.25 cm. the total distance to be advanced is 0.155 cm. (Equation 22). The rate of advance of the metallization zone is shown by the 3 to 4 mesh curve of Figure 10 to be 0.145 cm. per hour. Time for 95 per cent metallization is equal to 64 minutes, while the time for reduction to ferrous oxide under the same conditions is only 8 minutes.

#### FUTURE WORK

It is hoped that this investigation may be carried farther in the near future. A study of the rates of metallization at

higher and lower temperatures would be valuable. Further investigations of a wider range of particle sizes and gas velocities are needed. Increase of the gas velocity into the range used in blast furnace practice would give useful results. At higher gas velocities the Mesabi ore and the Moose Mountain briquet would probably approach a maximum rate similar to that shown by the Port Henry sinter at 50 liters per sq. cm. per hour.

A further study of the effect of gas composition is also desirable. The range of composition of carbon monoxide-dioxide mixtures should be increased. Gas mixtures containing various percentages of inert gas, such as nitrogen, should be studied. Finally the effect of small amounts of hydrogen and water vapor on the reaction should be given some attention.

#### ACKNOWLEDGMENT

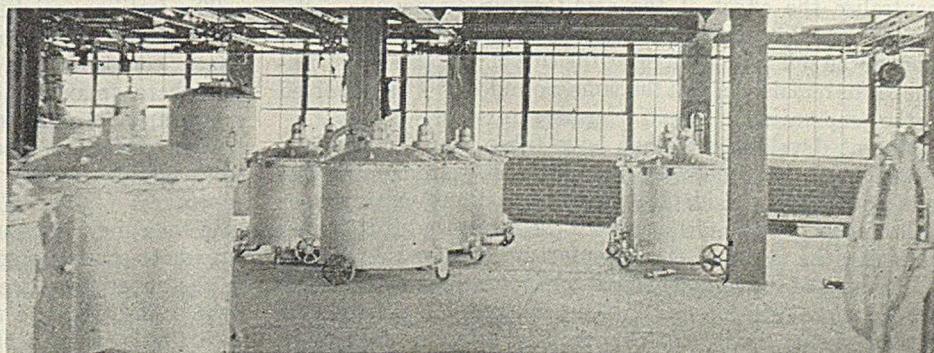
The authors wish to express appreciation to R. W. Cox for the samples of Moose Mountain briquet and Moose Mountain sinter used in this investigation; to the Bethlehem Steel Company for the Mesabi ore; and to the Witherbee, Sherman Company for the samples of Port Henry sinter.

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PORTABLE CHANGE CANS IN  
DULUX ENAMEL BUILDING,  
PHILADELPHIA, PA.





# Preparation of Physiologically Neutral Fertilizer Mixtures

## Reactions of Monoammonium Phosphate with Limestone and with Dolomite

KENNETH C. BEESON AND WILLIAM H. ROSS

Fertilizer Investigations, Bureau of Chemistry and Soils, Washington, D. C.

*Monoammonium phosphate reacts with limestone in all proportions at ordinary temperatures in the presence of moisture to evolve carbon dioxide. Loss of ammonia takes place also when the  $\text{CaCO}_3$  in the mixture exceeds one mole per mole of  $\text{P}_2\text{O}_5$ . At  $90^\circ \text{C}$ . loss of ammonia and carbon dioxide occurs in all proportions of the reacting materials. The rate of the reaction decreases as a rule with increase in the size of the limestone particles.*

*Dicalcium phosphate is formed at  $30^\circ \text{C}$ . in monoammonium phosphate-limestone mixtures containing up to one mole of  $\text{CaCO}_3$  per mole of  $\text{P}_2\text{O}_5$ , and more or less tricalcium phosphate is formed in mixtures containing in excess of this proportion of  $\text{CaCO}_3$ .*

*Monoammonium phosphate reacts with dolomite in the presence of moisture to evolve carbon dioxide, but no loss of ammonia or formation of tricalcium phosphate occurs in any proportion of the reacting*

*materials at ordinary temperatures. One-third of the ammonia entering into the reaction is changed into water-insoluble magnesium ammonium phosphate. Formation of some tricalcium phosphate and loss of ammonia may occur when mixtures of three or more moles of  $\text{CaCO}_3 \cdot \text{MgCO}_3$  are heated at  $90^\circ \text{C}$ . with five moles of monoammonium phosphate.*

*The use of dolomite as a neutralizing agent in fertilizer mixtures offers advantages over limestone: (1) It is much slower in its reaction with the phosphatic components of the mixture; (2) it does not cause loss of ammonia when mixed with monoammonium phosphate at ordinary temperatures; (3) it fixes in nonacid mixtures a portion of the ammonia in the form of a slowly soluble compound, magnesium ammonium phosphate; and (4) it does not cause any appreciable increase at ordinary temperatures in the citrate-insoluble  $\text{P}_2\text{O}_5$  in the mixture.*

FERTILIZER materials may be classified into three groups according as they exhibit an acid, neutral, or basic influence on the soil. The effect of a fertilizer material on the reaction of the soil may bear no relation to the chemical reaction of the material itself. Thus superphosphate which contains an acid salt is neutral as regards its influence on most soils. Liming materials, such as calcium hydroxide or carbonate, decrease the acidity of the soil but ammonium hydroxide increases soil acidity by nitrification to nitric acid. All ammonium salts are likewise acid-forming in the soil, but the nitrates of the alkali and alkaline-earth metals have an opposite effect. The potash salts most commonly used in fertilizers have little or no effect on soil reaction. By proper selection of their components it is thus possible to prepare fertilizer mixtures that are essentially neutral as regards their effect on the reaction of the soil.

For many years the consumption of the physiologically basic forms of fertilizer nitrogen was more than sufficient to neutralize the effect of the acid-forming ammonium salts. The average fertilizer mixture was therefore basic in its reaction on the soil (6). As long as the cost of nitrogen in its various forms remained about the same, no added cost was involved in the preparation of nonacid-forming mixtures.

Recent developments that have taken place in fertilizer manufacture have changed the situation. Ammonia nitrogen now costs considerably less than nitrate nitrogen or other forms of basic nitrogen with the result that it is largely replacing the latter in the manufacture of mixed fertilizers.

The bulk of the complete fertilizers now sold in this country are therefore acid-forming in their influence on the soil. If the use of such fertilizers is to continue, a serious decrease in

the crop-producing capacity of certain soils in the fertilizer-consuming sections of the United States is likely to result (2).

Two methods are available for preventing an injurious increase in the acidity of the soil with continued use of acid-forming fertilizers. The first consists in treating the soil with suitable separate applications of a liming material. This treatment is now being successfully practiced for many crops, but it is not so effective in the case of other crops, such as cotton, that are sensitive to excessive applications of lime. The second method consists in including a sufficient quantity of a basic or liming material in the fertilizer mixture to give a physiologically neutral product. By using the minimum quantity of liming material required to give a nonacid-forming mixture, danger from overliming is eliminated and the expense incident to a separate application of the material is avoided.

### CLASSIFICATION OF PHOSPHATE MIXTURES

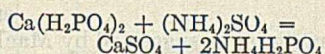
The fertilizer mixtures now on the market may be conveniently divided into three groups according as the phosphatic component of the mixture is present as a calcium phosphate, an ammonium phosphate, or both.

**CALCIUM PHOSPHATE MIXTURES.** The chemical reactions that take place in superphosphate mixtures containing limestone or dolomite have been studied by MacIntire and his co-workers (4, 5). Their results show that mixtures of limestone and superphosphate react with evolution of carbon dioxide to change more or less of the monocalcium phosphate in the superphosphate into di- or tricalcium phosphate, or both. The extent to which these reactions take place varies with the proportion of limestone present. Thus a mixture



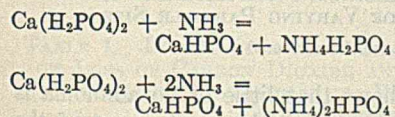
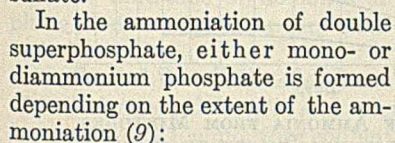
containing 8 parts of limestone to 90.5 parts of superphosphate showed no appreciable increase in citrate-insoluble  $P_2O_5$  in 146 days, whereas the citrate-insoluble  $P_2O_5$  in a mixture containing 30.5 parts of limestone to 60 of superphosphate increased from 0.09 to 2.81 per cent in the same length of time (5). No appreciable increase in citrate-insoluble  $P_2O_5$  was found to take place, however, when the limestone was replaced by an equivalent quantity of dolomite of any degree of fineness.

CALCIUM PHOSPHATE AND AMMONIUM PHOSPHATE MIXTURES. When superphosphate is mixed with ammonium sulfate, as is now common practice in the preparation of mixed fertilizers, reaction may take place between the ammonium sulfate and the monocalcium phosphate in the superphosphate:



Merz and his co-workers (7) have shown that calcium sulfate and monoammonium phosphate are the stable pair of these reciprocal salt pairs. A mixture of monocalcium phosphate and ammonium sulfate containing an excess of the former will therefore react in the presence of moisture until the ammonium sulfate no longer exists in the solid phase. The average fertilizer mixture contains almost equal molecular proportions of monocalcium phosphate and ammonium sulfate, and consequently there are possibilities for an extensive reaction between these two components of mixed fertilizers. Actually the low moisture content of most fertilizer mixtures will retard the reaction, but more or less monoammonium phosphate is no doubt present in all superphosphate mixtures containing ammonium sulfate.

In the ammoniation of double superphosphate, either mono- or diammonium phosphate is formed depending on the extent of the ammoniation (9):



An ammonium phosphate is thus present in all ammoniated mixtures containing double superphosphate.

AMMONIUM PHOSPHATE MIXTURES. Fertilizer mixtures are now being placed on the market in which an ammonium phosphate is the only source of phosphoric acid. These mixtures are of a concentrated nature and are usually made from materials that are readily soluble in water.

The present paper outlines the reactions that take place when a liming material is used in mixtures with monoammonium phosphate. A subsequent paper will describe the corresponding reactions in mixtures containing diammonium phosphate.

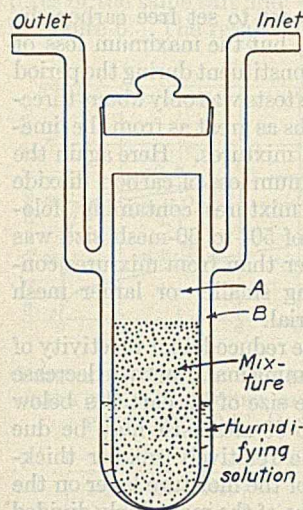


FIGURE 1. APPARATUS FOR STUDYING REACTIONS WITHOUT APPLIED PRESSURE

## EXPERIMENTAL PROCEDURE

MATERIALS. The liming materials used in the tests were calcium carbonate, limestone, and dolomite. The calcium carbonate was the analytical reagent. The compositions of the limestone and of the dolomite were as follows (in per cent):

	MOISTURE	VOLATILE MATTER	ACID-INSOL. MATTER	$\text{Fe}_2\text{O}_3$	MgO	CaO	$\text{CO}_2$	$\text{CaCO}_3$ EQUIVALENT
Limestone	0.06	0.14	Nil	Nil	0.11	55.74	43.76	99.50
Dolomite	0.08	0.87	9.76	0.55	17.10	29.01	41.87	95.22

The different sized particles of limestone and dolomite used in the tests showed little variation in  $\text{CaCO}_3$  equivalent. The purity of the ammonium phosphate was confirmed by analysis and by the pH value (4.38) of its 0.1 M solution.

APPARATUS. Fertilizer mixtures as produced in manufacturing plants are frequently stored in large piles, and portions of such mixtures are therefore necessarily subjected to considerable mechanical pressure. In order to simulate commercial conditions, certain of the mixtures used in these tests were subjected to a mechanical pressure corresponding to that developed in mixtures prepared on a factory scale. The apparatus used to give the pressures was described in a previous paper (1).

The glass apparatus represented in Figure 1 was used to study the reactions taking place without applied pressure:

The mixture under observation was placed in glass tube A which in turn was placed in the glass-stoppered vessel, B, having a gas inlet and an outlet. The annular space between the tube and the walls of the vessel was filled with a liquid or salt suspension having a vapor pressure corresponding to the mixture in tube A.

Duplicates of these two types of reaction vessels were supported in two oil thermostats of which one was maintained at 30° and the other at 90° C. A stream of air from which carbon dioxide and any ammonia present were removed was passed

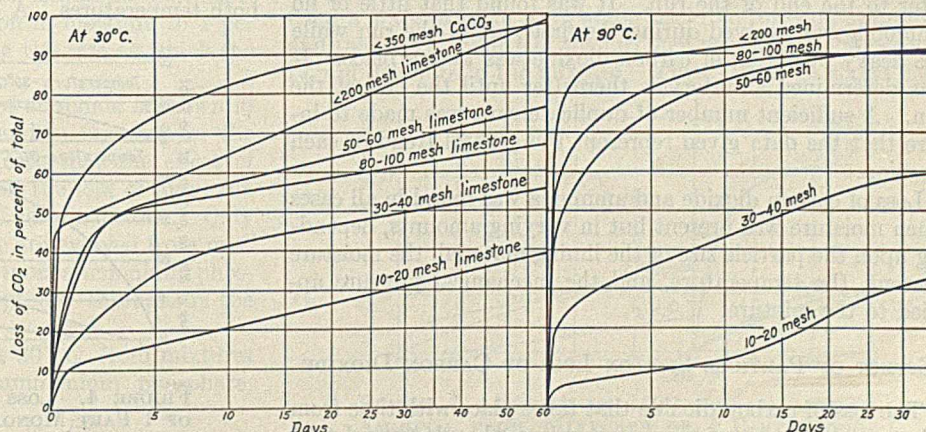


FIGURE 2. LOSS OF CARBON DIOXIDE FROM MIXTURES OF 1 PART MONOAMMONIUM PHOSPHATE AND 0.75 PART LIMESTONE (OR  $\text{CaCO}_3$ ) OF VARYING PARTICLE SIZE (Moisture, 10 per cent)

over the mixture in each vessel and subsequently passed successively through sulfuric acid and Ascarite to remove any ammonia and carbon dioxide that was evolved from the mixture.

COMPOSITION OF MIXTURES. Pierre (8) has shown that monoammonium phosphate has a physiological acidity equivalent to 107 pounds of  $\text{CaCO}_3$  per unit (20 pounds) of nitrogen. One part of pure monoammonium phosphate therefore requires 0.65 part of the limestone used in these tests, or 0.68 part of the dolomite to give a physiologically neutral mixture. A fertilizer mixture would ordinarily contain other acid-forming materials in addition to ammonium phosphate. The liming materials used were accordingly increased to 0.75



part per part of monoammonium phosphate in most of the tests but was varied in some of the tests from 0.25 to 1.3 parts per part of ammonium phosphate. To the mixture thus prepared was added the amount of moisture desired for the particular experiment. An attempt was made to control the moisture content of the mixture by passing the incoming air stream at the temperature of the bath through a saturated

mesh size than from those that are somewhat larger or smaller was invariably noted. In general, however, the carbon dioxide evolved increases with decrease in the size of the limestone particles.

The curves obtained when limestone was replaced with dolomite are shown in Figure 3. Mixtures of dolomite and monoammonium phosphate also react to set free carbon dioxide, but the maximum loss of this constituent during the period of the tests was only about three-fourths as great as from the limestone mixtures. Here again the maximum loss of carbon dioxide from mixtures containing dolomite of 50- to 60-mesh size was greater than from mixtures containing smaller or larger mesh material.

The reduced final reactivity of the liming material with decrease in the size of its particles below 50- to 60-mesh size may be due to the relatively smaller thickness of the moisture layer on the surface of the more finely divided

material as suggested by MacIntire and Shuey (5).

#### EFFECT OF PARTICLE SIZE OF LIMESTONE ON LOSS OF AMMONIA

The loss of ammonia under the same conditions as described for loss of carbon dioxide from limestone is given in Figure 4. These curves show that the rate of loss of ammonia increases with decrease in particle size as in the case of loss of carbon dioxide. The maximum loss of ammonia, however, is more than twice as great at 90° C. as at 30°, whereas the corresponding loss of carbon dioxide is approximately the same at both temperatures. A comparison of the curves in Figure 4

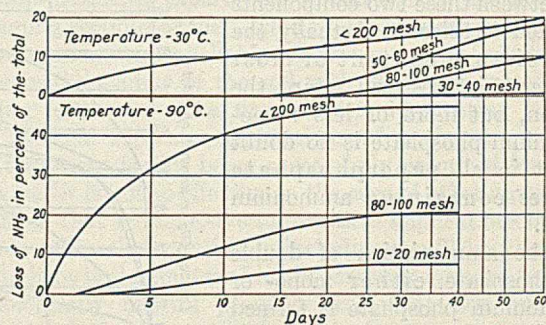


FIGURE 4. LOSS OF AMMONIA FROM MIXTURES OF 1 PART MONOAMMONIUM PHOSPHATE AND 0.75 PART LIMESTONE OF VARYING PARTICLE SIZE (Moisture, 10 per cent)

with those in Figure 2 shows that little or no ammonia is evolved in any given reaction until the greater part of the maximum loss of carbon dioxide has taken place. At 30° C. the loss of ammonia from limestone mixtures of 30- to 40-mesh size, or larger, amounts to less than 1 per cent of the total. There is no appreciable loss of ammonia at 30° C. from dolomite mixtures of any particle size, but at 90° a maximum loss of about 20 per cent of the total present may take place from mixtures containing <200-mesh dolomite as shown in Figure 8.

MacIntire and Sanders (3) have shown that there is no appreciable loss of ammonia at ordinary temperatures from mixtures of limestone or dolomite with ammonium salts such as the sulfate and nitrate.

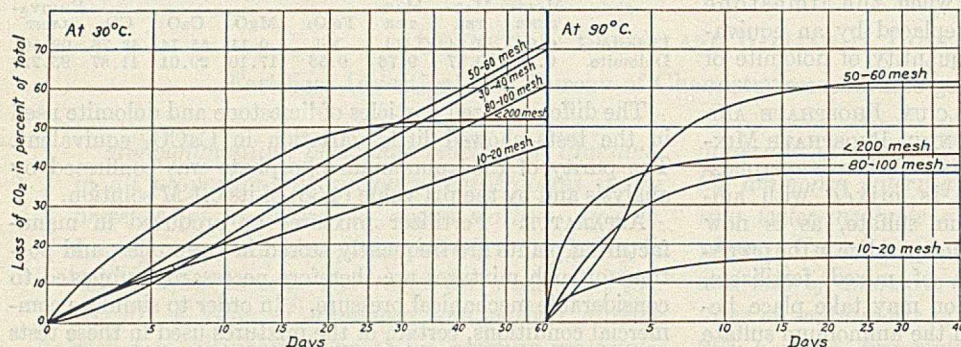


FIGURE 3. LOSS OF CARBON DIOXIDE FROM MIXTURES OF 1 PART MONOAMMONIUM PHOSPHATE AND 0.75 PART DOLomite OF VARYING PARTICLE SIZE (Moisture, 10 per cent)

solution of monoammonium phosphate. A saturated solution of the phosphate was also placed in the annular space surrounding the tube containing the mixture. This procedure was reasonably successful for the work at 30° C., but at 90° it was found necessary to increase the moisture content of the incoming air stream by passing it through water at 90°.

Each run at 30° C. was continued for approximately 60 days, and at 90° C. for 15 to 40 days until the carbon dioxide set free in 24 hours was less than 0.1 per cent of the total originally present. The carbon dioxide liberated was determined at the end of the first 6 hours and daily thereafter to the end of the run. It was found that little or no ammonia was evolved during the first part of the run while the heavy evolution of carbon dioxide was taking place. It was determined at intervals thereafter until the end of the run. A sufficient number of duplicate runs was made to insure that the data given represent the general trend of each reaction.

Loss of carbon dioxide and ammonia was found in all cases when moisture was present but in varying amounts, depending upon the particle size of the liming material, the moisture content, the temperature, and the mechanical pressure applied to the mixture.

#### EFFECT OF PARTICLE SIZE ON LOSS OF CARBON DIOXIDE

The loss of carbon dioxide that takes place with time from mixtures of 1 part of monoammonium phosphate and 0.75 part of limestone of varying particle size is shown by the curves in Figure 2 when the reacting mixture is maintained at 30° and at 90° C. The initial moisture content of each of the mixtures used in these tests was 10 per cent, and this remained more or less constant for several days. The changing partial vapor pressure of the mixture as the reaction proceeded made it impractical to maintain a fixed moisture content indefinitely at 90° C., and the samples gradually dried out towards the end of the run.

The results show that the loss of carbon dioxide in 30 days at 90° C. is approximately the same as that which takes place in double the time at 30°. With the smaller sized particles of limestone, about half of the carbon dioxide is evolved during the first quarter-day period at 30° C. The curves for particles of 50- to 60-mesh size cross those of 80- to 100-mesh. A greater loss of carbon dioxide from particles of 50- to 60-



EFFECT OF MOISTURE ON LOSS OF CARBON DIOXIDE AND AMMONIA

The effect of moisture on the loss of carbon dioxide from mixtures of monoammonium phosphate and <200-mesh limestone is shown by the curves in Figure 5, and from mixtures of the same salt and <200-mesh dolomite by the curves in Figure 6. The results indicate that a change in the mois-

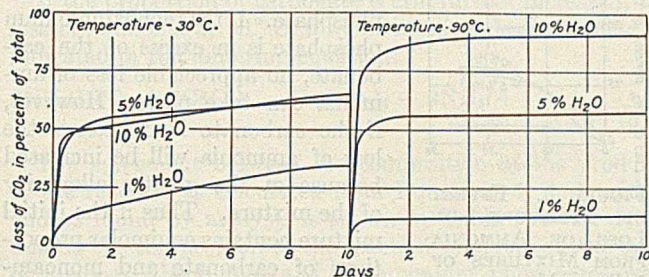


FIGURE 5. EFFECT OF MOISTURE ON LOSS OF CARBON DIOXIDE FROM MIXTURES OF 1 PART MONOAMMONIUM PHOSPHATE AND 0.75 PART <200-MESH LIMESTONE

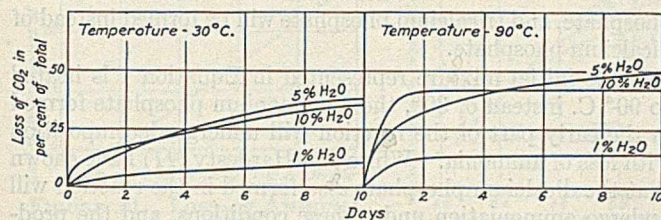


FIGURE 6. EFFECT OF MOISTURE ON LOSS OF CARBON DIOXIDE FROM MIXTURES OF 1 PART MONOAMMONIUM PHOSPHATE AND 0.75 PART <200-MESH DOLOMITE

ture content from 5 to 10 per cent has little effect on the carbon dioxide evolved, except when the limestone mixture is heated to 90° C., but that a reduction in moisture to 1 per cent has a marked effect in decreasing the rate at which the carbon dioxide is evolved.

The effect of moisture on the loss of ammonia is shown in Figure 7 for the limestone mixtures and in Figure 8 for the dolomite mixtures. The curves indicate that the effect of a variation in the moisture content on the loss of ammonia is, in general, the same as on the loss of carbon dioxide. Only traces of ammonia and carbon dioxide are evolved from mixtures of limestone or dolomite and monoammonium phosphate that are made up dry and kept dry throughout the test.

No loss of ammonia takes place at 30° C. from mixtures of <200-mesh dolomite and monoammonium phosphate, irrespective of the moisture content.

EFFECT OF MECHANICALLY APPLIED PRESSURE

The effect of increased pressure on the reaction between monoammonium phosphate and limestone or dolomite is shown in Table I. The results indicate that increased pressure at 30° C. has little effect on the loss of either ammonia or carbon dioxide. Mechanically applied pressures of 914 grams per sq. cm. at 90° C., however, seem to have the effect of reducing the loss of both ammonia and carbon dioxide in all mixtures. The decreased loss of these gases with increased pressure may be explained on the assumption that they are retained in the hard, caked mass resulting from the applied pressure. A pressure of 914 grams per sq. cm. is equal to the estimated maximum developed in a 1000-ton (907-metric-ton) pile of the ordinary mixed fertilizer, or in a bin filled with fertilizer to a depth of 30 feet (9.14 meters).

LOSS OF CARBON DIOXIDE AND AMMONIA WITH CHANGE IN RATIO OF PHOSPHATE TO LIMING MATERIAL

The rate of loss of carbon dioxide from mixtures of monoammonium phosphate and <200-mesh limestone when the proportion of the latter is changed from 0.25 to 1.3 parts per part of the former is shown in Figure 9. The effect of the same change in the proportion of the reacting materials on the loss of ammonia is shown in Figure 10. The curves in both figures show that, whereas a change in the ratio of the reacting materials has little effect on the rate of loss of carbon dioxide, it has a very marked effect on the loss of ammonia. Thus Figure 10 shows that the ammonia loss of more than 30 per cent of the total that occurs when the mixture contains equal parts of phosphate and limestone drops to little more than a trace when the ratio of limestone is decreased to one-fourth of the phosphate.

Although no loss of ammonia takes place at ordinary temperatures when dolomite is mixed with any proportion of monoammonium phosphate, it was found that a greater or less proportion of the nitrogen in mixtures of this kind changes from a water-soluble to a water-insoluble form on standing, and that the solubility of the nitrogen varies with the proportion of dolomite in the mixture. Thus Figure 11 shows that

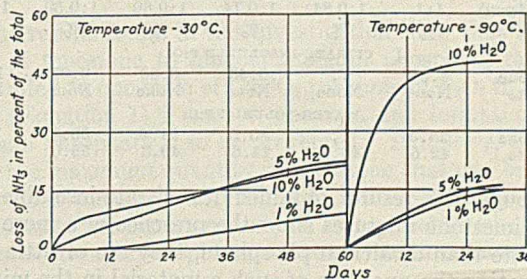


FIGURE 7. EFFECT OF MOISTURE ON LOSS OF AMMONIA FROM MIXTURES OF 1 PART MONOAMMONIUM PHOSPHATE AND 0.75 PART <200-MESH LIMESTONE

the water-insoluble nitrogen in mixtures of equal parts of <200-mesh dolomite and monoammonium phosphate amounts to about one-third of the total present. As the proportion of dolomite in the mixture is decreased, the ratio of water-insoluble to total nitrogen also decreases.

