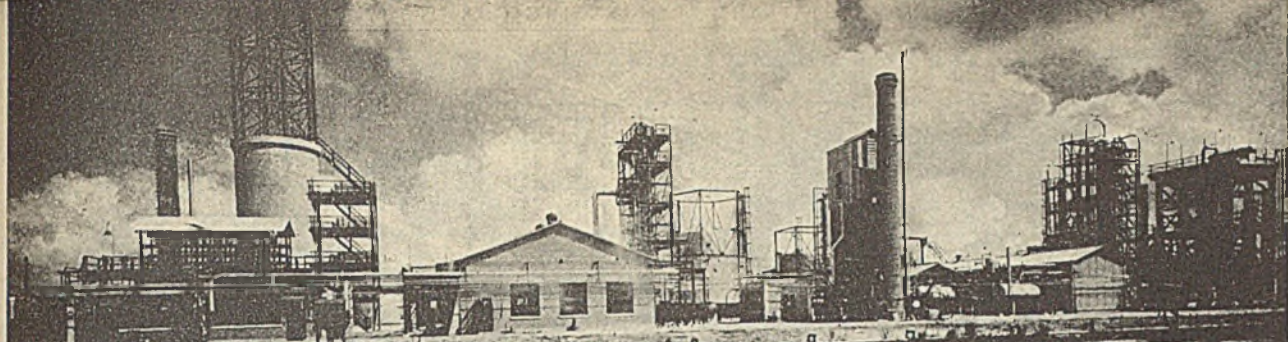


Industrial and Engineering Chemistry

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INDUSTRIAL AND ENGINEERING CHEMISTRY • INDUSTRIAL EDITION

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Above is a view of one of the first 100-octane aviation plants built by The Lummus Company.

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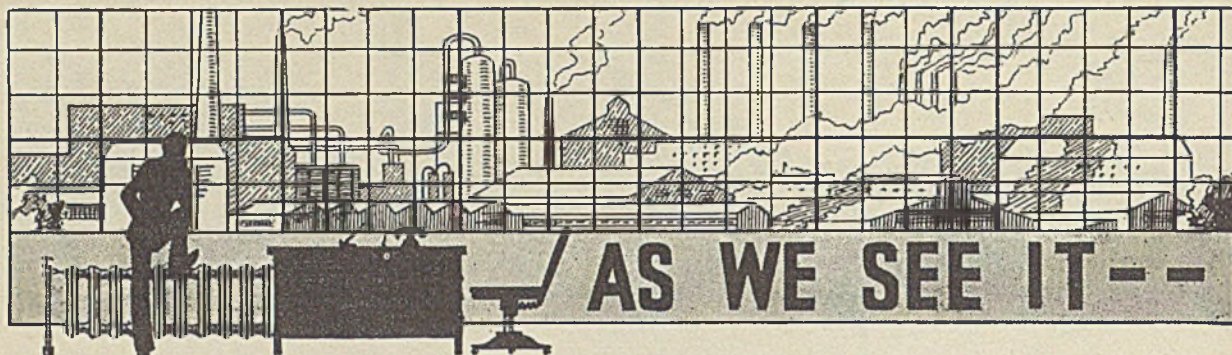
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► **AUTOCLAVES** for carrying out reactions under controlled pressure and temperature are practically universal tools in chemical industry. That lends special interest and importance to an exhaustive discussion of the many factors involved in their design and use provided by Gooch (page 927). Characteristics of the vessel itself, heating methods, agitation, drives, instrumentation, and safety precautions are all treated in some detail.

► **SYNTHETIC ELASTOMERS** continue as high priority problems as the huge program for their production approaches completion. Nine papers in this issue present as many aspects of this general subject and provide new data of great value.

► **HEAT GENERATED** during flexing of both rubber and synthetics is a vital factor in designing tires. Gehman, Jones, and Woodford (page 964) describe a simple, convenient flexometer for measuring this value and give comparable results obtained with it for rubber and GR-S. Effects of several important variables are shown.

► **BLENDS** of the several available synthetic elastomers possess important characteristics which indicate their widening use. Martin and Laurence (page 986) have made blends of Thiokol FA with synthetics of three other types and report the properties of the blends in some detail. They find variations from the expected linear relation with composition.

► **HEAT RESISTANCE** of neoprene vulcanizates is improved by a high state of cure, according to Forman (page 952). Data on Neoprene GN are given and principles applicable to heat resistance of all types of neoprene are developed.

► **BUNA S VULCANIZATES** with sulfur in varying percentages have been prepared by Cheyney and Robinson (page 976), and their chemical and physical properties determined. The range covered extends from soft rubbers to compounds resembling ebonites. Compositions of intermediate sulfur content, unlike rubber, possess intermediate properties.

► **CARBON REINFORCEMENT**, vital in the use of rubber, is also important in compounding synthetics. Turner and his co-workers (page 958) have determined the effects of different types of carbon on Butyl rubber and find important differences between its behavior and that of rubber.

► **STRUCTURE OF CARBONS** of several types has been investigated by Rossman and Smith (page 972) in an effort to relate this property to reinforcing effect in rubber. Density determined by helium displacement is compared with x-ray data.

► **COLD'S EFFECT** on the rubberlike properties of synthetic elastomers is noted by King (page 949) to be determined by bend-brittle and shatter points. These two points are measured for a variety of synthetics in a number of different compositions.

► **SWELLING EFFECT** of gasolines on neoprene vulcanizates has been found by Fraser (page 947) to be indicated by the aniline point or the Diesel index of the fuel. Tests have been made with a variety of motor fuels and blends.

► **MOLECULAR WEIGHTS OF POLYMERS** of large molecular size are difficult to determine accurately, yet this value is often important in gaging their properties. Huggins (page 980) critically examines methods used for this purpose and makes specific recommendations for improvement applicable to both resins and synthetic elastomers.

► **MATURING OF WHISKY** has been studied by Liebmann and Rosenblatt (page 994) using a large sampling (108 barrels) and analyzing each barrel annually over a period of five years. The large number of analyses provides a basis for statistical study of the changes occurring during aging. Both Bourbon and rye whiskies were included in the sample. The data presented are suggested as a basis for whisky specifications.

► **COPPERAS** can be crystallized from spent pickle liquor, and the acid content of the liquor recovered for re-use, by the addition of large volumes of acetone, according to Gehm (page 1003). Acetone, he found, is superior to methanol for this purpose. Application of the method depends upon the efficiency of recovering acetone.

► **CYCLOPENTANE** has been isolated by Tooke (page 992) from the pentane-hexane fraction of natural gasoline from the Burbank field. His results indicate the presence of 2.4 per cent cyclopentane in the original natural gasoline.

► **COMMERCIAL SOAPS** owe their properties to the proportions in which three separate crystalline phases of sodium soap are present in the product, according to Ferguson, Rosevear, and Stillman (page 1005). These phases, together with a fourth of less importance in commercial products, are identified by their x-ray patterns, and their properties are described. The balance between them is determined by the conditions of soap boiling and establishes the characteristics of the product.

► **HIGHLY PURIFIED LIQUIDS** have been found by Foulk and Barkley (page 1013) not to form films as do those containing minute amounts of impurities. Experimental results with seven typical liquids representing as many classes are presented.

D. H. Killeffer



EVEN though this summer of 1943 failed to bring the usual vacation atmosphere with it, its end is a signal to accelerate from the slowed gait of summer back to a swift pace again. That transition, we hope, will be helped by our continuing provision of significant papers bearing on the important problems of the present and others that loom ahead.

Solvents will be the leading topic of our October offering, with a group of informative papers to bring us up to date in this broad field. Each of the important families of solvents—hydrocarbons, alcohols, ketones, aldehydes, esters, and chlorinated compounds—will be discussed from the several points of view involved in their many applications. Products of petroleum, coal, pine trees, fermentation, and synthetic processes will receive attention. Many of the commoner uses of solvents are covered briefly, and others, such as selective solution, will be emphasized. The present availability of large numbers of solvents having widely diverse properties suggests consideration or reconsideration of many processes based on their action which have been overlooked or shelved in the past. The refining of wood rosin and of lubricating oils by the use of furfural's selective solvency suggests the possibilities in other fields, many of which await exploration.

Surface characteristics of asphalt are more important in most applications than its mass properties, and that has suggested the development of a method of testing of relatively thin layers. The method devised and some of its applications will be found in our October issue.

Efficiency of soap as the world's No. 1 cleansing agent and detergent is usually modified by the inclusion of inorganic compounds in the commercial product to act as builders. Few subjects have continued for so long to be so highly controversial as the usefulness of these various additives. Many variables affect results, and agreement on test methods has been difficult, almost impossible, to reach. However, a comparative evaluation of a number of common builders by a specified method will appear in October as new information on this important subject.

Another subject of much divergence of opinion, the estimation of molecular weights of polymers by measurement of the viscosity of their solutions, will also receive attention. Data to be presented on viscosity of solutions of normal paraffins in *n*-hexane agree perfectly with the Staudinger relation and suggest the value of this method for linear polymers.

Stability of furnace oils has been investigated because of its effect on the operation of heating systems and methods of test devised to determine suitability of oils.

Lignin, recoverable from pulp making wastes, is a cheap plentiful and interesting raw material. Some of its esters with aliphatic acids will be described for us.

Waste disposal, always important, involves special problems in war time when high explosives manufacture adds to their difficulty. This time it will be TNT waste discussed for us.

There will, of course, be much more, but that should at least encourage us to look into the issue assured there will be in it a spur to our imaginations and a probable help with pressing problems.

YOUR HUMBLE SPY

THE ads this month seem uniformly to have an engineering slant and they are all interesting reading. The first to strike our attention is that of the Corhart Refractories Company and the data

they have given on the operation of a Corhart electrocast furnace in the glass industry. They have been collecting facts and figures since 1935 on the performance of a furnace lined with Corhart electrocast, and, let us quote in effect "(in) 1937 we published figures for a record breaking furnace which produced 76,446 tons of soda lime glass in 556 operating days. When the furnace was let out (on an arbitrary date) the operators found they could have run 12 more months without failure." Now this same furnace has completed a run of another 12 months—a total of 36 months during which it produced 122,200 tons of soda lime glass. Corhart supplies us with a table in which an analysis of the various performances is given. The message they wish to get over is the following: If this refractory does such a outstanding job in the glass industry, perhaps there is some job for it in the chemical equipment you now use.

The Marley Company ad this month strikes us as being especially good. The diagrams of cooling towers are quite revealing, and they have a message which ought to be read and considered by every engineer interested in water cooling problems.

Babcock and Wilcox are designers and builders of special equipment for the process industries. To fabricate these parts accurately requires ponderous and rare machinery, and in their ad this month is shown a few of the giants used.

Good news for our Texas readers inasmuch as this month's message from the American Smelting and Refining Company announces the opening of a new Houston plant devoted to service on lead products and lead burning.

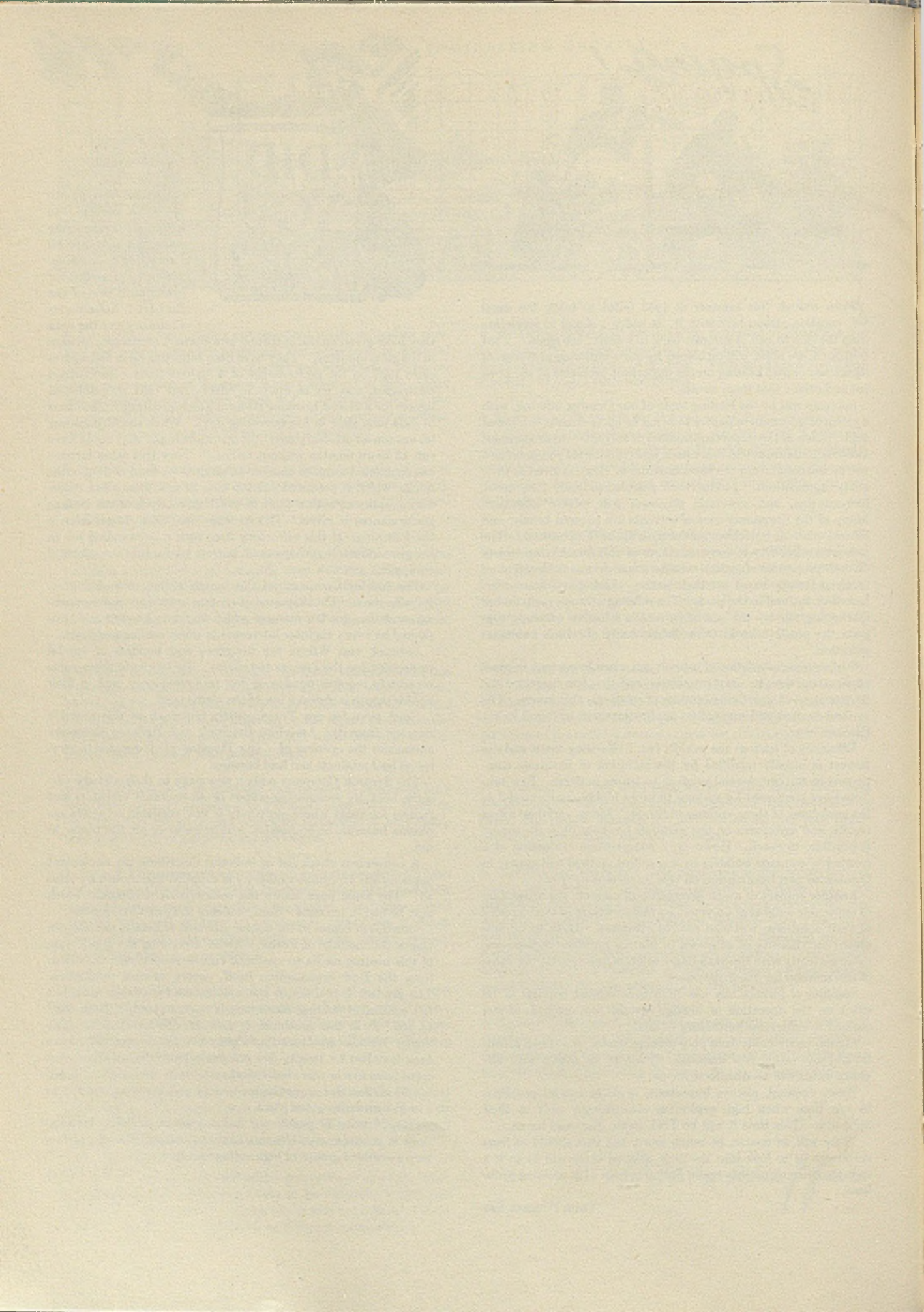
The Syntron Company adds a new page to their already versatile book by announcing water- or air-operated vibrators and feeders for spots where electricity is not available or where explosion hazards, or economics, makes water or air the power to use.

A convenient check list of bulletins describing the equipment made by the Hardinge Company is supplied this month by their ad. The same page shows the countercurrent classifier which may be had in ten sizes—from 18 inches to 10 feet in diameter.

Dowtherm comes in for double-barreled emphasis this month. One is the message of Foster Wheeler describing the application of this heating media to synthetic rubber processing; the other, from the Dow organization itself, covers varnish production. The product Dowtherm is too well known for review here, but the controlled heating conditions it makes possible, from 400° to 700° F. at low pressures, is an achievement of note. The Foster Wheeler ad states that eighty-two Dowtherm units have been installed by twenty-five companies, and five of these concerns have five or more individual systems in operation. Shown is a 24 million B. t. u. per hour capacity unit installed recently in a large synthetic rubber plant.

Simplification of purchasing and layout of electrical installations is possible, says General Electric, through the use of factory-assembled groups of high voltage equipment.

A. SID. ULATE



INDUSTRIAL AND ENGINEERING CHEMISTRY

PUBLISHED BY THE AMERICAN CHEMICAL SOCIETY • WALTER J. MURPHY, EDITOR

EDITORIALS

A Modern Version of the Loaves and Fishes?

ALTHOUGH but recently removed from the hush-hush category of scientific developments, "Food Yeast", the name which has been applied to dried *Torula utilis*, an organism with properties similar to those of *Saccharomyces cerevisiae*, the yeast of bakers and brewers, is now receiving considerable publicity in the lay press. Its meaty flavor and high content of protein and vitamin B complex offer intriguing possibilities. Whether or not the enthusiastic description provided by *Time Magazine*—"nearly as succulent as the sirloin steak it takes two years to raise on the hoof, much cheaper, and much richer in proteins and vitamins"—is an overstatement or understatement remains, of course, to be demonstrated by a still wider use of the product in diets under many diverse conditions.

We know that the Germans during World War I used food yeast as a source of protein for human consumption, but, according to authentic reports, the project was not considered to have been an outstanding success, since the amounts fed were probably too large to be well tolerated by the human system. It is believed that Germany currently is producing more than 100,000 tons a year. It is likely that this quantity is being used both as a feeding stuff for animals and for human consumption.

In Great Britain in the dark days of 1940-41 the idea was taken up enthusiastically by Thaysen and his staff at the Chemical Laboratory of the Department of Scientific and Industrial Research in an effort to find a product that could be substituted for the fast-dwindling supplies of meat. He did succeed in developing a new strain with a pleasant, nutty flavor, and the British Government is now erecting a plant in the West Indies to produce some 2,500 tons a year.

Now, according to reports, two Americans, Dr. and Mrs. Carl Lindegren, in the St. Louis laboratories of Anheuser-Busch, have succeeded in developing a number of entirely new strains with a meaty, nutty, or celery flavor, depending upon the variety.

The raw materials necessary for the production of "Yeast Food" are available to us in large quantities—sugar in some form, preferably molasses, ammonia (which the yeast converts into protein) and phosphorus which can be supplied either as superphosphate of lime or as ammonium hydrogen phosphate.

The nitrogen can be supplied by either liquid ammonia or ammonium sulfate and this introduces an angle of greatest significance, yet one whose portent seems to have been overlooked.

Developments by Haber and others of processes for fixing nitrogen have been viewed as a sort of mixed blessing. For without huge quantities of nitrogen for the production of explosives, no country, and certainly not Germany, Italy, or Japan, is capable of waging war.

At times sensational writers have pointed the finger of scorn at the chemist for having developed ways and means of extracting large quantities of nitrogen from the air, failing of course to give proper recognition to the fact that the same material serves not only to produce explosives but also nitrogen-bearing fertilizers which have removed forever fear of world-wide famine. Now the chemist appears to have accomplished a still greater step in the betterment of mankind. If the Thaysens, the Lindegrens, and others have actually succeeded in producing highly palatable foods, varying in flavor, high in protein and vitamin B content, then they have eliminated the steps heretofore necessary through plant growth to produce an important food product. Perhaps the chemist working quietly in the laboratory now has adequate solutions to two problems—one, the "quart of milk for every hottentot", and the other, a peacetime use for surplus fixed nitrogen. Perhaps you are still inclined to say "I'll still take steak—when I can get it", but to the millions of human beings who never have experienced the delights of a juicy steak or a thick cut of roast beef and who have no appreciation of the pleasures of the gourmet, the chemist offers at least the possibilities of a diet varied and vastly superior in nourishment to that which these unfortunates have been forced to consume in the past.

Women Chemists

JUST four years ago at the Boston meeting of the AMERICAN CHEMICAL SOCIETY the Division of Chemical Education sponsored a Symposium on Training and Opportunities for Women in Chemistry. In the light of the manner in which our women chemists have helped to bridge, partially at least, the present scarcity of well-trained technologists, it is interesting to recall the views expressed several years ago. Ethel L. French opened the program with the following state-

ment: "During the past few years women chemistry graduates have found it difficult to secure employment in positions for which their training has supposedly qualified them."