CITRATE-INSOLUBLE P<sub>2</sub>O<sub>5</sub> IN MIXTURES OF MONOAMMONIUM PHOSPHATE AND LIMESTONE

Table II gives the water-soluble and citrate-insoluble P<sub>2</sub>O<sub>5</sub> in monoammonium phosphate-limestone mixtures of varying moisture content when allowed to stand for 60 days at 30° C. and 20 days at 90°. The results obtained for citrate-insoluble P<sub>2</sub>O<sub>5</sub> indicate that more or less tricalcium phosphate is formed under these conditions and that the

TABLE I. EFFECT OF A MECHANICALLY APPLIED PRESSURE ON LOSS OF CARBON DIOXIDE AND AMMONIA FROM MIXTURES OF MONOAMMONIUM PHOSPHATE AND TWO LIMING MATERIALS

LIMING MATERIAL	MESH OF LIMING MATERIAL	(Moisture, 5 per cent)			
		0 GRAM/SQ. CM.		914 GRAMS/SQ. CM.	
		Loss of CO <sub>2</sub> %	Loss of NH <sub>3</sub> %	Loss of CO <sub>2</sub> %	Loss of NH <sub>3</sub> %
TEMPERATURE, 30° C.					
Limestone	< 200	90.5	21.6	99.4	27.2
Limestone	80-100	31.5	0.2	57.2	0.4
Limestone	10-20	25.5	0.2	45.7	0.7
Dolomite	< 200	58.6	0.2	45.6	0.1
Dolomite	80-100	60.2	0.2	60.5	0.2
TEMPERATURE, 90° C.					
Limestone	< 200	57.3	23.1	21.5	13.4
Limestone	80-100	40.8	7.6	48.3	10.6
Limestone	10-20	13.5	9.3	17.6	2.2
Dolomite	< 200	62.8	14.0	42.7	1.7
Dolomite	80-100	77.0	12.8	11.0	1.3
Dolomite	10-20	15.1	4.4	8.2	0.8



quantity formed increases with the temperature, the moisture content, the mechanical pressure applied, and the fineness of the limestone particles. The water-soluble  $P_2O_5$  as a rule decreases as the citrate-insoluble  $P_2O_5$  increases, but not uniformly so.

TABLE II. WATER-SOLUBLE AND CITRATE-INSOLUBLE  $P_2O_5$  IN MIXTURES OF 1 PART MONOAMMONIUM PHOSPHATE AND 0.75 PART LIMESTONE

MESH OF LIMESTONE	(In per cent of total $P_2O_5$ )							
	CITRATE-INSOLUBLE $P_2O_5$				WATER-SOLUBLE $P_2O_5$			
	0 g./sq. cm. $H_2O$	10% $H_2O$	914 g./sq. cm. $H_2O$	10% $H_2O$	0 g./sq. cm. $H_2O$	10% $H_2O$	914 g./sq. cm. $H_2O$	10% $H_2O$
	TEMPERATURE, 30° C.							
< 200	0.24	0.32	0.08	9.28	42.07	30.01	76.27	41.40
80-100	0.24	0.20	0.08	0.10	46.11	50.94	83.63	55.62
10-20	0.15	0.10	0.06	0.14	83.73	75.33	91.92	68.30
	TEMPERATURE, 90° C.							
< 200	0.19	23.80	18.84	...	90.05	43.20	34.00	...
80-100	0.19	3.94	...	0.49	91.86	54.09	...	59.25
10-20	0.09	0.67	...	1.21	97.73	85.42	...	80.18

The product formed by reaction of 1 part of monoammonium phosphate with 0.75 part limestone at 30° C. is alkaline in reaction, owing to the formation of diammonium phosphate. If the reaction is carried out at 90° C., little or no diammonium phosphate will be formed and the product will remain acid in reaction. This acid condition of the product will, on leaching, increase the solubility of any di- or tricalcium phosphate that may be present and explains the higher results obtained at 90° C. for water-soluble  $P_2O_5$  than at the lower temperature.

Table III shows that the citrate-insoluble  $P_2O_5$  increases and the water-soluble  $P_2O_5$  decreases with increase in the proportion of limestone to phosphate. No citrate-insoluble  $P_2O_5$  is formed when the limestone is replaced with dolomite. The water-soluble  $P_2O_5$  in the dolomite mixtures, however, drops to less than one-half of the total present when the mixture contains equal parts of the reacting materials.

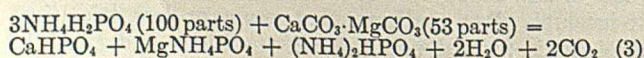
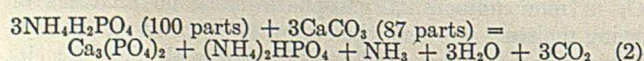
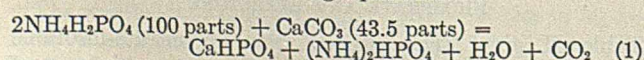
TABLE III. WATER-SOLUBLE AND CITRATE-INSOLUBLE  $P_2O_5$  IN MIXTURES OF VARYING RATIOS OF MONOAMMONIUM PHOSPHATE TO LIMING MATERIAL

LIMING MATERIAL (< 200-MESH)	RATIO OF $NH_4H_2PO_4$ TO LIMING MATERIAL					
	1:1	1:0.84	1:0.74	1:0.60	1:0.50	1:0.25
	CITRATE-INSOLUBLE $P_2O_5$					
Limestone	3.37	0.43	0.63	0.07	None	None
Dolomite	None	None	None	None	None	None
	WATER-SOLUBLE $P_2O_5$					
Limestone	28.5	45.5	54.4	59.8	77.2	77.2
Dolomite	42.5	43.7	44.6	49.3	55.0	78.0

Although the results obtained for citrate-insoluble  $P_2O_5$  in the limestone mixtures show the presence of a more basic phosphate than dicalcium phosphate, they are of little value in indicating the quantity of such a material in the mixture. According to Ross, Jacob, and Beeson (10), the greater part of any tricalcium phosphate formed in the mixtures under the conditions of the tests should be citrate-soluble.

#### INTERPRETATION OF RESULTS

The loss of carbon dioxide and ammonia, and the changes that take place in the solubility of the phosphoric acid in various mixtures of monoammonium phosphate with limestone and with dolomite may be explained on the assumption that the reactions taking place at ordinary temperatures are as represented in the following equations:



A mixture of 1 mole of calcium carbonate to 2 of monoammonium phosphate, as represented in Equation 1, gives an acid reaction at first because of the greater solubility of the ammonium phosphate. If the components of the mixture react as indicated in this equation, the mixture will finally become alkaline, and, when this occurs, a slight loss of ammonia should begin corresponding to that evolved from a mixture containing diammonium phosphate. If the monoammonium phosphate is in excess of the carbonate, no appreciable loss of ammonia can take place. However, if the carbonate is in excess, the loss of ammonia will be increased because of the greater alkalinity of the mixture. Thus if the initial mixture contains equimolar proportions of carbonate and monoammonium phosphate, as represented in Equation 2, more ammonia will be evolved than that due to the decomposition of the diammonium

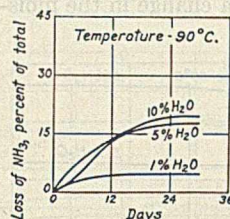


FIGURE 8. EFFECT OF MOISTURE ON LOSS OF AMMONIA FROM MIXTURES OF 1 PART MONOAMMONIUM PHOSPHATE AND 0.75 PART <200-MESH DOLOMITE

phosphate, and tricalcium phosphate will be formed instead of dicalcium phosphate.

If the initial mixture represented in Equation 1 is heated to 90° C. instead of 30°, the diammonium phosphate formed in the early part of the reaction will undergo decomposition with loss of ammonia. White and Hardesty (11) have shown that the dicalcium phosphate also formed in the reaction will undergo ammoniation under these conditions, and the products of the reaction will then consist of a mixture of di- and tricalcium phosphates and of mono- and diammonium phosphates. The proportions of these components of the mixture will vary with the conditions of the tests. An analysis of the residue obtained when the mixture was heated at 90° C. for 40 days showed that 20 per cent of the dicalcium phosphate formed in the reaction had been changed to tricalcium phosphate, and that about 55 per cent of the residual ammonia was still combined as diammonium phosphate.

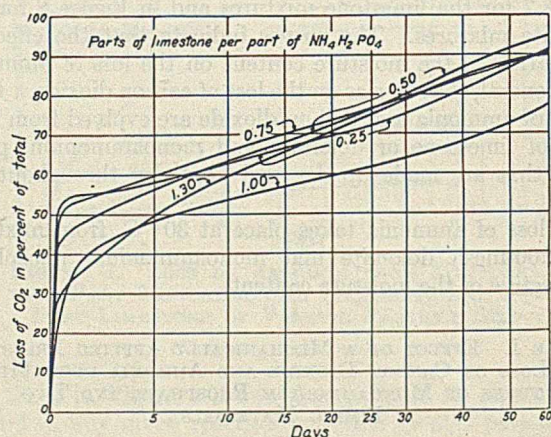


FIGURE 9. LOSS OF CARBON DIOXIDE AT 30° C. WITH CHANGE IN RATIO OF <200-MESH LIMESTONE TO MONOAMMONIUM PHOSPHATE

(Moisture, 5 per cent)

When equal moles of carbonate and phosphate are allowed to react at 90° C., the loss of ammonia will be more rapid and the reaction within the period of the tests may then be represented as follows:

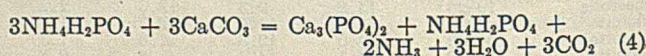
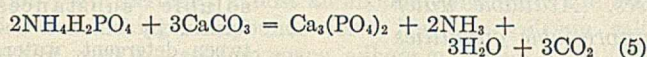




TABLE IV. PRODUCTS OF REACTION BETWEEN MONOAMMONIUM PHOSPHATE AND &lt;200-MESH LIMESTONE

MIXTURE	TEMP. ° C.	EVOLVED IN PER CENT OF TOTAL			COMPONENTS OF RESIDUAL PRODUCT								
		CO <sub>2</sub> found	NH <sub>3</sub>		NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>		(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>		CaH <sub>2</sub> PO <sub>4</sub>		Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>		CaCO found
			Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	
2NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> (100 parts) + CaCO <sub>3</sub> (43.5 parts)	30	98.5	0.1	0.0	1.3	1.3	48.3	48.3	49.8	49.8	0.0	0.0	0.6
3NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> (100 parts) + 3CaCO <sub>3</sub> (87 parts)	30	96.4	29.9	32.1	0.1	0.0	30.4	28.2	0.0	0.0	65.5	66.3	2.4
3NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> (100 parts) + 3CaCO <sub>3</sub> (87 parts)	90	76.8	41.5	51.2	36.1	37.7	0.0	0.0	0.0	0.0	43.8	49.3	14.5
2NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> (100 parts) + 3CaCO <sub>3</sub> (130.5 parts)	90	51.0	54.7	51.0	25.0	28.1	0.0	0.0	6.6	0.0	33.0	37.8	35.2

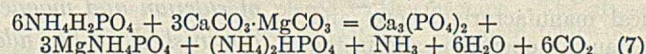
If the proportion of carbonate is still further increased, the loss of ammonia at 90° C. may be more or less complete as indicated in the following equation:



The agreement between the composition of the products of the reaction as calculated from Equations 1, 2, 4, and 5, and as found by analysis is shown in Table IV. In determining the composition of the reaction products on the basis of analysis, the mono- and diammonium phosphates were calculated from the total ammonia and that lost on heating

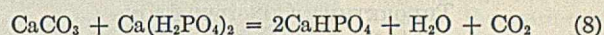
If this reaction were to go to completion, all of the calcium would be changed into tricalcium phosphate, two-fifths of the ammonia would be set free, and the remaining three-fifths would be changed into a water-insoluble form. It was found, however, that the reaction taking place at 90° C. in a mixture of dolomite and monoammonium phosphate in the proportion represented in Equation 6 is only about 45 per cent complete within the period of the tests as indicated by the loss of carbon dioxide. The loss of ammonia from a mixture of this kind should therefore amount to about 18 per cent of the total present, and about 27 per cent should be changed into a water-insoluble form. The values actually found were 20 per cent and 28 per cent, respectively (Figures 8 and 11).

If the mixture is heated in a closed vessel, diammonium phosphate will be formed on cooling, and the reaction may then be represented as follows:



If the reaction does not go to completion, the ammonia set free will combine on cooling with the excess of monoammonium phosphate and no loss of ammonia may then take place.

It has long been known that the citrate-insoluble P<sub>2</sub>O<sub>5</sub> in a superphosphate may be increased by the addition of limestone. If the quantity added does not exceed one mole of CaCO<sub>3</sub> per mole of P<sub>2</sub>O<sub>5</sub> in the superphosphate, the reaction will proceed for the most part to the formation of dicalcium phosphate, and little or no increase in citrate-insoluble P<sub>2</sub>O<sub>5</sub> will take place:



The results found in this investigation show that the addition of limestone to monoammonium phosphate must also be limited to one mole of CaCO<sub>3</sub> per mole of P<sub>2</sub>O<sub>5</sub> in the mixture (Equation 1) if loss of ammonia and formation of tricalcium phosphate is to be prevented. It follows, therefore, that the maximum quantity of limestone that can be used in a fertilizer mixture without loss of available plant food constituents is the same per unit of P<sub>2</sub>O<sub>5</sub>, whether the mixture contains a superphosphate, monoammonium phosphate, or both.

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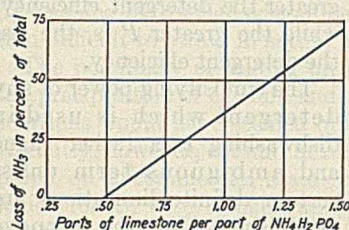


FIGURE 10. LOSS OF AMMONIA AT 30° C. WITH CHANGE IN RATIO OF <200-MESH LIMESTONE TO MONOAMMONIUM PHOSPHATE (Moisture, 5 per cent)

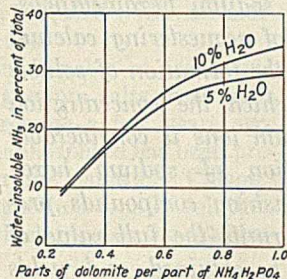


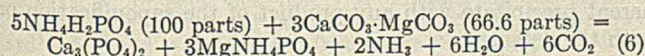
FIGURE 11. WATER-INSOLUBLE AMMONIA IN MIXTURES OF <200-MESH DOLomite AND MONOAMMONIUM PHOSPHATE

at 105° C. for 24 hours. The di- and tricalcium phosphates were calculated from the calcium not present as carbonate, and the remainder of the phosphoric acid by means of simultaneous equations. While it is assumed for the purpose of this paper that tricalcium phosphate can be formed and exists under the given experimental conditions, there is no direct experimental proof that a more basic phosphate (calcium hydroxyphosphate) may not also be formed.

The failure of the reactions to go to completion at 90° C. within the period of the tests was no doubt due to the gradual drying out of the mixture as already explained.

The reactions are somewhat different when the limestone is replaced with dolomite. If the dolomite contains calcite, this will react with the phosphate as already described. Any dolomite entering into the reaction at ordinary temperatures will form dicalcium phosphate, magnesium ammonium phosphate, and diammonium phosphate, as represented in Equation 3. As a result of this reaction one-third of the ammonia entering into the reaction is rendered insoluble in water. Figure 3 shows that only 50 per cent of the total carbon dioxide was evolved in the tests with <200-mesh dolomite, which indicates that the reactions involving the dolomite mixtures proceed more slowly than in the case of the limestone mixtures. No appreciable loss of ammonia can take place at ordinary temperatures as a result of the slow decomposition of the diammonium phosphate, owing to its association in the mixture with the unchanged monoammonium phosphate.

If the mixtures are heated to 90° C. in an open vessel, diammonium phosphate will not be formed and the reaction will proceed as follows:





# Sodium Metaphosphate in Mechanical Dishwashing

CHARLES SCHWARTZ<sup>1</sup> AND BERNARD H. GILMORE, Mellon Institute of Industrial Research, Pittsburgh, Pa.

THE critical examination of detergent processes has in recent years assumed an aspect of some importance, as evidenced by numerous papers on metal cleaning, laundering, and textile scouring, but the field of dishwashing has been almost entirely neglected. Upon superficial examination the problems involved in dishwashing might seem trivial; however, when one considers the tremendous amount of such activity in the bottling industries, pharmaceutical manufacturing, hotel and restaurant operation, and in the home, where cleanliness is absolutely essential for both hygienic and esthetic reasons, the issues involved become of major importance.

This investigation was undertaken to determine how the performance of established commercial detergents could be improved and, if possible, to develop a composition which would have none of the shortcomings of present compounds.

## THEORETICAL CONSIDERATIONS

The detergent efficiency of any washing process depends upon the following factors:

- (1) The mechanical efficiency of the process.
- (2) The temperature at which the washing operation is carried out.
- (3) The amount and concentration of the detergent agent.
- (4) The amount and type of soil.
- (5) The emulsifying power of the detergent—in other words, its power of suspending dirt, oil, and grease.
- (6) The saponification power of the detergent, or its ability to form soaps by interaction with fatty soil which may thus be washed away.
- (7) The formation of adherent and insoluble substances during the washing process.
- (8) The corrosive effect of the detergent upon the articles to be cleaned.

For the sake of expediency let it be assumed that the first four factors enumerated remain constant, and let the last one be temporarily neglected. Then there might be formulated a speculative, but reasonable, mathematical expression for the detergent efficiency of any substance:

$$D = f(E, S, P)$$

where  $D$  = detergent efficiency  
 $E$  = emulsification or soil-suspending power of the substance under investigation  
 $S$  = saponification or soap-forming power of the substance under investigation

*The precipitation factor is an important phase of detergent processes. Available water supplies usually contain appreciable quantities of calcium and magnesium salts which have the property of forming insoluble and adherent precipitates of calcium and magnesium compounds from the alkaline salts added as detergents and the soaps resulting from the interaction of an alkaline detergent with fatty soil. It has been shown that sodium hexametaphosphate has the property of sequestering calcium and magnesium ions by the formation of soluble complex molecules in which the concentration of calcium and magnesium ions is considerably diminished. The addition of sodium hexametaphosphate to dishwashing compounds prevents film formation, permits the full value of the detergent mixture to be obtained, and yields results that are superior with respect to brightness and freedom from film.*

$P$  = precipitation factor, or, the amount of adherent insoluble substances formed by reaction between detergent, water, and soil, and deposited on the articles being washed during the washing process

The following interrelation exists among these variables: The greater  $E$  and  $S$  are the greater the detergent efficiency; while the greater  $P$  is, the less the detergent efficiency.

The emulsifying power of any detergent which is used in dishwashing is a rather vague and ambiguous term unless certain definite limitations are established. For the purpose of this work the discussion may be limited, (1) to the type of difficultly removable soil which includes fats and solid materials commonly occurring in food products, and (2) to detergents such that when made up to a concentration in water of 0.25 to 0.5 per cent by weight, the pH will be between 10 and 12. With these two limits fixed, the effect of various alkalies in solution at that pH upon soils of a greasy type may be considered.

While no alkali has a marked emulsifying effect upon soil which is completely free from fatty acid, all alkalies have a marked emulsifying effect upon soil containing a small amount of free fatty acid, owing to the formation of alkali soaps which have excellent emulsifying properties in the presence of alkali. If the amount of soap present is the same in each case, the emulsifying properties of the commonly used alkalies are of the same order of magnitude. Thus, it may be seen: (1) In order for any alkali to be a rapid emulsifier, there must be free fatty acid present in soil to be removed, or the alkali must be compounded with a soap or a similar emulsifying agent; (2) if this is true, the selection of the alkali to be used in a detergent must rest upon other considerations than the emulsifying power, as will be shown.

The saponifying power of any substance depends in general upon its pH in solution and the temperature. Thus, when any alkaline detergent is used at relatively elevated temperatures in the presence of fats, a greater or lesser amount of saponification and neutralization takes place with the formation of soap. This soap in turn acts as an emulsifying agent upon the soil to be removed. Thus,  $E$  and  $S$  are closely related, and, if the alkali used is of such a nature as to cause the formation of enough soap during the washing process, the emulsifying power of the detergent mixture will be sufficient to clean off any soiled article, provided that the soil or the wash water is free from any substance which will form an adherent precipitate with any product of the saponification or with the detergent.

<sup>1</sup> Present address, Hall Laboratories, Inc.



The precipitation factor depends upon the tendency of the soil, the detergent, and the mineral content of the water to form insoluble precipitates of an adherent character. It is well known that water as ordinarily used contains appreciable amounts of calcium and magnesium, which too may be present in the soil on the articles to be cleaned. Hence, just as fast as soap formation takes place, insoluble calcium and magnesium soaps will precipitate at the grease-water interface, thereby preventing complete access of the detergent to the soil, and also preventing the formation of soluble soaps in the slight but necessary amount to obtain good emulsification. Furthermore, almost all alkaline salts which are used in dishwashing compounds form insoluble calcium salts which, with the calcium soaps, adhere and build up as films on the dishes and in the washing machine. Thus, the ideal detergent must, in addition to saponifying part of the soil and emulsifying the remainder, have the unique property of preventing in alkaline solution the formation of insoluble soaps and other calcium and magnesium precipitates which inhibit detergency by actually adding to the soil on the dishes and washing machine. These effects may of course be overcome by washing in distilled or completely softened water, a condition difficult to attain in actual practice.

The possibility of finding an agent capable of preventing the precipitation of calcium and magnesium salts in alkaline solutions would have seemed quite remote a few years ago. Recently, however, sodium hexametaphosphate has been prepared on a commercial scale under the name of "Calgon" which forms, with calcium and magnesium ions in solution, a very stable soluble complex and which reduces the calcium- and magnesium-ion concentration far below that necessary to satisfy the solubility product relationships for the formation of any of their known insoluble salts. This property has been named by Hall (2) "calcium (and magnesium) sequestration."

If the theoretical deductions made thus far are correct, this substance should be an ideal adjunct to any dishwashing compound. It should facilitate detergency and should prevent entirely the formation of film and insoluble precipitate on the dishes washed with it.

The following experiments were performed in order to establish these points and to indicate the ideal composition of a detergent for dishwashing.

#### WASHING OF GLASSWARE

The first set of experiments was performed on glassware on which the slightest differences in soil and film deposit may be easily seen:

Glass tumblers (all of the same type) and a number of flat glass plates, 5 × 5 inches, were used. A standard soil was prepared by mechanically mixing 1 pound of peanut butter, 0.5 pound of lard, 0.5 pound of butter, and 0.88 ounce (25 grams) of calcium

hydroxide until a homogeneous mass was obtained. A rather large proportion of peanut butter was used because of the fact that such soil is difficult to remove. The calcium hydroxide was added to make the wash water moderately hard (equivalent to 190 p. p. m. of calcium carbonate), thereby increasing the severity of the test. Experiments performed under less severe conditions are described later.

Two machines of the domestic type, equipped with spray heads and a motor-driven propeller which agitated the detergent solution during the washing process, were used. Both machines were connected side by side to the same water supply. The wash water ranged between 128° and 140° F., temperatures recommended by the manufacturers of the machines. For operation, the machine is equipped with a single triangular control knob which is labeled on the three sides "spray," "wash-rinse," and "off," respectively. When the knob is in the spray position, water enters the machine through the revolving spray head at the rate of about 6 gallons per minute and runs out through the open drain. With the control in the wash-rinse position the drain is closed automatically, and water runs into the machine until its back pressure on the revolving propeller reaches a pre-set amount whereupon the incoming water is shut off. The volume of water retained in the machine is approximately one gallon. After the washing time has elapsed, the knob is turned to the off position. This turns off the motor and drains the machine.

For any individual run three glass tumblers and three glass plates were thoroughly washed by scouring with a brush and soap, and rinsed, first in tap water and then in distilled water until perfectly clean. Some of the standard soil was smeared on the inside of each tumbler and some was smeared evenly by means of a large spatula on one side of each glass plate. The six pieces were then placed in the machine. The glasses were inverted, as in regular procedure; the glass plates were put in on edge with the soiled side inclined slightly towards the water inlet in the center of the machine. The machine was run in the spray position for about 30 seconds to remove any of

the loosely adherent soil, and then it was drained. Next the machine was run in the wash-rinse position until it automatically shut off the incoming water at a volume of one gallon, whereupon the motor was shut off, the detergent poured in, and the machine run in the wash-rinse position for 4 minutes. At the end of this time the water was drained, and the dishes were rinsed for 30 seconds, followed by another rinse 1 minute in length. This is the standard procedure for this type of washer.

At the end of the second rinse the glasses and plates were allowed to drain for a few minutes. They were then resoiled in the same manner, except that the glass plates were soiled on the reverse side, and their positions in the machine were changed

to allow for any difference in the force with which the water strikes in different parts of the machine. The plates were always soiled on alternate sides and their positions in the machine changed after each wash. All runs except where otherwise noted were of twenty-five washes. The amount of detergent in each case was 0.36 ounce (10 grams) unless otherwise noted. At the end of a run the vessels and plates were removed and permitted to drain and dry without wiping.

The light transmission of each of the glass plates washed was read in a Zeiss photometer and compared with the transmission of a plate which was scoured with soap and rinsed thoroughly in distilled water. In every case the reading was

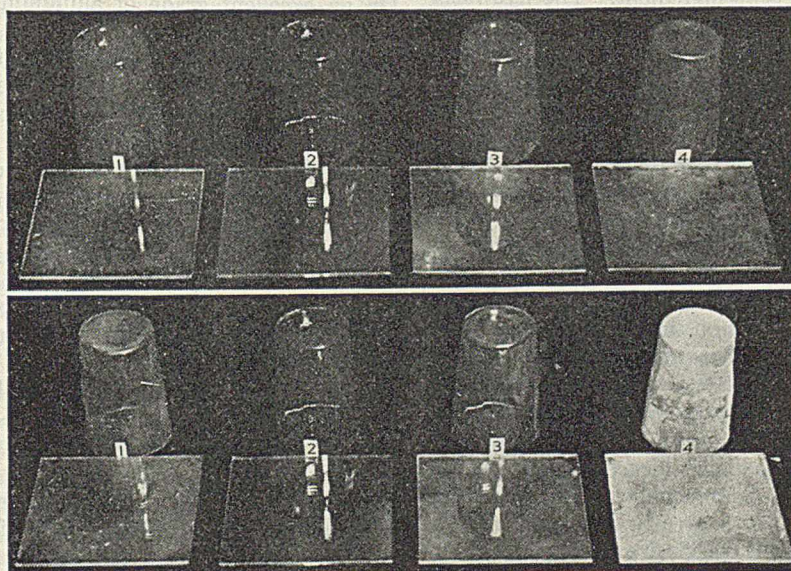


FIGURE 1. GLASSWARE AFTER TWENTY-FIVE WASHES WITH SOILING

Above: 1. Proprietary C  
2. Metaphosphate formula 1  
3. Sodium metasilicate  
4. Proprietary E

Below: 1. Trisodium phosphate  
2. Metaphosphate formula 1  
3. Proprietary A  
4. Soap and sodium carbonate



taken at the point on the plate where the film was most dense. The results are shown on Table I.

TABLE I. EFFECT OF DETERGENTS IN WASHING GLASSWARE

DETERGENT <sup>a</sup>	LIGHT TRANSMISSION OF GLASS PLATES AS COMPARED WITH ORIGINAL %
Soap 50%, sodium carbonate 50	0.9
Sodium aluminate	2.2
Sodium carbonate	4.2
Proprietary E <sup>b</sup>	24
Proprietary D	62
Sodium metasilicate	65
Proprietary C	71
Trisodium phosphate	72
Proprietary B	79
Proprietary A	82
Soap 33 $\frac{1}{3}$ %, sodium carbonate 33 $\frac{1}{3}$ %, sodium metaphosphate 33 $\frac{1}{3}$	89
Formula 1 (%): trisodium phosphate 45, sodium metaphosphate 53, sodium hydroxide 2	100
Formula 2 (%): trisodium phosphate 55, sodium metaphosphate 43, sodium hydroxide 2	98
Formula 4 (%): trisodium phosphate 75, sodium metaphosphate 23, sodium hydroxide 2	99
Formula 5 (%): trisodium phosphate monohydrate 15, sodium metasilicate 40, sodium metaphosphate 40, sodium hydroxide 5	97

<sup>a</sup> Proprietaries A, B, and C are mixtures containing large amounts of trisodium phosphate; D is a commonly used neutral domestic flake soap; E is a sulfated fatty alcohol.

<sup>b</sup> Two washes were performed with 0.36 ounce (10 grams), but suds formed to such an extent that they could not be rinsed out with the technic used. Hence, after two washes the amount of detergent was cut to 0.18 ounce (5 grams), and twenty-five washes were completed using 0.18 ounce in each.

Table I and Figure 1 show clearly that the choice of detergents on the basis of cleansing efficiency and absence of film formation is definitely limited to those compounds of which sodium hexametaphosphate is an ingredient. The five most widely known and commonly used detergents—namely, proprietary A, proprietary B, proprietary C, trisodium phosphate, and sodium metasilicate—are very close in efficiency; proprietary A is slightly better than the others. Proprietary D is not as good as any of these, owing undoubtedly to the fact that the mechanical efficiency of the process is reduced by the cushion of suds formed within the machine. This also accounts, perhaps, for a large part of the film formed when proprietary E was used. The heavy films formed when sodium carbonate, sodium aluminate, and sodium carbonate and soap were used were probably due both to a precipitation *in situ* of calcium salts and soaps on the glassware and to incomplete removal of the soil. This incomplete soil removal may have been in part the result of the calcium precipitates preventing ready access of the detergent to the soiled surfaces.

While sodium metaphosphate lacks the powerful soap-forming action of the more alkaline detergents as exemplified by trisodium phosphate and sodium metasilicate, its admixture with these salts has led to greatly improved results. Speaking in terms of the mathematical expression, this enhanced detergent efficiency has not been caused by increasing *S*, the saponifying power, or *E*, the emulsifying power. Hence the improvement must have been attained by reducing *P*, the precipitation factor, to a minimum. As anticipated on the basis of its known properties, the function of the sodium metaphosphate has been to prevent the precipitation of the insoluble compounds of calcium and magnesium. The detailed mechanism of the reaction by which this is effected is to be the subject of future publications and has been discussed elsewhere (1, 3).

Thus it may be concluded that the addition of sodium metaphosphate to any ordinary detergent, which possesses those minimal soil-suspending and soap-forming values necessary for soil removal, will prevent completely the formation of insoluble adherent films of calcium and magnesium precipitates which lead to unsatisfactory results in dishwashing. Therefore the choice of alkali to be used with sodium meta-

phosphate must rest upon other considerations which will be brought out later.

## WASHING OF ALUMINUM WARE

In addition to possessing proper detergent qualities, cleaning compounds must be of such a nature that they will not injure the articles with which they come in contact during the washing process. In view of the fact that an increasingly large number of utensils are being made from aluminum, the possible corrosive action of the various detergent compositions on aluminum was investigated. Several aluminum pans of a very cheap quality were purchased and, without soiling, each was given five washes as described above with the following substances:

DETERGENT	CORROSION
(1) Sodium metaphosphate 40%, trisodium phosphate 40, sodium metasilicate 20	Marked
(2) Sodium metaphosphate 40%, trisodium phosphate 30, sodium metasilicate 30	Less than (1)
(3) Sodium metaphosphate 40%, trisodium phosphate 20, sodium metasilicate 40	Very little, if any
(4) Sodium metaphosphate 50%, sodium metasilicate 50	None
(5) Proprietary A	Marked
(6) Proprietary B	Marked

A similar series of experiments was performed on a better grade of aluminum with the following results:

DETERGENT	CORROSION
(1) Sodium metaphosphate 40%, trisodium phosphate 50, sodium metasilicate 10	Marked
(2) Sodium metaphosphate 40%, trisodium phosphate 40, sodium metasilicate 20	Less than (1)
(3) Sodium metaphosphate 40%, trisodium phosphate 30, sodium metasilicate 30	None

On an excellent grade of aluminum exactly similar results were noted.

Thus, it appears that any detergent of this type, which is to be used to clean aluminum for household use, should contain at least 30 per cent of sodium metasilicate and preferably 40 per cent to protect very cheap ware.

In order to see whether the common electrolytic method of removing silver tarnish would work in the presence of a detergent which did not visibly corrode aluminum, a silver spoon was blackened with ammonium sulfide, placed in an aluminum pan, and washed in the machine by the regular procedure. The spoon was thoroughly cleaned in one wash in spite of the fact that the aluminum pan remained apparently unaffected.

Hence, two facts have been established—namely, that the presence of sodium metaphosphate in a dishwashing compound produces superior results, and that sodium metasilicate to the extent of at least 30 per cent is necessary to inhibit corrosion of aluminum. It remains to prove that such a compound will clean common soil from dishes, and will not, of itself, leave a deposit on the dishes.

## WASHING OF CHINAWARE

Thirty china dishes varying from moderately priced ones to a few rather expensive ones with both overglazed and underglazed patterns were divided into two sets, each set containing an equal number of the same kind of dishes.

Each dish in set 1 was dipped into a mixture of 2 pounds of lard, 2 pounds of tallow, and 2.65 ounces (75 grams) of ferric chloride at a temperature of 140° F. (60° C.). The dish was then allowed to drain and the grease to harden for about 30 minutes. Then the set of dishes was washed by the method described above with proprietary A as the detergent. This was repeated for five washes, the immersion in the fat mixture taking place between each wash. At the end of the fifth wash the dishes were permitted to dry without wiping, and each dish was covered with a solution of yellow ammonium sulfide. The sulfide was used so that the ferric chloride remaining in the fat film on the dish would be changed to black iron sulfide which



would show up photographically. After one hour the sulfide was rinsed off with tap water. The same procedure was followed with set 2 except that a detergent containing sodium metaphosphate (formula 5) was used.

In appearance the dishes of set 2 were far superior to those of set 1. After five washes, the dishes in set 1 had accumulated a film of grease which was quite noticeable, both visually and by feel. Set 2 on the other hand was, as far as could be seen, perfectly washed.

#### PREVENTION OF FILM FORMATION

The previous experimental work has shown that a detergent mixture containing sodium metaphosphate, as exemplified by formula 5, will clean soiled glasses leaving them free of film, will not corrode aluminum in a few washes, and will remove heavy grease deposits from china-ware.

In order to determine to what extent the detergent itself was responsible for film formation, some additional washing experiments were conducted in which the articles were not soiled before washing. For this purpose two sets of dishes, each consisting of ten ordinary china dishes, three glass salad plates, two glass tumblers, and one aluminum pan of a cheap grade were washed one hundred times in Pittsburgh city water (60 p. p. m. of hardness as calcium carbonate) according to the previously described routine, using proprietary A in one machine and formula 5 in the other.

At the end of one hundred washings all of the dishes and glasses washed with proprietary A were covered with a distinct film, and the aluminum pan had lost about 30 per cent of its original weight together with its lustrous appearance and was very heavily etched by the corrosive action of the detergent. The dishes washed with sodium metaphosphate, on the other hand, were entirely free from film (Figure 2), and the aluminum pan lost only about 6 per cent of its original weight but retained its luster and seemed practically new in appearance. The results of these experiments leave no doubt that the precipitation effect of the detergent itself is an important factor in film formation, and that the addition of a calcium sequestering agent to a detergent formula greatly improves the quality of the work.

#### DISCUSSION OF RESULTS

From a consideration of the experimental results as a whole, one finding stands out clearly: The precipitation factor, or the formation of insoluble products from the inter-

action of the calcium and magnesium in the water and in the soil with the detergent, constitutes a serious problem in the washing of dishes. While this has been more or less clearly recognized for a long time, the work reported in this paper confirms it under exactly controlled conditions. The seeming neglect of this factor up to the present time is not the fault of detergent manufacturers, for they have gone to great trouble and expense in many unsuccessful attempts to remedy this serious failing of their preparations.

In view of the fact that nearly all the alkaline salts commonly used for detergent purposes form insoluble compounds with alkaline earth salts, it is evident that their use with any but a completely softened water supply will result in precipitation and film formation. Since completely softened water is so infrequently available in establishments where the greatest volume of dishwashing is done, the only remedy for the condition is an agent capable per se of effecting complete

sequestration of calcium and magnesium. The commercial development of sodium metaphosphate, which by its great avidity for the ions of calcium and magnesium is able to prevent formation of films of alkaline earth salts and which may be used with any detergent, represents a distinct advance in detergent technic.

#### CONCLUSIONS

The effect of the admixture of sodium metaphosphate with detergent compounds has been investigated and compared with the behavior of several commercial dishwashing preparations. Such mixtures containing sodium hexametaphosphate were, in every case, found superior to the products now available.

By reason of its excellent detergent properties, its non-corrosive action on aluminum, and its complete prevention of film, the following composition was judged the best of all studied (in per cent): sodium metaphosphate 40, trisodium phosphate monohydrate 15, sodium metasilicate pentahydrate 40, and sodium hydroxide 5; or the dehydrated equivalent: sodium metaphosphate 48, trisodium phosphate 18, sodium metasilicate 28, and sodium hydroxide 6.

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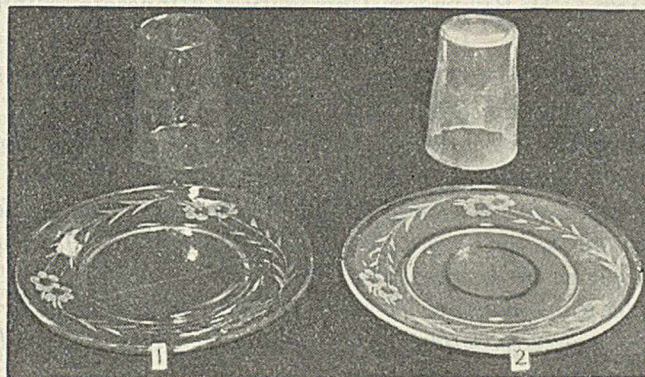


FIGURE 2. GLASSWARE AFTER ONE HUNDRED WASHES WITH NO SOILING

1. Metaphosphate formula 5

2. Proprietary A

ENGLAND SEEKS NEW USES FOR COAL. England, faced with a decline in the demand for coal, of which that country is generously endowed and upon which its industrial structure has been reared, is making determined efforts to find new uses for coal and its derivatives, according to the Chemical Division of the Department of Commerce.

Motor fuel, said to be of high antiknock value, is being produced by the British Fuel Research Board from coal and tar, according to a report from the American Consulate, London, which points out that from one treatment of tar 45 per cent of motor spirit is recovered and by reprocessing a total volume of

98 per cent of motor fuel is derived from the original tar. The aim of the board is the highest possible yield of valuable products from coal and affects not only motor fuel and gas, but pulverized fuel, lubricating oils, gas coke, and other smokeless fuels for the domestic grate. In carrying out its laboratory tests the board uses more than 8000 tons of coal per annum.

Production of motor fuel from coal is not new in England. One company has been producing and marketing coal gasoline at the rate of 1000 gallons daily since September, 1933, and plans to erect 20 plants at different points, which, when completed, are expected to produce approximately 6,000,000 gallons annually.



# Production of High-Hydrogen Water Gas from Younger Coal Cokes

## Effect of Carbon Dioxide upon Cokes

R. E. BREWER AND L. H. REYERSON, University of Minnesota, Minneapolis, Minn.

*The experimental data show, for measured volumes of dry carbon dioxide passed over heated carbon, that, in addition to a large amount of carbon monoxide and a small amount of carbon dioxide appearing in the products, there is an appreciable portion of the carbon dioxide fixed as a solid carbon-oxygen complex. This evidence is supported by the exothermic character of the reaction at the temperatures of the experiments. For an approximately constant time of contact at a given temperature, the percentage of carbon dioxide fixed by carbon reaches a fairly constant value after several hours' passage of carbon dioxide over heated carbon. Two alternate hypotheses are*

*suggested to explain the results. The limitations of the use of theoretical equilibrium constants in interpreting apparent equilibrium data from dynamic experiments are discussed. The calculated values of the velocity constant,  $k_1$ , for the forward reaction  $C + CO_2 \rightleftharpoons 2CO$  from data at different temperatures are in accord with the kinds of carbon used. The possible error in the carbon dioxide-carbon monoxide ratio due to thermal separation in the exit gases is judged to be small. It is concluded that the speed of the reaction between carbon dioxide and heated carbon is governed chiefly by chemical changes rather than by diffusion.*

EXPERIMENTAL results for water gas rich in hydrogen produced by the action of steam upon younger coal cokes presented in an earlier paper in this series (4) do not appear to have an adequate explanation in some of the older mechanisms for water gas formation. The object of the present study is the investigation of some of the factors affecting the surfaces of different kinds of carbon materials and the ways that surface changes, either in area or composition or both, may contribute to these mechanisms. The experimental data definitely indicate the formation of a solid carbon-oxygen complex in addition to carbon dioxide and carbon monoxide in the products. This complex is known to play a very important role in "surface" reaction mechanisms. Additional evidence concerning the mechanism of the heterogeneous reaction  $C + CO_2 \rightleftharpoons 2CO$  in its relationship to water gas formation is afforded from this study.

### APPARATUS AND PROCEDURE

The apparatus employed was the same as that shown in Figure 1 of the earlier paper (4), except that the steam-generating unit—i. e., that portion connected to the superheater at cock  $X_w$ —was replaced by suitable equipment for furnishing measured dry carbon dioxide. Tank carbon dioxide, measured by a calibrated wet gas meter, dried by passing through a large calcium chloride tower, and with its rate of flow indicated by passage through a calibrated flowmeter, entered the main apparatus through cock  $Q$ . The assembled apparatus was first swept with carbon dioxide for several hours to insure saturation of the water in the wet gas meters. As a further precaution carbon dioxide was again passed through the assembled apparatus until the exit gases were free of air before starting an experimental run.

The general method of operation was essentially the same as previously used (4):

A weighed sample of either lignite char or electrode carbon, obtained from the same sources and prepared as previously described (4), was placed in the sillimanite reaction tube of the furnace. The furnace was heated until no more gas due to carbonization was evolved at the temperature selected for passage

of carbon dioxide over the heated carbon. Dry measured carbon dioxide (99.8 per cent pure) was then introduced at a uniform rate during a given run. Frequent observations of temperatures, pressures, and volumes were made to insure complete knowledge of operating conditions. Analyses of the collected gas samples were made for carbon dioxide, oxygen, carbon monoxide, and, whenever possible, explosion of the residue to determine hydrogen and methane.

### PRESENTATION OF DATA

A general summary of the experimental data for the main portion of this paper, together with certain calculated data, is shown in Table I. A separate fresh carbon sample was used for each series. The apparatus was allowed to cool overnight between experiments 1A and 1B, 2B and 2C, and 2D and 2E. Experiment numbers within the same bracket in column 1 indicate that such experiments were run consecutively. The bracketed data in column 14 show the percentage by weight of carbon sample used up in each series. In computing these percentages, the original weights of carbon material were first corrected for carbonization loss (4). The "percentage of carbon used up" can be considered only approximate, since, as will be shown later, the residue finally removed from the cooled furnace does not represent the weight of solid product left after making a simple deduction of the carbon required for carbon monoxide formation. The volume percentages of carbon dioxide and carbon monoxide in the products are shown for each experiment in columns 15 and 16. Explosive residues (hydrogen and methane) were found only in the A experiments of series I, II, and III. The total time (expressed to the nearest second decimal place in hours) of passage of carbon dioxide over heated carbon samples from the beginning of experiment A in each series to the end of a later experiment in the series is shown in column 17. Thus, the time opposite the B experiments in each series equals the sum of the times of passage of carbon dioxide in experiments A and B; that opposite the C experiments, the sum of the times for experiments A, B, and C, etc. The duration of each experiment is, therefore, the difference between the time recorded opposite that experiment number and the time recorded opposite the preceding experiment



TABLE I. SUMMARY OF DATA

EXPT. NO.	TEMP. ° C.	ABS. PRESSURE Mm.	TIME OF CONTACT Seconds	DRY CO <sub>2</sub> TAKEN <sup>a</sup> Liters	DRY GASEOUS PROD-UCTS <sup>a</sup> Liters	DRY CO FORMED <sup>a</sup> Liters	DRY CO <sub>2</sub> <sup>a</sup> DISTRIBUTED AS:			TOTAL DRY CO <sub>2</sub> DISTRIBUTED AS:			CARBON USED UP %	GAS ANALYSIS			ELAPSED TIME Hours	VALUE OF <i>k</i> <sub>1</sub> <sup>a</sup>
							CO	CO <sub>2</sub>	C <sub>2</sub> O <sub>2</sub>	CO	CO <sub>2</sub>	C <sub>2</sub> O <sub>2</sub>		%	%	%		
SERIES I, LIGNITE CHAR																		
1A	886	738.1	2.1555	5.783	8.577	6.227	3.113	1.758	0.912	53.8	30.4	15.8	43.11	72.6	20.5	0.50	0.5999	
1B	941	738.2	2.7887	4.738	7.788	6.892	3.446	0.428	0.864	72.7	9.0	18.2		88.5	5.5	1.11	0.7751	
1C	966	743.6	2.7685	4.784	7.785	6.897	3.448	0.273	1.063	72.1	5.7	22.2		88.6	3.5	1.73	0.7835	
SERIES II, LIGNITE CHAR																		
2A	1087	735.1	5.7737	8.438	15.139	13.760	6.880	0.121	1.437	81.5	1.4	17.0	53.14	90.9	0.8	2.80	0.4186	
2B	1116	734.9	4.2488	6.288	10.033	9.652	4.826	0.050	1.412	76.7	0.8	22.5		96.2	0.5	4.49	0.7688	
2C	1102	727.2	6.7723	11.614	16.353	15.470	7.735	0.065	3.814	66.6	0.6	32.8		94.6	0.4	8.07	0.4306	
2D	1119	727.2	12.7021	2.466	2.924	2.766	1.383	0.029	1.054	56.1	1.2	42.7		94.6	0.1	9.29	0.2296	
2E	1081	733.4	10.5436	4.724	5.954	5.532	2.766	0.083	1.875	58.6	1.8	39.7		92.9	1.4	11.29	0.2506	
2F	1094	733.3	8.8198	5.905	10.584	9.968	4.984	0.190	0.731	84.4	3.2	12.4		94.5	1.8	14.59	0.3284	
SERIES III, LIGNITE CHAR																		
3A	1090	731.0	5.4398	9.562	15.164	13.284	6.642	0.137	2.783	69.6	1.4	29.2	60.77	87.6	0.9	2.65	0.3833	
3B	1115	731.0	5.7875	9.562	14.788	14.169	7.084	0.104	2.374	74.1	1.1	24.8		95.8	0.7	5.45	0.5471	
3C	1136	731.0	6.1033	11.986	18.188	17.624	8.812	0.127	3.047	73.5	1.1	25.4		96.9	0.7	9.12	0.5685	
3D	1150	731.0	5.6137	7.168	10.497	10.717	5.358	0.033	1.777	74.7	0.5	24.8		97.9	0.3	11.17	0.6874	
SERIES IV, ELECTRODE CARBON																		
4A	1100	736.1	4.5797	9.458	12.508	9.180	4.590	3.002	1.866	48.5	31.7	19.8	24.13	73.4	24.0	2.15	0.2888	
4B	1134	736.3	6.0627	9.436	13.505	13.060	6.530	0.405	2.501	69.2	4.3	26.5		96.7	3.0	5.30	0.5621	
4C	1145	735.9	4.8496	9.467	14.555	14.046	7.023	0.393	2.051	74.2	4.2	21.7		96.5	2.7	8.02	0.6905	
4D	1150	736.9	5.6328	9.454	14.014	13.524	6.762	0.393	2.329	71.3	4.1	24.6		96.5	2.8	11.08	0.5945	

<sup>a</sup> The units in which *k*<sub>1</sub> is expressed are given later in the paper in the section entitled "The Equilibrium Constant."

number. Column 18 shows the calculated values for the direct velocity constant, *k*<sub>1</sub>, of the forward reaction for the equilibrium  $C + CO_2 \rightleftharpoons 2CO$ . From this stoichiometrical relation between carbon dioxide and carbon monoxide the calculated volumes in column 8 are obtained from the experimental volumes in column 7 by dividing by 2. The volumes in column 9 are experimental, while those in column 10 are the differences between the volumes in column 5 and the sum of the volumes in columns 8 and 9. The data in the other columns of Table I are self-explanatory.

Figure 1 shows the time in hours for the duration of the experiments of series III for lignite char and of series IV for electrode carbon, plotted against the corresponding percentage distributions of carbon dioxide into the products carbon monoxide, carbon dioxide, and carbon-oxygen complex.

Table II gives certain weight relationships between the reactants and products for series III and for series IV. The values in columns 2, 3, and 5 were calculated from the corresponding volumes (at normal temperature and pressure) in columns 5, 7, and 9 of Table I, using the accepted weights of normal liters of carbon dioxide and carbon monoxide given in the International Critical Tables (27). The values in column 8, Table II, represent the experimental loss in weight between the original weight of carbon material taken (first corrected for carbonization loss, 4) and the weight of the cooled solid residue removed from the furnace after a series run.

TABLE II. WEIGHT RELATIONSHIPS BETWEEN REACTANTS AND PRODUCTS

SE-RIES NO.	(In grams)							LOSS OF CARBON SAMPLE
	DRY CO <sub>2</sub> TAKEN	DRY CO FOUND	DRY CO <sub>2</sub> REQUIRED FOR CO	DRY CO <sub>2</sub> FOUND	DRY CO <sub>2</sub> FIXED BY CARBON	CARBON REQUIRED FOR CO	LOSS OF CARBON	
III	75.672 <sup>a</sup>	69.742 <sup>a</sup>	54.797 <sup>b</sup>	0.793 <sup>a</sup>	20.082 <sup>c</sup>	14.945 <sup>d</sup>	15.52 <sup>a</sup>	
IV	74.816 <sup>a</sup>	62.263 <sup>a</sup>	48.921 <sup>b</sup>	8.289 <sup>a</sup>	17.606 <sup>c</sup>	13.342 <sup>d</sup>	13.55 <sup>a</sup>	

<sup>a</sup> Experimental values.

<sup>b</sup> Column 3 times 44/56.

<sup>c</sup> Column 2 minus the sum of columns 4 and 5.

<sup>d</sup> Column 3 times 12/56.