War has changed this as every one knows who has ready access to laboratories. Not only do personnel departments eagerly seek graduate women chemists, but young women are being given special courses to fit them to become laboratory technicians.

The women chemists of America have a golden opportunity to refute now and for all time many of the standard arguments raised in the past against wider use of their talents. Leading women chemists are adopting a realistic viewpoint on the subject. Lois Woodford, for example, writing in the *Journal of Chemical Education* late last year summed up the situation admirably: "Employers are accepting the entrance of women into industrial laboratory work with grave misgivings. To find a chemical position at the present moment is the simplest thing in the world; to hold onto it while we are in the midst of war preparations is going to require only a minimum of effort on your part; to carve out a place for yourself so secure that you can hold onto it when the days of keen competition return is quite another matter."

Possibly incurring the displeasure of the male members of the SOCIETY (they outnumber the females twenty to one), we boldly express the belief that the women will come through with flying colors. But it must be on merit alone, and the ladies, God bless them, would not, we are certain, want it otherwise. This is the "Chemical Age", and in a proper postwar world there will be work for all good chemists, male and female.

Deferment of Government Chemists

DEPARTMENTS and agencies of the Federal Government are not following a policy of asking for deferments of their chemists and chemical engineers.

Within the past month a chemist in the employ of the U. S. Department of Agriculture with a Ph.D. degree and seven years of varied research experience has been advised by his superior that a replacement is now available and no further occupational deferments will be sought for him. This man, facing imminent induction into the Armed Forces, possesses the rating of associate chemist and is engaged in important food research work. This case, moreover, is not an isolated one.

Must the services of this chemist in the war effort and of others like him be sacrificed because of political expediency? Stung to the quick by the criticism leveled at the previous policy of seeking deferments for large numbers of slide-rule boys, would-be publicists, propagandists, and others of doubtful value to the proper prosecution of the war, the Government now seems prepared to jettison much worthwhile research only because it cannot differentiate between the value of

a well-trained scientist doing vital war work and a slide-rule boy in the OPA. Government officials are likely to object to the word "differentiate", preferring to substitute the word "discriminate". In any case, the net result is that valuable talent will be lost to the Production Army.

It is nonsense to excuse this action by saying that a replacement has been found. This government chemist, about to be drafted and eventually to wind up either shouldering a gun or driving a jeep cannot impart to his successor the accumulated experience of months, possibly of years. Research chemists of accepted worth are not replaceable like stenographers. Are the research programs of the Federal Government so unessential that they should be delayed and handicapped while new personnel, no matter how well trained, are fitted into the positions vacated by drafted men?

The situation of this government chemist is not the result of any unintelligent action by a local draft board. If he were performing similar work in private industry, his employer would seek and obtain deferment on occupational grounds. Certainly the present government policy on deferments is far less enlightened than that of industry. Continuance by government departments of the existing plan to obtain so-called replacements for all men under twenty-five years of age, and for as many as possible of those over that age, will have the effect of driving promising and valuable technologists into private industry to the detriment of federal research programs.

Depletion of Natural Resources

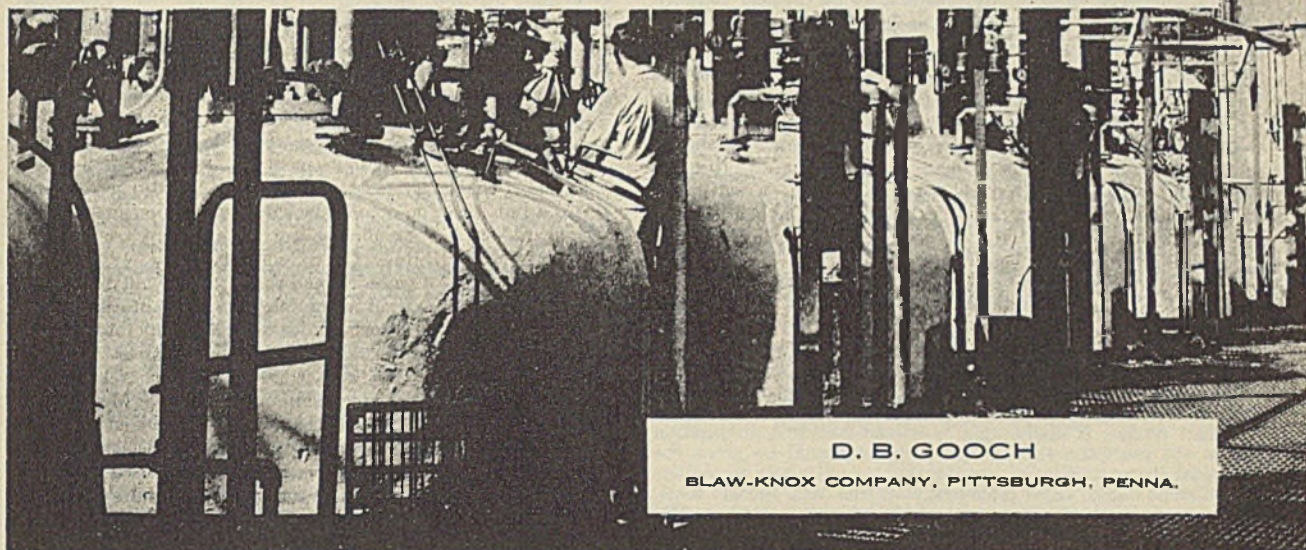
IN A RECENT article in *Chemical and Engineering News* (June 25, 1943, page 939) Benjamin T. Brooks points out that the American petroleum industry has entered a new phase of its existence, characterized by a decreasing rate of finding new oil in this country and an increasing dependence upon foreign sources. In our role as the "Arsenal of Democracy" it is evident that we are draining off at a terrific pace not only supplies of petroleum but other important natural raw materials, notably high-grade iron ore and the better grades of ores and minerals of the non-ferrous group, particularly copper. Little can be done until the war is won, but conservation of our high-grade deposits and sources of vital natural raw materials should be of definite concern to all, and should have serious consideration at the peace table and in the framing of future foreign trade policies. It is difficult for Americans to believe that we may in the not-too-distant future be without adequate reserves of certain raw materials, but evidence is piling up to support the contention that we may face possible shortages. Now is the time to formulate a policy with, of course, the interest of the country as a whole the paramount and single consideration.

AUTOCLAVES

for

The increasing complexity of modern processing is reflected in present trends of autoclave design and construction. These closed reaction vessels are now being manufactured to operate at elevated temperatures and high pressures. Many of today's important industrial pressure processes owe their existence to modern metallurgy and engineering which have made it possible to furnish the type of batch or continuous autoclave that can successfully function under such severe operating conditions. Limitations of existing laws and safety codes, materials of construction, and component parts must be studied on the basis of sound engineering reasoning in conjunction with a thorough understanding of process conditions as a prerequisite for the design of safe and efficient autoclaves.

Pressure-Temperature Reactions



D. B. GOOCH

BLAW-KNOX COMPANY, PITTSBURGH, PENNA.

AN AUTOCLAVE may be defined as a closed vessel in which chemical reactions are effected under controlled conditions of pressure and temperature, where either or both of these factors accelerate the reaction or give a higher yield. Usually autoclaves are provided with means for agitation to accelerate further the reaction or to increase heat transfer rates and thus secure a shorter cycle.

This definition is so broad that a great variety of chemical processing equipment falls under it, including such diverse types as digesters, stills, kettles, reactors, nitrators, sulfonators, vulcanizers, cookers, etc. This article, therefore, will be restricted to a discussion of the applications and design features of autoclaves for moderate or high pressures and temperatures, the type of autoclave that is particularly adapted to such unit processes as hydrogenation, dehydrogenation,

amination, ammonolysis, carbonation, hydrolysis, oxidation, hydration, polymerization, and other organic syntheses.

As a further restriction, no attempt will be made to discuss the pipelike type of autoclave (extensively used in the petroleum industry and beginning to be widely used in the strictly chemical industry) utilized in high-pressure catalytic circulatory plants for the synthesis of ammonia, the synthesis of methyl alcohol, the hydrogenation of crude oils, and similar unit processes; for although internal structures for heat interchange and support of the catalyst may be quite complicated, such autoclaves are essentially heavy-walled tubes and do not, in general, present such a diversity of design problems as does the batch-type autoclave discussed here. Dodge's treatment of the subject (2) is recommended, both because it describes the applications of high pressure autoclaves to the

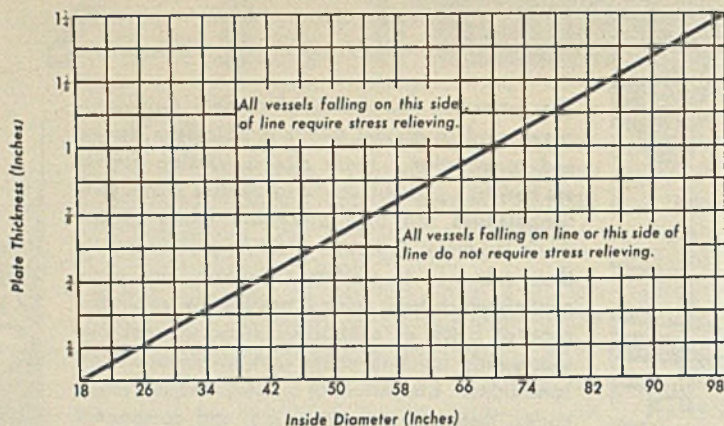


Figure 1. Necessity for Stress Relieving Depends upon Relation between Plate Thickness and Inside Diameter

most important industrial pressure processes and because it includes a bibliography which comprehensively covers the field.

BASIC DESIGN

The design of process equipment may be divided roughly into two parts. The physical design is concerned chiefly with strength and satisfactory mechanical engineering. The functional design is in the realm of chemical engineering. Unless a thorough understanding of the process variables is obtained, and all requirements of the particular chemical reactions and phase changes are provided for, the finest mechanical design possible will not ensure a satisfactory product. The autoclave designer must have a thorough understanding of fluid flow, heat transfer, mixing, and other unit operations as related to the high pressure autoclave; the chemical engineer entrusted with the design of an autoclave is not in position adequately to analyze the problem until he has the following information:

1. Where it is permissible, he should be furnished complete information about the process, the product, and the reaction. Where a secret process is involved or a radically different new product renders it inadvisable to release complete information as to the reactants and the product, he should be given the physical characteristics of the reactants, particularly viscosities at different stages, vapor pressures, corrosion data, specific heats, boiling points, specific gravities, and the heat of reaction. He will also require the time-temperature-pressure cycle data. The more complete the information, the better the engineer's position to select the best design possible.
2. If the manufacture of more than one product in the autoclave is anticipated, the engineer should be given the range of working pressures, range of temperatures, maximum volumetric capacity desired, and the maximum and minimum working capacities desired. From these (and preferably more complete data) the engineer may be able to develop a flexible design suitable for a number of products.
3. If not specified, the engineer must select the materials of construction; hence, he should be furnished complete information regarding past experience as to corrosion and contamination. If a new product is involved, laboratory data on corrosion tests should be made available. Since they have no control over operating conditions, equipment manufacturers obviously cannot make guarantees against corrosion; it is therefore doubly important that great care be exercised in selecting suitable materials of construction.

SAFETY FACTOR

Because of the trend toward higher pressures and temperatures, it is imperative that the design engineer keep abreast of the latest data on materials of construction, on design

stresses, and on practicable, economical shop fabricating methods. The A. S. M. E. Code (1) crystallizes seasoned and tried ideas into a valuable and workable handbook of pressure vessel design. The code is constantly in process of revision; special cases are reviewed by the Boiler Code Committee, and their findings are published as Addenda. Normally, the code is revised as a whole and reissued about every second year. In many of our states and in Canada the A. S. M. E. Code is mandatory for all pressure vessels; in other states it is the recognized unofficial authority. In all cases the principles and rules set up should be followed as minimal requirements if the user is to be assured of receiving process equipment which embodies the latest accepted principles of design and manufacture. If the manufacturing engineer is experienced in the high pressure-high temperature field, he is in position to handle special items properly, the design

of which is not within the scope of the code. It is on such points that the skill and experience of the manufacturing engineer is of most value to the prospective user; no code, no matter how comprehensive, can cover completely so diversified and complicated a field as that of process equipment or anticipate the new problems requiring original designs that are constantly arising. Only a manufacturing engineer of wide experience is in position to exercise sound judgment in such cases and thus assure to users the type of equipment which incorporates a high safety factor. At present the A. S. M. E. Code provides for a safety factor of 4 and this should be the minimal requirement in the design of all autoclaves. (The safety factor was only recently changed from 5 to 4 but for some details the safety factor remains at the higher value. For specific applications, refer to Case No. 979 of the A. S. M. E. Boiler Code Committee.)

Only the best of materials and the highest quality of workmanship should be used in the fabrication of autoclaves. A large proportion of autoclaves for pressure-temperature reactions are designed for such high working pressures and operating temperatures that Class I welding is required; this means that under the provisions of the A. S. M. E. Code for Unfired Pressure Vessels the procedure specified in Paragraph U-68 must be followed, as pressure vessels constructed in accordance with this procedure may be used for any service. For more moderate conditions, the rules of Paragraph U-69 may be followed. To comply with the rules of Paragraph U-68 the fabricator must:

1. X-ray all longitudinal and all circumferential butt welds. A prerequisite of the x-ray investigation is the grinding of welds inside and outside for uniformity in comparing the results of exposures.
2. Stress relieve the entire vessel in an annealing furnace to relieve local stresses induced by heat of welding. For carbon steels, the code requires stress relieving at 1150° F. for a period equal to one hour per inch of thickness of the vessel wall.
3. Prepare test plates, using the same technique and material as for the tank proper. These test plates are checked for tensile strength, ductility, and density of weld. All welding must be performed by welders who have demonstrated their ability by definite prescribed tests given periodically.
4. Subject the completed vessel to a hydrostatic test of double the maximum design pressure.

When a vessel is constructed in accordance with Paragraph U-68, the longitudinal seam is recognized as having an efficiency of 95 per cent for computing the wall thickness.

As stated above, where service conditions are only moderately severe, an autoclave or pressure vessel may be constructed in accordance with the rules of Paragraph U-69 of

the code. The following limitations, however, apply, and exceeding any of them makes it mandatory to adhere to the rules of Paragraph U-68 as summarized above:

1. The vessel must not be used for the storage of lethal gases or liquids (hydrocyanic acid, carbonyl chloride, cyanogen, mustard gas, and xylol bromide).
2. The maximum working pressure cannot exceed 600 pounds per square inch.
3. The shell thickness cannot exceed 1.5 inches.

Under this class of construction the welders must also have shown their ability to comply with the requirements of good welding by periodic tests. No x-ray of the welds is made, nor are test plates prepared. Vessels are stress-relieved only when:

1. The plate thickness exceeds 1.25 inches.
2. The wall thickness is greater than 0.58 inch and the shell diameter is less than 20 inches.
3. The diameter is less than $120t - 50$, where t = thickness in inches.

Figure 1 shows graphically when such vessels must be stress-relieved, as evaluated by item 3 above. For a vessel so constructed, the efficiency of its welded longitudinal seam is 85 per cent of that of the solid plate in computing its wall thickness.

As in all engineering work, the final design of a pressure vessel represents a number of compromises between conflicting conditions. The job of the designer is to see that optimum conditions are realized. For example, since the volume of a vessel is usually determined by process requirements, the mechanical design of the vessel involves a balance between wall thickness and diameter. The smaller the diameter of the vessel, the thinner will be the wall thickness for a given pressure, as indicated by the formula for a cylinder subjected to internal pressure:

$$t = PR/SE \quad (1)$$

where t = shell thickness, inches
 P = maximum working pressure, lb./sq. in.
 R = inside radius of cylindrical shell, inches
 S = allowable working stress = $1/4$ of minimum tensile strength, lb./sq. in.
 E = efficiency of longitudinal joint

A small-diameter vessel may greatly magnify the problem of placing openings in the top head of the autoclave, or it may mean more circumferential welds, or it may increase the problems of agitation. A large-diameter vessel may run afoul of railroad clearances, size of annealing furnace, or size of shell and head plates normally rolled at the steel mill. Also a large-diameter vessel may mean that the wall thickness will become excessive. Too frequently the dimensions of the autoclave are decided upon without real engineering thought being given to the problem.

After a satisfactory balance between diameter, length, and shell thickness has been determined, the next consideration is the selection of proper type of head or end closure. Hemispherical, A. S. M. E., and semiellipsoidal heads are the three principal types used in vessels for high internal pressures.

While the hemispherical head is the strongest for a given plate thickness, it is difficult to form, and frequently special forming dies are required which tend to make its cost prohibitive.

The semiellipsoidal head is next to the hemispherical head in strength for a given plate thickness. This type, in which half the minor axis or depth of head is equal to at least one fourth of the inside diameter of the head, is readily available in a wide range of sizes, with no premiums for special dies. Because of its strength it is extensively used for the higher pressure ranges (Figure 2). The minimum plate thickness is calculated by formula 1 (when the head is formed from a single plate, the joint efficiency $E = 1.0$).

For moderate pressures a two-radius head may be employed. The most widely used pressure vessel head of this type is the A. S. M. E. head, in which the principal radius is equal to or less than the diameter of the head, and the corner or knuckle radius is at least three times the thickness of the head plate or at least 6 per cent of the diameter of the head, whichever is the greater. The thickness of an A. S. M. E. head is calculated from the formula:

$$t = 8.33PL/2TSE \quad (2)$$

where t = thickness of plate, inches
 P = maximum working pressure, lb./sq. in.
 L = radius to which head is dished, measured on concave side of head, inches
 TS = tensile strength of plate, lb./sq. in.
 E = efficiency of weakest joint used in forming head ($E = 1.0$ when head is formed from single sheet)

Thus far we have discussed vessels subjected to internal pressures. The engineer may also be confronted by a situation where the pressures are external to the vessel. For a dished head subject to pressure on the convex side, as in the case of a steam-jacketed head, the maximum allowable working pressure is only 60 per cent of that permitted for the same head with pressure on the concave side. In other words, formulas 1 and 2 are modified by the insertion of the factor 0.6 in the denominator. Figure 2 shows the dimensions and capacities of the heads in question. Likewise, for cylindrical shells subjected to external pressure, special provisions must be made in the design. Figure 3 may be used to determine the thickness of the cylindrical shell when the pressure is external.

In many autoclaves the wall thickness is large compared to the diameter of the vessel. For this condition circumferential stresses cannot be considered as being uniformly distributed throughout the vessel wall, and therefore special

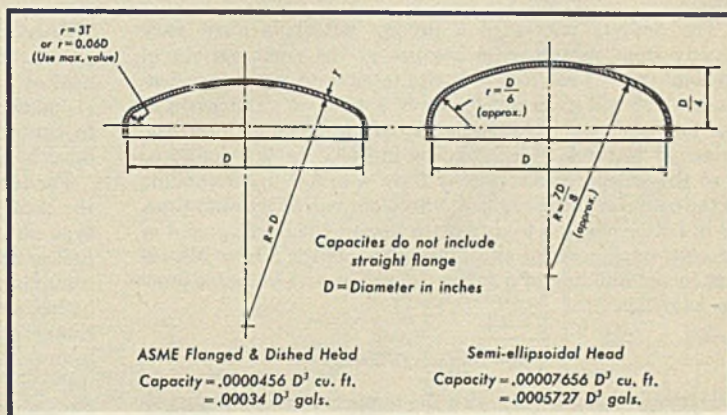


Figure 2. Diagrams of Most Commonly Used, A. S. M. E. Code Approved, Types of Pressure Vessel Heads

For most conditions, the A.S.M.E. head will be thicker than the shell; it is normally used only for moderate or low pressures. Generally, elliptical heads are no thicker than the shell and are therefore normally used for higher pressures.