### DISCUSSION OF RESULTS

The cooled residue left in the furnace after a series run, if no weight changes due to "side effects" take place, would be expected to include the carbon dioxide apparently fixed by heated carbon plus that portion of the original carbon sample not required for carbon monoxide formation or that appearing directly as volatile products in the exit gases. The weights of carbon dioxide apparently fixed by heated carbon

(column 6, Table II) are greater than the corresponding weights of carbon required for carbon monoxide formation (column 7, Table II). This would indicate that the weight of the cooled residue should be greater than that of the original carbon sample. The experimental values in column 8, Table II, show instead an appreciable loss of sample between weighings during the series run. This loss may be partly accounted for by the weight of gaseous products, other than carbon dioxide and carbon monoxide, resulting during the carbon dioxide treatment of heated carbon. The weights of these gases—i. e., oxygen (hydrogen, methane) and nitro-

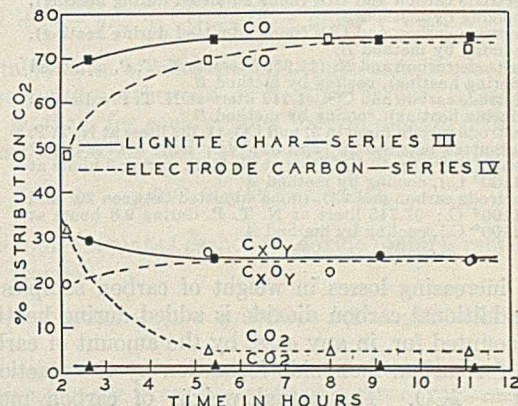


FIGURE 1. DISTRIBUTION OF CARBON DIOXIDE AS CARBON MONOXIDE, CARBON-OXYGEN COMPLEX, AND CARBON DIOXIDE

gen, calculated from the volumetric analyses—are 3.031 grams for series III (lignite char) and 0.787 gram for series IV (electrode carbon). As may be seen, these gases account for only a portion of the respective losses in the two series. Other distributions of material must, therefore, be sought. Possible losses of products which might escape ready detection are: (1) loss of hot exit gases by leakage or diffusion; (2) mechanical loss of carbon (dust) in exit gases; (3) loss of carbon by deposition (resulting from carbon monoxide decomposition) upon the porcelain packing in the exit end of the reaction tube; and (4) incomplete removal and weighing back of all the solid cooled residue left in the furnace after a series run. These possibilities were carefully checked and found to be negligible. Two plausible causes of weight changes remain to be considered. These are: (5) possible weight changes—other than that corrected for by the carboni-



zation loss (4)—resulting from side effects upon the carbon sample during the preheating before the treatment with carbon dioxide proper; and (6) weight changes occurring during the cooling of the activated residue after the carbon dioxide treatment. A number of check experiments were carried out to establish the magnitude of these side effects. The measured loss (algebraic sum) in weight representing such weight changes furnished a plausible answer to what, at first, appeared to be an unaccountable loss of material. These experiments covered separate studies of the effects of heating and cooling equal-size electrode carbon samples with the gases—air, nitrogen, and carbon dioxide—under known conditions for gas admission, time and temperature of heating, and manner of cooling. The general procedure was as follows:

The assembled apparatus, with electrode carbon sample (approximately 56.2 grams in each case, weighed accurately to four decimal places) in position in the reaction tube, was first swept at room temperature with the gas under study until the exit gas showed the same composition. The furnace and contents were then heated at a uniform rate to 1100° C., with or without further admission of gas, and finally cooled under one of two conditions: (A) with one small opening to air to equalize pressures, or (B) slight positive pressure of the gas under study. Modifications of this general procedure were made in two experiments—one on an electrode carbon sample previously used with carbon dioxide and one on a fresh sample—to study the effects of continued treatment with carbon dioxide at 1100° C.

A brief summary of the results of separate experimental runs show weight losses for the original electrode carbon samples as follows:

CONDITIONS OF EXPERIMENT	Wt. Loss %
(1) Electrode carbon and air (none admitted during heating), cooling by method A	0.174
(2) Electrode carbon and CO <sub>2</sub> (none admitted during heating), cooling by method A	0.153
(3) Electrode carbon and CO <sub>2</sub> (none admitted during heating), cooling by method B	0.167
(4) Electrode carbon and N <sub>2</sub> (11.959 liters at N. T. P. admitted during heating), cooling by method B	0.141
(5) Electrode carbon and CO <sub>2</sub> (1.112 liters at N. T. P. admitted during heating), cooling by method B	0.753
(6) Electrode carbon (used in 5) and CO <sub>2</sub> (1.122 liters at N. T. P. admitted between 26° and 521° C.; none between 521° and 1100° C.; 10.307 liters at N. T. P. during 3 hours at 1100° C.), cooling by method A	8.29
(7) Electrode carbon and CO <sub>2</sub> (none admitted between 29° and 1100° C.; 37.745 liters at N. T. P. during 9.8 hours at 1100° C.), cooling by method A	22.67

The increasing losses in weight of carbon samples found when additional carbon dioxide is added during heating are not accounted for, in any case, by the amount of carbon required for carbon monoxide formation by the reaction  $C + CO_2 \rightleftharpoons 2CO$ . The actual weight of carbon monoxide found, as calculated from the volumetric analyses of the total collected gases in each series, when multiplied by 12/56 gave a required value for the "carbon used up" always lower than the experimental loss represented by the weighings before and after the series run. Furthermore, the nonappearance of an appreciable portion of the total carbon dioxide added, either as carbon dioxide or as carbon monoxide in the gaseous products, would lead to the conclusion that such portion of carbon dioxide must have been taken up by the samples during the heating in the furnace. The algebraic sum of the carbon required for carbon monoxide formation and the carbon dioxide taken up by carbon during the heating indicates an actual gain in weight of original sample. This would be the situation at the end of the heating period before cooling was started. Apparently then, the residue, now activated by carbon dioxide and heat treatment, must undergo further change in weight during cooling. The mechanism of such change has a plausible explanation in the work of Shilov and co-workers. These investigators have shown that the adsorptive power of active charcoal is due to three surface ox-

ides, A, B, and C (34, 35). The structural differences in these oxides lies in the carbon-carbon and carbon-oxygen linkages. These workers (36) found that sugar charcoal activated by heating in carbon dioxide at about 900° C. forms chiefly oxide B. This oxide at temperatures between 300° and 700° C. oxidizes partially in air to form a less stable oxide, C, which splits out carbon dioxide and leaves a new oxide B surface. The process repeats itself again and again, thus losing weight by the elimination of carbon dioxide. At 700° C. and higher temperatures the oxide B splits out carbon monoxide with considerable velocity and is reformed by oxidation with air, so that carbon is continually oxidized to carbon monoxide through the formation and decomposition of oxide B. At temperatures under 300° C. oxide B is stable; therefore, if the decomposition of oxide B is not completed during the cooling of the activated residue of unused carbon and carbon-oxygen complex from furnace temperature down to 300° C., a portion of the complex will remain. For details of the mechanism showing the elimination of carbon dioxide and carbon monoxide from oxides B and C, as well as the properties and structures of oxides A, B, and C, reference should be made to the original papers (34, 35, 36).

In the present work a much larger excess of carbon sample was originally taken than is stoichiometrically required by the added carbon dioxide for carbon monoxide formation according to the reaction  $C + CO_2 \rightleftharpoons 2CO$ . If this were the only reaction taking place and proceeded completely to the right, all of the carbon dioxide added should be used up and carbon monoxide should be the only gaseous product (except such gaseous products as might result by direct heating or from side effects during heating). A study of the data in Tables I and II reveals that all of the carbon dioxide introduced did not go into the formation of carbon monoxide. Some carbon dioxide was always found in the gaseous products, and an appreciable portion was seemingly fixed during heating as a solid surface complex by the carbon. As shown above, this solid surface carbon-oxygen complex partially decomposes during cooling with elimination of carbon dioxide and carbon monoxide, and hence the final amount of complex stable under 300° C. represents only a portion of that formed during heating.

The conception of a solid oxide of carbon, stable at ordinary temperatures, is not new. In addition to the oxides that obey the law of definite proportions, there are a number of solid oxides of variable composition (1, 2, 3, 5, 7, 13, 15, 17, 20, 21, 22, 24, 25, 30, 32, 37, 38). The literature citations mentioned give only a partial list of some of the known solid oxides of carbon. The latter class of oxides (low in oxygen and high in carbon content) frequently result as surface complexes when oxygen or oxygen-containing gases (air, carbon dioxide, or steam) react with carbon. Extensive experimental support for the formation of such oxides has been amply shown for both oxygen and carbon dioxide with carbon. Rhead and Wheeler (31), Taylor and Neville (38), and Thiele and Haslam (39) suggest a similar complex for steam and carbon. The solid carbon-oxygen complex is considered by most investigators to be a "physico-chemical" or "quasi-chemical" oxide of carbon, which may be represented by the formula  $C_xO_y$ . Other workers express the complex as  $C\text{---}O$  solid. Shah (33) and Keyes and Marshall (19) prefer to regard the oxygen as being adsorbed in a special state by the carbon. As yet there is not sufficient evidence to warrant definite expression of the chemical nature of the solid carbon-oxygen complex with any finality. Undoubtedly the composition will vary under different conditions of formation and after-treatment. It may possibly be the result of adsorbed oxygen (30, 32), dissolved oxygen (13, 26, 37), or adsorbed carbon monoxide (6). The extent of the formation of the solid carbon-oxygen surface complex, or the resultant of adsorbed

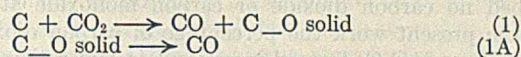


gas by carbon, is known to be dependent upon the relative amounts of gases and carbon present, surface of carbon exposed, time of contact, reactivity of the carbon surface, temperature, and probably other factors. The complex is fairly stable below 300° C. but, with increased time, temperature, and vacuum, breaks down partially into carbon dioxide and carbon monoxide. The ratio of carbon dioxide to carbon monoxide in the products decreases with rising temperatures and, as shown recently by Burrage (7), changes according to the mode of evacuation and flushing.

Whether the solid carbon-oxygen complex is considered to be an oxide of variable composition with high carbon and low oxygen content, or the result of dissolved or adsorbed gas in carbon, the present experiments indicate that at least for temperatures above 925° C. its formation appears to be exothermic. Below 925° C., in keeping with the experimental data of the present paper, the observations of Mayers (24), and the explanation for spontaneous decomposition of the activated residue during cooling by Shilov and co-workers (36), the reaction appears to be endothermic. The average furnace temperature for each experiment is shown in column 2, Table I. In series I it was found that, with an approximately steady current through the furnace circuit for each experiment, the temperature in experiment 1A tended to fall off slightly. This is probably due to the fact that in this experiment some heat was required for further carbonization at this temperature and that the rates of formation of carbon monoxide and especially carbon-oxygen complex are slow under 900° C. The temperatures in experiments 1B and 1C rose slightly during these runs. In series II, III, and IV the temperatures tended to rise in all cases. To overcome this, the furnace resistance was increased so as to maintain, as nearly as possible, a uniform temperature during each experiment. The general tendency of the furnace temperature to increase during the runs indicated an exothermic effect due to the fixation of carbon dioxide by heated carbon greater than the endothermic effect of the reaction  $C + CO_2 \rightleftharpoons 2CO$ . This evidence, together with the disappearance of an appreciable portion of the added carbon dioxide from the gas phase, gives strong support for the formation of a solid surface carbon-oxygen complex when carbon dioxide is heated with carbon above 925° C.

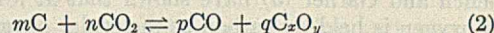
The curves for carbon monoxide, carbon-oxygen complex, and carbon dioxide shown in Figure 1 for series III and IV indicate the distribution of the reactant carbon dioxide going into these products plotted against the total time of carbon dioxide passage expressed in hours. The times of contact for series III (lignite char) and for series IV (electrode carbon) were considered constant for the purpose of plotting the curves. Comparison of the curves for lignite char and electrode carbon shows marked differences for elapsed times up to about 5 hours, while above 5 hours the respective curves are very nearly parallel. Except for the carbon dioxide curve for lignite char (series III) the general shape of the curves for the shorter elapsed times indicates that about 5 hours were required before the proportional distribution of carbon dioxide into the products as carbon monoxide, carbon dioxide, and carbon-oxygen complex became constant. The curves show also that lignite char reaches equilibrium more rapidly than does electrode carbon. This is in keeping with the reactivities of these kinds of carbon materials. The numerical values from which the curves were constructed are shown in columns 11, 12, 13, and 17 of Table I. The effect of allowing the furnace to cool between experiments is shown by comparing series II and III of Table I. Although the total time of carbon dioxide passage is greater in series II than in series III, the percentage of carbon monoxide in the final experiments of series II is less, even though the temperatures are comparable.

The mechanism of the reaction between carbon dioxide and heated carbon may be formulated by two general expressions. To simplify the stoichiometry, the excess carbon and gaseous carbon dioxide found in the products may be omitted from consideration, as these would appear on both sides. One of the general expressions is that offered by Mayers (24), who makes use of the following reactions:

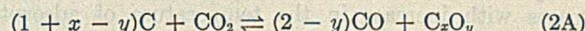


The relative rates of the two reactions govern the amounts of solid carbon-oxygen complex and carbon monoxide found under given experimental conditions. This mechanism would indicate that one mole each of carbon and carbon dioxide take part in the reaction. Broom and Travers (6) and Langmuir (21) found that, when carbon dioxide reacted with carbon at temperatures ( $T < 1250^\circ K.$ ), carbon monoxide was formed at the same rate as that at which carbon dioxide disappeared. This is in accordance with reaction 1. Mayers (24) has shown that the rate of reaction 1A increases with temperature so that at higher temperatures (between 925° and 950° C., 24) the second reaction, 1A, follows the first reaction, 1, so rapidly that there is no further accumulation of the solid oxide.

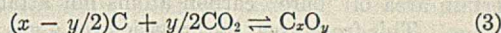
A second mechanism is offered by the authors for the data of the present work. This mechanism may be summarized in the expression,



The experimental data in this paper indicate that  $p$  is not equal to  $2n$ . If, as in the expression by Mayers,  $n$  is taken as 1 mole of carbon dioxide, then  $m = 1 + x - y$ ,  $p = 2 - y$ , and  $q = 1$ . The general equation may now be written,



The total amount of solid carbon-oxygen complex formed and undecomposed at the end of heating carbon dioxide with carbon is, then, for each mole of carbon dioxide used up for both carbon dioxide and carbon-oxygen complex formation,



and the total amount of carbon monoxide found is represented by the reaction,



The relative numerical values of  $m$  and  $n$  may be determined with fair accuracy from the ratios of moles of carbon (values in column 8, Table II, divided by 12) to the moles of carbon dioxide (sum of values in columns 4 and 6, divided by 44). The values of  $m$  and  $n$  for series III (lignite char) are 1.293 and 1.702, respectively. The corresponding values in series IV (electrode carbon) are 1.129 and 1.512. For  $n = 1$  mole,  $m = 0.759$  mole in series III, and  $m = 0.747$  mole in series IV. Since  $m = 1 + x - y$ , then  $y$  must be greater than  $x$ . The exact magnitude of  $x$  and  $y$  cannot be determined from the experimental data. From the ratios of the values of  $m$  and  $n$  it seems more reasonable to use the mechanism given in reactions 2 or 2A rather than that given by Mayers (reactions 1 and 1A) as a representation of the reaction between carbon dioxide and heated carbon in the present work. Mayers used much higher velocities of carbon dioxide and much less carbon surface in his experiments than were used here. Figure 1 shows that the proportional distribution of carbon dioxide into carbon monoxide and fixed by carbon as a solid carbon-oxygen complex is, after equilibrium is established, about the same in series III as in series IV. The close agreement in values of the ratios of  $n$  to  $m$  as shown above

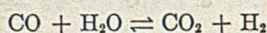


would indicate also that the composition of the solid carbon-oxygen complex is very similar in the two cases. For the sake of brevity and convenience the complex will be generally denoted by  $C_xO_y$  in the following discussion of the related work of other investigators.

Rhead and Wheeler (32) have shown that charcoal previously exhausted of gases at 950° and heated to 400° C. absorbed no carbon dioxide or carbon monoxide at 400° C. In the present work the percentage of carbon dioxide fixed by carbon as  $C_xO_y$  formed in series I is lower than the corresponding percentages for the other series at higher temperatures. This may be due in part to a lower time of contact, but temperature no doubt plays an important part. The fact that Rhead and Wheeler used a different kind of carbon from that used in the present investigation and that their carbon had been preheated to 950° C. may be significant. It should be further noted that wider variations in the percentages of carbon monoxide and carbon dioxide in the gases as well as in the percentage distribution of carbon dioxide as carbon monoxide, carbon dioxide, and  $C_xO_y$  appear in the data of series I and series II than in the data of series III. This is no doubt due in part to the interruption in series I and II between certain experiments as stated above. The marked drop of the carbon dioxide fixed as  $C_xO_y$  in experiment 2F compared with that in 2E may be due to an increase in decomposition of  $C_xO_y$  on account of the long time of the run, 14.59 hours, for series II.

Blench and Garner (3) have shown that at low temperatures oxygen is held by carbon as molecular oxygen without chemical change; i. e., no primary valences are broken. At higher temperatures intimate combination occurs with formation of  $C_xO_y$  groups on the surface of the carbon. Some of these groups are stable and some unstable at any particular temperature. The heat of formation of the stable groups increases with increase in the temperature of adsorption caused by the mode of orientation of the oxygen atoms on the surface with temperature.

The total amount of  $C_xO_y$  formed during the duration of the run must be greater than that left at the end, since  $C_xO_y$  is known to break down partially. This would always allow a certain area of "bare" carbon atoms not attached to the complex. This fresh area, by provision for a gas film of carbon monoxide on the carbon, especially in the presence of catalytic materials in the ash, would afford favorable conditions for the surface reaction



to take place in the manufacture of water gas. There is also the possibility that  $C_xO_y$  and steam react to form carbon dioxide and hydrogen. Rhead and Wheeler (31) found that decomposition of this complex seems to be accelerated by the presence of steam. If this is true, then the evidence of the formation of a solid carbon-oxygen complex, shown by the data in the present work, furnishes a possible partial explanation for the composition of water gas formed from younger coal cokes.

Confirmatory evidence of the formation of  $C_xO_y$  has been obtained by Burrage (7). A very plausible hypothesis substantiated by later experimental proof of the mechanism of the process is stated by Burrage as follows:

It would appear that the carbon dioxide, which is adsorbed, changed over continuously into the complex,  $C_xO_y$  (a kind of surface compound), dependent on the pressure. As the pressure of carbon dioxide is increased, more  $C_xO_y$  will form and vice versa. This means that with increase of pressure the complex builds itself up outwards from the surface of the charcoal, forming a spongy mass, of which molecules nearest the charcoal actually form the complex, with a continuous gradation to ordinary carbon dioxide molecules on the surface.

## THE EQUILIBRIUM CONSTANT

The values of the equilibrium constant

$$K = (CO)^2 / (CO_2) = k_1 / k_2$$

obtained by the use of a dynamic type of apparatus has been criticized by Rhead and Wheeler (30) on the grounds that equilibrium is not reached in dynamic experiments. These authors found that the gases must be maintained in contact with heated carbon in some cases for several days even in a static type of apparatus before equilibrium was reached. They have shown also (29) that carbon dioxide should, theoretically, be reduced by carbon at a temperature of 315° C. or less, but that the rate of reduction was extremely slow even at 700° C. At 850° C. Rhead and Wheeler (28) showed that under the same experimental conditions the reduction of carbon dioxide by carbon to carbon monoxide is 166 times as fast as the dissociation of carbon monoxide. At higher temperatures the equilibrium is displaced still farther in the direction of carbon monoxide. The relative rates of reaction at different temperatures are practically proportional to the time of circulation of gases over the carbon. Rhead and Wheeler (30) object to the calculated time of contact commonly used in computing the data of experiments from the dynamic type of apparatus in that it involves too many arbitrary assumptions. Rhead and Wheeler's values for the relative rates of reduction of carbon dioxide at different temperatures for 5 minutes of circulation in each case are:

TEMP. ° C.	REACTION VELOCITY, $k_1$ ( $t = 1$ MIN.)	CO <sub>2</sub> REDUCED AFTER 10 MIN. %
900	0.00660	1.4
950	0.00374	8.3
1000	0.01764	33.3
1050	0.05760	73.4
1100	0.10570	91.3

The time of contact would probably be under one second for these values.

Although the time of contact is a valid objection, the use of a time of circulation cannot be made for a dynamic type of apparatus in which the gases are not recirculated. Therefore, a usual plan in obtaining the values of the direct velocity constant,  $k_1$ , for the forward action  $C + CO_2 \rightleftharpoons 2CO$  has been followed for the values recorded in column 18 of Table I. These values were calculated according to an equation of Haslam and Russell (16) who developed it from the reaction-rate equation of Clement, Adams, and Haskins (9A). The latter authors found that the values of  $k_1$  vary with the kind of carbon and believe that the decomposition of carbon monoxide yields only one kind of carbon (lampblack). The value of  $k_2$  cannot, therefore, be calculated from the expression  $K = k_1 / k_2$ .

The values of  $k_1$  obtained by Clement, Adams, and Haskins (9) for charcoal lie above and those for bituminous coke lie below the calculated values of  $k_1$  for lignite char and electrode carbon of the present paper for the corresponding temperatures. This is in keeping with the relative reactivities of these four kinds of carbon. When equilibrium conditions are not readily realized, the calculation of  $k_1$  from the equation of Haslam and Russell (16) is not strictly applicable. This equation, rewritten with  $k_1$  instead of carbon monoxide as the unknown, becomes:

$$k_1 = \frac{2.3 \log_{10} \frac{1}{1 - CO}}{t}$$

where CO = volume percentage of carbon monoxide expressed as a decimal  
 $t$  = time, seconds



It is seen that, as the percentage of carbon monoxide approaches 100, the numerical values of  $\log_{10} \frac{1}{1 - \text{CO}}$  increase. In the use of the above expression for calculating  $k_1$ , the reverse velocity constant,  $k_2$ , for the decomposition of carbon monoxide is neglected. This neglect of  $k_2$  should only be made, however, when the decomposition of  $2\text{CO} \rightleftharpoons \text{C} + \text{CO}_2$  is extremely slow. The calculated values of  $k_1$ , if computed by the method developed by Haskins (9B) would give better values. Since the worth of the values of  $k_1$  calculated from data obtained by the use of the dynamic type of apparatus is questionable, these more complicated computations were omitted in the present paper.

Falcke (14) gives a fairly complete bibliography upon the  $\text{C} + \text{CO}_2 \rightleftharpoons 2\text{CO}$  equilibrium. From thermodynamic consideration he calculates that there may be more than one kind of carbon formed by carbon monoxide decomposition. From the results of his calculations Falcke believes that the values of the equilibrium constants for temperatures above  $1000^\circ \text{K}$ . indicate, except for those obtained from data by Mayer (23), only graphitic carbon, while for temperatures below  $1000^\circ \text{K}$ . the equilibrium is not well defined, but that amorphous carbon is probably involved. Falcke concludes, therefore, that the reaction  $2\text{CO} \rightleftharpoons \text{C} + \text{CO}_2$  proceeds with the deposition of graphite carbon above  $1000^\circ \text{K}$ . and extremely slowly below  $1000^\circ \text{K}$ ., with probable deposition of amorphous carbon. In the present work a very small amount of carbon was found upon the porcelain packing and the walls of the reaction tube near the gas exit end of the furnace. From all indications this deposit was amorphous carbon (lampblack). This agrees with the observations of Clement, Adams, and Haskins (9) rather than those of Falcke (14).

Drakeley (10) has shown that the values of the direct velocity constant,  $k_1$ , and of the reverse velocity constant,  $k_2$ , for the reaction  $\text{C} + \text{CO}_2 \rightleftharpoons 2\text{CO}$  vary with the temperature at which the coke is prepared. A typical Durham gas coal was carbonized at different temperatures to prepare a number of test cokes. Drakeley found that the value of  $k_1$  diminished slowly as the temperature of coking was increased from  $450^\circ$  to  $700^\circ \text{C}$ . At  $700^\circ \text{C}$ . the value of  $k_1$  diminished rapidly and again more slowly between  $900^\circ$  and  $1100^\circ \text{C}$ . On the other hand, the value of  $k_2$  showed an abrupt rise at about  $700^\circ \text{C}$ ., after which the temperature of carbonization had little effect. Direct velocity constant  $k_1$  is increased, while reverse velocity constant  $k_2$  is diminished by a rise in the temperature of the reaction between carbon dioxide and coke. For cokes prepared at temperatures ranging from  $450^\circ$  to  $1100^\circ \text{C}$ ., the approximate ratios of the extreme values of  $k_1$  at reaction temperatures  $950^\circ$ ,  $1000^\circ$ , and  $1100^\circ$  are 4.5 to 1, 2.5 to 1, and 1.5 to 1, respectively; at the same reaction temperatures the ratios for  $k_2$  are 1 to 4.7, 1 to 3.8, and 1 to 1.9, respectively. Drakeley's work presents an excellent argument for always giving a complete description of the conditions under which the coke was prepared.

#### POSSIBILITY OF THERMAL SEPARATION

One other point that may be mentioned, although this should have but little effect on the equilibrium constant  $K = k_1/k_2$ , is the possible change of the carbon dioxide-carbon monoxide ratio due to thermal diffusion of these gases. According to the theory of thermal diffusion worked out by Enskog (12) and by Chapman (8) and verified for certain gas mixtures by other workers, if two gases of different molecular weights are placed in a tube, one end of which is heated while the other remains cold, the ratio of the heavy gas to the light rapidly becomes and remains larger in the cold end than in the hot end of the tube. Calculations made by Emmett and Schultz (11) based upon the thermal diffusion measurements

of Ibbs and Underwood (18) show "that if equilibrium with respect to thermal diffusion were established, the 'cold end' carbon dioxide-carbon monoxide ratios for the iron-ferrous oxide system might be higher than the 'hot end' values by as much as 6.3 per cent at  $600^\circ \text{C}$ . to 7.9 per cent at  $1000^\circ \text{C}$ ." Emmett and Schultz state, however, that the actual errors that can be attributed to thermal separation of carbon dioxide and carbon monoxide is uncertain for two reasons: (1) In the values of the published data (ratio of carbon dioxide to carbon monoxide) it is not always stated whether they are for the cold or hot end of the apparatus; and (2) at about one atmosphere of pressure, where diffusion is slow, convection currents are likely to cut down the amount of thermal separation between the hot and cold ends of the usual reaction vessel.

Since it is impracticable to draw off the gases for analysis from the hot zone of the reaction and since the  $\text{C} + \text{CO}_2 \rightleftharpoons 2\text{CO}$  reaction is usually studied in a dynamic type of apparatus, it is possible to have some thermal separation. On the other hand, since the molecular weights of carbon dioxide and carbon monoxide, as compared, for example, with those for water and hydrogen, lie close together and since at about one atmosphere pressure convection currents reduce thermal diffusion, the actual error in the ratio of carbon dioxide to carbon monoxide which can be attributed to thermal diffusion would probably be small.

#### REACTION KINETICS

The coefficient of reaction velocity rises with temperature for the heterogeneous system  $\text{C} + \text{CO}_2 \rightleftharpoons 2\text{CO}$ . The observed increase in reaction velocity is many fold greater than the calculated increase in the diffusion constant. The speed of the reaction under consideration is, therefore, governed chiefly by the velocity of chemical combination rather than by diffusion.

The velocity of the reverse reaction—i. e., decomposition of carbon monoxide to form carbon and carbon dioxide—is extremely slow as compared with the forward reaction.

From the work of other investigators it is believed that reaction velocity plays a more important role in explaining the apparent equilibrium constants obtained in a dynamic type of apparatus than does the lack of agreement of the experimental equilibrium constants with the theoretical values. It is intended to continue these types of experiments using other rates of carbon dioxide supply and also to extend the work to other gases and heated carbon. This should help to establish with certainty which factor plays the most important role.

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# Styrene and Indene from Persian Natural Gas

S. F. BIRCH AND E. N. HAGUE, Anglo-Persian Oil Company, Ltd., Sunbury-on-Thames, England

CONSIDERABLE attention, as indicated by the patent literature and such communications as that of Natelson (11), has been directed to the production of styrene and indene on account of the ease with which these hydrocarbons can be converted into colorless polymerides of potential industrial value.

While the classic researches of Berthelot indicated that certain hydrocarbons yielded styrene and indene in greater or lesser amount when passed through a tube at a moderate red heat, it is only comparatively recently that the development work on the pyrolysis of waste hydrocarbon gases for the production of benzene has opened up this source of these materials. The enormous possibilities of this source can best be judged from the figures given below for the actual yields of styrene and indene obtained under semi-commercial scale conditions.

These results<sup>1</sup> were obtained during the period 1928-29 when the pyrolysis products of certain Persian natural gases were being investigated. An account of the plant and the gases used has already been published by Cadman (3). A rough distillation of the crude pyrolysis product was first effected on the plant with the production of a distillate boiling up to 200° C. and a dark brown tarry residue. The former, the crude motor benzene, was then fractionated in the laboratory from a gas-heated copper can with a capacity of 4.5 liters, through an iron column 65 inches (165.1 cm.) in length and 1.4 inches (3.6 cm.) internal diameter, lagged with asbestos and packed with Lessing rings. A charge of 4 liters was distilled in one operation and a standard rate of distillation of 8 cc. per minute was maintained. The volume of distillate obtained for every 5° C. was carefully noted, and fractions were collected over selected ranges of temperature. The results of a typical distillation of the crude motor ben-

zene obtained from an unstripped gas are given in Table I. The composition of the gas employed, which was desulfurized before use, was as follows:

	% by vol.		% by vol.
Hydrogen sulfide	12	Propane	21
Methane	29	Butanes	10
Ethane	24	Pentanes and higher	4

Desulfurization was effected by partial oxidation with air using an activated charcoal catalyst at 300° C., the reaction involved being:



This method was used for the purpose of sulfur recovery but possessed the disadvantage that it loaded the pyrolysis plant with about 22 per cent by volume of nitrogen. The pyrolysis conditions were as follows: gas temperature in reaction zone, 850° C.; outside skin temperature of reaction tubes, 1000° C.; space velocity (expressed as volumes of cold gas per volume of heated space per hour), approximately 400; absolute pressure, 20 pounds per square inch (1.4 kg. per sq. cm.). The tube material in the reaction section was Hadfield's Era H.R.4 steel containing 26 per cent chromium, 1.5 per cent manganese, 0.9 per cent silicon, 0.15 to 0.2 per cent carbon, and not more than 0.3 per cent nickel.

## FRACTION I

BUTADIENE AND CYCLOPENTADIENE. Although these compounds are outside the scope of the present paper, it is interesting to note that both were identified in the pyrolysis products. Passage of the gases evolved in the early stages of the distillation of the crude product through chloroform containing bromine gave, on removal of the solvent and liquid dibromides by distillation under reduced pressure, a solid bromide. After crystallization from alcohol, from which it separated in colorless plates, this melted at 114° C. and was

<sup>1</sup> Since this paper was written, Cambron and Bayley [*Can. J. Research*, 10 145 (1934)] have published the results of their investigation on the chemical composition of the products of pyrolysis of gaseous paraffins. Their findings are in general agreement with those of the present authors.



identified by the method of mixed melting points as butadiene tetrabromide.

The presence of cyclopentadiene was suspected at the time this work was originally carried out, but it was only when the excellent method of Diels and Alder (5) of using the maleic anhydride addition compound as a means of identifying diolefins became available that the presence of cyclopentadiene in the low-boiling products of pyrolysis was definitely established. On adding maleic anhydride to the fraction boiling up to 45° C. from the fractionation of the fresh pyrolysis product, heat was immediately evolved and cooling became necessary. Almost immediately a colorless crystalline solid separated which, on recrystallization from a mixture of benzene and petroleum ether (boiling point, 60° to 80° C.), separated in long, fine needles which melted at 163° to 164° C. and did not depress the melting point of a genuine specimen of *cis*-endomethylene-3,6-tetrahydrophthalic anhydride.

TABLE I. RESULTS OF TYPICAL DISTILLATION OF CRUDE MOTOR BENZENE

TEMP. ° C.	DISTILLATE PER 5° C. % of charge	FRACTIONS COLLECTED		
		No.	Range ° C.	% of charge
30	0.12			
35	0.12			
40	0.12	I	Up to 45	1.73
45	0.12			
50	Nil			
55	0.17			
60	0.07			
65	0.12	II	45-75	2.73
70	0.37			
75	2.50			
80	72.5			
85	0.37			
90	0.37	III	75-95	73.61
95	0.37			
100	0.25	IV	95-105	1.37
105	0.75			
110	7.00	V	105-115	7.25
115	0.25			
120	0.12			
125	0.25	VI	115-135	0.61
130	0.12			
135	0.12			
140	0.87			
145	0.87	VII	135-150	6.74
150	0.25			
155	0.25			
160	0.12			
165	0.12	VIII	150-170	0.86
170	0.12			
175	0.50			
180	0.50	IX	170-180	2.00
Residue	2.00			

#### FRACTION VIII

**STYRENE.** In a batch of fractions which had been allowed to stand in the laboratory for some weeks it was observed that, while the lower fractions remained colorless, several of those in the 130° to 180° C. range darkened. Steam distillation of these fractions gave a nonvolatile residue which on standing became converted into transparent, light brown solids or resins. After the lower fractions had been examined, an attempt was made to refractionate the xylene fraction (VIII) at atmospheric pressure. As soon as the liquid commenced to boil, an extremely violent reaction set in, and clouds of lachrymatory vapors were disengaged. The source of heat was at once removed, but sufficient heat was developed spontaneously to continue the boiling for nearly an hour in spite of water cooling. When cold, the product in the flask was a hard, glassy, fairly transparent mass with a dark brown color. A yield of 800 grams of polymeride was recovered from a still charge of 2000 cc. (1760 grams). Definite proof of the presence of styrene in this fraction was obtained by treating with bromine a portion of the original fraction diluted with chloroform and removing the solvent and excess of bromine under reduced pressure, when a good yield of a solid dibromide was left. On crystallization from alcohol, it separated in stout needles melting at 73° C.; styrene dibromide melts at 73° C. (10). Gentle refluxing of

the dibromide with a zinc-copper couple in alcoholic solution in the usual way (cf. Manning, King, and Sinatt, 9) gave pure styrene which boiled completely at 144.6° C. (740 mm.).

Styrene was also obtained by refractionation of the crude fraction (boiling point, 135° to 150° C.) under reduced pressure, a liquid boiling at 73° to 74° C. (73 mm.) being obtained, which had the following properties: specific gravity at 16° C., 0.9085;  $n_D^{20}$ , 1.5430; boiling point, 141.5° C. at 740 mm. (Beilstein gives specific gravity as 16.5° C. as 0.9080 and  $n_D^{21}$  as 1.5446 for styrene, 1).

Finally, dry or steam distillation of the solid polymer gave a liquid boiling at 144° to 146° C. which possessed all the characteristics of styrene; this solid agrees in its properties with metastyrene.

An approximate estimation of the styrene content of the crude 135° to 150° fraction was made as follows: 100 cc. (88 grams) of the fraction were mixed with 200 cc. of chloroform and well cooled. A solution of bromine in the same solvent (10 per cent) was then slowly added until the yellow color persisted, which necessitated adding approximately 110 grams of bromine. On removal of the chloroform and fractionation of the residue at 50 mm. pressure, a distillate was obtained, boiling at 55° to 62° C. (50 mm.) leaving a residue of styrene dibromide which solidified on cooling and weighed 182 grams. This corresponded with a styrene content for the original fraction of 80 per cent.

**m-XYLENE AND p-XYLENE.** The fraction mentioned above (boiling point 55° to 62° C. at 50 mm.), obtained during the estimation of the styrene content, had a volume of 18 cc. and distilled at atmospheric pressure over the same range as the original fraction. It possessed an odor similar to that of xylene and was treated with a mixture of concentrated nitric and sulfuric acids. The products of the reaction were poured into water, and the solid nitro compound, after thorough washing with water to remove any acid, was crystallized from alcohol. Pale yellow plates of 2,4,6-trinitro-*m*-xylene separated and, after a further crystallization, melted sharply at 182° C. and did not depress the melting point of a genuine specimen. Another compound melting at 135° C. was isolated from the alcoholic mother liquids and identified as 2,3,5-trinitro-*p*-xylene. It formed colorless needles when recrystallized from alcohol (Fittig, Ahrens, and Mattheides give 139° to 140° C., 7).

No evidence for the presence of *o*-xylene was obtained.

#### FRACTION IX

**INDENE.** The fraction boiling from 170° to 180° C. darkened on standing and exposure to light; in view of the surprisingly high styrene content of fraction VII, the presence of indene in this fraction was suspected. The fraction was therefore diluted with chloroform and well cooled, and bromine in chloroform (10 per cent) was slowly added until the yellow bromine color persisted. After the chloroform had been removed under reduced pressure, the residue solidified on cooling. It was freed as far as possible from contained liquid on a cooled filter funnel, and the residue was crystallized from petroleum ether. It formed colorless prisms of 1,2-dibromohydroindene which melted at 32° C. (Kraemer and Spilker give 31.5° to 32.5° C., 8). Treated with a zinc-copper couple in boiling alcoholic solution, it gave pure indene which boiled at 180° to 181° C. and solidified on cooling in a freezing mixture.

The almost quantitative yield of dibromide obtained from the original fraction indicated that it must have consisted almost entirely of indene, and no further examination was made.

**HIGH-BOILING RESIDUE.** An investigation of the tarry residue left on removal of the crude motor benzene in

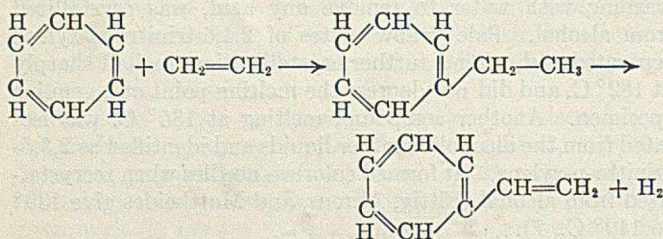


the original distillation indicated the presence of the usual high-boiling products of pyrolysis. Of these, naphthalene, anthracene, phenanthrene, and chrysene were isolated and definitely identified. While it is obvious that the formation of these hydrocarbons can be explained in many ways, it is interesting to note that Ferko (6) obtained phenanthrene and anthracene by the passage of styrene through a glowing tube while Spilker (13) isolated chrysene from the products obtained by treating indene in the same way.

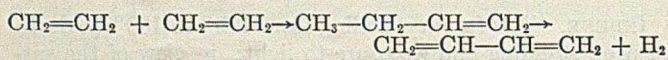
**YIELDS OF STYRENE AND INDENE.** Some indications of the quantities of styrene and indene can be obtained from the above results. The yields of the fractions containing the styrene and indene were, respectively, 6.74 and 2.0 per cent based upon the crude motor benzene. Thus the actual yields of styrene and indene became approximately 5 and 2 per cent. Using as raw material for pyrolysis a gas rich in propane and butane, the yields would be 2.4 liters of styrene and 0.95 liter of indene per 100 cubic meters or 0.15 and 0.06 Imperial gallon per 1000 cubic feet of gas treated, respectively. Thus a plant capable of dealing with a throughput of 5,000,000 cubic feet (142,000 cubic meters) per day of such gas would produce 13,000 Imperial gallons (59,000 liters) of motor benzene containing 750 Imperial gallons (3400 liters) of styrene and 300 Imperial gallons (1360 liters) of indene.

**MECHANISM OF THE REACTION.** The mechanism of the formation of styrene and indene is of particular interest in view of the possible commercial utilization of these hydrocarbons.

The formation of styrene can be accounted for by the pyrolysis of (1) acetylene, (2) benzene and acetylene together, (3) xylene, (4) ethylene, (5) ethylbenzene, and (6) a mixture of ethylene and benzene. Of these, the reaction probably responsible for the styrene formed when natural gas is pyrolyzed is as follows:



This is analogous to the mechanism suggested for the formation of butadiene from ethylene:



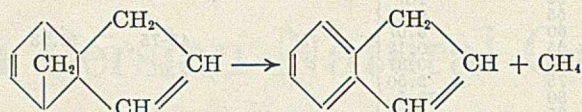
While it is not impossible, it is extremely unlikely that acetylene played any part in the formation of styrene in these experiments since acetylene was never found in the products. The suggestion that acetylene is so reactive that it is not found in the reaction products has been vitiated by Davidson (4) and by the present authors, using synthetic mixtures of acetylene and paraffins for pyrolysis when acetylene was invariably found in the gaseous products.

Berthelot (2) pyrolyzed xylene at a "moderate red heat" and obtained toluene as the principal product, benzene in considerable quantities, and a small amount of an unsaturated hydrocarbon boiling in the xylene range. The quantity of the unsaturated hydrocarbon was, however, so small that it did not permit of further study, but it was probably styrene.

In 1915 Pittman, Byron, and Egloff (12) investigated the pyrolysis of xylene and confirmed Berthelot's observation that toluene and benzene are the chief products; at the same time they isolated naphthalene and anthracene as well. In view of the ratio of xylene to styrene of 1 to 4 in the 135° to 150° C. fraction, it does not appear probable that the styrene obtained in the present experiments can be accounted for by the pyrolysis of xylene.

Reactions 4, 5, and 6 above constitute the present writers' view of the mechanism for styrene formation; i. e., ethylene is the parent hydrocarbon producing benzene, which in turn then reacts with a further molecule of ethylene to give styrene via ethylbenzene. An equimolecular mixture of ethylene and benzene subjected to pyrolysis at 820° C. showed that, of the products boiling higher than benzene, 40 per cent consisted of styrene. This appears to be definite confirmation of the suggested mechanism.

It is not so easy to account for the formation of indene. Of the many possibilities, the three most likely are the following: (1) reaction between propylene and benzene to give propylbenzene which is then converted into indene by ring closure and dehydrogenation, (2) a somewhat similar reaction between toluene and ethylene involving the formation of ethyltoluene or propylbenzene followed by ring closure and dehydrogenation, (3) demethanation of dicyclopentadiene thus:



Rough experiments carried out in the laboratory at 800° to 820° C. to test these suggestions, however, gave negative results. While these experiments were little more than qualitative, if indene had been formed as a major product it would certainly have been found; without an exhaustive study, however, it is not definitely possible to preclude any of these possibilities. Pyrolysis of dicyclopentadiene in a silica tube at 800° to 820° C. gave considerable quantities of solid aromatic hydrocarbons, including naphthalene and anthracene, which confirms the observation made by Weger (14).

#### ACKNOWLEDGMENT

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# Factors Affecting Lubricating Properties of a Petroleum Oil

F. H. RHODES AND ARTHUR W. LEWIS  
Cornell University, Ithaca, N. Y.

WILSON and Barnard (3) have shown that the lubricating power of a petroleum oil, as measured by the effect of the oil on the coefficients of static friction between metallic surfaces to which it has been applied, is due largely to the presence of some component that is very firmly adsorbed by the metal. This as yet unidentified constituent appears to be present in very small amounts only. The investigation described in the present article was undertaken for a twofold purpose: (1) to isolate and to identify the component that is primarily responsible for the "oiliness" of petroleum lubricants; and (2) to discover, if possible, other substances that, when added to an oil, will have a similar effect in improving the lubricating properties. The first of these problems has not yet been solved; the second objective has been attained.

## MEASUREMENT OF THE COEFFICIENT OF STATIC FRICTION

The method used for measuring the coefficient of static friction was similar to that described by Rhodes and Allen (2):

It consisted essentially of a light rider resting at three points on a flat metallic surface lubricated by the oil that was being examined, which surface could be tilted slowly until slipping of the rider occurred. The tangent of the angle of inclination at which the rider began to slide was taken as a measure of the coefficient of static friction.

The rider itself consisted of a triangular plate of sheet aluminum, in each corner of which was mounted a polished-steel ball bearing that served as a point of support. The bed plate on which the rider rested was a brass block in which were set three chromium-plated lugs so spaced that each bearing of the rider rested on a separate lug. The flat upper faces of the lugs were in the same plane so as to give, in effect, a horizontal plane surface. The plate carrying the bearing was mounted on a frame which was hinged at one end and was so arranged that it could be tilted slowly. The bearing block was provided with electrical heating coils for varying and controlling the temperature and was enclosed in a chamber through which either dry air or dry nitrogen could be circulated.

With this apparatus it is possible to obtain results that are consistent to within 3 per cent. For example, in two determinations made with the same oil the following results were obtained:

RUN 1		RUN 2	
Temp. ° C.	Coefficient of friction	Temp. ° C.	Coefficient of friction
24.5	0.1595	24.5	0.159
33.5	0.156	33.5	0.159
50	0.1605	52	0.162
65	0.157	70	0.160
81	0.157	83	0.164
88.5	0.172	90	0.174
90	0.177		

It was observed, however, that in order to obtain consistent results, the bearing surfaces had to be cleaned meticulously before the lubricant was applied. Both the rider and the block

The effect of a petroleum lubricant in reducing the static coefficient of friction in a bearing appears to be due primarily to the presence of a small amount of some substance that is firmly adsorbed on the surface of the bearing to form a film of high lubricating power. This film does not form instantly on a freshly oiled surface; an appreciable length of time elapses before equilibrium is established.

The constituent that is primarily responsible for the lubricating power may be removed from the oil by adsorption on finely divided metal—for example, on powdered Wood's metal. It is retained so tenaciously by the metal that attempts to recover it in a relatively pure form have not been successful.

When a petroleum lubricant is heated in the presence of air, a marked loss of lubricating power occurs at about 75° C. This change appears to be the result of oxidation. It may be inhibited by adding small amounts of certain substances to the oil. Cyclohexanol and  $\beta$ -naphthol are among the addition agents that show this effect. These particular addition agents also improve the lubricating power of the oil at ordinary temperatures.

bearing the polished lugs were boiled in absolute alcohol, rinsed with absolute alcohol, and dried in a vacuum desiccator over phosphorus pentoxide before being used in making a determination of the coefficient of friction. The absolute alcohol used had to be carefully purified, since certain impurities, when present even in small amounts, are adsorbed on the metal and decrease the accuracy of the results obtained.

In each series of tests the apparatus was allowed to stand for at least an hour after the fresh oil had been applied to the bearings before the determination of the frictional coefficient was made. The adsorbed film, to the presence of which the lubrication is due, forms rather slowly so that, if the coefficient is determined very soon after the oil is applied, erroneous results may be obtained (1). A sample of typical petroleum oil gave the following results:

TIME AFTER OIL WAS APPLIED Minutes	COEFFICIENT OF FRICTION	TIME AFTER OIL WAS APPLIED Minutes	COEFFICIENT OF FRICTION
5	0.1535	30	0.242
9	0.160	34	0.173
15	0.169	38	0.167
18	0.211	50	0.151
24	0.250	56	0.152

It was also observed that, in making a series of determinations with the same sample of oil, less consistent results are obtained if the individual measurements are taken at intervals of less than 3 minutes. Apparently a short time is required for the film to be restored to its equilibrium condition after the slight disruption caused by the motion of the bearing.

## SELECTIVE ADSORPTION OF LUBRICATING COMPOUNDS ON METALS

The lubricating oil used in these experiments was a commercial oil of "medium" grade, prepared from pure Pennsylvania crude by the usual process of steam-distillation followed by



chilling and filtration to remove wax. It showed the following characteristics:

Density at 20° C., 0.88  
Carbon residue (Conradson), 0.81 %

TEMP.		Viscosity Saybolt seconds
° C.	° F.	
30.6	87	651
37.8	100	445
54.4	130	205.4
98.9	210	64

Very finely divided Wood's metal was prepared by atomizing the molten alloy (melting point, 65° C.) with a jet of steam and collecting the mist in cold water. The resulting powder was dried and passed through a 150-mesh sieve. A

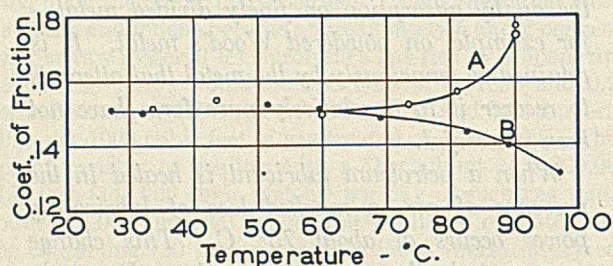


FIGURE 1. CHANGE IN COEFFICIENT OF STATIC FRICTION ON HEATING

A. In dry air      B. In dry nitrogen

portion of the lubricating oil was shaken with an equal weight of the metal and centrifugalized to remove the solid material. The coefficient of static friction of the original oil was 0.149; that of the oil which had been treated with the Wood's metal was 0.1852. After standing for several days exposed to the air, the treated oil showed a coefficient of 0.155. In a second experiment 50 grams of an oil that had a coefficient of friction of 0.141 was treated with two successive portions (50 grams each) of Wood's metal. The treated oil showed a coefficient of 0.189; on standing for 7 days exposed to the air, the coefficient decreased to 0.141. The metal removes a small amount of some substance that is primarily responsible for the lubricating power of the oil; this material is slowly regenerated when the oil stands in the air at room temperature.

Several portions of powdered Wood's metal that had been shaken with separate portions of fresh oil were combined and dropped into boiling water. The metal melted but did not coalesce, even on long-continued heating and stirring. The droplets remained separate, like globules of dirty mercury. Only a part of the adhering oil was liberated to float on the water. The liberated oil showed a coefficient of friction of 0.171, only slightly less than that of the main portion of the oil that had been separated from the metal by centrifugalizing. The experimental evidence indicates that the material which is most effective in increasing the lubricating power of the oil is so firmly adsorbed on the finely divided metal that it is retained even when the metal is melted. The presence of this film of adsorbed oil on the surface is apparently responsible for the failure of the metal to agglomerate.

Attempts were made to recover the adsorbed oil from the Wood's metal by heating gently with dilute hydrochloric acid. Even in the presence of the acid, however, the agglomeration of the finely divided metal was very incomplete. The recovered oil, after washing to remove traces of acid, showed a coefficient of friction of 0.175.

Somewhat analogous results were obtained when the original oil was treated with finely divided iron powder. One hundred grams of the oil were shaken with 20 grams of the iron and allowed to stand for 12 hours in contact with the metal. The clear oil was then separated and again treated with 20 grams of the iron. After the removal of the second

portion of the metal, the clear oil showed a coefficient of friction of 0.1601. The recovered iron was extracted with warm benzene, and from the extract the benzene was removed by distillation in a vacuum. The oil thus recovered from the iron showed a frictional coefficient of 0.1508. These results are qualitatively similar to those obtained with Wood's metal. Any component of especially high lubricating power that was adsorbed by the metal was so firmly retained that it was not removed even by extraction with benzene.

#### EFFECTS OF TEMPERATURE AND OF THE PRESENCE OF OXYGEN

Two series of experiments were made in which the coefficients of static friction of the lubricating oil at different temperatures were measured. In one set of measurements the gas passed through the apparatus was dry air; in the other, dry nitrogen. The results are shown in Figure 1. In each series the coefficient remained about constant until a temperature of around 75° C. was reached. Above that temperature the sample exposed to air showed an increase in the frictional coefficient, gradual at first and then more and more rapid. In nitrogen the coefficient of friction decreased somewhat at the higher temperatures.

A fresh sample of oil was tested in a current of dry air. The temperature was raised gradually to 99° C. and was then decreased to 34° C. The coefficient of friction increased at the higher temperatures but decreased again only slightly when the temperature was again lowered (Figure 2).

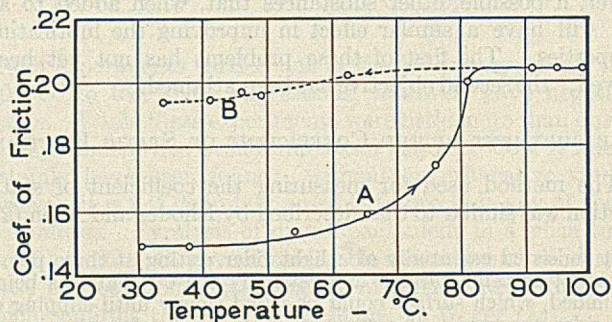


FIGURE 2. EFFECT OF HEATING AND SUBSEQUENT COOLING, IN AIR, ON COEFFICIENT OF STATIC FRICTION

A. Results obtained during heating  
B. Results obtained during cooling

These experiments indicate that the decrease in lubricating power that occurs at the higher temperatures is caused by the oxidation of some constituent of the oil. They do not indicate whether the decrease is due to the destruction of the material that is primarily responsible for the lubricating power or to the formation of some substance that has a marked effect in increasing the frictional coefficient.

#### EFFECTS OF PRELIMINARY OXIDATION AND OF TREATMENT WITH ALKALI AND ACID

If the decrease in the coefficient of static friction that occurs when the oil is heated in air is due simply to oxidation, it should be more pronounced when the oil has been subjected to a preliminary oxidation—for example, to exposure to oxygen under ultraviolet light. A sample of the original oil through which oxygen was being passed was exposed for 2 hours, in a thin flat quartz vessel, to the light from a mercury lamp (Hanovia). The coefficients of friction of the resulting oil at various temperatures are shown in Figure 3. At comparatively low temperatures the lubricating power of the treated oil was not much inferior to that of the original material; at higher temperatures the coefficient of static friction increased very rapidly. These results indicate that the decrease in lubricating power that takes place when



the oil is heated in air is not due directly to the primary products of the oxidation but is to be attributed to the presence of substances formed by the polymerization or other secondary reactions of these primary products.