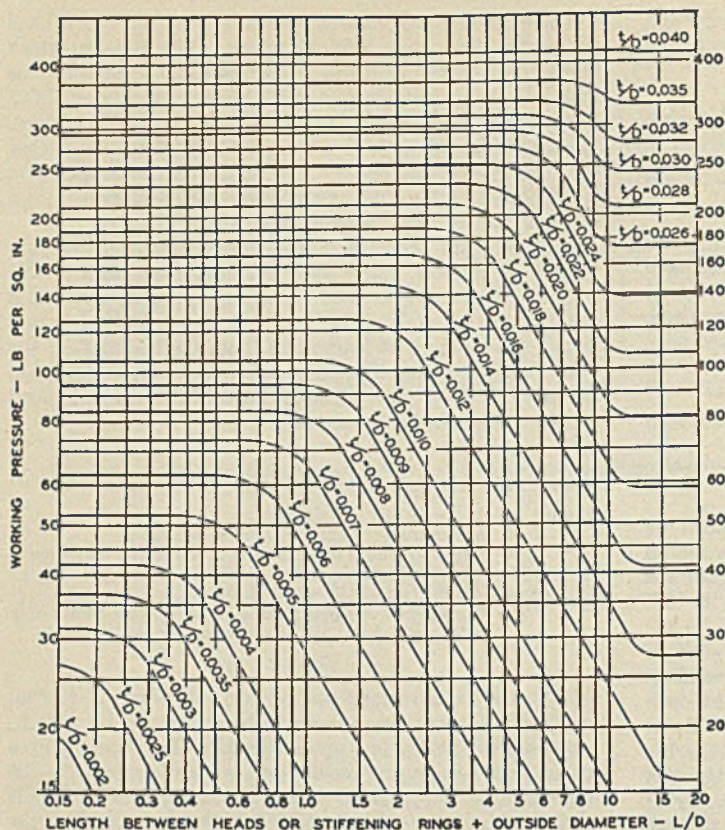


FIG. U-19 CHART FOR DETERMINING SHELL THICKNESS OF UNFIRED CYLINDRICAL VESSELS SUBJECTED TO EXTERNAL PRESSURE WHEN CONSTRUCTED OF STEEL COMPLYING WITH SPECIFICATIONS S-1, S-2, S-4, S-17, S-18, S-25, S-26, S-27

Figure 3. Chart (Reproduced from A. S. M. E. Code) to Facilitate Calculation of Shell Thickness of Unfired Pressure Vessels Subject to External Pressure

design methods must be applied. For many high pressure installations, therefore, the autoclave shell cannot be treated as a thin-walled vessel so the Lamé equation is used instead of formula 1 to determine the proper wall thickness. Thick-walled vessel design is separately discussed later in this article.

The design features of a process autoclave must vary greatly from case to case because of the great variety of applications. Therefore it is not feasible to write specifications which will cover a "standard" autoclave. The intent of the following specifications is to outline, in brief form, the principal features which may be included in the design so that the prospective user may have a better understanding of the manufacturing engineer's problem and, at the same time, be in better position to cooperate toward the development of an efficient functional and mechanical design which will result in the building of a safe, economical, and workable process autoclave.

HEATING SYSTEMS

Heating methods vary with the temperatures that must be reached, the time available to bring the charge up to heat, the degree of control required, the necessary forced cooling, existing plant facilities, and cost and availability of fuels. No single method may be universally applied; all methods have specific advantages as well as limitations, and each case

must be studied in order to select the heating system with most merit.

Based on the maximum working temperature of the charge, autoclaves may be arbitrarily classified as:

1. Low temperature type, with a maximum operating temperature of 350° F.
2. Medium temperature type, with operating temperatures from 350° to 525° F.
3. High temperature type, with operating temperatures ranging from 525° F. upward.

An attempt is made below to evaluate the various heating methods available with respect to general operating characteristics, initial cost, and comparable cost per unit of utilized heat. Since operating costs are contingent to a large extent upon local conditions, plant facilities, and availability of the fuel under discussion, it is obviously difficult to draw conclusions, except in a general and relative way.

HOT WATER HEATING. In some few cases there are applications for an autoclave where the reaction or the product is particularly sensitive to heat. In these instances hot water circulating systems may be used. Such systems are simple and inexpensive, and permit close control of temperature. Two types of systems are in general use. The simplest is the open system and consists principally of a circulating pump, an open reservoir tank holding water into which live steam is sparged, necessary interconnecting piping between the reservoir tank and the autoclave, and a thermostatically controlled steam valve for controlling the water temperature. In the closed system a heat exchanger is substituted for the open reservoir tank, an

air vent valve is provided, and the system is usually designed to operate under a pressure of 20 to 30 pounds per square inch. The closed system responds better to automatic control than does the open system and is also somewhat more flexible in applications.

STEAM HEATING. "Vapor", or steam at less than atmospheric pressure, is sometimes used instead of hot water for heating when temperatures less than 212° F. are required. Its main disadvantage lies in the fact that it is rather difficult to control and that normally some device such as a pump must be used to remove condensate.

For temperatures from 212° to 350° F., saturated steam is the most common heating medium for a low temperature type autoclave. Unlike the relatively thin-walled ordinary processing vessel, the internal pressures in autoclaves are commonly so high that the inner shell is quite thick and thus higher steam pressures in the jacket are possible at only a comparatively slight increase in initial cost. Hence, if there is an existing source of steam at 300 to 500 pounds per square inch gage, it can be used for jacket heating, and an operating temperature of 400° to 450° F. is thus obtained. In most plants, however, steam is available only at a maximum pressure of 150 pounds per square inch gage, corresponding to an operating temperature of 350° F.

Steam jackets may readily be designed for water cooling and permit excellent control over exothermic processes.

Where internal steam coils are used instead of, or to supplement, steam jackets, the same results follow.

Saturated steam for low temperature processing has all the advantages of high rate of heat transfer, excellent control, and, generally, low cost per utilized B. t. u.

DIRECT FIRING. This has been, and probably still is, the most common method of obtaining medium and high temperatures. The fuel may be gas, oil, coal, or coke; the first two are preferable because of ease of control. There are no temperature limitations within the range under consideration. The initial cost is comparatively low, the mechanism of the system is simple, and the relative cost per utilized B. t. u. is low. Heat is more quickly available, starting cold, than is the case with an indirect heating system employing a heat transfer medium such as Dowtherm or hot oil. Also the rate of heating in the higher temperature range may be more rapid than with an indirect heating system. Thus, heating cycles may be much shorter when direct firing is used. For small units the heating furnace may be shop-assembled and shipped ready for operation. The complete autoclave and heating system is self-contained and does not involve boilers, pressure piping, and other auxiliary equipment (Figures 4 and 5).

While direct firing has certain inherent disadvantages, in too many cases this method of heating has fallen into disrepute undeservedly. Too commonly, for instance, a processing vessel is purchased for direct-fired service with stress being laid on such elements of design as working pressures, operating temperatures, process agitation, mechanical features such as connections, etc., whereas little or no stress is placed on the fact that the vessel is to be direct-fired, on the temperature differences that will obtain, and on other equally important considerations. Then, when received in the field, a furnace is hurriedly designed and the vessel installed. This practice is to be deprecated as it too frequently results in improper processing, local overheating, and burned-out equipment, not to speak of poor fuel economy.

The method of heating process equipment is as functional and inherently an element of design as any other feature; this statement is especially applicable to direct-fired equipment. In so far as autoclaves are concerned, the temperatures and conditions prevailing in the setting should be given consideration in selecting the materials of construction. Thermal stresses must receive more careful consideration than for most methods of heating. If local overheating and even danger of burning the shell of the autoclave are to be avoided, the agitator design will have to be based not only on the necessary process agitation but temperature gradients through the shell, the specific heat, and the viscosity of the charge in order to ensure that liquid velocities past the heated shell are adequate to take away heat as fast as it is transmitted and to reduce the inert film next to the shell to a minimum in the interest of efficient heat transfer.

It follows, then, that furnace design is equally important. Not only must direct impingement of the flame on the shell be avoided to prevent carburization, oxidation, and hot spots, but the design must ensure both proper and uniform temperatures around the shell. In addition, if good fuel economy is to be obtained, efficient burners must be selected and the furnace must be designed to ensure proper combustion. As a safety precaution interlocking controls or alarms should be provided to prevent overheating or damage to the autoclave or the charge in the event that power failure stops agitation. Furnaces should be so insulated that the working area around the autoclave will not become uncomfortably hot. Direct-fired autoclaves should be isolated from combustible vapors, and carbon dioxide or steam smothering systems provided to minimize fire hazard.

It is recommended that direct-fired autoclaves be purchased as complete units with efficient burners, furnaces, and controls from one manufacturer in order to ensure integration and proper functioning of the equipment.

It should be borne in mind that direct-fired autoclaves may be arranged for forced cooling through refluxing, internal

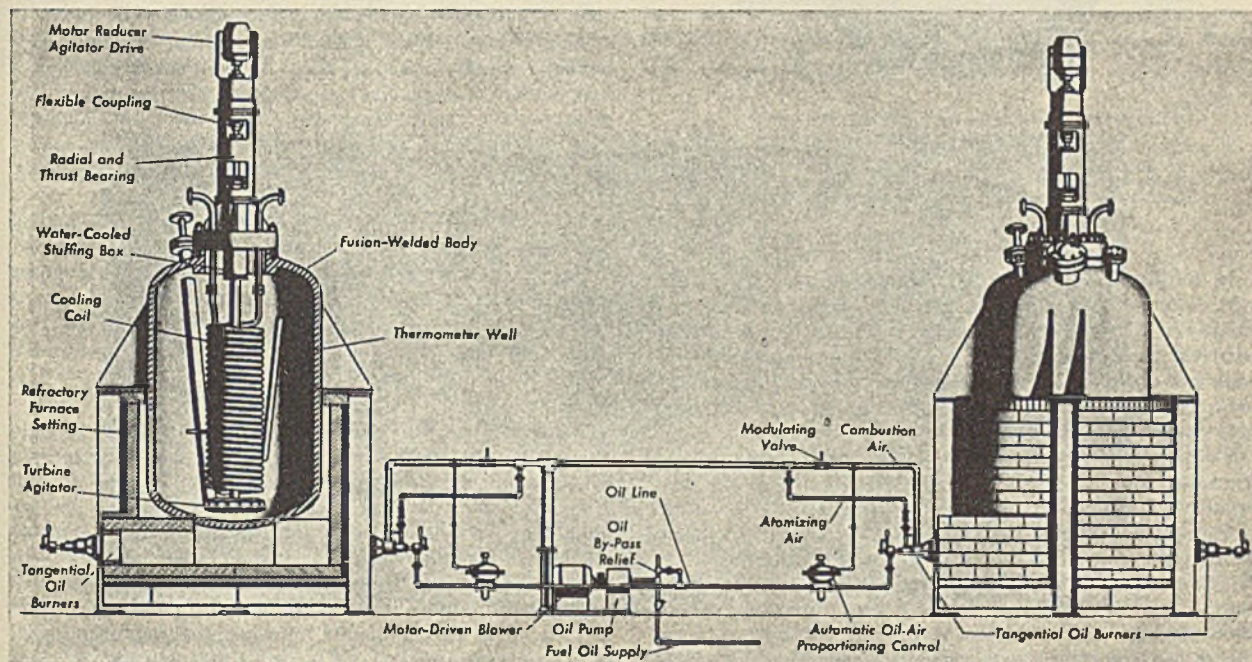


Figure 4. Installation of Two Direct-Fired Autoclaves

Furnace setting and arrangement of oil burning equipment and controls are shown; each autoclave is equipped with cooling coil for control of reaction and quick cooling before discharge.

coils, and/or external water jackets or water spraying systems to provide for control of exothermic reactions as well as quick cooling before discharge at the end of the cycle. Air also may be used for cooling, but it is difficult to secure good results, not only because air is a poor cooling medium but because it is difficult to design a firebox that does not have a large heat capacity to add to the duty; however, there are special cases for which it is adaptable.

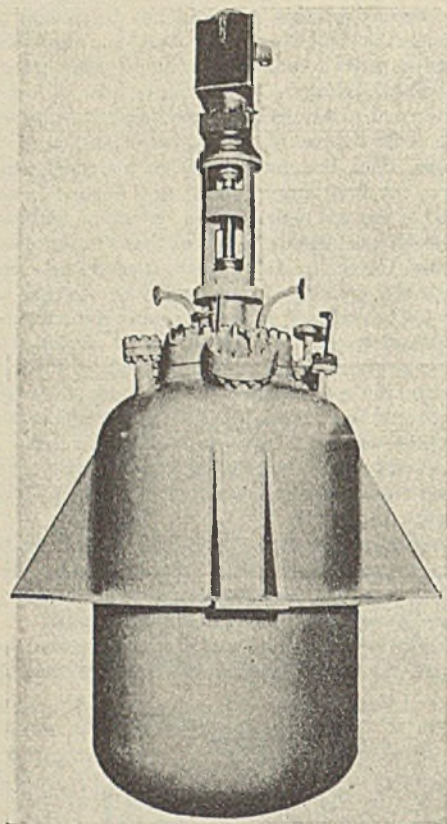


Figure 5. Shop Photograph of One of the Autoclaves Featured in Figure 4

It measured 4 feet 8 inches i. d. and 5 feet 7 inches high, straight shell, and was constructed of firebox quality steel for a pressure of 950 pounds per square inch at 730° F.

In addition, it is frequently necessary to cool direct-fired autoclaves to prevent scorching of the film during the interval occurring between discharging and the introduction of the following batch. Also, in all process applications involving cooling of direct-fired autoclaves, the insulating value of furnace refractories must be carefully balanced against their heat storage capacity, since this heat is lost on cooling.

Unless special designs are resorted to, there is considerable fire hazard around direct-fired equipment. The large heat capacity of most fireboxes tends to cause upward coasting of temperatures long after burners have been shut off and thus makes it difficult to get accurate temperature control. However, these inherent disadvantages can be reduced by proper, coordinated design of both the autoclave and the heating equipment. It should be pointed out, however, that such designs are considerably more expensive (in so far as the heating equipment is concerned) than the usual inefficient, hazardous, "home-made" furnaces; but in the long run the extra expense is well justified.

INDIRECT FIRING. Indirect firing of the type where the products of combustion are recirculated around the autoclave has a definite advantage over direct firing in that somewhat better temperature control is possible; in addition, it is possible to apply the heat to the autoclave in horizontal bands or sections (through which the hot circulating gases are admitted by a blast gate), and it then becomes feasible to process either large or small batches without heating the autoclave above the liquid level (Figure 6). Indirect firing is of particular value for heating a battery of autoclaves with one furnace serving the entire battery; not only are the over-all initial costs reduced, but control is simplified. Finally, indirect firing may be so designed as to eliminate fire hazard.

When forced cooling of an indirect-fired autoclave is desired, any of the methods suitable for cooling direct-fired units may be used. Air cooling is utilized more frequently than with direct-fired units, particularly for units where the furnace or burner is separate from and connected to the autoclave by ducts.

Indirect firing systems, however, tend towards high initial cost and must be carefully designed and provided with well engineered baffling systems if local overheating and hot spots are to be avoided.

HOT OIL HEATING. Hot oil, heated in a direct-fired furnace and circulated through the autoclave jacket or coils by a pump, has reasonably good temperature control; where the installation is of sufficient size, the cost per utilized B. t. u. is average or better.

Heating oils, even of the best grades available today, are limited to a maximum operating temperature in the neighborhood of 600° F., and if operated at this maximum temperature continuously, excessive carbonization is likely to occur. Carbon deposits may then accumulate in the tubes of the heater and cause them to burn out, and the resulting fire may be both dangerous and expensive. The maximum operating temperature in an oil-heated autoclave is limited to about 525° F. Owing to the high viscosity of heating oils at room temperature (particularly in winter), a considerable length of time is required to heat up the system initially.

The oil in a system of this type operates at a moderate working pressure of around 20 to 30 pounds per square inch maximum. The auxiliary equipment, such as pumps, expansion tanks, and piping system, can become quite elaborate; together with the oil heating furnace required, this makes the initial cost of a heating system of this type relatively expensive.

Attempts at forced cooling have been made with hot oil systems where the same oil used for heating is circulated through a water cooler and then through the autoclave jacket or coils. The resultant cooling effect has been small and unsatisfactory, principally as a result of the difficulty of extracting heat from a fluid whose viscosity increases rapidly with drop in temperature.

DOWTHERM LIQUID HEATING. Dowtherm A is a eutectic mixture having a composition of 26.5 per cent diphenyl and 73.5 per cent diphenyl oxide, a melting point of 53.6° F., and a boiling point of 500° F. at atmospheric pressure. The hot liquid may be used in place of mineral oil as the heat-carrying medium. The Dowtherm is heated to a maximum temperature of 525° F., corresponding to 5 pounds per square inch gage pressure, in a direct-fired heater using either gas or oil as fuel. It is then circulated by a pump through the jacket or coils of the autoclave and returned to the heater. Except that a closed instead of an open system is used, the equipment requirements are essentially the same as for a hot oil circulating system. The maximum autoclave working tem-

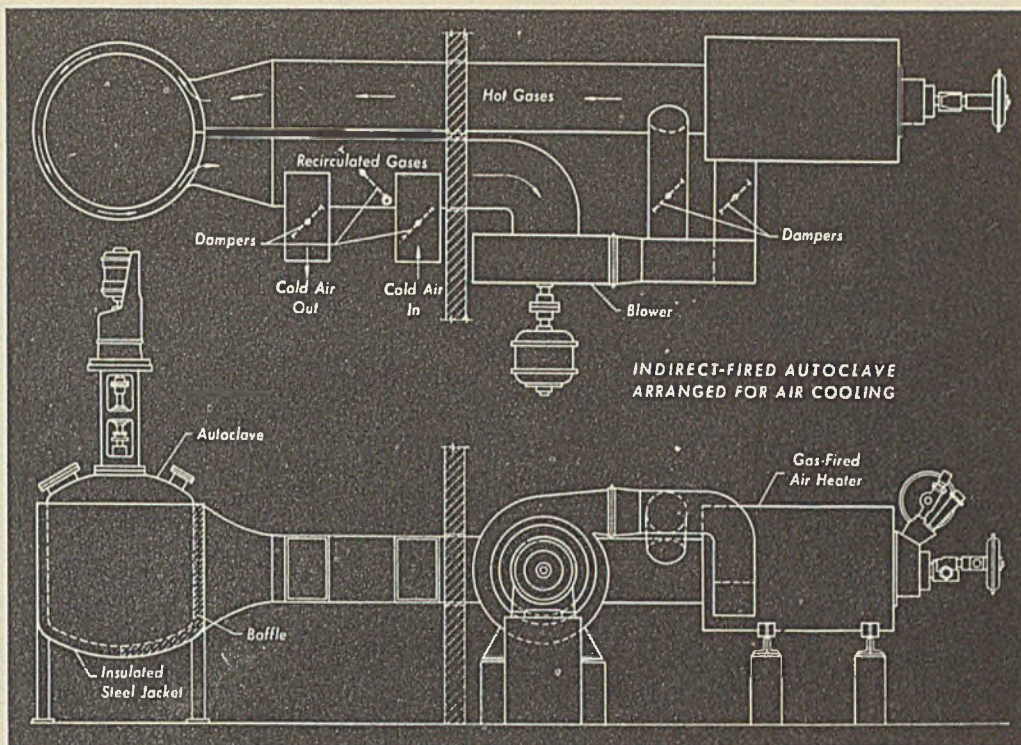


Figure 6. Method of Indirect Firing Where Combustion Products Are Recirculated around the Autoclave by an Alloy Steel High-Temperature Fan; by Closing Off Burner, Cold Air May Be Blown around the Autoclave for Cooling

perature with this method of heating is around 475°F . (Figure 7).