A portion of fresh oil was washed with a concentrated solution of sodium hydroxide, then with dilute sulfuric acid, and finally with water. The final clear neutral oil was dried in a vacuum. The coefficients of friction of the washed

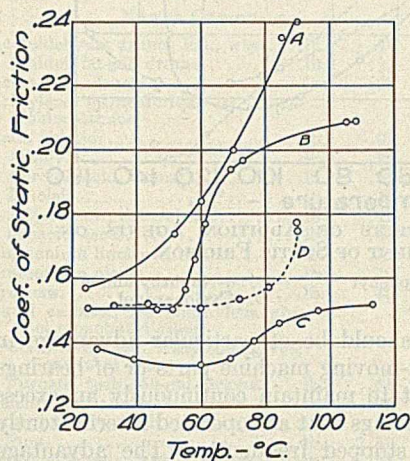


FIGURE 3. EFFECT OF OXIDATION UNDER ULTRAVIOLET LIGHT AND OF TREATMENT OF ALKALI

- A. Original oil treated with oxygen under ultraviolet light
- B. Original oil washed with alkali and subsequently treated with air under ultraviolet light
- C. Original oil washed with alkali and acid
- D. Original oil untreated

A portion of the original oil through which oxygen was being blown was exposed to the ultraviolet light for 4 hours and was then shaken with a 30 per cent solution of sodium hydroxide, washed, neutralized, and dried. The resulting oil showed a coefficient of friction of 0.177 at 76° C. and 0.169 at 94° C. This experiment indicates that the product that is formed when the oil is oxidized in the presence of ultraviolet light and that is assumed to be responsible for the reduction in lubricating power is largely removed when the treated oil is extracted with alkali.

#### EFFECTS OF ADDITION AGENTS ON THE LUBRICATING PROPERTIES

The effects of small amounts of various addition agents upon the coefficient of static friction of the lubricating oil and upon the variation of the coefficient with temperature were measured:

SUBSTANCE	CONCN. %	SUBSTANCE	CONCN. %
<i>p</i> -Cresol	0.08	<i>p</i> -Hydroxydiphenyl	Satd.
$\alpha$ -Naphthol	0.05	<i>m</i> -Dimethylaminophenol	Satd.
$\beta$ -Naphthol	0.05	<i>p</i> -Aminophenol	Satd.
$\beta$ -Naphthol	0.01	1,5-Dihydroxynaphthalene	Satd.
$\beta$ -Naphthol	0.001	Menthol	0.05
Thymol	0.05	$\alpha$ -Naphthylamine	0.05
Cyclohexanol	0.05		

Those substances for which no exact value of the concentration is stated were not soluble to the extent of 1 part in 200 parts of the oil. With these compounds, saturated solutions were used.

The results obtained with oil containing these substances are shown by Figures 4, 5, and 6. Of the various addition agents tested,  $\alpha$ -naphthol has the least effect. *p*-Hydroxydiphenyl, *m*-dimethylaminophenol, and *p*-aminophenol have relatively little influence on the frictional coefficient. With each of these substances an increase in temperature causes

first a decrease and then an increase in the frictional coefficient. The final rise in the coefficient begins only at temperatures much higher than that at which the rapid loss of lubricating power of untreated oil occurs. Cyclohexanol,  $\beta$ -naphthol, *p*-cresol, and  $\alpha$ -naphthylamine show the most marked effects on the lubricating characteristics. With each of these addition agents the coefficient diminishes rapidly as the temperature rises until it becomes approximately one-half as great as at room temperature. At still higher temperatures the coefficient again rises rapidly, but this final increase does not occur until relatively high temperatures are reached. Menthol, thymol, and 1,5-dihydroxynaphthalene have a similar but less pronounced influence on the lubricating power.

The effect of the variation of concentration of an active addition agent is depicted in Figure 4 where are plotted the results obtained with oils containing 0.001, 0.01, and 0.05 per cent, respectively, of  $\beta$ -naphthol. Even in extremely low concentrations this substance has an appreciable influence in improving the lubricating power at moderate temperatures and in retarding the rise in the frictional coefficient at higher temperatures. With increasing concentrations, these effects become more and more marked.

In general, the addition agents most suitable for commercial use in improving lubricating oil appear to be  $\beta$ -naphthol and cyclohexanol. Both of these substances reduce considerably the frictional coefficient at ordinary temperatures as well as at elevated temperatures; both are relatively

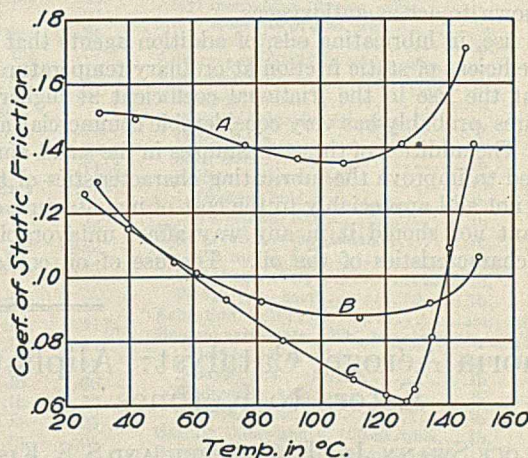


FIGURE 4. EFFECT OF  $\beta$ -NAPHTHOL

- A.  $\beta$ -Naphthol concentration = 0.001 per cent
- B.  $\beta$ -Naphthol concentration = 0.01 per cent
- C.  $\beta$ -Naphthol concentration = 0.05 per cent

stable and nonvolatile; neither should have any corrosive action on the metal of the bearings. Both of these materials have been used by the writers as addition agents in automobile oils with satisfactory results. Oil containing cyclohexanol has been used in the lubrication of a ruling engine in which the bearings operate at heavy load and at very low speed; the use of this treated oil eliminates the chattering and sticking that occurs when a similar oil without addition agent is employed.

The exact cause of the beneficial effects of these addition agents is not obvious. Those substances that decrease the static coefficient at low and moderate temperatures appear to owe at least a part of their effect to the absorption of the added material on the surface of the bearing, with the formation of a film of high lubricating power. This assumption is consistent with the fact that these substances are polar compounds that should be adsorbed rather strongly on metal. Minor differences in structure, however, may greatly influence either the extent of adsorption or the lubricating



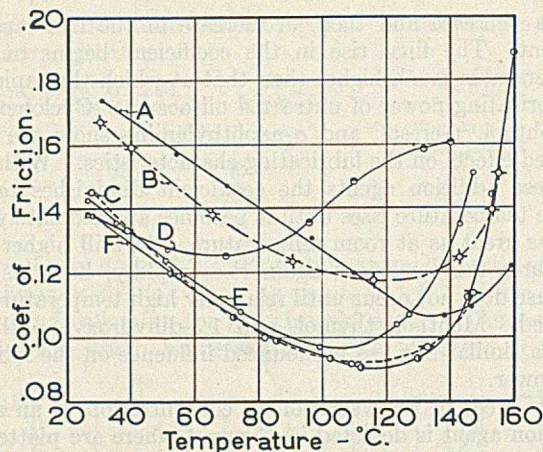


FIGURE 5. EFFECT OF ADDITION AGENTS ON COEFFICIENT OF STATIC FRICTION

A. Menthol  
B. *m*-Dimethylaminophenol  
C. *p*-Aminophenol  
D.  $\alpha$ -Naphthol  
E. Thymol  
F. 1,5-Dihydroxynaphthalene

properties of the adsorbed film, or both. For instance,  $\alpha$ -naphthol has very little beneficial effect while  $\beta$ -naphthol very greatly increases the lubricating power both at room temperature and at elevated temperatures. The inhibition of the decrease in "oiliness" on heating may be due to the action of the addition agents as negative catalysts in the oxidation of the oil; this hypothesis is supported by the fact that most of the substances that have beneficial effects are known to act as antioxidants.

The use, in lubricating oils, of addition agents that lower the coefficient of static friction at ordinary temperatures and prevent the rise in the frictional coefficient at higher temperatures probably has very considerable commercial advantage. The addition of these substances in the small amounts required to improve the lubricating characteristics of the oil would not add appreciably to the cost of manufacture of the lubricant nor should it in any way affect unfavorably the other characteristics of the oil. The use of oil containing

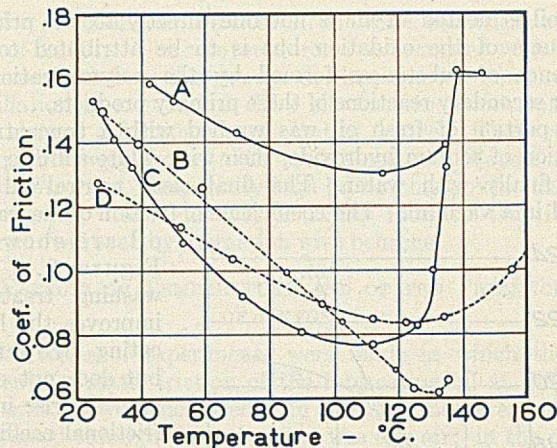


FIGURE 6. EFFECTS OF ADDITION AGENTS ON COEFFICIENT OF STATIC FRICTION

A. *p*-Hydroxydiphenyl  
B. *p*-Cresol  
C.  $\alpha$ -Naphthylamine  
D. Cyclohexanol

such addition agents should be of particular advantage in the lubrication of slow-moving machine parts or of bearings on which it is difficult to maintain continuously an excess of oil, as well as on bearings that are operated intermittently and are started and stopped frequently. The advantage would, perhaps, be less evident when the lubricant is used on bearings that are operated at high speed and with flood lubrication, although even under such conditions the addition to the oil of a substance that increases its lubricating power should be of some benefit.

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- (2) Rhodes and Allen, *IND. ENG. CHEM.*, 25, 1275 (1933).
- (3) Wilson and Barnard, *Ibid.*, 14, 683 (1922).

RECEIVED April 9, 1934.

## Thoria Aëroge! Catalyst: Aliphatic Esters to Ketones

SHERLOCK SWANN, JR., E. G. APPEL, AND S. S. KISTLER  
University of Illinois, Urbana, Ill.

IN THE first part of this communication<sup>1</sup> it was shown that ketones could be prepared in excellent yield by distilling the corresponding acid over thoria aëroge! at atmospheric or under reduced pressures. The size of the ketone which can be conveniently prepared is limited by the volatility of the acid and ketone. In order to extend the scope of the method to higher ketones, the conversion of ethyl esters was studied. The esters have a much lower boiling point than their corresponding acids and, therefore, may often be employed when the use of the free acid is not feasible.

Ethyl laurate was chosen as a typical example. The results of its conversion to laurone are shown in the following table:

RUN No.	ESTER <sup>a</sup> Grams	RATE OVER CATALYST Grams/min.	TEMP. OF CATALYST ° C.	ESTER RECOVERED Grams	KETONE Grams	CONVERSION %
1	57	3-4	300	20.0	27	64.8
2	57	3-4	360	4.0	39	92.5
3	57	4-6	360	10.0	34.8	82.5
4	57	8	360	17.0	29.6	70.0

<sup>a</sup> The ethyl laurate was distilled over the catalyst at 150° to 160° C. at 25 to 30 mm. pressure.

<sup>1</sup> *IND. ENG. CHEM.*, 26, 388-91 (1934).

The ketone was purified by distillation under reduced pressure and by two recrystallizations from ethanol. The melting point was 68° to 69° C.

The best yields of laurone reported in the literature are 10 to 30 per cent from lauric acid over thoria at 400° C. (3), from lauric acid with phosphorous pentoxide (2), and 91 per cent by heating small quantities of the acid in an iron dish for about 4 hours. The preparation of laurone described in this paper gives better yields than the first two methods and produces laurone at a much higher rate than the third.

Besides laurone, undecylenone,  $\text{CH}_2 = \text{CH}(\text{CH}_2)_9\text{CO}(\text{CH}_2)_9\text{CH} = \text{CH}_2$  (melting point, 43° C.) was prepared from ethyl undecylenate in 86 per cent yield. This is a new ketone. The microanalysis in per cent is as follows: calculated for  $\text{C}_{21}\text{H}_{38}\text{O}$ : C = 82.30, H = 12.42; found: C = 82.39, H = 12.47.

This method may be used successfully to prepare in large quantities aliphatic ketones of high molecular weight which were formerly obtained only with difficulty.

The microanalysis was carried out by K. Eder of the Chemistry Department of the University of Illinois.

#### LITERATURE CITED

- (1) Gruen, A., Ulbrich, E., and Krczil, F., *Z. angew. Chem.*, 39, 421 (1926).
- (2) Kipping, F. S., *J. Chem. Soc.*, 57, 981 (1890).
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RECEIVED June 9, 1934.



# MARKET REPORT—AUGUST, 1934

THESE PRICES UNLESS OTHERWISE SPECIFIED ARE THOSE PREVAILING IN THE NEW YORK MARKET, AUGUST 15, FOR COMMERCIAL GRADES IN CARLOAD QUANTITIES

## NEWER CHEMICALS

Acetaldehyde, drums, 1c-1, wks....lb.	.16	Acetic anhydride, 92-95%, obys....lb.	.21	Aluminum chloride, anhyd., commercial, wks., drums extra, c/l....lb.	.04
Acetaldol, 50-gal. drums.....lb.	.27	Acetone, drums, wks., c/l.....lb.	.11	Aluminum stearate, 100-lb. bbl....lb.	.17
Acetamide, drums.....lb.	.38	Acetphenetidin, bbls.....lb.	1.30	Aluminum sulfate, comm'l, bags, wks.....100 lbs.	1.35
Acetylene tetrachloride, see Tetrachloroethane		Acid, acetic, 28%, c/l, bbls...100 lbs.	2.68	Iron-free, bags, wks.....100 lbs.	1.90
Acid, abietic.....lb.	.07	56%, c/l, bbls.....100 lbs.	5.50	Aminoazobenzene, 100-lb. kegs....lb.	1.15
Adipic.....lb.	.72	Glacial, c/l, bbls.....100 lbs.	9.13	Ammonia, anhydrous, cyl., wks....lb.	.15½
Furoic, tech., drums.....lb.	.35	Glacial, U. S. P., c/l, carboys.....100 lbs.	9.63	50,000-lb. tanks, wks.....lb.	.04½
Linoleic.....lb.	.16	Acetylsalicylic, bbls.....lb.	.70	Ammonia, aqua, 26°, tanks, wks., contained NH <sub>3</sub> .....lb.	.05½
Naphthenic, drums.....lb.	.12	Anthranilic, 99-100%, drums.....lb.	.85	Ammonium acetate, kegs.....lb.	.33
Sebacic, tech.....lb.	.58	Benzoic, tech., bbls.....lb.	.40	Bifluoride, bbls.....lb.	.15½
Ammonium linoleate, drums.....lb.	.12	Boric, bbls.....lb.	.04	Bromide, bbls.....lb.	.39
Ammonium oleate.....lb.	.10	Butyric, 100% basis, obys.....lb.	.80	Carbonate, tech., casks.....lb.	.08
Aroclors.....lb.	.40	Chloroacetic, mono-, bbls., wks....lb.	.18	Chloride, gray, bbls.....100 lbs.	5.50
Butyl carbitol, see Diethylene glycol monobutyl ether		Di-, obys.....lb.	1.00	Lump, casks.....lb.	.10½
Cellosolve, see Ethylene glycol monobutyl ether		Tri-, bbls.....lb.	2.50	Iodide, 25-lb. jars.....lb.	4.30
Furoate, tech., 50-gal. drums....lb.	.65	Chlorosulfonic, drums, wks.....lb.	.04½	Nitrate, tech., cryst., bbls.....lb.	.08½
Calcium furoate, tech., drums....lb.	.25	Chromic, 99%, drums.....lb.	.15½	Oxalate, kegs.....lb.	.24
Capryl alcohol, tech.....lb.	.85	Cinnamic, bottles.....lb.	3.25	Persulfate, cases.....lb.	.20
Pure.....lb.	2.50	Citric, U. S. P., cryst., bbls.....lb.	.28	Phosphate, dibasic, tech., bbls....lb.	.08½
Crotonaldehyde, 50-gal. drums, c/l..lb.	.26	Cresylic, pale, drums.....gal.	.60	Sulfate, bulk, wks.....ton	24.00
Dichloroethyl ether, 50-gal. drums, c/l.....lb.	.21	Formic, 90%, obys., N. Y.....lb.	.11	Amylene, tanks, wks.....lb.	.09
Diethylene glycol, drums.....lb.	.14	Gallic, U. S. P., bbls.....lb.	.77	Amyl acetate, tech., from pentane, tanks, delivered.....lb.	.135
Monobutyl ether, drums.....lb.	.26	Glycerophosphoric, 25%, 1-lb. bot.....lb.	1.40	Amyl chlorides, mixed, tanks, wks. lb.	.10½
Monoethyl ether, drums.....lb.	.15	H, bbls., wks.....lb.	.65	Amyl chloride, normal, drums, wks. lb.	.56
Diethylene oxide, 50-gal. drums....lb.	.26	Hydriodic, 10%, U. S. P., 5-lb. bot.....lb.	.67	Amyl lactate, drums, wks.....lb.	.50
Diglycol oleate, drums.....lb.	.18	Hydrobromic, 48%, obys., wks. lb.	.45	Amyl mercaptan, drums, wks.....lb.	1.10
Dimethylamine, pure 25 & 40% sol. —100% basis, drums.....lb.	1.20	Hydrochloric, 20°, tanks, wks. 100 lbs.	1.35	Amyl stearate, drums, wks.....lb.	.31
Dioxan, see Diethylene oxide		Hydrofluoric, 30%, bbls., wks....lb.	.07	Aniline oil, drums.....lb.	.16½
Diphenyl.....lb.	.15	60%, bbls., wks.....lb.	.15	Anthracene, 80-85%, casks, wks....lb.	.75
Ethyl acetoacetate, 110-gal. drums. lb.	.37	Hydrofluosilic, 35%, bbls., wks....lb.	.11	Anthraquinone, subl., bbls.....lb.	.45
Carbonate, 90%, 50-gal. drums. gal.	1.85	Hypophosphorus, 30%, U. S. P., 5-gal. demis.....lb.	.75	Antimony, metal.....lb.	.08½
Chlorocarbonate, carboys.....lb.	.30	Lactic, 22%, dark, bbls.....lb.	.04	Antimony chloride, drums.....lb.	.13
Ether, absolute, 50-gal. drums....lb.	.50	48%, light, bbls., wks.....lb.	.11½	Oxide, bbls.....lb.	.09½
Furoate, 1-lb. tins.....lb.	5.00	Mixed, tanks, wks..... N unit	.07	Salt, dom., bbls.....lb.	.22
Ethylene chlorhydrin, 40%, 10-gal. obys.....lb.	.75	S unit	.08	Sulfide, crimson, bbls.....lb.	.25
Dichloride, 50-gal. drums.....lb.	.05½	Molybdic, 85%, kegs.....lb.	1.25	Golden, bbls.....lb.	.16
Glycol, 50-gal. drums.....lb.	.25	Naphthionic, tech., bbls.....lb.	nom.	Vermilion, bbls.....lb.	.38
Monobutyl ether, drums, wks....lb.	.20	Nitric, c. p., obys.....lb.	.11	Argols, red powder, bbls.....lb.	.07
Monoethyl ether, drums, wks....lb.	.15	Nitric, 36°, c/l, obys., wks. 100 lbs.	5.00	Arsenic, metal, kegs.....lb.	.44
Monoethyl ether acetate, drums, wks.....lb.	.16½	Oxalic, bbls., wks.....lb.	.11½	Red, kegs, cases.....lb.	.15
Monomethyl ether, drums.....lb.	.21	Phosphoric, 50%, U. S. P.....lb.	.14	White, c/l, kegs.....lb.	.04½
Oxide, cyl.....lb.	.75	Picramic, bbls.....lb.	.65	Asbestine, bulk, c/l.....ton	15.00
Furfuramide (tech.), 100-lb. drums. lb.	.30	Picric, bbls., c/l.....lb.	.30	Barium carbonate, bbls., bags, wks. ton	45.00
Furfuryl acetate, 1-lb. tins.....lb.	5.00	Pyrogallic.....lb.	1.60	Chloride, bbls., wks.....ton	74.00
Alcohol, tech., 500-lb. drums....lb.	.35	Salicylic, tech., bbls.....lb.	.33	Dioxide, drs., wks.....lb.	.12
Glyceryl phthalate.....lb.	.28	Stearic, d. p., bbls., c/l.....lb.	.09	Hydroxide, bbls.....lb.	.05
Glycol phthalate, drums.....lb.	.28	Sulfanilic, 250-lb. bbls.....lb.	.18	Nitrate, casks.....lb.	.08½
Glycol stearate.....lb.	.20	Sulfuric, 66°, c/l, obys., wks. 100 lbs.	1.60	Barium thiocyanate, 400-lb. bbls....lb.	.27
Isopropyl ether, drums.....lb.	.07	66°, tanks, wks.....ton	15.00	Barytes, floated, 350-lb. bbls., wks. ton	23.00
Magnesium peroxide, 100-lb. cs....lb.	1.15	60°, tanks, wks.....ton	10.50	Benzaldehyde, tech., drums.....lb.	.60
Methyl acetate, 82%, drums.....lb.	.12	Oleum, 20%, tanks, wks.....ton	18.50	F. F. C., obys.....lb.	1.40
99%, tanks.....lb.	.15	40%, tanks, wks.....ton	42.00	U. S. P., obys.....lb.	1.15
Cellosolve, see Ethylene glycol monomethyl ether		Sulfurous, U. S. P., 6%, obys....lb.	.05	Benzidine base, bbls.....lb.	.65
Methyl hexyl ketone, pure.....lb.	1.20	Tannic, tech., bbls.....lb.	.23	Benzol, tanks, wks.....gal.	.19
Paraldehyde, 110-55 gal. drums, c/l..lb.	.16	Tartaric, U. S. P., cryst., bbls....lb.	.26½	Benzoyl chloride, drums.....lb.	.40
Phloroglucinol, tech., drums.....lb.	15.00	Tungstic, kegs.....lb.	1.35	Benzyl acetate, F. F. C., bottles....lb.	.75
C. P.....lb.	20.00	Valeric, c. p., 10-lb. bot.....lb.	2.50	Alcohol, drums.....gal.	.85
Phosphorus oxychloride, 175 cyl....lb.	.20	Alcohol, U. S. P., 190 proof, bbls..gal.	4.485	Chloride, tech., drums.....lb.	.30
Potassium abietate.....lb.	.06	Amyl, from pentane, tanks.....lb.	.143	Beta-naphthol, bbls.....lb.	.24
Pyrocatechin, c. p., drums.....lb.	2.75	Amyl, tertiary, tech., tanks, del. lb.	.052	Beta-naphthylamine, bbls.....lb.	.58
Sodium abietate.....lb.	.06	Amyl, imp. drums.....gal.	1.75	Bismuth, metal, cases.....lb.	1.20
Sodium alginate.....lb.	.64	Butyl, drums, c/l., wks.....lb.	.11½	Bismuth, nitrate, 25-lb. jars.....lb.	1.20
Sodium naphthenate, drums.....lb.	.13	Denatured, No. 5, comp. denat., c/l, drums.....gal.	.34	Oxychloride, boxes.....lb.	3.05
Strontium peroxide, 100-lb. drums...lb.	1.25	Isoamyl, drums.....gal.	4.00	Subnitrate, U. S. P., 25-lb. jars...lb.	1.55
Sulfuryl chloride, 600-lb. drums, crude.....lb.	.15	Isobutyl, ref., drums.....gal.	.75	Blanc fixe, dry, bbls.....ton	65.00
Distilled.....lb.	.40	Isopropyl, ref., drums.....gal.	.50	Bleaching powder, drums, wks. 100 lbs.	1.90
Tetrachloroethane, 50-gal. drums....lb.	.08½	Propyl, ref., drums.....gal.	.75	Bone ash, kegs.....lb.	.06
Trichloroethylene, 50-gal. drums....lb.	.09½	Wood, see Methanol		Bone black, bbls.....lb.	.08½
Triethanolamine, 50-gal. drums....lb.	.35	Aldol, 95%, drums, c/l.....lb.	.21	Borax, bags.....lb.	.018
Trihydroxyethylamine linoleate....lb.	.40	Alpha-naphthol, bbls.....lb.	.65	Bordeaux mixture, bbls.....lb.	.10½
Trihydroxyethylamine stearate....lb.	.35	Alpha-naphthylamine, bbls.....lb.	.33	Bromine, bot.....lb.	.36
Vinyl chloride, 16-lb. cyl.....lb.	1.00	Alum, ammonia, lump, bbls., wks. 100 lbs.	3.00	Bromobenzene, drums.....lb.	.50
Zinc perborate, 100-lb. drums....lb.	1.25	Chrome, casks, wks.....100 lbs.	7.00	Bromoform, jars.....lb.	1.80
Peroxide, 100-lb. drums.....lb.	1.25	Potash, lump, bbls., wks....100 lbs.	3.00	Butyl acetate, drums, c/l.....lb.	.12
		Soda, bbls., wks.....100 lbs.	4.00	Butyl carbinol, nor., drums, wks....lb.	.60
		Aluminum, metal, N. Y.....100 lbs.	22.90	Butyl carbinol, sec., wks.....lb.	.60
				Butyl carbinol, iso, tanks, wks....lb.	.328
				Cadmium bromide, 50-lb. jars....lb.	1.25
				Cadmium, metal, cases.....lb.	.55
				Cadmium sulfide, boxes.....lb.	.60