Although seldom done, it is feasible to circulate liquid Dowtherm at pressures up to 135 pounds per square inch, corresponding to a maximum Dowtherm temperature of 750°F . and an autoclave working temperature of around $675\text{--}700^{\circ}\text{F}$. This would be done only in exceptional cases, however,

since for autoclave operating temperatures above 500°F . it would be preferable to use Dowtherm vapor as the heating medium and to utilize its latent heat of condensation.

Due to the low viscosity of Dowtherm liquid at all temperatures above its melting point of 53.6°F ., the comparable heat transfer coefficients are excellent and the over-all heat efficiency may be very good.

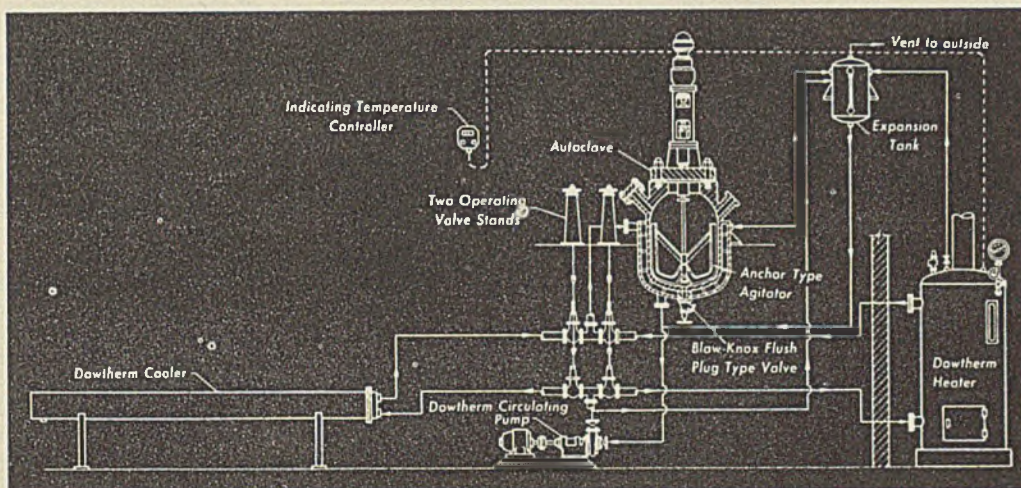


Figure 7. Liquid Dowtherm Heating and Cooling System Developed to Secure Quick and Effective Temperature Control for Medium Temperature Type Autoclaves Operating within a Range of $350^{\circ}\text{--}525^{\circ}\text{F}$.

By means of only two valve handles, full flow of either hot or cold liquid Dowtherm may be secured. Partial movement of valve handles permits any desired intermediate combination of hot and cold liquids, and thus provides exceptionally quick and easy temperature control.

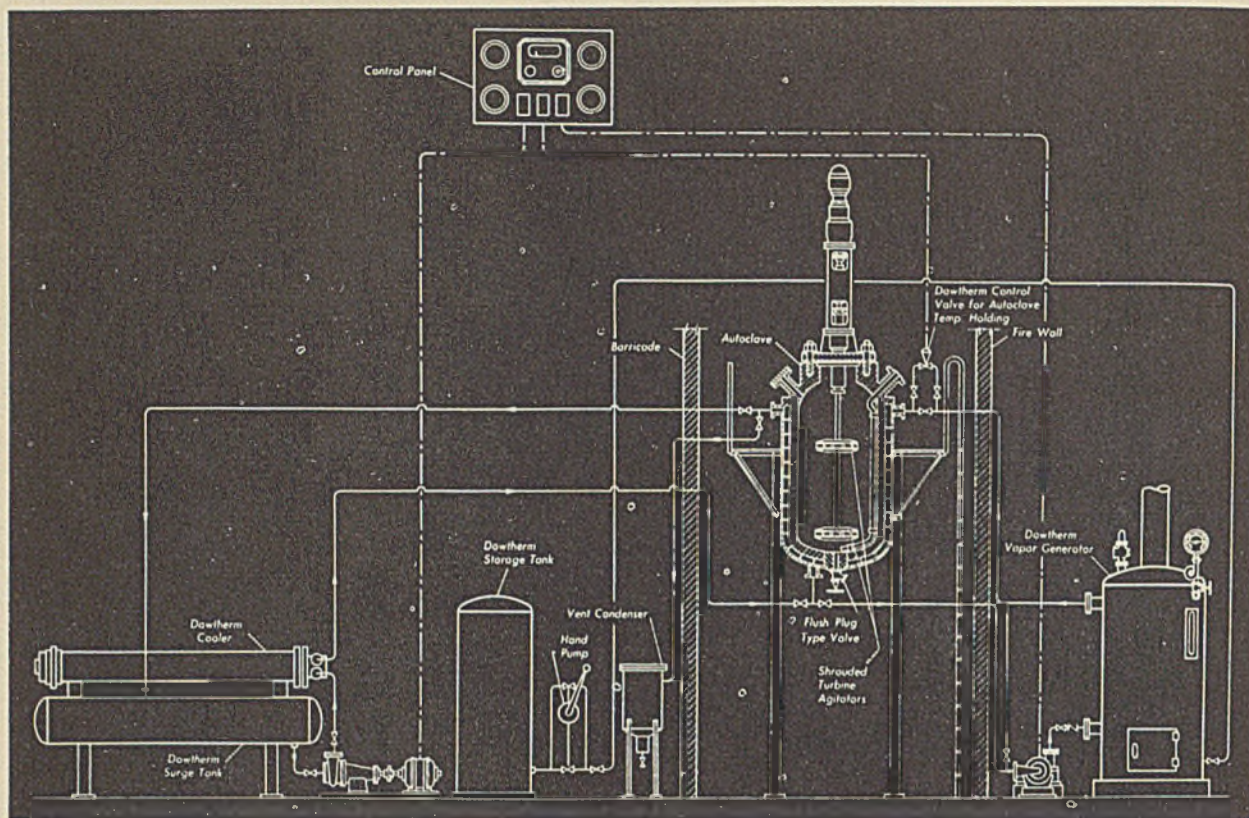


Figure 8. Typical Arrangement of Dowtherm Vapor-Heated Liquid-Cooled Autoclave

Effective and efficient forced cooling can readily be obtained by an independent cooling system using liquid Dowtherm as the cooling medium. Such a combined heating and cooling system permits close control of operating temperatures within the autoclave.

DOWTHERM VAPOR HEATING. Dowtherm A vapor is undoubtedly the most flexible and readily controlled heating medium available today for operating temperatures up to 675° F. (Figure 8). A gas- or oil-fired boiler generates Dowtherm vapor at 560° to 700° F. which correspond to 15 and 88 pounds per square inch gage, respectively. For intermittent duty, Dowtherm vapor temperatures have been carried as high as 750° F., corresponding to a gage pressure of 135 pounds per square inch. However, at present for continuous service, the recommended maximum working temperature is 700° F., due to the possibility of overheating and partial breakdown of the Dowtherm.

In transferring the heat from the direct-fired vapor generator to the autoclave, the Dowtherm vapor acts in exactly the same manner as saturated steam by condensing in the autoclave jacket and giving up its latent heat of vaporization to the charge. As in all condensing vapor systems, the overall heat transfer coefficient is excellent, and the resultant heat flow into the material is smooth and gentle, since there is a low mean temperature difference. Local overheating problems are eliminated or reduced.

Taking into consideration its flexibility and ease of temperature control, a Dowtherm vapor heating system will meet, and in most cases exceed, the performance of any other high temperature heating system commercially available at

present. Operating temperatures readily available range from 350° to 675° F. In the lower temperature range the Dowtherm vapor system operates under partial vacuum rather than pressure, but this does not involve any difficulties in design, control, or operation.

Probably no other high temperature heating system can be so readily equipped with effective forced cooling as the Dowtherm vapor type. After the heating period is over, the vapor and condensate valves are closed and Dowtherm liquid is circulated through the jacket from an independent, closed cooling system equipped with a separate circulating pump. If the autoclave has been designed with a divided heating jacket, it is necessary only to provide a cross-over valve connection between the two jackets in order to establish series flow of cooling liquid through the jacket. A system of spiral baffles in the jacket space directs the flow and materially increases turbulence of the cooling medium and thus increases the heat transmission from the charge to the circulating liquid. When sufficient cooling has been obtained to permit discharge, the circulating pump is stopped and the liquid Dowtherm drained by gravity down to the cooler and storage tank, after which the jacket is again ready for another heating cycle.

Although the initial cost of a combined heating and cooling system of this type is comparatively high, the actual operating and maintenance cost is low, comparing favorably with any direct or indirect method of high temperature heating.

ELECTRIC HEATING. Heating of process autoclaves by strip heaters clamped or otherwise fastened on the outside of the autoclave shell proper or by radiant heaters mounted at a

slight distance from the shell has excellent and simple heat control; the equipment is compact, neat, and clean, requires no pumps, furnaces, stacks, or settings; has a reasonably small fire hazard, and provides heat quickly merely by pushing the starting button. Depending on the temperature increase rate required, the practical upper limit of operating temperatures is probably in the neighborhood of 750° F. for strip heaters (Figure 9). With radiant heaters much higher operating temperatures may readily be obtained.

The initial cost of an electrically heated installation is relatively low, but the operating costs are above those of other high temperature heating systems. The over-all thermal efficiency, however, is practically 85 per cent, and higher operating costs are sometimes partially offset by the improvement in the over-all power factor of the plant, due to the 100 per cent resistance load.

Forced cooling can be obtained to some extent by blowing cold air around the dead air space between the autoclave and the insulating jacket. On an autoclave of appreciable size, where the ratio of square feet of cooling surface per gallon of charge is small, the rate of cooling is necessarily slow because of the low over-all heat transfer coefficient obtained. Better forced cooling may be obtained by internal cooling coils or by arranging the heating elements so that a portion of the autoclave shell may be water-jacketed.

Electric heating elements can be grouped in any way desirable, permitting sectionalized heating to accommodate batches of varying size. The usual arrangement is three horizontal bands all automatically controlled by thermostat, but manually subject to the operator's choice.

On special heat requirements involving long holding periods at appreciable loads, it may become advisable to arrange the heating elements in both delta and star grouping, the delta arrangement to be used for full load heat capacity during the heating up period and the star arrangement when merely holding the temperature. Such an arrangement is excellent as far as heater life is concerned, but the additional wiring and switch gear required add appreciably to the initial cost.

Usual wiring for all heating elements for alternating current is delta, with balanced phase loading on any one or all heating sections. Although it is possible to arrange electric heating elements for 440 volt current, the safest and most satisfactory voltage is 220. For small pilot units 110 volt, single phase current lends itself most readily to a simple and flexible, yet thoroughly satisfactory, control wiring.

INDUCTION HEATING. Because of the thick wall, the typical high pressure autoclave is particularly adaptable to induction heating

(Figures 10 and 11). Electric current is passed through an induction coil which consists of flat copper tubing wound on edge with insulation between each turn and mounted in a transit box as a complete unit. Water is circulated through the primary coil to keep it cool. The secondary "coil" consists of the metal walls of the autoclave, heat being generated by the eddy (Foucault) currents. Thus the induction or primary coil is cool at all times, and the heat is generated directly in the shell of the autoclave. This is important in high temperature work since uniform wall temperatures reduce the thermal stresses in the autoclave.

More heat per unit of time can be put into an autoclave shell by induction heating than by any other method. If small, induction-heated autoclaves are usually designed for single-phase current but if large, may be designed for two- or three-phase current. Low-frequency induction heating is applicable only to autoclaves fabricated of magnetic materials of construction.

OTHER METHODS OF HEATING. In addition, high temperature systems employing mercury, molten salts, or eutectic mixtures of low-melting-point metals as heat transfer media may be utilized for certain special applications. Such systems, however, are best adapted to processing temperatures above 700° F. Below that range Dowtherm vapor heating

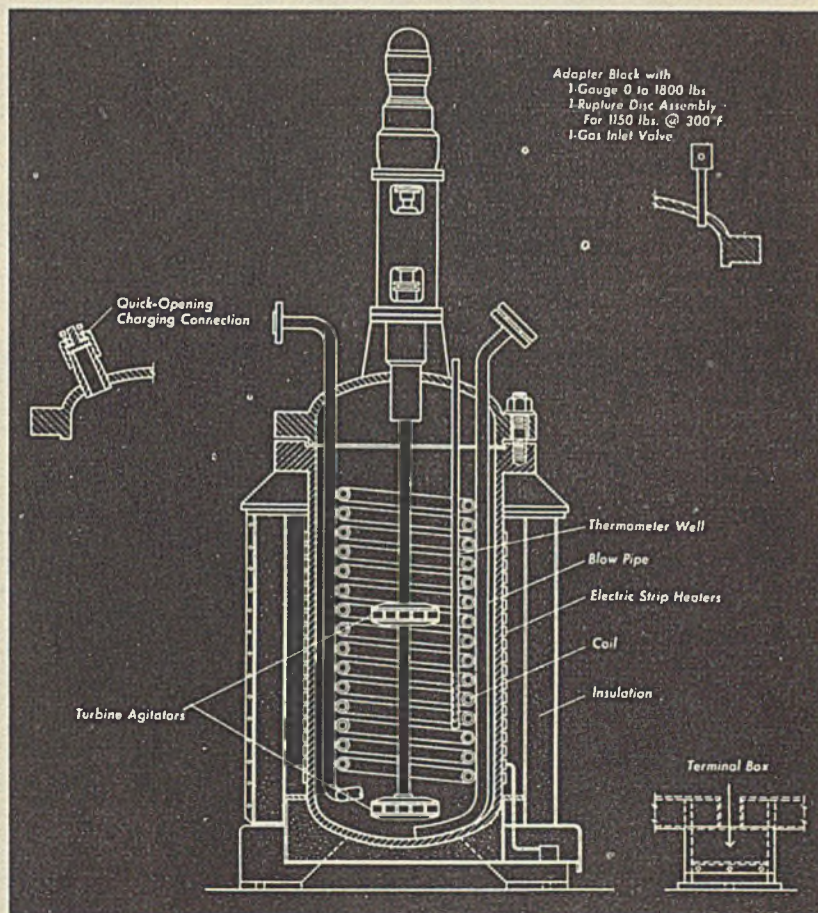


Figure 9. Electrically Heated, 134-Gallon Stainless Steel Autoclave for a Pressure of 900 Pounds per Square Inch at 375° F.

A coil is provided for steam boosting heating or water cooling. Heating elements are arranged in separately controlled bands to permit economical heating and to avoid the application of heat above the liquid level line. Two turbines are used to ensure good gas dispersion, strong agitation, and efficient heat transfer.

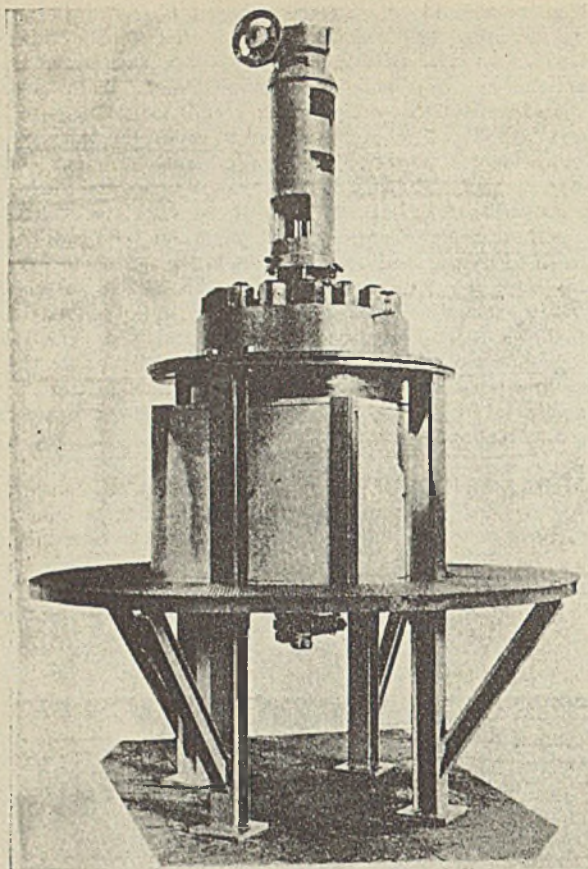


Figure 10. Induction-Heated, 42-Gallon Autoclave for Hydrogenation at a Pressure of 2000 Pounds per Square Inch

may be blended or dispersed as emulsions, fluids and finely divided solids dispersed as suspensions, gases dispersed in fluids, or soluble substances dissolved.

The general theory of mixing has received as little attention as any of the chemical engineering unit operations. The empirical nature of our knowledge of mixing and the wide variation in physical properties of the materials encountered in mixing problems have resulted in the development of many different agitator types. In most autoclave operations the primary function of agitation is to aid heat transfer and increase reaction rates. Anchor type agitators, turbines, and high speed propellers have generally proved to be the most suitable agitators and therefore are more frequently used in autoclaves than other types.

PROPELLER AGITATORS. Propellers are most effective for liquids of low viscosity, with or without the presence of light solids. They are also used effectively for circulating and mixing gases. Frequently one propeller is mounted high in the vessel to push a liquid or gas stream downward, and a second propeller on the same shaft is mounted low in the vessel to force a stream upward. The meeting of the two streams results in mixing and radial flow in a horizontal plane, a highly desirable change of direction. Excessive swirling of the charge may be overcome by locating the propeller shaft off-center with respect to the vertical center line of the autoclave. Draft tubes are frequently resorted to for single turbines to improve over-all circulation within the autoclave.

TURBINE MIXERS. The turbine mixer is best described as a centrifugal pump without a casing, and its work can be translated into pumping capacity. Liquid or gas enters the impeller axially through the central opening, is accelerated by the vanes, and finally discharges tangentially from the impeller at high velocity. In the case of two opposed propeller mixers, the directional change from vertical to horizontal is

systems are recommended as having a lower initial cost and higher efficiency, and requiring less maintenance.

AGITATION

Agitation of the charge in an autoclave is used to promote reaction and to produce some particular physical state. Chemical reaction rates usually increase with temperature and with more intimate contact between the reactants. Mechanical agitation promotes the flow of heat by forcing convection in the mass and by reducing the film resistance at the vessel wall. Also, agitation breaks up agglomerated solids and thereby increases the surface of contact and the rate at which reacting particles come into close proximity.