## CHEMICALS PREVIOUSLY QUOTED

Acetanilide, U. S. P., powd., bbls....lb. 26



Caffeine, U. S. P., 5-lb. cans..... lb.	1.85	Hydrogen peroxide, 25 vol., bbls..... lb.	.05½	Phthalic anhydride, bbls..... lb.	.14½
Calcium acetate, bags..... 100 lbs.	2.50	Hydroquinone, kegs..... lb.	1.20	Platinum, metal..... oz.	36.00
Arsenate, bbls..... lb.	.05	Indigo, 20%, paste, bbls..... lb.	12	Potash, caustic, drums..... lb.	.07½
Carbide, drums..... lb.	.05½	Iodine, crude, 200-lb. kgs..... kilo	15s. 1d.	Potassium acetate, kegs..... lb.	.27
Chloride, drums, wks., flake..... ton	19.50	Iodine, resubl., jars..... lb.	1.90	Bicarbonate, casks..... lb.	.07½
Cyanide, 100-lb. drums..... lb.	.30	Iron acetate, liq., 17°, bbls., c/l..... lb.	.03	Bichromate, casks..... lb.	.08½
Nitrate, bags, 15% N..... ton	25.50	Kieselguhr, bags..... ton	50.00	Binoxalate, bbls..... lb.	.14
Phosphate, monobas., bbls..... lb.	.07½	Lead, metal, N. Y..... 100 lbs.	3.75	Bromide..... lb.	.35
Tribas., bbls..... lb.	.11	Lead acetate, bbls., white..... lb.	.11	Carbonate, 80-85%, calc., casks..... lb.	.07
Calcium carbonate, tech., bags, ..... 100 lbs.	1.00	Arsenate, bbls..... lb.	.08	Chlorate, kegs..... lb.	.09
U. S. P., precip., 175-lb. bbl..... lb.	.06½	Oxide, litharge, bbls., 20-ton lots..... lb.	.05½	Chloride, crystals, bbls..... lb.	.04½
Camphor, Jap., slabs..... lb.	.51	Peroxide, drums..... lb.	.20	Cyanide, cases..... lb.	.55
Carbazole, bbls..... lb.	.75	Red, bbls., 20-ton lots..... lb.	.0655	Meta-bisulfite, bbls..... lb.	.10½
Carbon, activated, drums..... lb.	.08	Sulfate, bbls..... lb.	.06	Muriate, fert., bulk, per K <sub>2</sub> O unit... .	.40
Carbon bisulfide, drums..... lb.	.051	White, basic carb., bbls..... lb.	.06½	Permanganate, drums..... lb.	.18½
Carbon black..... lb.	.04½	Lime, hydrated, bbls..... 100 lbs.	.85	Prussiate, red, casks..... lb.	.39
Carbon dioxide, liq. cyl..... lb.	.06	Lime, live, chemical, bbls., wks., ..... 280 lbs.	1.70	Yellow, casks..... lb.	.18
Carbon tetrachloride, drums..... lb.	.05½	Limestone, ground, bags, wks..... ton	4.50	Titanium oxalate, bbls..... lb.	.32
Casein, stand. gr., bbls..... lb.	.12½	Lithopone, bbls..... lb.	.04½	Pyridine, drums..... gal.	1.25
Cellulose acetate, bbls..... lb.	.80	Magnesium, calcined, 500-lb. bbls., wks..... ton	60.00	Resorcinol, tech., kegs..... lb.	.75
Cerium oxalate, kegs..... lb.	.25	Magnesium, metal, wks..... lb.	.30	Rochelle salt, bbls., U. S. P..... lb.	.13½
Charcoal, willow, powd., bbls..... lb.	.08	Magnesium carbonate, bags..... lb.	.06½	R salt, bbls..... lb.	.44
China clay, bulk..... ton	8.00	Chloride, drums..... ton	36.00	Saccharin, cans..... lb.	1.70
Chloral hydrate, drums..... lb.	.70	Fluosiicate, cryst., bbls..... lb.	.10	Salt cake, bulk..... ton	13.00
Chlorine, liq. c/l., cyl.*..... lb.	.055	Oxide, U. S. P., light, bbls..... lb.	.42	Saltpeter, gran., bbls..... lb.	.06
Chlorine, tanks..... 100 lbs.	1.85	Manganese chloride, casks..... lb.	.07½	Silica, ref., bags..... ton	22.00
Chlorobenzene, mono-, drums..... lb.	.06	Dioxide, 80%, bbls..... ton	80.00	Silver nitrate, 16-oz. bot..... oz.	.35½
Chloroform, tech., drums..... lb.	.20	Sulfate, casks..... lb.	.09	Soda ash, 58%, light, bags, contract, wks..... 100 lbs.	1.23
Chromium acetate, 20° soln., bbls..... lb.	.05	Mercury bichloride, cryst., 100 lbs. lb.	.88	Soda, caustic, 76%, solid, drums, contract, wks..... 100 lbs.	2.60
Coal tar, bbls., wks..... bbl.	8.50	Mercury flasks, 76 lbs..... flask	74.50	Sodium acetate, bbls..... lb.	.05
Cobalt, metal, kegs..... lb.	2.50	Meta-nitroaniline, bbls..... lb.	.67	Benzoate, bbls..... lb.	.45
Cobalt oxide, bbls..... lb.	1.25	Meta-phenylenediamine, bbls..... lb.	.82	Bicarbonate, bbls..... 100 lbs.	1.85
Cod liver oil, bbls..... bbl.	27.00	Meta-tolylenediamine, bbls..... lb.	.67	Bichromate, casks..... lb.	.06½
Coppers, c/l., bulk..... ton	14.50	Methanol, pure, synthetic, drums, delivered, c/l..... gal.	.37½	Bisulfite, bbls..... lb.	.03
Copper, metal, elec..... 100 lbs.	9.00	Tanks, delivered..... gal.	.35½	Bromide, bbls., U. S. P..... lb.	.35
Copper carbonate, bbls., 52/54%..... lb.	.15½	Methyl acetone, drums..... gal.	.55½	Chlorate, kegs..... lb.	.05
Chloride, bbls..... lb.	.17	Methyl chloride, cylinders..... lb.	.45	Chloride, bags..... ton	12.00
Cyanide, drums..... lb.	.37	Methyl propyl carbinol, drums, wks. lb.	.60	Cyanide, cases..... lb.	.15½
Oxide, red, bbls..... lb.	.15	Methyl salicylate, cases..... lb.	.42	Fluoride, bbls..... lb.	.07½
Sulfate, c/l., bbls..... 100 lbs.	3.85	Michler's ketone, bbls..... lb.	2.50	Metallic, drums, 12½-lb. bricks... lb.	.19
Cotton, soluble, bbls..... lb.	.40	Monoamylamine, drums, wks..... lb.	1.00	Metasilicate, cryst..... 100 lbs.	3.25
Cream tartar, bbls..... lb.	.18½	Naphthalene, flake, bbls..... lb.	.06	Metasilicate, gran., bbls..... 100 lbs.	2.65
Cyanamide, bulk, N. Y..... ..... Ammonia unit	1.07½	Nickel, metal..... lb.	.35	Naphthionate, bbls..... lb.	.52
Diaminophenol, kegs..... lb.	3.80	Nickel salt, single, bbls..... lb.	.11½	Nitrate, crude, 200-lb. bags, N. Y..... ..... 100 lbs.	1.315
Diamylamine, drums, wks..... lb.	1.00	Double, bbls..... lb.	.11½	Nitrite, bbls..... lb.	.07½
Diamylene, tanks, wks..... lb.	.08½	Niter cake, bulk..... ton	11.50	Perborate, bbls..... lb.	.17
Diamyl sulfide, drums, wks..... lb.	1.10	Nitrobenzene, drums..... lb.	.09	Peroxide, cases..... lb.	.20
Dianisidine, bbls..... lb.	2.35	Oil, castor, No. 1..... lb.	10½	Phosphate, disodium, bags. 100 lbs.	1.90
Dibutylphthalate, drums, wks..... lb.	.20½	China wood, bbls..... lb.	.09	Phosphate, trisodium, bbls. 100 lbs.	2.70
Dichloropentanes, tanks, wks..... lb.	.02½	Coconut, tanks..... lb.	.02½	Pieramate, kegs..... lb.	.67
Diethylaniline, drums..... lb.	.52	Cod, N. F., bbls..... gal.	.40	Prussiate, bbls..... lb.	.11½
Diethylene glycol, drums..... lb.	.14	Corn, crude, tanks, mills..... lb.	.05½	Silicate, drums, tanks, 40°... 100 lbs.	.80
Diethyl carbinol, drums, wks..... lb.	.60	Cottonseed, crude, tanks..... lb.	.05	Silicofluoride, bbls..... lb.	.05
Diethyl phthalate, drums..... lb.	.23	Linseed, bbls..... lb.	.095	Stannate, drums..... lb.	.34
Diethyl sulfate, tech., drums..... lb.	.20	Menhaden, crude, tanks..... gal.	.18	Sulfate, anhyd., bbls..... 100 lbs.	2.20
Dimethylaniline, drums..... lb.	.29	Neat's-foot, pure, bbls..... lb.	.12	Sulfide, cryst., bbls..... lb.	.02½
Dimethyl ethyl carbinol, drums, wks. lb.	.60	Oleo, No. 1, bbls..... lb.	.06½	Solid, 60%..... lb.	.03½
Dimethylsulfate, drums..... lb.	.45	Olive oil, denat., bbls..... gal.	.84	Sulfocyanide, bbls..... lb.	.30
Dinitrobenzene, tech., drums..... lb.	.17	Foods, bbls..... lb.	.07½	Thiosulfate, reg., cryst., bbls..... lb.	.02½
Dinitrochlorobenzene, bbls..... lb.	.14½	Palm, Lagos, casks..... lb.	.03½	Tungstate, kegs..... lb.	.83
Dinitronaphthalene, bbls..... lb.	.34	Peanut, crude, tanks..... lb.	.06	Strontium carbonate, tech., bbls..... lb.	.07½
Dinitrophenol, bbls..... lb.	.23	Perilla, bbls..... lb.	.09½	Nitrate, bbls..... lb.	.09½
Diphenylamine, bbls..... lb.	.31	Rapeseed, bbls..... gal.	.37	Sulfur, bulk, mines, wks..... ton	18.00
Diphenylguanidine, bbls..... lb.	.36	Red, bbls..... lb.	.06½	Sulfur chloride, red, drums..... lb.	.05
Epsom salt, tech., bbls., c/l., N. Y..... ..... 100 lbs.	1.70	Soy bean, crude, tanks..... lb.	.065	Yellow, drums..... lb.	.03½
Ether, nitrous, bot..... lb.	.75	Sperm, 38°, bbls..... lb.	.108	Sulfur dioxide, commercial, cyl..... lb.	.07
Ether, conc., drums..... lb.	.09	Whale, bbls., natural, winter..... lb.	.072	Sulfuryl chloride, drums..... lb.	.10
Ethyl acetate, tanks, c/l..... lb.	.07½	Ortho-aminophenol, kegs..... lb.	2.15	Thiocarbamid, bbls..... lb.	.25
Bromide, drums..... lb.	.50	Ortho-dichlorobenzene, drums..... lb.	.08	Tin..... lb.	.55
Chloride, drums..... lb.	.22	bbls..... lb.	.28	Tin tetrachloride, anhydrous, drums, ..... lb.	.26
Methyl ketone, drums..... lb.	.30	Ortho-nitrochlorobenzene, drums..... lb.	.85	Oxide, bbls..... lb.	.56
Ethylbenzylamine, 300-lb. drums... lb.	.88	Ortho-nitrophenol, bbls..... lb.	.85	Titanium dioxide, bbls., wks..... lb.	.17½
Ethylene chlorohydrin, anhyd. drums. lb.	.75	Ortho-nitrotoluene, drums..... lb.	.05½	Toluene, tanks..... gal.	3.00
Glycol, c/l., wks..... lb.	.26	Ortho-toluidine, bbls..... lb.	.14	Triamylamine, drums, wks..... lb.	1.00
Feldspar, bulk..... ton	10.00	Para-aminophenol, kegs..... lb.	.78	Triamyl borate, drums, wks..... lb.	1.40
Ferric chloride, tech., bbls..... lb.	.05	Para-dichlorobenzene..... lb.	.16	Tribromophenol, cases..... lb.	1.10
Ferrous chloride, cryst., bbls..... lb.	.06	Para-formaldehyde, cases..... lb.	.38	Triphenylguanidine, drums..... lb.	.58
Ferrous sulfide, bbls..... 100 lbs.	2.50	Paraldehyde, tech., drums..... lb.	.20½	Triphenyl phosphate, bbls..... lb.	.37
Fluorspar, 98%, bags..... ton	31.00	Para-nitraniline, drums..... lb.	.48	Tungsten, powder..... lb.	1.65
Formaldehyde, bbls..... lb.	.06	Para-nitrochlorobenzene, drums... lb.	.25	Urea, pure, cases..... lb.	.15
Formaniline, drums..... lb.	.37½	Para-nitrophenol, bbls..... lb.	.45	Whiting, bags..... ton	7.00
Fuller's earth, bags, c/l., mines... ton	6.50	Para-nitrosodimethylaniline, bbls... lb.	.92	Xylene, 10°, tanks, wks..... gal.	.29
Furfural, drums, tech., contract, works..... lb.	.10	Para-nitrotoluene, bbls..... lb.	.35	Xylidine, drums..... lb.	.36
Glauber's salt, bbls..... 100 lbs.	1.10	Para-phenylenediamine, bbls..... lb.	1.15	Zinc, metal, E. St. Louis..... 100 lbs.	4.30
Glucose, 70°, bags, dry..... 100 lbs.	3.14	Para-tertiary amyl phenol, drums, wks..... lb.	.50	Zinc ammonium chloride, bbls..... lb.	.05
Glycerine, C. P., drums..... lb.	.13½	Para-toluidine, bbls..... lb.	.56	Chloride, granulated, drums..... lb.	.05½
G salt, bbls..... lb.	.42	Paris Green, 250-lb. kegs..... lb.	.23	Oxide, Amer., bbls..... lb.	.06½
Hexamethylenetetramine, tech., drums..... lb.	.37	Phenol, drums..... lb.	.14½	Stearate, bbls..... lb.	.18
..... 100 lbs.	1.10	Phenolphthalein, drums..... lb.	.52	Zinc dust, bbls., c/l..... lb.	.0630
..... 100 lbs.	3.14	Phenylyethyl alcohol, 1-lb. bot..... lb.	3.75		
..... 100 lbs.	3.14	Phosphorus, red, cases..... lb.	.45		
..... 100 lbs.	3.14	Phosphorus trichloride, cyl..... lb.	.18		

† This is the approximate F. O. B. shipping point price. Quotations are now all on a delivered basis and vary with the section.

\* F. O. B. destination.

‡ Less certain discounts depending upon time of purchase and delivery.



When crude is high you can't afford to skim it because you get too little gasoline and it sells at too low a price

When crude is cheap you can't afford to skim it either, because too many other refiners are skimming it, there is too much knocking gasoline and the price is too low—or you can't sell it at all

Be crude oil high or low, Dubbscracking is the way to make gasoline

Universal Oil Products Co  
Chicago, Illinois



Dubbs Cracking Process  
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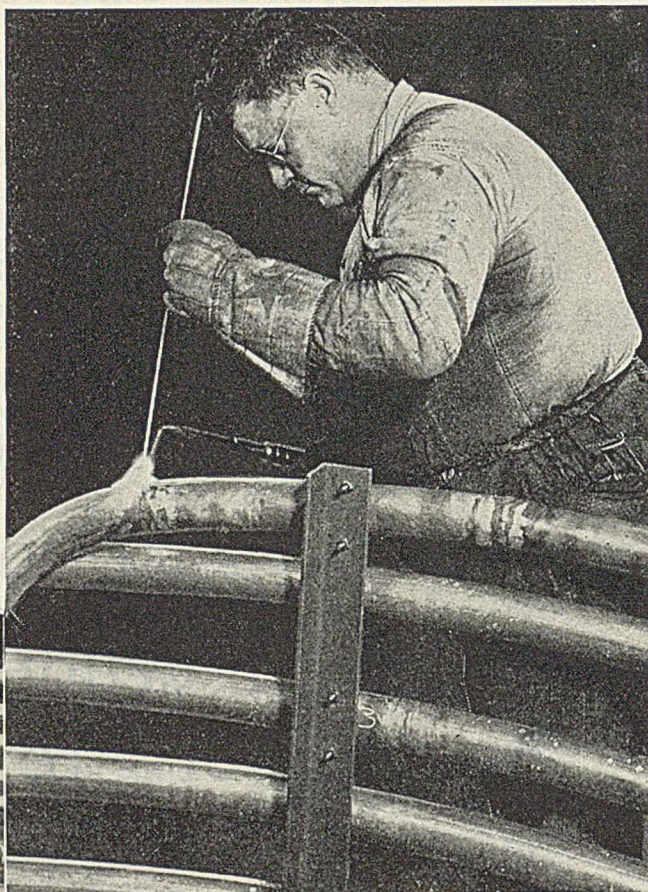
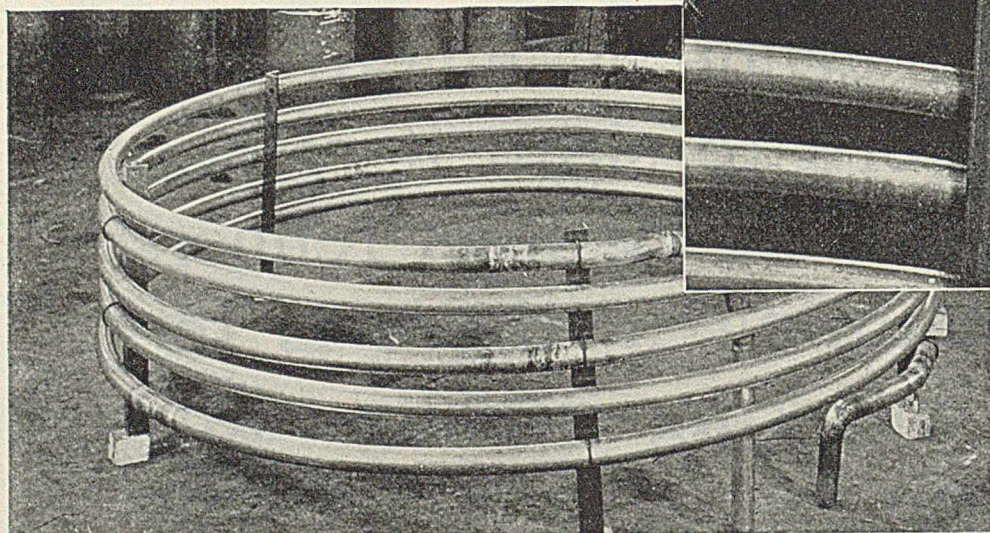
# Sil-Fos brazed

for

## PERMANENCY

plus

## ECONOMY



*This mash tank cooling coil built by National Valve & Manufacturing Co., Pittsburgh, Pa., is 9' in diameter and subjected to approximately 40 lbs. pressure.*

Here is a large mash tank cooling coil where eight lengths of 2½" O. D. copper tubing were brazed with SIL-FOS—the low temperature brazing alloy—into one solid, leak-proof unit. SIL-FOS did the job quickly, economically and permanently.

Free flowing at 1300° F., SIL-FOS joined the thin 16-gauge tubing without over-heating or damaging the metal. It penetrated deeply into the copper, actually alloying with it to give a strength in the joints as high as the metal itself.

SIL-FOS is the MODERN brazing alloy to use for jobs like this. It works fast, saves labor and gas and keeps cleaning expenses down. Close-fitting joints require but little brazing alloy—the cost per joint is low. SIL-FOS joints stay tight permanently under temperature changes, shock and vibration—and resist corrosion.

Try SIL-FOS on your work—wherever non-ferrous metals are to be joined. Order a small quantity and test it thoroughly—it has solved problems for others—it can help you too.

SIL-FOS can be obtained from all distributing stations of the AIR REDUCTION SALES COMPANY, as well as from many prominent supply houses.

WRITE FOR BULLETIN NO. 59-1 AND PRICES

**HANDY AND HARMAN** 82 Fulton St., New York



# LONG LIFE

One of the many reasons why Leading Chemical Manufacturers choose Hackney Containers



Hackney containers for shipment of acids have established enviable records for long life and economy.

The Hackney seamless cold drawn, two-piece acid drum for handling and shipment of sulphuric acid, is one of this group.

Flanges and flange threads are extra heavy. The surface of these containers is smooth

*\* Two-piece Hackney acid drum for shipment of concentrated sulphuric acid, aqua ammonia, and caustics.*

and free from pits, scale or uneven spots.

Top and bottom halves are pressed together from circular sheets of steel. There are no longitudinal or chime seams.

The wide preference for Hackney containers by leading chemical manufacturers is based on economy and long life.

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MILWAUKEE

**CONTAINERS FOR GASES, LIQUIDS AND SOLIDS**



"In its preparation it has not been regarded as sufficient merely to point out the special properties of the argentiferous and arsenical coppers, but as a background for an understanding of these there has been compiled a general account of copper itself in all its phases. The monograph constitutes one of the most authentic and complete, as it is certainly the most up-to-date, of compendiums on the properties and uses of the metals. Nowhere else will such modern knowledge of this ancient metal be found in so few pages."—  
*From the foreword.*

# ARSENICAL and ARGENTIFEROUS COPPER

By J. L. Gregg, Metallurgist, Battelle Memorial Institute

With a Foreword by H. Foster Bain

Director, Copper and Brass Research Association

8 Chapters  
192 Pages  
Illustrated  
\$4.00

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## CHAPTER CONTENTS

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Copper and Its Alloys in Ancient Times—The History and Development of Copper Mining—The Development of Copper Refining—Classification of Copper by Origin and Uses.

### PROPERTIES AND USES OF COPPER

Physical Properties—Electrical Conductivity—Chemical Properties—Uses of Copper.

### ARSENICAL AND ARGENTIFEROUS COPPER

Geology of Lake Copper—Concentration—Smelting and Refining—Casting—Mechanical Working.

### CONSTITUTION OF ARSENICAL AND ARGENTIFEROUS COPPER

The Copper-oxygen System—The Copper-arsenic System—The Copper-silver System—Complex Alloys.

### ELECTRICAL AND THERMAL PROPERTIES OF ARSENICAL AND ARGENTIFEROUS COPPER

The Effect of Oxygen on Electrical Conductivity—The Effect of Arsenic on Electrical Conductivity—Electrical Conductivity of Argentiferous Copper—Influence of Magnetic Field on Electrical Conductivity—Thermal Electromotive Force—Thermal Conductivity—Thermal Expansion.

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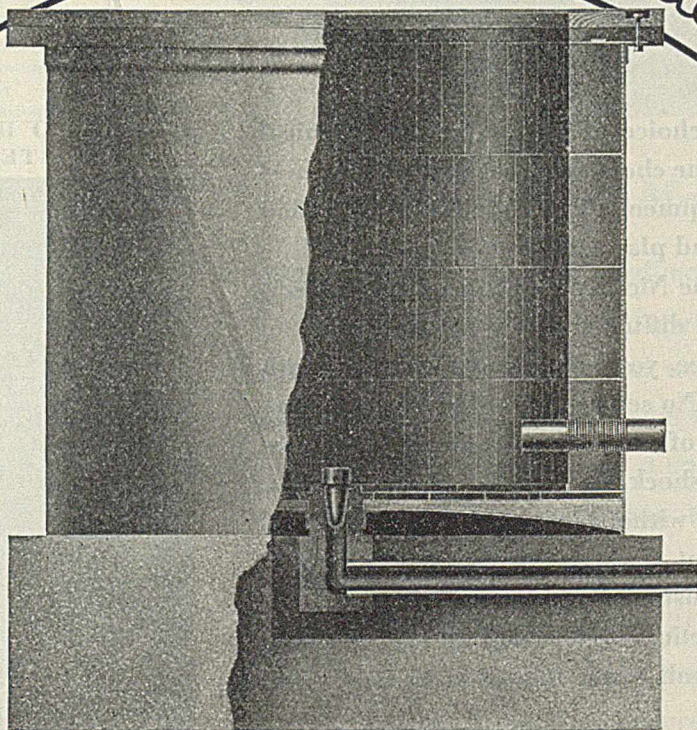


# NATIONAL Carbon Brick

## ABSOLUTELY NO REACTION

### WITH HYDROFLUORIC ACID OR FLUORINE COMPOUNDS

A NEW Construction Material



... National Carbon Brick, in conjunction with carbon pipe, tile and special shapes, provides a corrosion proof material of construction for all types of acid proof masonry, including flues, towers, vats, tanks and like equipment.

Typical Carbon Brick and Carbon Tile Lining for Circular Tank. Note also Corrosion Proof Carbon Drain and Connections.



Carbon is immune to reaction with most of the products in chemical manufacturing plants. It is unaffected by all acids, alkalies and salt solutions except hot concentrated solutions of highly oxidizing character. Maximum safe temperature under oxidizing conditions, 750°F.

**IMPERVIOUS CARBON** When required, National Carbon Brick and other chemical carbon products can be supplied in a form impervious to the seepage or absorption of liquids and gases.

ITS THERMAL CONDUCTIVITY AND LOW COEFFICIENT OF EXPANSION AFFORD HIGH RESISTANCE TO THERMAL SHOCK

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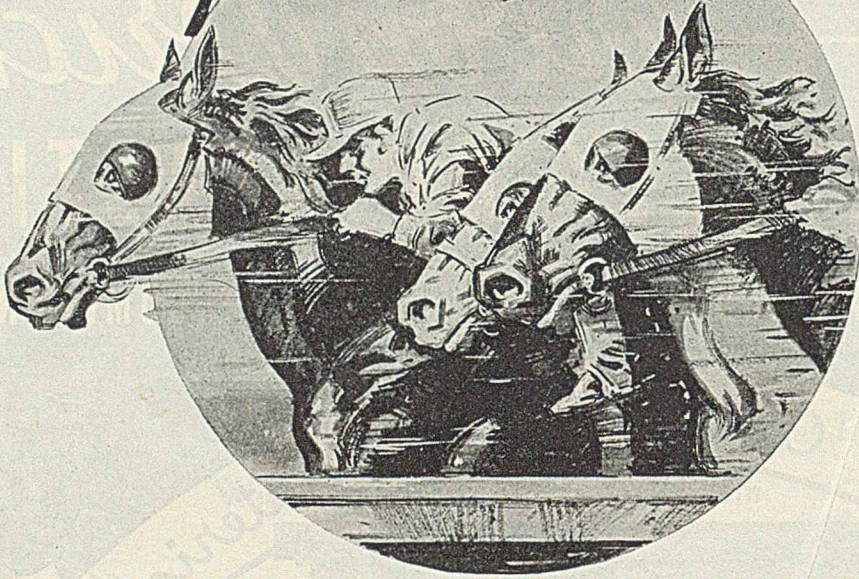
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Among clad metals, the choice of leaders in the chemical and allied industries . . . the choice that has proved a winner in a wide variety of equipment . . . is Lukens Nickel-Clad Steel! Play the favorite and play safe!

Because the bond of the Nickel layer to the steel base is obtained through thermal diffusion which forms a solid solution alloy at the interface, you need have no worries with Lukens Nickel-Clad Steel. No separation of the layers occurs under normal conditions of temperature change, pressure, vacuum or mechanical shock. It can be sheared, bent, flanged, welded or riveted without cracking or peeling.

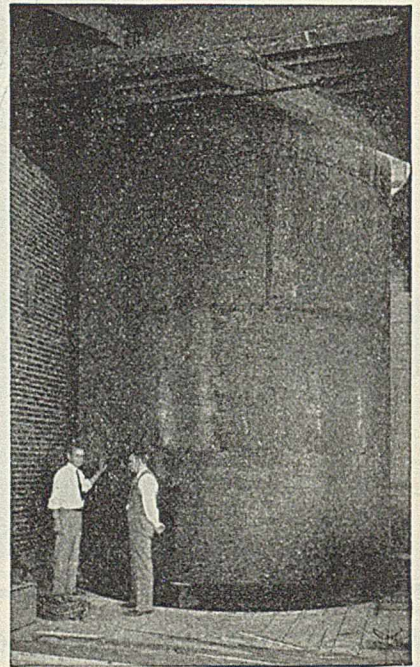
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Be sure you have complete data on Lukens Nickel-Clad Steel . . . its advantages, its economies . . . before you invest in new equipment. Write us today. Lukens Steel Company, World's Largest Plate Mill, Coatesville, Pa.



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IT HAD TO HAVE QUALITY  
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*Soap boiling kettle under construction in the plant of a large soap manufacturer, being fabricated throughout from Lukens Nickel-Clad Steel, 10% Nickel-cladding. Heating coils and discharge spout are pure Nickel.*

*This booklet gives complete data on Lukens Nickel-Clad Steel and its extensive use in the chemical and allied industries. Write for a copy.*



# Lukens NICKEL-CLAD Steel



# DRYERS

*for*

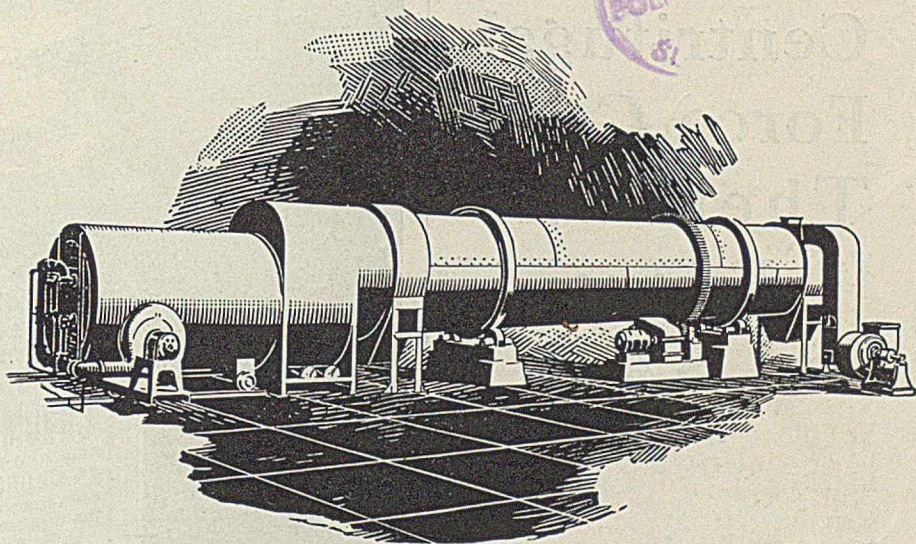
- Acetates . . .** Cellulose
- Acids . . . . .** Oxalic Crystals
- Carbonates .** Calcium  
Magnesium  
Sodium  
Zinc
- Chlorides . . .** Ammonium  
Sodium
- Fluorides . . .** Sodium
- Nitrates . . .** Ammonium  
Sodium
- Nitrites . . .** Sodium
- Oxides . . . .** Iron  
Silicon  
Titanium  
Zinc
- Sulphates . .** Ammonium  
Ferrous  
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The installation of Bartlett-Snow conveyors, elevators, storage bins, feeders, crushers, screens, and other auxiliary drying or kiln equipment insures the successful operation of the complete assembly as a unit and enables you to cover the entire installation with a single Bartlett-Snow guarantee.



### *Automatic or Manual Control*

**F**OR stone or sand, ores, and many minerals, manual control frequently suffices. Not so with sodium nitrate, tobacco, or spent grain. For these and other heat sensitive materials, thermo-elements connected with recording or indicating dials and operating valves, insure a constant grade of product . . . automatically adjust performance to the load.

The ability of Bartlett-Snow engineers to control moisture in the finished product to within 2/100 of 1%, with an oil fired direct heat dryer, when faced with feeds ranging from 18 to 53 tons per hour and a moisture variance of from 3 to 5%, has proved of interest to many chemical engineers. It's one of the reasons these purchasers turn instinctively to Bartlett-Snow with every drying problem.

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50 YEARS' EXPERIENCE—THOUSANDS OF INSTALLATIONS



# Centrifugal Force Gave Them The Extra 5%

**T**HOUGH trite, the bromide originally credited to Ben Franklin about a penny saved being a penny earned is a live truth that modern industry is applying with telling results.

If, for example, the 5% loss of valuable mercurochrome through absorption by solids could be eliminated—that 5% saved would be 5% earned for the profit side of the ledger. So Sharples engineers were called in to see what centrifugal force might do. Centrifugal force was put to work on the entire output of mercurochrome before it went to settling tanks—with the result that the quantity of sludge deposited in the settling tanks was so small, that it could be reworked into the next batch to

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Thus another valuable use of centrifugal force is demonstrated—recovery. Your product may be thoroughly unlike mercurochrome—yet it is very likely that centrifugal force can make its definite contribution somewhere in your separating, clarifying or recover-

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*Sharples Super Centrifuge, rotating at a speed of 15,000 R. P. M., generates a centrifugal force of over 13,000 times gravity.*

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*... And you can be*  
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"U. S." Rainbow Sheet Packing began to build its reputation more than four decades ago . . . and through all that time its imitators have never been able to equal its record of service to industry. Its color, its trade mark, its name—everything about it has been copied . . . except its performance!

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There's nothing else like "U. S." Rainbow! Made in two styles: No. 9 for average steam, air and hydraulic joints; No. 19 brass wire inserted, for heavy service. Made in rolls, 36 inches wide, weighing from 100 to 200 pounds; standard thicknesses— $\frac{1}{32}$  inch,  $\frac{1}{16}$  inch,  $\frac{3}{32}$  inch,  $\frac{1}{8}$  inch,  $\frac{3}{16}$  inch and  $\frac{1}{4}$  inch.

Write or call the "U. S." Branch nearest you, or direct to United States Rubber Company, 1790 Broadway, New York City.

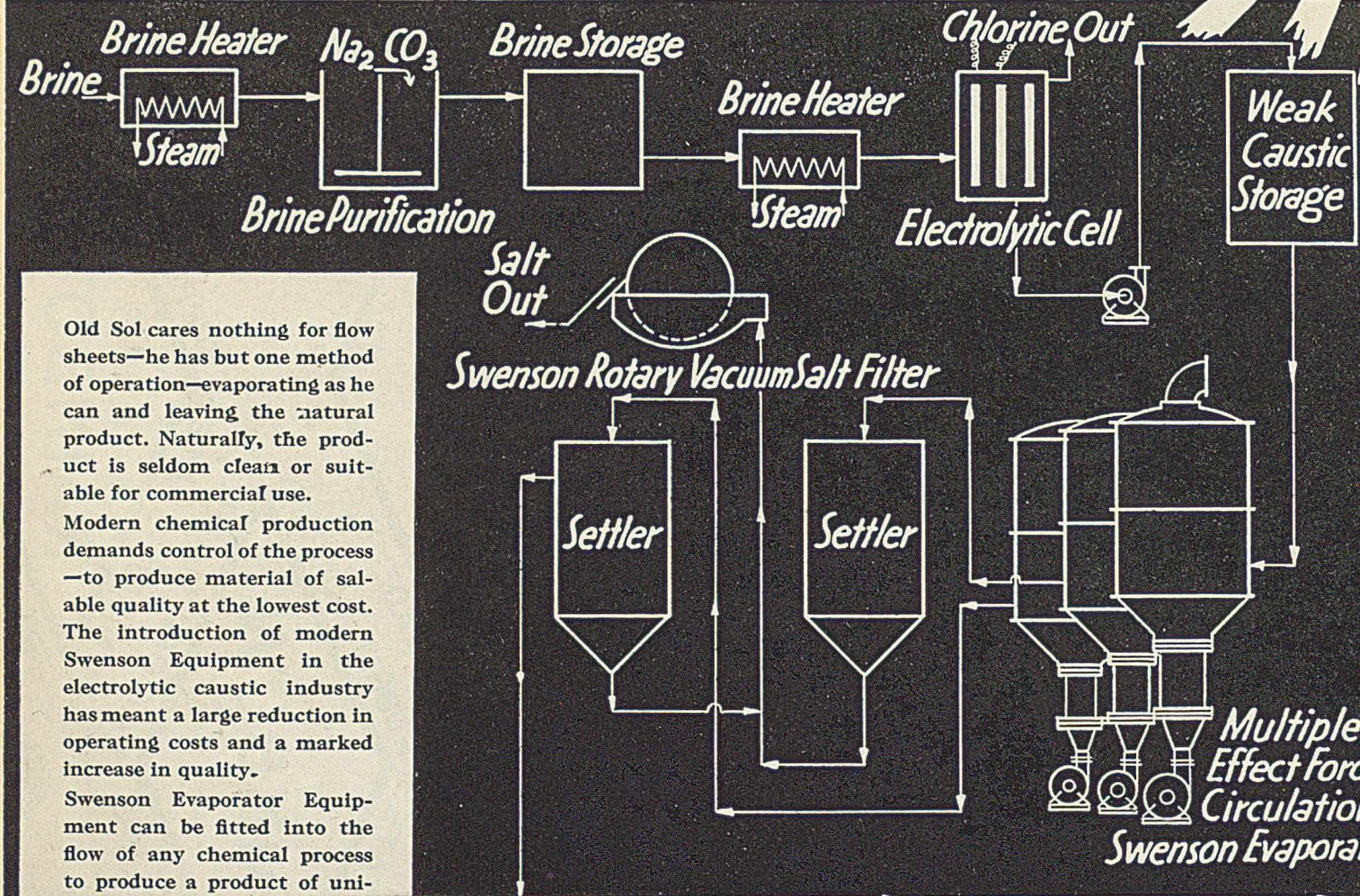


United States Rubber Company





# Equipment that Fits the Process ... With Economy

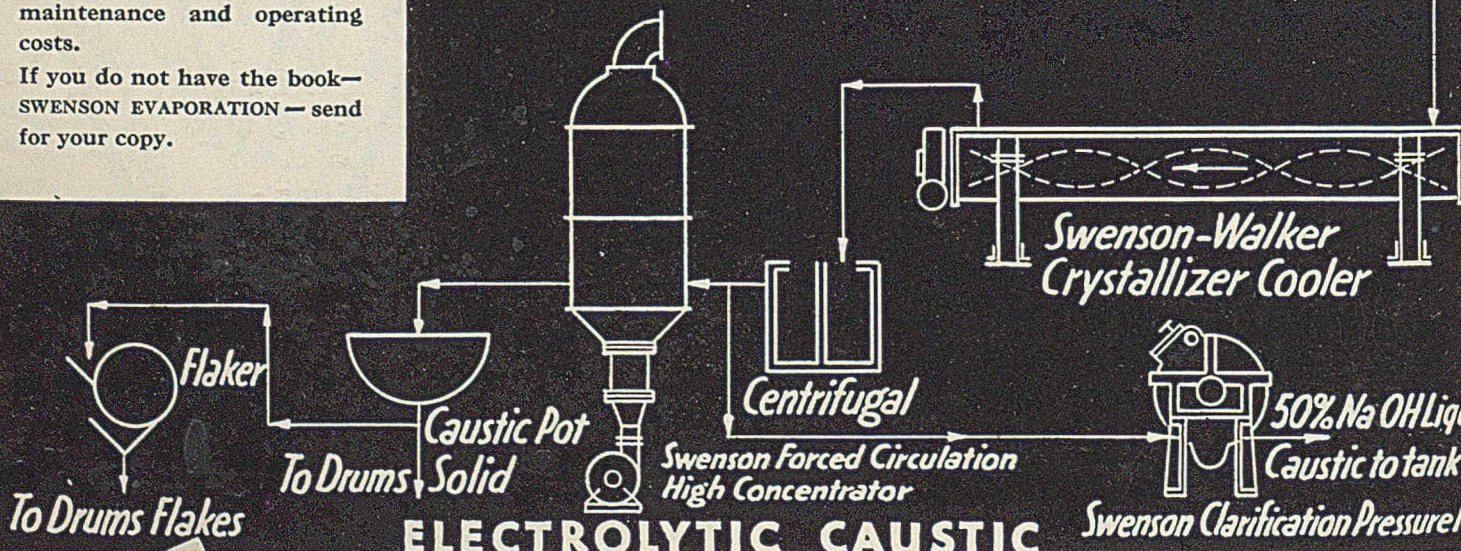


Old Sol cares nothing for flow sheets—he has but one method of operation—evaporating as he can and leaving the natural product. Naturally, the product is seldom clean or suitable for commercial use.

Modern chemical production demands control of the process—to produce material of salable quality at the lowest cost. The introduction of modern Swenson Equipment in the electrolytic caustic industry has meant a large reduction in operating costs and a marked increase in quality.

Swenson Evaporator Equipment can be fitted into the flow of any chemical process to produce a product of uniform quality with economy in maintenance and operating costs.

If you do not have the book—SWENSON EVAPORATION—send for your copy.



## ELECTROLYTIC CAUSTIC

### SWENSON EVAPORATOR COMPANY

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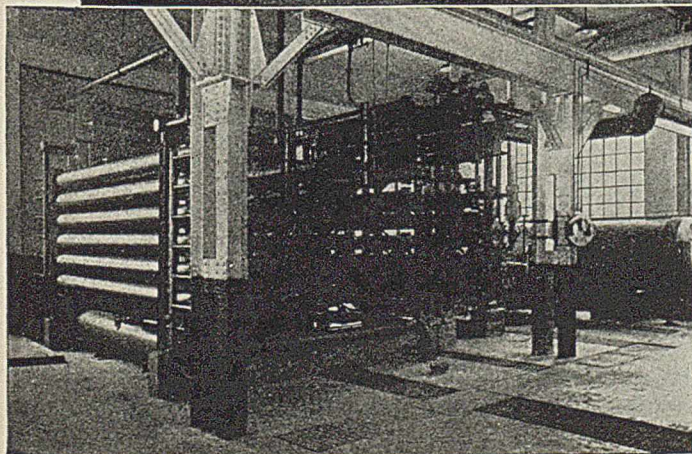
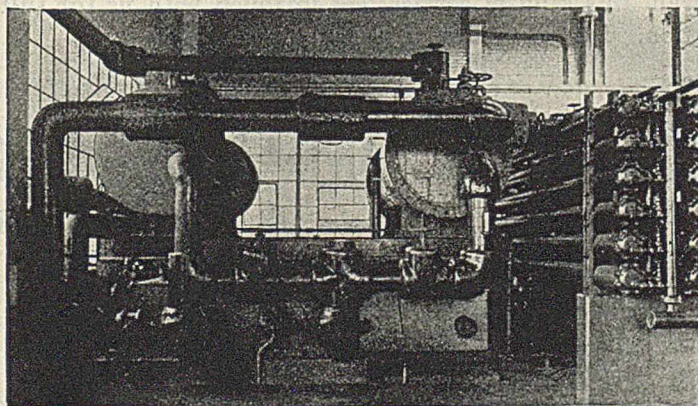
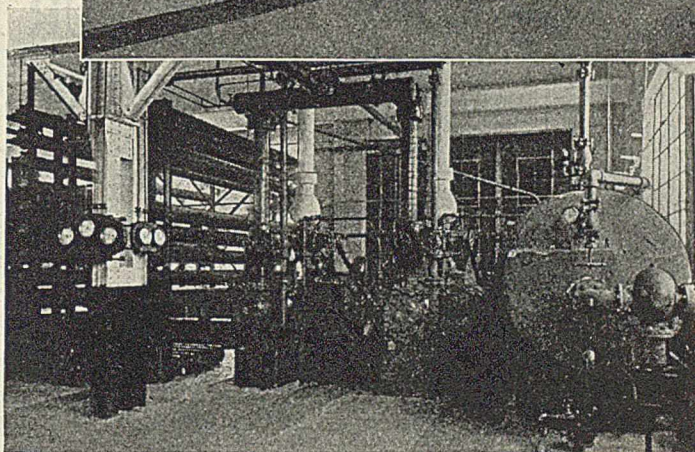
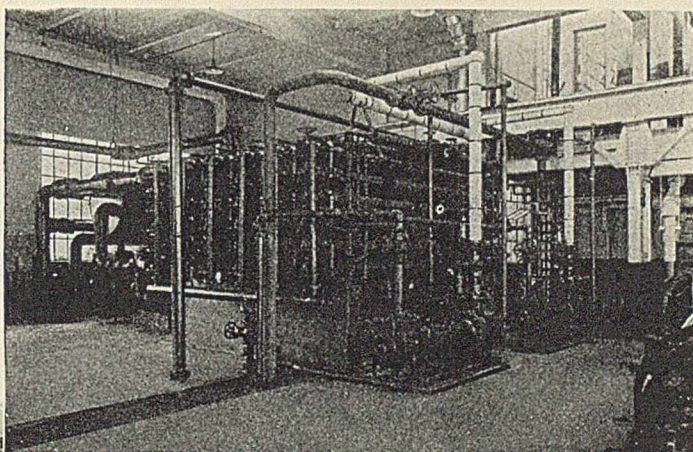


# Chemical Plants

with the most varied demands for refrigeration of any industry find a ready solution of their problems with . . . . .

# Vogt Refrigeration Equipment

SINCE 1880



The illustrations show a combined Vogt Exhaust Steam Absorption and Compression Refrigerating Unit operating on sixty pounds pressure exhaust from a turbine driven power generating set. One hundred and sixty tons refrigeration is developed as a by-product and the final condensate from the absorption machine is returned to the boiler, completing a most economical cycle of performance.

**Vogt**  
FOR BETTER REFRIGERATION



We shall be glad to cooperate in the solution of your refrigeration problems.

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**LOUISVILLE, KY.**

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Manufacturers of: Oil Refinery Equipment, Drop Forged Steel Valves and Fittings, Water Tube Boilers, Ice Making and Refrigerating Machinery, Heat Exchangers.



# One Winner Helps Another



## LABOUR Pumps in Contact Acid Service at Rumford Plant

Makers of a quality product themselves, The Rumford Chemical Works appreciate quality in the equipment they buy. Nobody knows better than they do that there's a difference in pumps, just as there's a difference in baking powders. The mere fact that this widely known company is a good LaBour customer is in itself a recommendation.

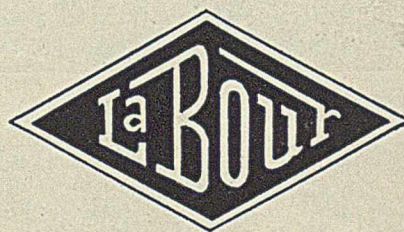
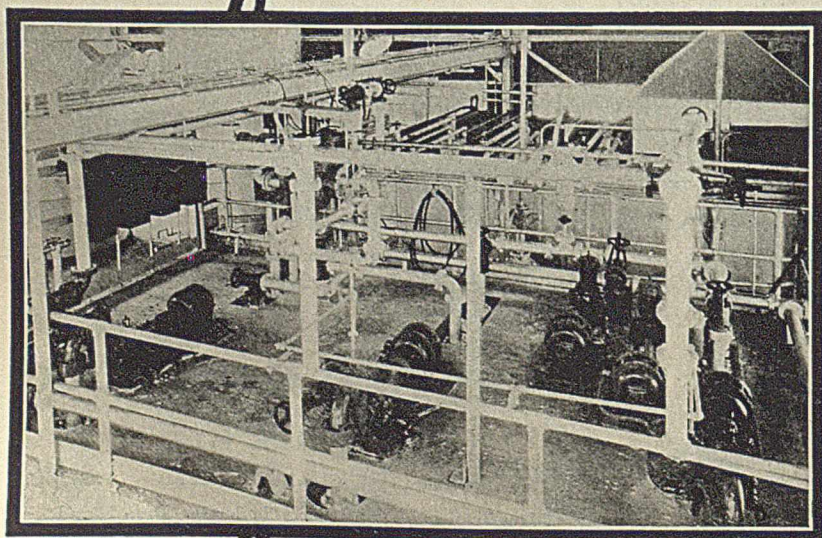
E. L. Wilson, general superintendent, tells us that the five LaBour pumps illustrated are circulating sulphuric acid in their contact system and have been operating continuously for more than four years, with only "five or six brief shutdowns." Each pump is handling 40 tons of 98-99% acid, at 180° F., per hour.

Service like this is the reason why LaBour pumps predominate in most of the difficult spots in the process industries. If you want this kind of service, get in touch with us for full information. It costs you nothing.

## The LABOUR COMPANY, INC.

1001 Sterling Ave.

ELKHART, INDIANA



Photograph by courtesy of the Rumford Chemical Works, Rumford, R. I., showing the five LaBour pumps referred to in Mr. Wilson's statement.



**\$4,100**  
**LOUISVILLE**

**DRYER**

**RE-CLAIMS**

**WASTE—SAVES**

**\$7,740**

**ANNUALLY**

**T**HIS is the story of a company which formerly threw away one of its processing materials because of its wet and supposedly "worthless" condition after use.

The cost of the material itself is \$30.00 per ton. After considerable research, our Louisville Dryer engineers demonstrated that the wet material could be completely recovered for use by means of a Louisville Rotary Dryer and at a drying cost of \$4.20 per day. *Net saving to the customer—\$25.80 per day—\$645.00*

#### **PROBLEM**

To develop a drying system for reclaiming wet processing material that was formerly thrown away.

#### **SOLUTION**

A Louisville Rotary Dryer operating at total cost of \$4.20 per day, including fixed charges, reclaims \$30 worth of material.

#### **RESULT**

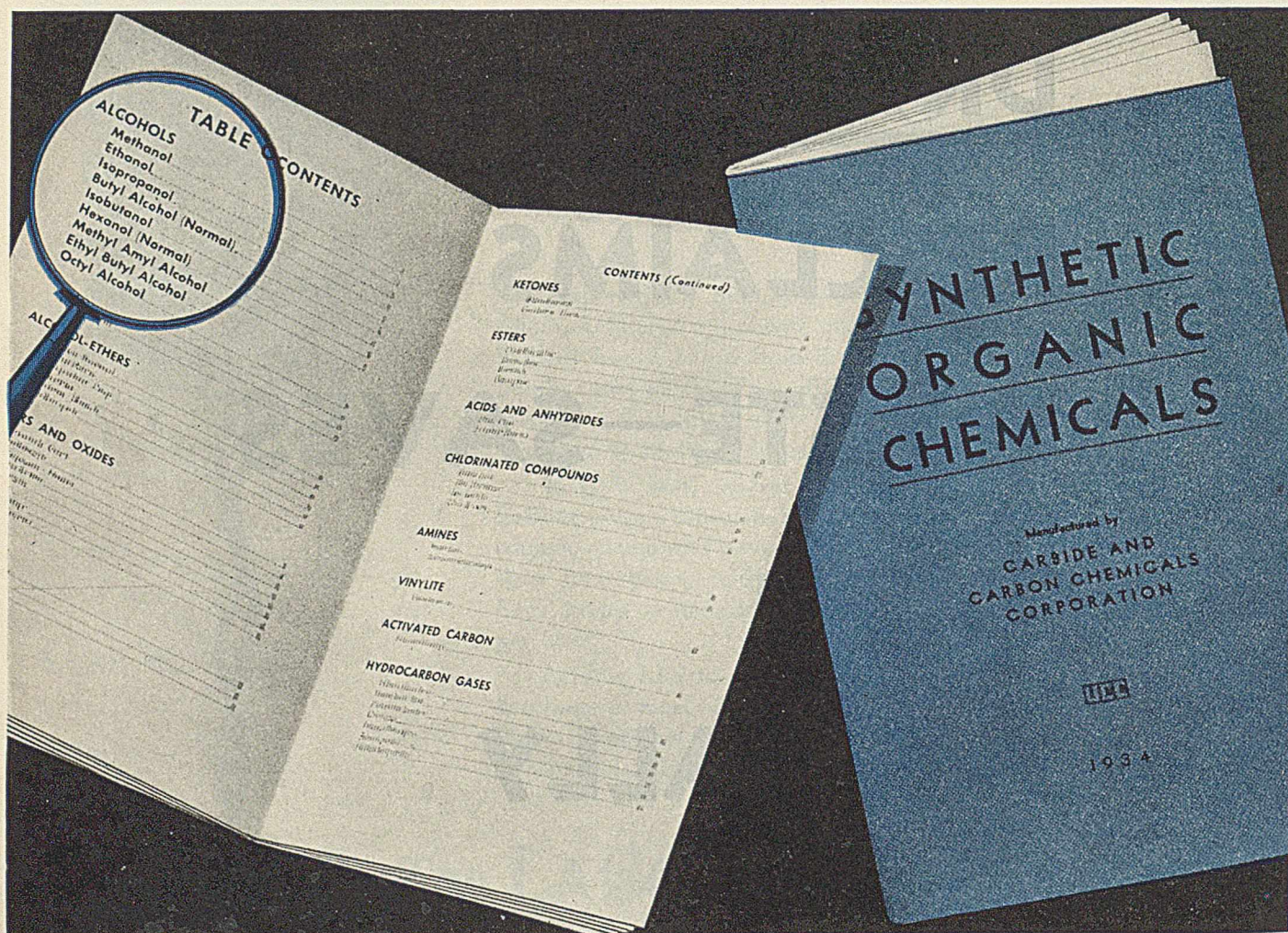
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*per month—\$7,740 per year.* And all for a capital expenditure of \$4,100, which was entirely paid for in the first seven months after installation!

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