An important purpose of agitation or mixing is to bring a number of materials together in a physically homogeneous mixture. Thus, two or more fluids

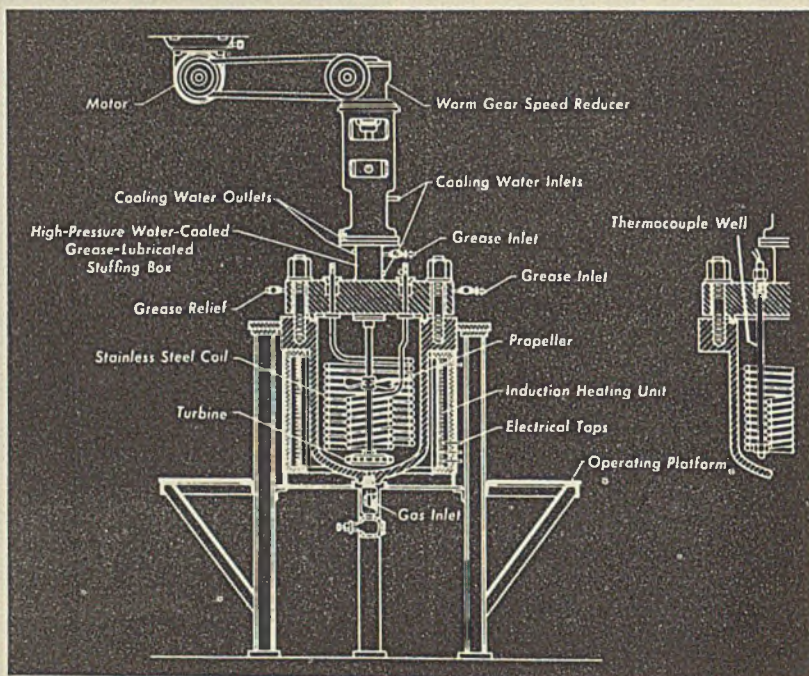


Figure 11. Arrangement of Induction-Heated Autoclave Shown in Figure 10

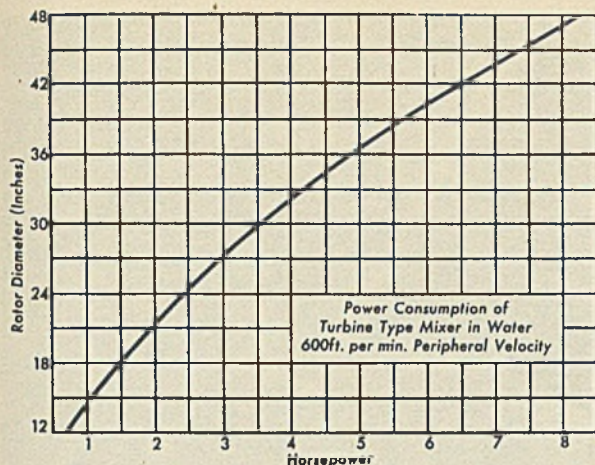


Figure 12. Power Consumption of Turbine Type Agitators with Respect to Rotor Diameter

accomplished by the meeting and deflection of two streams of currents, resulting in a certain amount of turbulence and considerable loss of kinetic energy. In the case of the turbine mixer, this deflection is accomplished mechanically, smoothly, and with little loss of kinetic energy so that the radial currents are still traveling at high velocity at the remote parts of the vessel. Turbines have a wide range of applicability and are especially adaptable to heat transfer, gas absorption, dispersion, and general mixing problems. Their power consumption is moderate (Figure 12). They are also the most satisfactory mixers for continuous work. They have a low starting torque and so can readily dig themselves out of sand, sediment, or a crystalline precipitate even when covered to a depth of several feet. Although the turbine mixer imparts a velocity to the liquid as high as does the high speed propeller, the turbine does so at a slower shaft speed than does a propeller. This condition greatly prolongs the life of shaft bearings and stuffing box packing. Another important attribute of the shrouded type turbine is that its power consumption does not materially increase with higher viscosity of the liquid charge. Although the surface drag (due to viscosity) increases, the pumping capacity of the turbine decreases, and the net result is only a slight increase in the power consumed. To offset these advantages, their structure is more complex than that of a propeller and, because of the greatly reduced shaft speed at which turbines rotate, they require larger speed reduction units than do propeller agitators.

For fluid materials having a viscosity up to approximately 5000 centipoises, the shrouded turbine (Figures 13 and 14) operating at moderate shaft speed has proved satisfactory and popular. For high viscosities the open type turbine of either straight or curved blade construction (Figures 13, 15, and 16) provides more positive turnover of material. Several stationary vertical swirl breakers attached to the straight shell will discourage the tendency of the mass of the charge to rotate at the same speed as the turbine and thus will greatly increase liquid turnover in the vertical direction. These can be located directly on the shell, or if supported on a heel plate, can be placed 1 to 3 inches from the shell in order to prevent dead corners or areas. Stators, consisting of ring type, stationary, deflecting baffles, are seldom used in autoclaves, as they tend to cut down the pumping capacity of the turbine and thus decrease the rate of flow of the material and lower the over-all heat transfer coefficient. Ring type deflecting baffles also add appreciably to the horsepower consumed. Only

where the primary object of the agitator is to disperse a gas or where some shearing action is desired is there any justification for the use of stationary ring baffles.

ANCHOR TYPE AGITATORS. When properly designed, anchor type agitators have the widest range of application of any of the mixing devices used in autoclaves. Anchor (sometimes referred to as horseshoe) agitators conform to the wall contour of the autoclave and, depending on service requirements, there may be either a wide gap or very little clearance between the agitator and the shell.

Many autoclaves are built to handle liquids having a wide range of viscosities. If an anchor agitator is designed to handle effectively an extremely viscous liquid, it may also be used for mixing liquids of very low viscosity. As a result of strength considerations, the reverse is not necessarily true. Consequently, a stout anchor agitator is the most popular type for multipurpose autoclaves.

The agitating action of the anchor type agitator may be made very effective. By varying the speed of rotation, the optimum turnover for a liquid of given viscosity may be obtained.

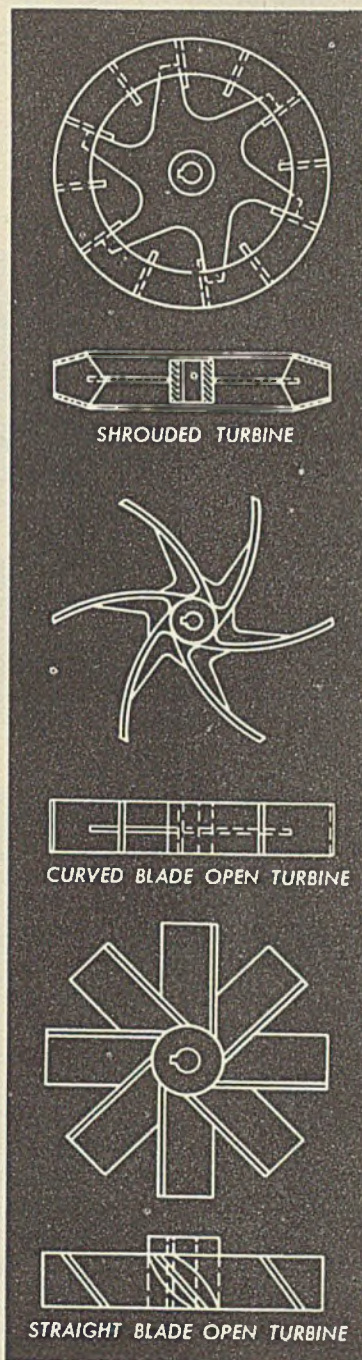


Figure 13. Most Commonly Used Types of Turbine Agitators

The shrouded turbine mixer has highest efficiency and greatest turnover for the mixing of low viscosity liquids. The curved-blade open turbine thoroughly mixes liquids and slurries at high viscosity. The straight-blade open turbine is particularly adapted to the breaking up of large, solid particles and incorporating them into a liquid to form a solution or suspension.

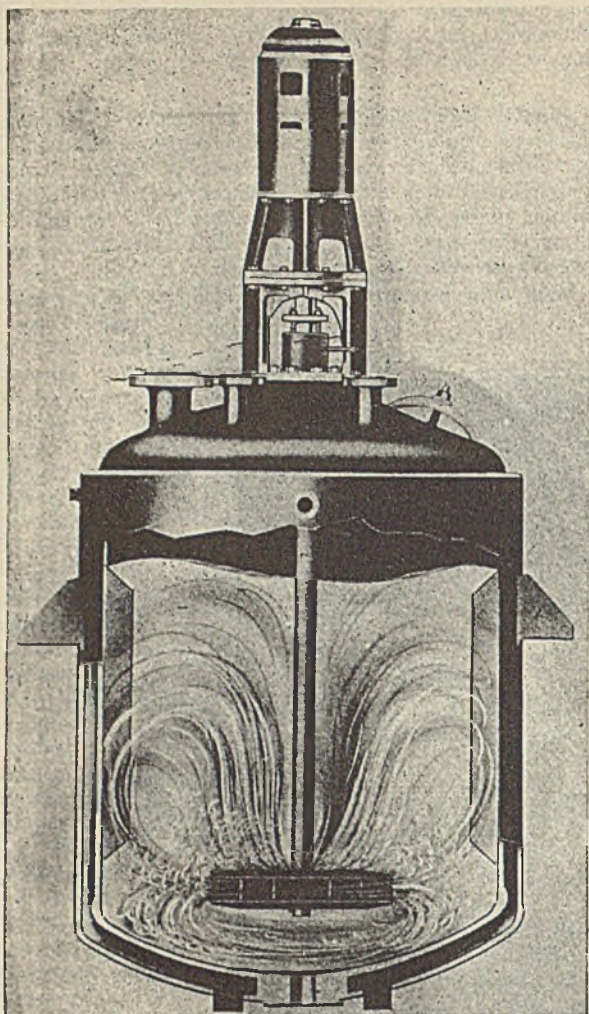


Figure 14. Flow Lines and Type of Agitation Secured with a Shrouded Turbine

Hence multispeed motors are frequently used for anchor-agitated autoclaves handling a variety of materials. Swirl stoppers should be provided to prevent rotation of the mass as a whole.

In heating viscous liquids, a close-clearance anchor agitator is very effective. If the agitator is revolved at fairly high speeds, stagnant films are swept from the wall through the "hydraulic brush" action of the liquid on the leading side of the blade. Excellent heat transfer is obtained in the case of more slowly revolved anchor agitators provided with spring-loaded scraping blades. The latter type is also used for solutions being evaporated where a cake of solid material tends to build up on the wall.

A well designed anchor agitator is versatile and effective, and operates with an efficiency that compares favorably with any other type of mixing device.

DOUBLE-MOTION AGITATORS. These are infrequently used in high pressure autoclaves because of the difficulty of designing and building a tight stuffing box of the intricate type required. By taking special precautions or by using upper and lower stuffing boxes, this difficulty can be overcome; but since it greatly increases both initial and maintenance costs, it is seldom done. When special processing problems do

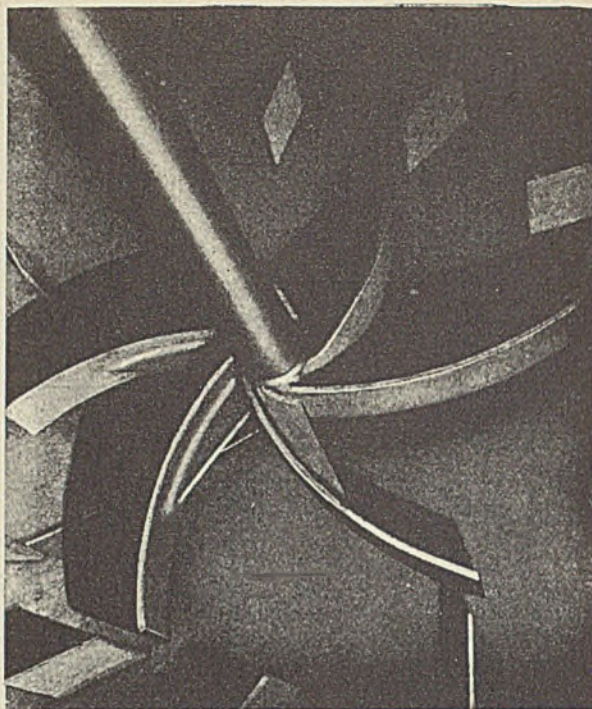


Figure 15. Curved-Blade Open Turbine for Handling a Solution with a Viscosity of 300,000 Centipoises. The fixed stator blades were used in this case to increase shearing action.

render a double motion agitator advisable, special combination agitators can be devised to fit requirements (Figure 17). The usual combination consists of a relatively slow moving gate or scraping outer agitator revolving in one direction and a blade type agitator mounted on the central shaft revolving in the other. If the charge is of high viscosity, a spiral agitator is frequently used instead of the inner or blade type agitator. Another good combination consists of the outer scraper agitator and propellers or turbines for the inner agitator. Double-motion agitators are applicable to the mixing of viscous or semiplastic materials such as soaps or greases and where the nature of the material is such that it must be scraped off the heated shell in the interest of good heat transfer.

SPECIAL AGITATORS. In cases where the autoclave is designed for one particular operation, the advantages of a highly specialized agitating mechanism may be considerable. Frequently a standard agitator may be modified for a given case, or several simple types may be combined to form a highly efficient compound agitator. At times properly selected tests should be made in the laboratory to secure data for design. Agitation problems such as the mixing of viscous and plastic materials (Figure 18), the suspension of finely divided metallic catalysts in solutions of low viscosity, and the dispersion of a liquid in another immiscible liquid of greatly different density, have been successfully solved by specially designed agitators.

EXTERNAL-CIRCULATION AND REVOLVING OR SHAKING AUTOCLAVES. In addition to placing an agitating device inside the autoclave body, proper, two other methods of securing agitation are worthy of comment.

External-circulation agitation may be secured by connecting a circulating pump through suitable piping to the autoclave

and recirculating the liquid charge. This method normally does not give as satisfactory agitation as the internal agitator. It is of real value, however, when short heating or cooling cycles are necessary and sufficient heat transfer surface is not available through the autoclave shell and any internal coils that may have been provided. In such cases the addition of a heat exchanger to the external circuit may furnish a satisfactory solution to the problem.

In dealing with gaseous pressures with a magnitude of several thousand pounds per square inch, mechanical limitations of available packing materials make it difficult to build a stuffing box that will be gastight over an extended time. There are a few reactions, in which the end point is determined by the gas pressure dropping to a predetermined point, which are so delicate that even minute gas leakage would interfere with accuracy of control. In such cases agitation may be secured by revolving or shaking the autoclave body. In other instances it is desirable to run several batches in the autoclave at the same time; this may be accomplished by using a shaking or oscillating autoclave and placing each charge in a separate bottle or container. Again, if the charge is extremely corrosive, a loose corrosion-resistant liner or a

spiral mixer. For liquid charges turbine or propeller type agitators may also be used. Figures 22, 23, and 24 illustrate typical horizontal autoclaves.

COMPONENT PARTS

DRIVES. The subject of mixing naturally brings up the means of transmitting power to the agitator. Although still supplied in occasional instances, the line shaft method of power transmission has given way to individual drives; these not only present neater installations but provide greater flexibility of operation and lower maintenance cost.

The gear-head motor or motor reducer is one of the most satisfactory means of delivering power to the mixer shaft at the speeds required for propeller or turbine agitators. The supporting structure for such a drive unit is of the simplest character. Motors can be of the open, enclosed, or explosion-proof type as required. This drive unit is perhaps the least expensive of the individual drives in current use.

Where headroom is low, another good arrangement for a constant-speed direct drive consists of a worm gear reducer coupled to a separate motor by means of a flexible coupling.

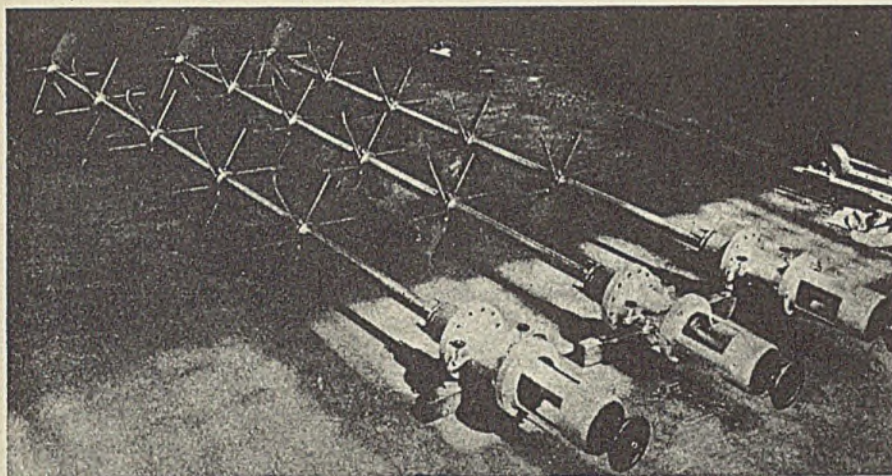


Figure 16 (Left). Open Type, 24-Inch-Diameter, Straight Blade, Nickel Multiturbine Mixers for Material Having a Viscosity of 200,000 Centipoises under a Working Pressure of 300 Pounds in a 36-Inch-Diameter Autoclave

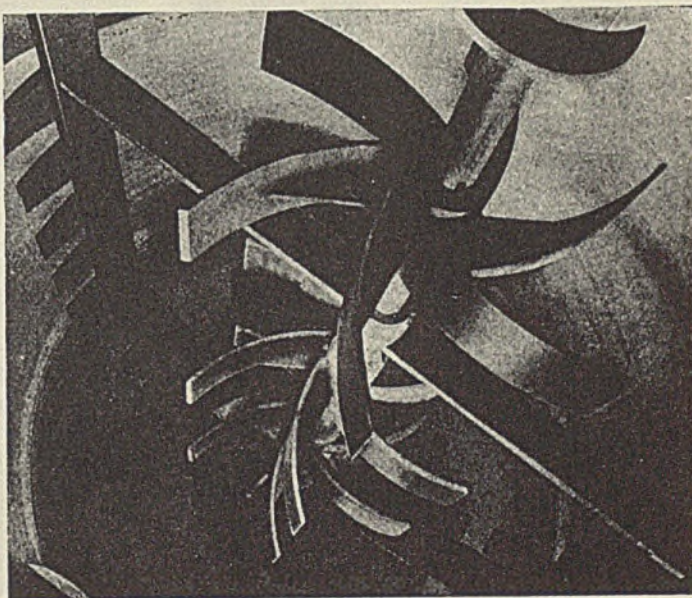


Figure 17 (Below). Double-Motion Agitator

A high-speed curved-blade open turbine on a solid shaft and a low-speed scraping agitator on a quill shaft turning in the opposite direction solved a difficult problem involving the quick cooling of a viscous liquid.

glass or ceramic bottle may be placed in a shaking, oscillating, or revolving autoclave to hold the charge; the bottle or liner is firmly anchored in place and, if necessary, surrounded by a suitable liquid heat transfer medium to transmit heat from the autoclave heating jacket. Figures 19, 20, and 21 illustrate the types of autoclaves utilized in solving such problems.

HORIZONTAL AUTOCLAVES. This type is used mainly for the processing of slurries, granular materials, or solids which do not readily flow and where agitation can best be secured by turning or lifting and dropping the charge; in order to offer greater liquid surface for evaporation or gas absorption, to secure a special mixing action, or to compensate for headroom limitations, the engineer occasionally resorts to horizontal agitated autoclaves. These involve no design problems that are radically different from those of the conventional vertical autoclave except that the style of agitator is normally limited to a horizontal shaft, blade type, or



A variation of this arrangement is to connect the motor to the worm gear reducer by a V-belt and pulley. By varying the effective diameter of the pulleys, the final output or mixer shaft speed can be varied over a rather wide range. This drive arrangement is more expensive than the gear-head motor combination and requires a more complex supporting structure, but has the advantage of lower headroom and easier replacement of either the motor or the speed reducer, and provides a relatively easy way of changing agitator speeds.

Because of viscosity changes during the processing cycle or because more than one product can be made in the same autoclave, several mixing speeds may be desired; the motors for either of these combinations may be of the two-, three-, or even four-speed type. When working with new products, it is not always possible to predetermine the most efficient agitator speed. In such cases it is sometimes wise to insert a variable-speed drive unit in the drive combination.

THRUST BEARINGS AND COUPLINGS. The agitator shaft should, whenever possible, be connected to the speed reduction unit by a flexible coupling. In addition, the radial and thrust loads on the shaft (which may be of large magnitude when an autoclave operates under high pressure) should be carried by an independent bearing assembly. Such an ar-

angement protects the shaft against possible misalignment and relieves the speed reduction unit of excessive loads.

STUFFING BOXES. The heart of an agitated autoclave is the stuffing box, for no agitated autoclave can function properly without an effective seal at the point where the agitator shaft passes through the autoclave body to join the prime mover. A good stuffing box must seal the pressure within the autoclave, and yet permit the agitator shaft to rotate freely and without undue overheating. It must have an internal bearing designed to provide proper guidance for the shaft to maintain its alignment and thus prevent "whipping". It must provide means for removing excess heat which may be conducted through the shaft from the charge, or which may be generated from the friction of the bearing and packing. Finally, it must be so constructed that all sections are easily accessible for assembly or replacement.

CONNECTIONS. For autoclaves designed for moderate working pressure, no particular trouble is encountered in laying out connections, but where high pressures are involved, the reverse is the case (Figure 25). High pressure autoclaves tend to be small in diameter to avoid excessive wall thickness; the top cover is usually of flanged and bolted construction, which means that studs and nuts must be massive to withstand the high stresses involved. Furthermore, the stuffing box is usually water-jacketed and therefore much larger in outside diameter than a low pressure stuffing box. The net result is that frequently little available space is left on the top cover; consequently, connections have to be kept to a minimum number.

Nozzles are flanged wherever possible, but where space does not permit, threaded connections are used. In the latter case, for high pressures parallel threads are preferred, backed up by a gasket so that the joint may be broken frequently and readily made tight again.

Because of space limitations, a connection frequently has to do double duty. For instance, after charging, a flanged thermometer well may be installed in the charging nozzle. Another device sometimes resorted to is to connect a forged, rectangular adapter block to an opening. This block may have connections on three or more sides and normally may be equipped with a pressure gage, a gas injection

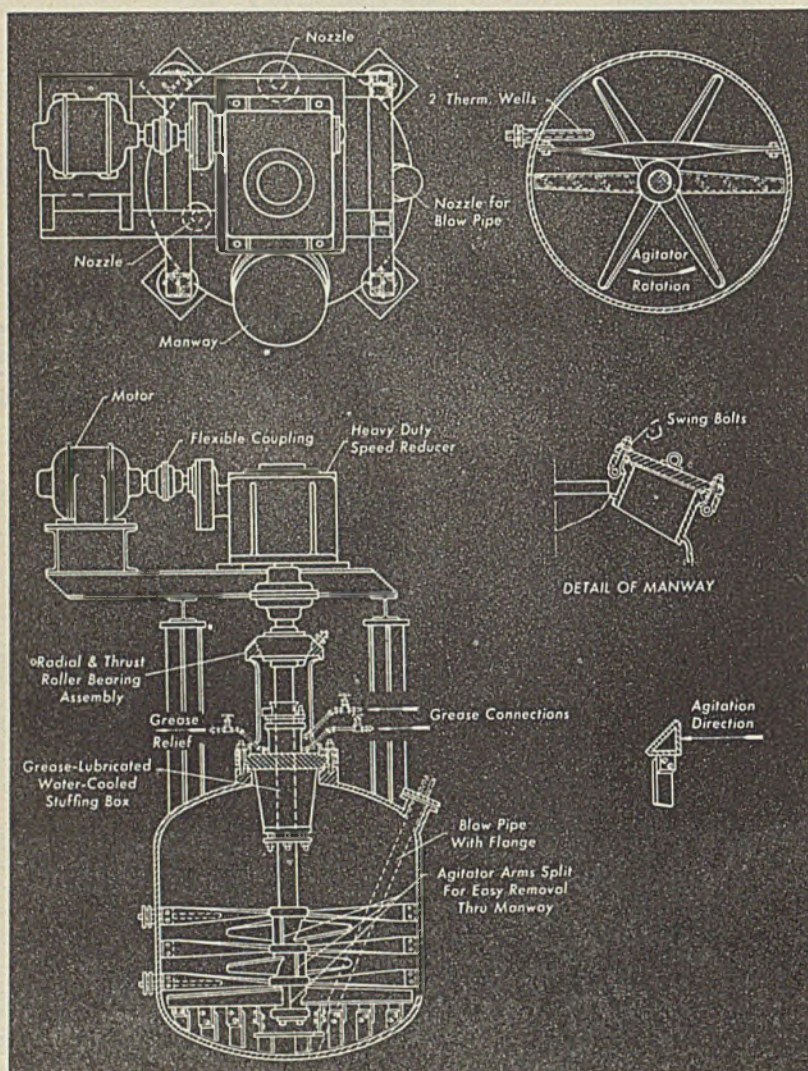
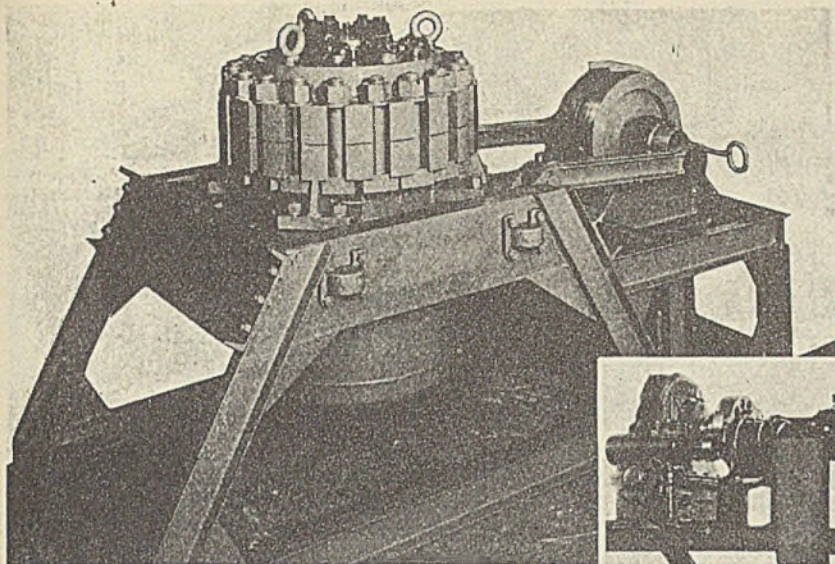
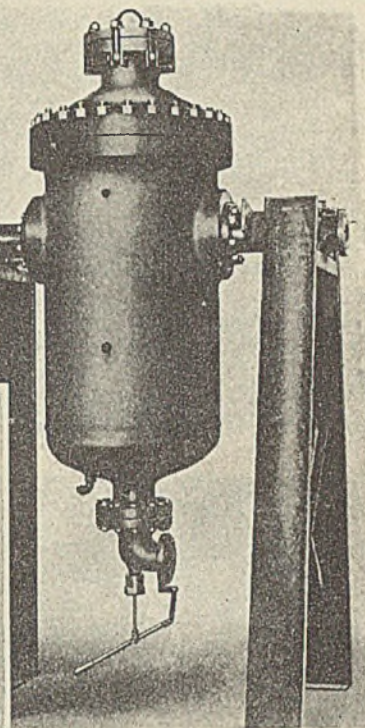
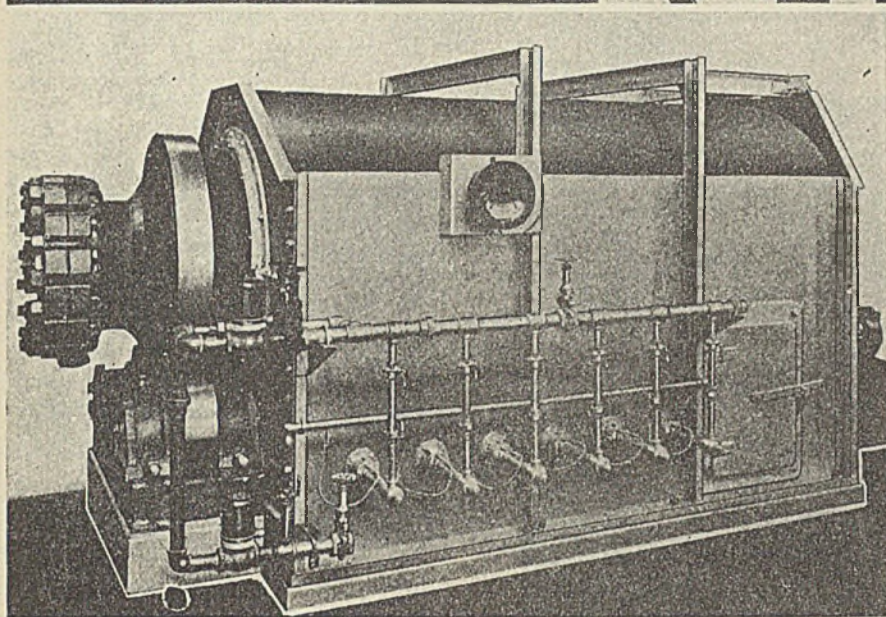


Figure 18. Direct-Fired Autoclave with a Heavy-Duty Agitator Designed for Mixing Problems Formerly Considered Too Difficult for Vertical Autoclaves



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Figure 19. A 45-Gallon Shaking Type Autoclave for Hydrogenation at 1500 Pounds per Square Inch



↑
Figure 20. Jacketed Stainless Steel, Tumbling Autoclave, 2 Feet I. D. x 3 Feet 4 Inches High, for Experimental Digestion at 400 Pounds per Square Inch

←
Figure 21. Gas-Fired, Revolving Autoclave, 30 Inches I. D. x 8 Feet 2 Inches Long, for 700 Pounds Working Pressure

valve, and a safety head, but other valves or devices may also be connected to it.

In cases where a large-diameter charging nozzle is required for the charging of solids, it may be advisable to go to the additional expense of providing a quick-opening cover. This will save considerable time on each cycle. For discharging the finished product, either a siphon pipe or a bottom discharge valve may be used. It is advisable to provide a renewable siphon or blowpipe where these are used, particularly if the product is abrasive or corrosive, since the life of the siphon pipe or blow pipe may be short.

CLOSURES. In most cases access to the inside of a high pressure autoclave is necessary for inserting agitators, coils, or other internal devices, or for cleaning purposes. Small diameter vessels are generally provided with a full-sized flanged opening at the top, closed with a bolted flat plate. Large diameter vessels are furnished with a dished and flanged, bolted top

head, or with a welded dished head provided with a suitable manway with cover plate (Figures 26 and 27).

Practically every closure for high pressure service involves a special flange design. The correct proportioning of the flange proper and of the hub can result only from a careful analysis of the stresses involved for a given loading. Experience and technical skill are required in obtaining a proper balance between gasket and bolt loads and flange dimensions and fabrication costs.

A leaking closure can cause a great deal of maintenance and operational trouble; hence the correct type of joint must be selected for each working condition, and a gasket chosen of the proper dimensions and thermal and chemical properties. An attempt to apply standard gasket practices to conditions encountered in high pressure autoclaves will almost always result in trouble.

The abuse to which studs and nuts are necessarily subjected requires that special care be given to their design. Correct

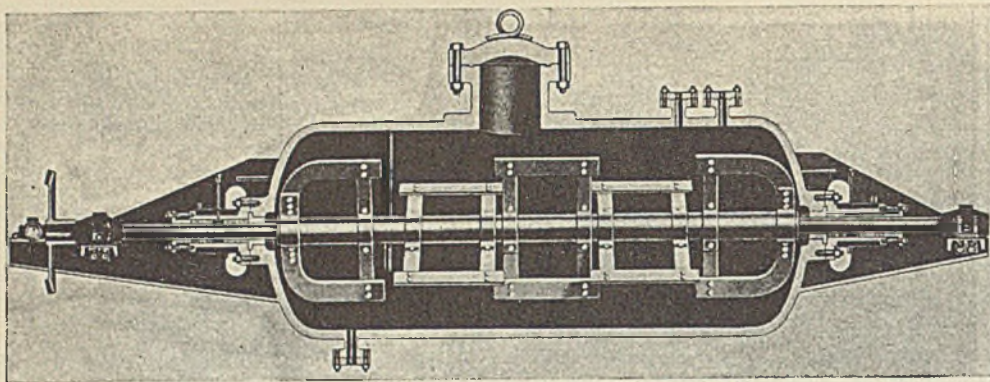


Figure 22. A 650-Gallon Horizontal Autoclave for a Pressure of 1000 Pounds

alloy materials must be selected, and the number, dimensions, and threading selected on the basis of sound engineering reasoning to ensure proper transmission of loads without exceeding allowable stresses.

Flat-plate end closures must satisfy the minimum requirements of the A. S. M. E. Code. Usually, external connections

and structures impose additional loads on the closure which require consideration in design. Many problems encountered in flange design, such as bolt spacing and joint selection, also must be considered in flat-plate closures.

INSTRUMENTATION

SAFETY DEVICES. The A. S. M. E. Boiler Code and most state safety departments require each pressure vessel to be protected by a safety device which will not permit the pressure within the vessel to rise above the point for which the equipment has been designed or which is stamped on the subject equipment (Figures 28 and 29). In most instances a spring-loaded safety valve is adequate, but where corrosive vapors may attack the vital elements of the safety valve or where sediment and gummy materials on the valve seat may cause the valve to function improperly, a supplementary safety device should be employed.

In conjunction with safety valves, the use of frangible diaphragms is recommended (commonly known as rupture disks), held between two specially machined flanges; the entire assembly is known as a safety head. These diaphragms are under careful control during fabrication, so that disks from the same factory lot will rupture within 5 per cent of their rated bursting pressure under standard test conditions. They are made in a variety of materials, both solid and plated, to resist corrosive agents within the autoclave or to resist the effects of either elevated or subzero temperatures.

For normal autoclave operation, where no severe pulsations of pressure occur or no violent fluctuations of pressures develop, it is recommended that the bursting pressure of the safety head be fixed at one and a half times the maximum design pressure stamped on the vessel. Where there is a possibility of violent changes in pressure, however, the bursting pressure of the diaphragm should be fixed at double that of the maximum design pressure (which in most cases corresponds to the hydrostatic pressure at which the autoclave is tested in the shop).

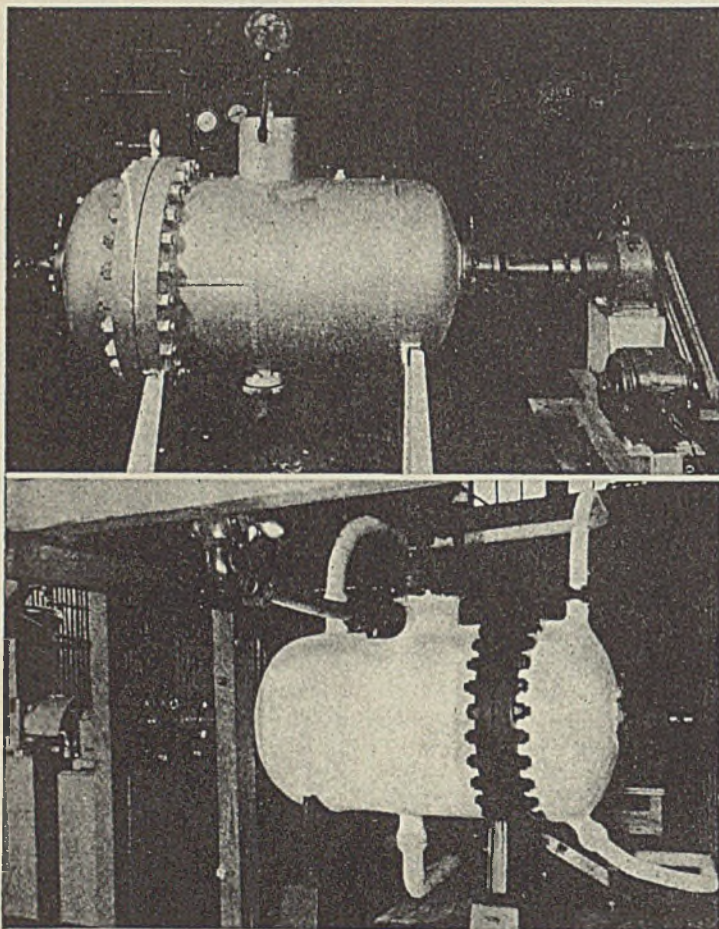


Figure 23 (Above). Steam-Jacketed, Horizontal, Experimental Autoclave, 2 Feet I. D. \times 4 Feet Long, Straight-Shell, with Helical Agitator, Designed for an Internal Pressure of 430 Pounds with a Jacket Pressure of 260 Pounds

Figure 24 (Below). A 300-Gallon, Dowtherm-Heated, Horizontal Autoclave with Special Agitator Drive

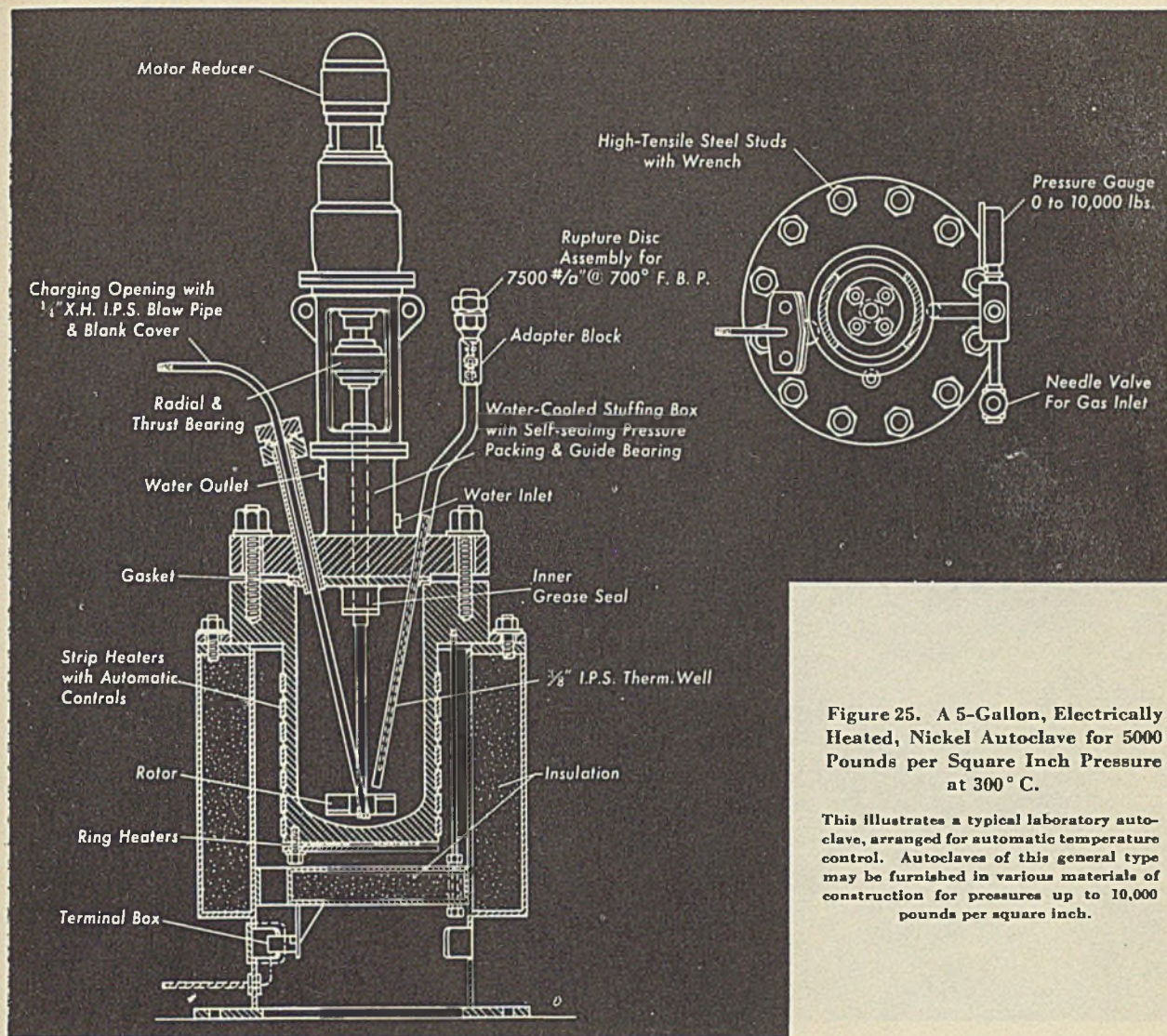


Figure 25. A 5-Gallon, Electrically Heated, Nickel Autoclave for 5000 Pounds per Square Inch Pressure at 300° C.

This illustrates a typical laboratory autoclave, arranged for automatic temperature control. Autoclaves of this general type may be furnished in various materials of construction for pressures up to 10,000 pounds per square inch.

CONTROL INSTRUMENTS. It is of extreme importance that all high pressure autoclaves be equipped with proper control instruments to ensure safety of operation as well as to give proper performance from a processing standpoint. As a minimum, each unit should be equipped with an indicating pressure gage and indicating thermometer, of high-quality rugged construction. In addition, certain autoclaves for special application should be equipped with additional instruments as dictated by the specific requirements.

If it is desirable to maintain a record of the internal pressure, a recording pressure gage should be used. A convenient additional safety feature is to use a pressure gage with built-in electric contacts so that it will sound an alarm when a predetermined pressure is reached and thus give warning before the pressure has built up to such a value as to blow the safety valve. Pressure gages on high pressure autoclaves should be recalibrated frequently so that they will always give correct readings.

When a record of the internal temperature is desired, a recording thermometer should be used. With a controlling thermometer it is often possible to control the heating or

cooling system automatically. When heating or cooling is by means of a jacket on the outside of the autoclave, it is necessary to take into consideration the temperature lag through the thick inner wall. Because of this lag it is usually necessary to use a throttling type temperature-control instrument with automatic reset to prevent overshooting the operating temperature.

It is frequently desirable to purchase the control instruments as well as certain other auxiliary equipment with the autoclave proper to ensure that they will be of the proper type to perform their intended functions.

MATERIALS OF CONSTRUCTION

In the design of a pressure vessel, an important consideration is the choice of the materials of construction. Such a choice must be governed by: (a) adequacy of the material to withstand the maximum pressure and temperature which will be encountered in the process; (b) adequacy of the material to resist corrosive agents or reactions where such conditions prevail; (c) adaptability of the material to the various

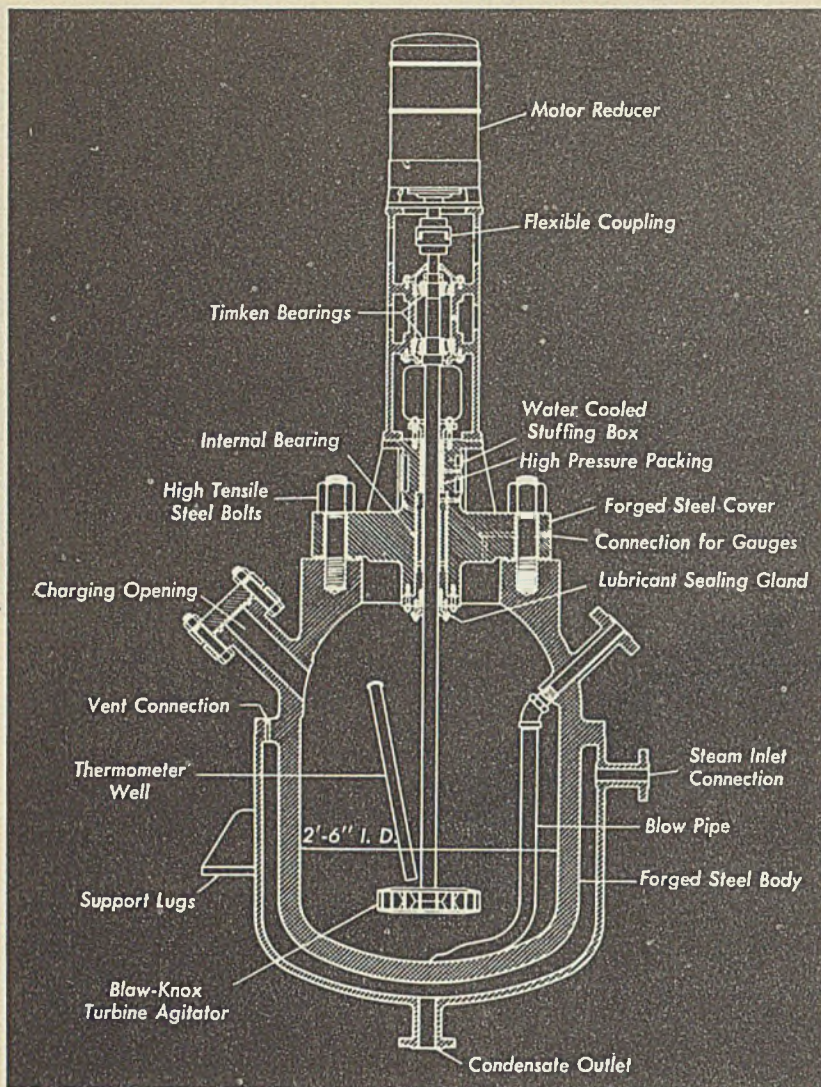


Figure 26. Diagram of Steam-Jacketed Autoclave Shown in Figure 27

methods of fabrication, such as forming it into various shapes, machining, finishing, welding, etc.; and (d) relative cost and time of delivery of the several available materials. The following summary will be useful in arriving at a solution to this problem. It does not embrace all available materials but will serve as a guide.

GENERAL PURPOSES. The most widely used steel for general purposes in the construction of pressure vessels is that complying with A. S. T. M. Specification A-70. This steel has an ultimate tensile strength of 55,000 pounds per square inch through a range of metal temperatures from -20° to 650° F., with a yield point at approximately one half its tensile strength. Besides possessing good ductility, it forms, welds, and machines easily. It is also the least expensive of the steels suitable for pressure vessels.

HIGH PRESSURES. For higher pressures or for larger diameter vessels, the thickness of the wall and consequently the weight of the vessel can be reduced by using a steel of higher tensile strength, complying with A. S. T. M. Specification A-212,

Grade B. This steel has a tensile strength of 70,000 pounds per square inch, so that the vessel wall is reduced in the direct proportion of 55/70, or to about 79 per cent. This steel also lends itself easily to fabrication.

HIGH TEMPERATURES. At elevated temperatures (over 650° F. metal temperature) most steels rapidly lose tensile strength and, even more seriously, decline in creep strength. For such conditions a steel complying with A. S. T. M. Specification A-204, containing 0.4 to 0.6 per cent molybdenum, has proved satisfactory because it retains not only a safe tensile strength but also a good degree of creep strength.

SUBZERO TEMPERATURES. Most steels gain in tensile strength at subzero temperatures but decline rapidly in ductility, making them subject to failure through sudden impact. A satisfactory steel for such conditions must therefore retain not only high tensile strength but continued ductility through the range of temperature. For temperatures down to about -50° F., a close-grain normalized carbon steel (modified A. S. T. M. Specification A-70) is adequate and meets the A. S. M. E. requirements. This material is the least expensive of the steels available for these service conditions. For still lower temperatures (down to -150° F.), it is necessary to use nickel steels. One such material having 2 to 2.75 per cent nickel, corresponding to A. S. T. M. Specification A-203, is satisfactory. On the basis of carbon content, three grades are available with minimum tensile strengths of 65,000, 70,000, and 75,000 pounds per square inch. The 18-8 chrome-nickel grades of stainless steel also possess excellent impact values at subzero temperatures, but their cost is much higher than the others.

STAINLESS STEELS. For corrosive service conditions where the use of stainless steel is indicated in the construction of a pressure vessel, the A. S. M. E. Code now recognizes the following types:

Type No.	Min. % Chromium	Min. % Nickel	Stabilizing Element
304	18	8	
316	17	10.0	Molybdenum (2% min.)
321	17	9.0	Titanium 5 X carbon
347	17	9.5	Columbium 10 X carbon

A tensile strength of 75,000 pounds per square inch is permitted by the code for figuring wall thickness with these grades of stainless steel. The most widely used are types 304 and 347. The latter, "stabilized" with columbium, permits

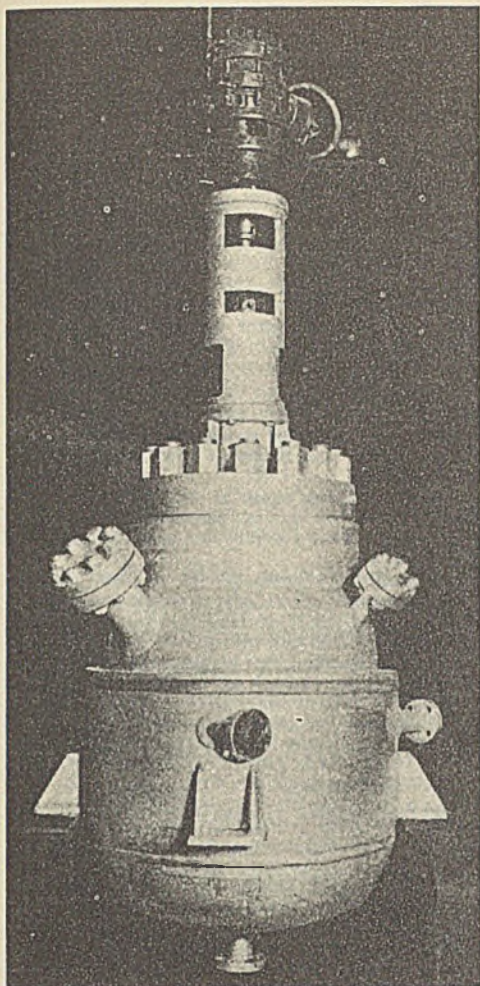


Figure 27. A 120-Gallon Steam-Jacketed Autoclave for Processing Organic Chemicals at 2000 Pounds per Square Inch and 300° F.

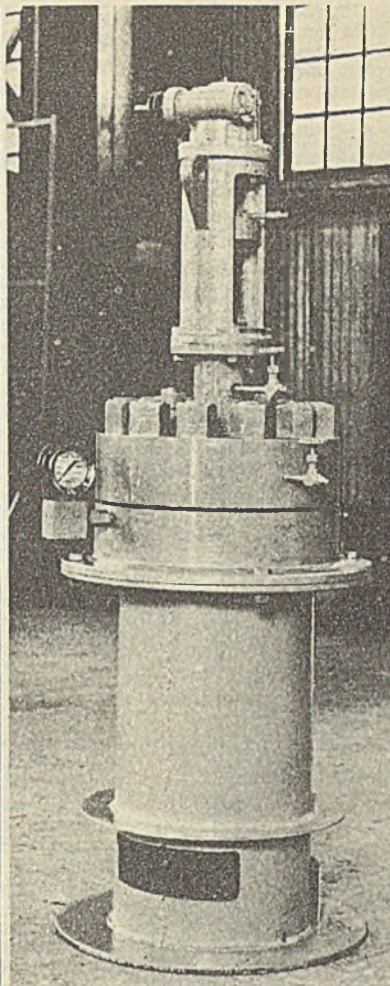


Figure 28. A 5-Gallon, 9-Inch I. D., Electrically Heated Autoclave for Industrial Research at 2500 Pounds per Square Inch

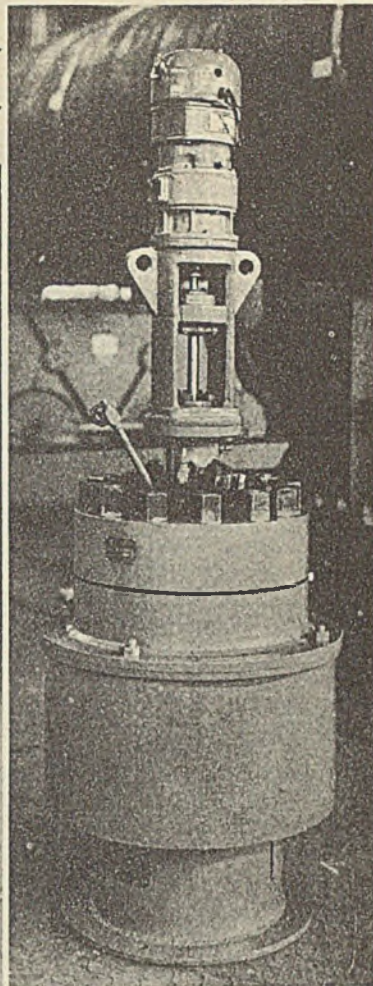


Figure 29. A 2-Gallon Electrically Heated Autoclave for a Pressure of 2500 Pounds per Square Inch, with Motor-Driven Turbine Agitator

welding with a minimum of carbide precipitation along grain boundaries, and thus gives greater assurance that the adjacent welds and areas will exhibit a resistance to corrosion substantially equivalent to the parent plate. Type 316 stainless steel (the most expensive of the code-recognized stainless steels) gives somewhat better resistance to corrosion from organic acids, such as acetic, than do the other three grades.

The straight chrome stainless steels (without nickel) have their important applications also, but much greater care and skill are required in fabrication. Their base prices are considerably lower than those of the 18-8 stainless steels, although fabrication costs are somewhat higher. Thus far they are not recognized by the A. S. M. E. Code but their adoption is under contemplation.

STAINLESS-CLAD STEELS. The stainless steels mentioned above can be obtained in clad form as well as in the solid, with the cladding usually 20 per cent of the total plate thickness. The A. S. M. E. Code has recently granted permission to utilize the total thickness of the clad plates in design computations. (Formerly only the carbon steel base material could be so treated in the determination of wall thicknesses.) The allowable tensile strength of the composite plate is that correspond-

ing to the base material. Obviously the chief advantage of clad plate over solid stainless steel plate is in its lower pound price, but since the clad plate must be 75/55 times as thick as the solid stainless plate, or approximately 36 per cent heavier, the total over-all cost of a pressure vessel may not be greatly reduced in changing to clad plate. This is particularly true where an agitated autoclave is concerned, since a large part of the cost is due to the closure, stuffing box, connections, agitator, and drive.

NONFERROUS METALS AND ALLOYS. Among the non-ferrous materials sanctioned by the A. S. M. E. Code may be listed:

1. Monel metal (approximately 65 per cent nickel, 35 per cent copper) with a tensile strength of 70,000 pounds per square inch from room temperature up to 400° F., dropping down to 62,500 pounds per square inch at 550° F.
2. Copper-silicon alloy, known commercially as Everdur or Herculoy (approximately 95 per cent copper, 3 per cent silicon) with a tensile strength of 50,000 pounds per square inch from room temperature up to 250° F., dropping to 25,000 pounds per square inch at 350° F.
3. Copper, with tensile strength of 30,000 pounds per square inch at room temperature and up to 150° F., dropping to 20,000 pounds per square inch at 400° F.

4. Nickel, not yet officially recognized by the A. S. M. E. Code, can be utilized for a pressure vessel only in the form of clad plate (from 10 to 20 per cent of the total plate thickness.) The tensile strength and thickness of the base plate only are used in computation of wall thickness for service temperatures above 250° F.

HYDROGEN PERMEATION. Reactions with hydrogen gas are becoming increasingly numerous, and here the engineer is confronted with the phenomenon of hydrogen penetration through most carbon steels. This takes place at a rapid rate at high pressures (1000 pounds per square inch and above) and at high temperatures (over 500° F.). Under such conditions the chrome-vanadium steels have been found adequate. One such alloy steel, SAE No. 6130, contains 0.80–1.10 per cent chrome, 0.15–0.18 per cent vanadium, 0.50–0.80 per cent manganese, and 0.25–0.35 per cent carbon. It has an ultimate tensile strength of 75,000 pounds per square inch. The 18–8 chrome-nickel stainless steels are also satisfactory but are more costly, except where the design of the autoclave lends itself to a stainless steel lining or to the use of stainless clad steel.

THICK-WALL CYLINDER FORMULA FOR HIGH PRESSURES. The A. S. M. E. Code outlines working stresses and computations of wall thickness for vessels operating within normal pressure ranges (less than 1000 pounds per square inch). When, however, higher pressures are encountered, such that the computed thickness of the wall exceeds 10 per cent of the inside radius of the cylindrical shell in the formula $t = PR/SE$, we must treat the autoclave body as a thick-walled cylinder, and the results obtained from this formula are not adequate. The A. S. M. E. Code now recognizes the Lamé equation for such conditions:

$$t = R \left(\sqrt{\frac{SE + P}{SE - P}} - 1 \right) \quad (3)$$

where t = thickness of cylindrical shell, inches
 R = inside radius of cylinder, inches
 S = allowable working stress, lb./sq. in.
 E = efficiency of longitudinal seam, per cent
 P = maximum design pressure, lb./sq. in.

Thus, if we design an autoclave with a 24-inch inside diameter, for a maximum working pressure of 3000 pounds per square inch at 500° F., employing a high-tensile carbon steel, such as A. S. T. M. A-212 (70,000 pounds per square inch minimum tensile strength), and a welding technique which allows 95 per cent efficiency of the longitudinal joints (Class I construction, Paragraph U-68, A. S. M. E. Code), the thickness of the wall will be:

$$t = 12 \left(\sqrt{\frac{\left(\frac{70,000}{4}\right) 0.95 + 3000}{\left(\frac{70,000}{4}\right) 0.95 - 3000}} - 1 \right) = 2^{13/32} \text{ in.}$$

The previous thin-wall formula would have resulted in a wall thickness of only $2^{3/16}$ inches. In addition to the specification of longitudinal joint efficiency, the code stipulates other controlling considerations.

SAFETY PRECAUTIONS FOR HIGH PRESSURE PLANTS

The manufacturing engineer devotes great care to the design and fabrication of high pressure autoclaves to provide a high factor of safety. His responsibility ends there, and that of the user begins; the user must accept as his responsibility the location and proper operation of the equipment in the field. However remote, he should bear in mind the possi-

bility of failure of the autoclave or auxiliary equipment and plan his layout so as to protect his workers and to localize the effects of any failure of equipment.

High pressure plants can be made as safe as any, when reasonable precautions are taken:

1. On receipt, internal and, if possible, external measurements should be made at specified locations of the diameter and height of the autoclave. Similar measurements should be made of auxiliary equipment. This data should be carefully filed. With the frequency depending on the severity of service conditions, these measurements should be rechecked at reasonably frequent intervals as a matter of routine to make certain that corrosion is not reducing wall thickness to a dangerous point.
2. If cautioned by the manufacturer, the rate of pressure rise should never exceed the maximum rate given by him.
3. If cautioned by the manufacturer, the rate of temperature rise should never exceed the rate given by him.
4. No pressure joint should be tightened under pressure.
5. When dealing with poisonous gases, two persons should always be present. Suitable gas masks at convenient locations should be on the premises.
6. If oxygen or an oxidizing agent is used in the process, under no conditions can oil or gas be permitted to enter the autoclave. *In such cases a special stuffing box, packing, and lubricant will have to be provided.*
7. Safety valves and safety heads should be piped so that any sudden release of pressure will be led to a safe place. Piping should be so arranged that there is no danger of fire or explosion if flammable materials are suddenly released to outside atmosphere. It should be borne in mind that neither safety valves nor heads will provide protection against an internal explosion in the autoclave. Therefore the autoclave and pipe line should be so arranged that chances of an explosion will be minimized. Piping should be grounded. Long straight runs of pipe should be avoided, and buffer chambers, packed with conducting materials, should be located at strategic positions.
8. It is desirable so to arrange the equipment that the operator will handle all operations from a distance, viewing gages, etc., through a system of mirrors.
9. A high pressure-high temperature autoclave and its auxiliary equipment should be isolated from the rest of the plant. Buildings housing such equipment should have heavy walls and light roofs but should also be well ventilated and special precautions should be taken to prevent the formation of gas pockets beneath the roof. In addition, it is sometimes desirable to surround the equipment with steel plate, concrete barricades, or woven rope mantlets.
10. A log book should be kept for each autoclave for the inclusion of all experimental data and records of repairs, tests, etc.
11. The extent of individual responsibility should be clearly defined.

ACKNOWLEDGMENT

The writer wishes to express thanks to those fellow workers who submitted helpful contributions or criticism, and is particularly grateful to H. L. Barnebey, A. Grodner, J. H. McLellan, and A. Olson for their help in summarizing the principal features of heating and mixing systems and of the A. S. M. E. Code pertinent to autoclave design.

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Effect of Petroleum Products on *Neoprene Vulcanizates*

Effect of Gasolines



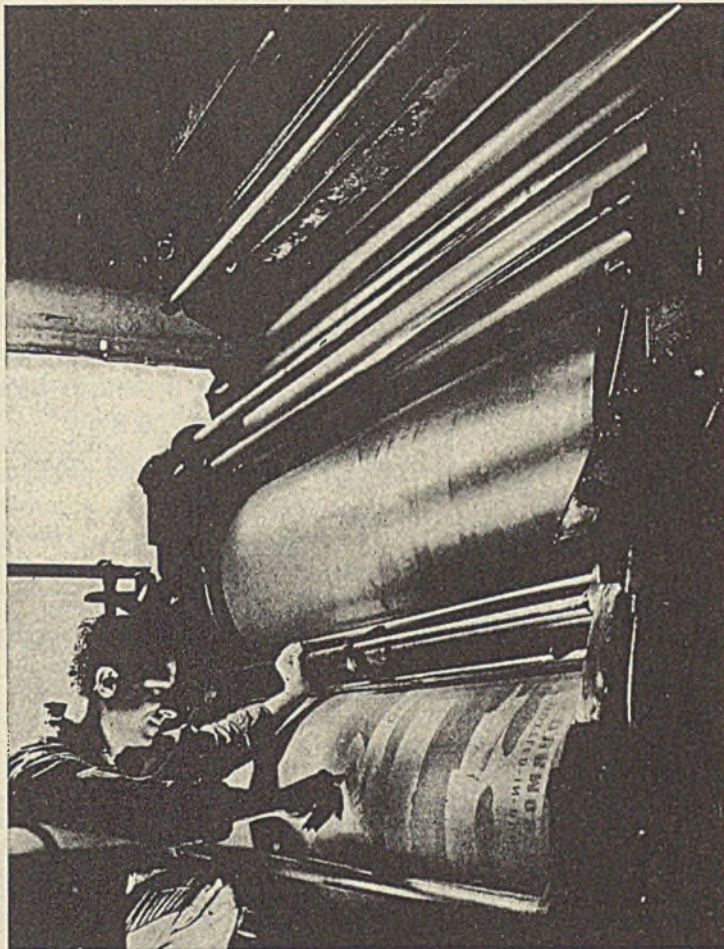
As with other petroleum products the aniline point may be used to indicate the swelling effect of commercial gasolines on neoprene vulcanizates. However, it is felt that the Diesel index is a more precise indication with products having A. P. I. gravities greater than 40 (kerosenes and gasolines). This may be particularly true in the case of recently proposed aromatic aviation gasoline blends.



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Robert Yarnall Richie photograph

**Neoprene Printing Blankets Maintain Their Original Properties
Despite Exposure to Oil, Ink, and Chemicals in Cleaning Solutions**

THE third paper of this series (3) showed that the Diesel index may be used as a criterion of the swelling effect on neoprene of kerosenes and kerosene-benzene blends. It was erroneously stated, however, that "swelling caused by kerosene is not a simple function of the . . . aniline point". A recheck of the data, together with additional work, indicates that the aniline point may be used as a criterion of the swelling power of kerosenes, but this correlation is not so precise as with the Diesel index. This is particularly true in the case of kerosene-benzene blends when benzene predominates in the blend. As with kerosenes, the aniline point or Diesel index may be used as an indication of the swelling power of gasolines, and thus these constants may be used to specify standard immersion media of these types.

The neoprene composition used in the work was identical with that used in the previous investigations (1, 2, 3). The specimens were prepared for the volume increase test as previously described. The physical data for and the description of the gasolines used in the swelling tests are shown in Table I. Also shown is the volume increase after immersion of the neoprene specimens in the gasolines at 27.8° C. (82° F.). The results shown are those of the maximum swelling. The immersions were continued for 14 days, but maximum swelling was attained, except in the case of isooctane, within 3 days. The volume increases at the end of 14 days were the same, within the experimental error, as the results shown in Table I. Because of the volatility of gasoline, care was taken

to make the necessary weighings as soon as possible after removal of the specimen from the gasoline.

In Figure 1 the logarithm of maximum swelling is plotted against Diesel index, and a straight-line relation is obtained. The plot for isooctane (sample 15) is the swelling after 14-day

For instance, in the case of samples 5, 6, 7, and 8 (showing the effect of the addition of tetraethyllead) no change was observed in the aniline point, but the Diesel index and swelling results showed that the addition of tetraethyllead did affect these properties.

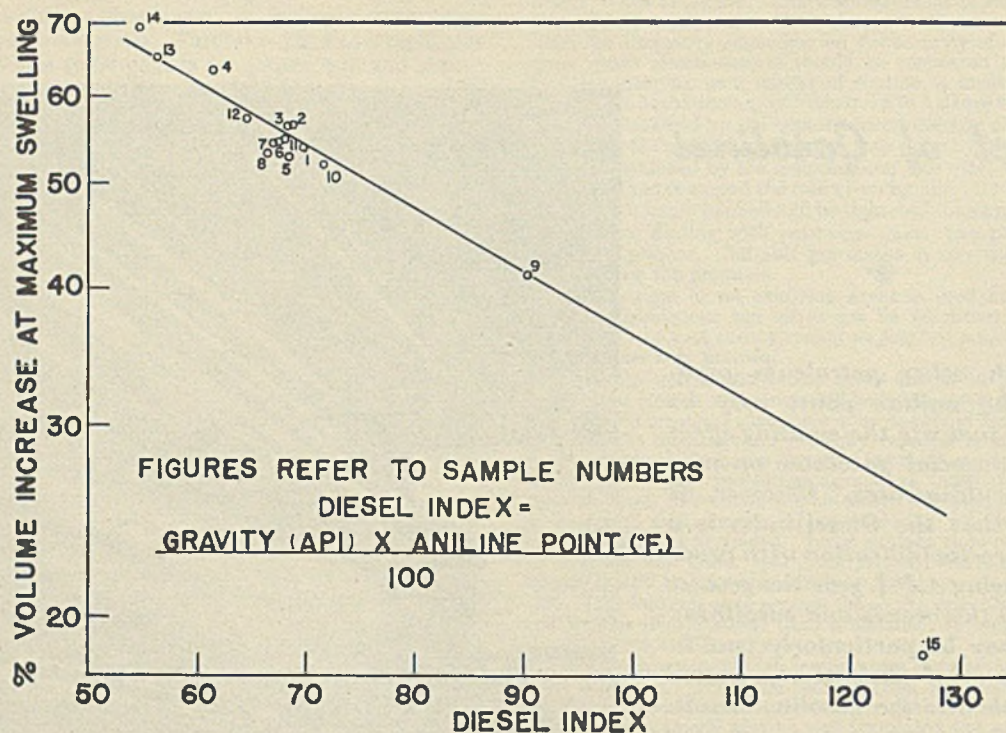


Figure 1

immersion and does not fall on the curve. This material has very little swelling power, and consequently the time necessary to reach maximum or equilibrium swelling is probably considerably in excess of 14 days. If the aniline point is substituted for the Diesel index, a good correlation is also obtained; but it is felt that the latter is a more precise criterion.

Practically all commercial motor fuels (gasolines) represent blends of straight-run and cracked stocks. However, the Diesel index may be used as a criterion of swelling of either type of stock or of intermediate blends as indicated by samples 9, 10, 11, 12, and 13. As would be expected, a straight-run stock has considerably less swelling effect than a cracked stock. Sample 14 was prepared by adding 0.0043 per cent of a commercial antioxidant (du Pont gasoline antioxidant, solution 14) to cracked stock sample 13. The swelling results indicate that some commercial antioxidants, at least, increase the swelling power of gasolines containing them.

Comparison of the swelling results in Table I with those in Table I of the preceding paper (3) shows that commercial gasolines do not vary in swelling power as much as commercial kerosenes and that the average swelling effect of the gasolines is a little greater.

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PRESENTED before the Division of Rubber Chemistry at the 105th Meeting of the AMERICAN CHEMICAL SOCIETY, Detroit, Mich.

TABLE I. SUMMARY OF DATA FOR GASOLINES

Sample Number	Description	A. P. I. Gravity (60° F.)	Aniline Point, °F.	Diesel Index	Refractive Index	Max. Vol. Increase of Neoprene at 27.8° C.
1	Commercial motor fuel	60.6	115.5	69.99	1.4340	54.0
2	Commercial motor fuel	62.4	110.5	68.95	1.4380	56.5
3	Commercial motor fuel	61.8	111.0	68.60	1.4375	56.5
4	Commercial motor fuel (unleaded)	59.7	103.0	61.49	1.4450	63.4
5	Commercial motor fuel (unleaded)	59.7	114.5	68.36	1.4165	52.9
6	No. 5 + 1 cc. Pb(C ₂ H ₅) ₄ per gal.	59.1	114.5	67.67	1.4160	54.5
7	No. 5 + 2 cc. Pb(C ₂ H ₅) ₄ per gal.	58.0	114.5	67.10	1.4175	54.3
8	No. 5 + 3 cc. Pb(C ₂ H ₅) ₄ per gal.	58.1	114.5	66.52	1.4151	53.1
9	Straight-run stock	67.7	133.5	90.38	1.4098	41.2
10	50:50 No. 9:No. 13	61.6	116.5	71.70	1.4276	52.0
11	40:60 No. 9:No. 13	60.3	113.0	68.15	1.4207	55.0
12	30:70 No. 9:No. 13	59.3	109.0	64.64	1.4282	57.3
13	Cracked stock	56.3	99.5	56.02	1.4372	65.0
14	No. 13 + antioxidant	56.0	98.0	54.88	1.4359	69.6
15	Isooctane	71.7	176.0	126.19	1.3904	18.5

Bend-Brittle and Shatter Points of Rubberlike Materials

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WITHIN the past two years the performance of rubberlike compositions at low temperatures has become important. A number of tests have been devised to measure the loss of rubberlike properties of many of these compositions.

As the temperature is lowered, the first indication of the loss of rubberlike properties is hardening of the material. As the temperature is lowered farther, the material continues to stiffen and harden to a point where it becomes quite inflexible; bending or striking with a solid object then causes breaking or shattering due to the brittleness of the material. Up to this time the temperature at which breaking occurs has been called the "brittle point" of the material, with no distinction made between the temperature at which breaking occurs upon bending and the temperature at which breaking occurs upon striking with a sharp blow from a solid object. It would be easy to assume that the two points occur at the same temperature.

Koch (9) tested the brittle point of elastic materials by measuring the bend stress with a micrometer gage placed in the center of the specimen that was supported at each end. By observing the distortion caused by weights, the elastic modulus could be measured to the breaking point which occurred at a definite temperature. This bend-brittle temperature was called the "high elasticity" temperature by Houwink (5) and the "elasticity" temperature by Whitby (14). An apparatus was developed by the Thiokol Corporation (11) for determining the flexibility of rubberlike materials at low temperatures. The samples are mounted between two plates and bent by turning a crank. The apparatus was designed so that the distance between the plates can be varied. The temperature of breaking was called the "brittle point".

Kohman and Peek (10) tested the brittle point by bending a strip through 90° with a hammer blow. They found that the brittle temperature was independent of the dimensions and the bending angle; however, a high rate of deformation was necessary for the duplication of results. Kemp (7) applied this test to rubber samples and likewise made no differentiation between a bend-brittle point and a shatter point. A similar method (6) was reported from Germany except that, in place of a hammer blow, a falling weight was used to break the sample which was bent back upon itself.

Selker and co-workers (13) mounted their samples on a wheel and, by rotation, caused the samples to strike against a

Many rubberlike materials possess two relative points of change in physical properties corresponding to the bend-brittle temperature and the shatter point. Since the bend-brittle point varies and approaches the shatter point, the shatter point seems to be the true brittle temperature. These points change although they hold their relative positions in respect to each other for various plasticizations and for time of freezing. The two points approach each other as hardness increases through loading. Although there is a minimum distance from which a weight must be dropped to shatter a given sample, a greater distance does not raise the shatter point.

projection on the frame to give a bend test. The rate of bending was not stated; however, a high rate of operation would probably simulate a shatter test. Recently (8) this apparatus was improved to control the rate as well as the magnitude of stress.

Garvey (3, 4) attempted to differentiate between a freezing temperature, a stiffness by bending under a load, and a brittle point. The brittle point was tested by placing a rod on the opposite end of a securely held sample and bending the sample by striking the rod with a hammer. The temperature of breaking was the brittle point.

A sample of plasticized polyvinyl chloride was tested at low temperature by Russell (12) for a break after cooling for 5 minutes at each temperature. The point of breaking occurred with no observable bending.

In making a bend test by cooling a sample and bending through an angle, it was noticed that the breaking temperature did not correspond to the shatter point when struck a sharp blow with a hammer, and that in the former case the break was usually a straight fracture while in the latter it was a shattering into a number of pieces. A recheck of the tests showed that shattering occurred at a higher temperature than the bend-breaking point. It was considered advisable to determine whether this condition existed in a large number of elastomers.

DETERMINATION OF POINTS OF CHANGE

BEND-BRITTLE TEST. An adaptation of the Hycar brittle test was run by dicing samples from a sheet 0.0625 inch thick to make the samples 3.0 inches long and 0.25 inch wide. Each end of the sample was placed in holes drilled in the test block. The holes were 0.25 inch in diameter and 2.0 inches from center to center. This caused the sample to form an arch approximately 1.25 inches high. The samples are bent by placing a rod on the sample and pushing firmly. The rate is sufficient to bend each sample in 1-1.5 seconds.

SHATTER POINT. The apparatus (Figure 1) consisted of a steel bar mounted vertically in a sleeve fitted with ball bearings for free sliding. The bar weighed 5 pounds and had a cutting edge at its lower end of a 90° wedge, 0.010 inch wide and 1.0 inch long. For very soft compounds the bar was dropped from a height of 3.0 inches. This distance was sufficient to shatter the sample without cutting it. For samples above 50 Shore hardness, a height of 5.0 inches was used. The base upon which the sample was placed was hardwood.

HAND BEND TEST. The sample was grasped by gloves kept in the cold box and bent with a continuous motion through 90° at a rate from 1-1.5 seconds. It was found that the hand bend test

TABLE I. EFFECT OF PLASTICIZERS ON BEND-BRITTLE AND SHATTER POINT IN A NEOPRENE FR COMPOUND*

Plasticizer (20.5 Parts by Wt.)	Bend-Brittle Point, ° F.	Shatter Point, ° F.
Butyl cellosolve acetate	-82	-69
Diisobutyl adipate	-90	-62
Dibutyl phthalate	-90	-67
Dibutyl sebacate	-90	-76
Diamyl phthalate	-82	-62
Dicapryl phthalate	-82	-67
Plasticiser SC	-90	-69
Dispersing oil No. 10	-82	-62
Tributoxy ethyl phosphate	-90	-62
TP-10 plasticizer	-74	-49

* Base formula: Neoprene FR 100.0, stearic acid 1.0, Flectol H (anti-oxidant) 2.0, sulfur 1.0, litharge 5.0, white factice 50.0, Thermax 100.0, paraffin 1.0, zenite 0.5.

sile, elongation, and hardness, were selected for the test. Table I shows the results of the bend-brittle and shatter points corresponding to the plasticizers used. In all these compounds two points were noted that had a difference from 5-18° F. There is an indication that, while some plasticizers act as freeze depressants, others, in spite of their low freezing points, do not depress the shatter point as would be expected. Some plasticizers act as freeze depressants although their freezing points are higher than the brittle or shatter point of the compound. Usually increasing the amount of plasticizer will lower the bend-brittle and shatter points. Hardness is

TABLE II. SYNTHETIC RUBBER FORMULAS

	Neoprene		OR-15	Hycar		OS-10	Thiokol		Buna S	Butaprene		Butyl B
	GN	ILS		OS-20	RD		FA	NM		NXM		
Synthetic	100.00	100.00	100.00	100.00	100.00	100.00	100.00	134.00	100.00	100.00	100.00	100.00
Stearic acid	0.50	0.50	0.50	0.50	0.50	0.50	0.50	1.00	0.50	0.50	0.50	0.50
Zinc oxide	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
Sulfur	...	1.50	1.50	1.50	1.50	1.50	1.50	1.25	1.25	1.25	1.25	2.00
P-33 black	80.00	80.00	80.00	80.00	80.00	80.00	80.00	80.00	80.00	80.00	80.00	80.00
Circo oil	5.00	5.00	5.00	5.00	5.00	5.00	5.00	...	5.00	5.00	5.00	5.00
Whiting	9.00	6.50	5.75	5.75	5.25	5.25	6.12	6.00	6.00	6.00	6.00	5.80
Paraffin	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Altax	1.50	1.50	1.50	1.50	1.50	0.50	1.50	1.50	1.50	...
Tbionex	0.25	0.25	0.25	0.25	0.25	...	0.25	0.25	0.25	...
DPG	0.13
Permalux	...	1.00
Captax	1.00
Tuade	0.50
Benzoic acid	0.50
Cure at 316° F., min.	20	15	15	15	15	15	20	10	10	10	10	20
Shore hardness	67	75	70	60	65	65	85	68	55	60	70	55

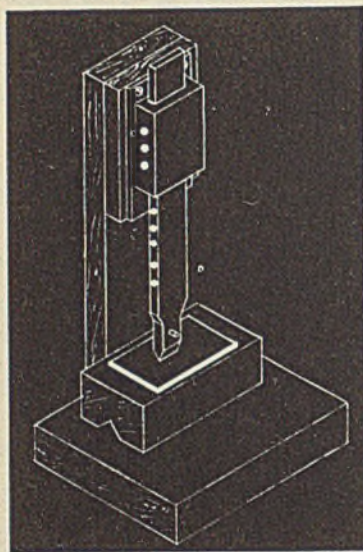


Figure 1. Shatter Point Apparatus

not an indication of the bend-brittle or shatter points, and this confirms the results found by others (1, 8). For example, dibutyl sebacate definitely has the better shatter point; however, diisobutyl adipate has a lower hardness at the breaking temperature.

COMPARISON OF ELASTOMERS. In order to determine whether the same phenomenon of shatter point and bend-brittle point existed in materials other than neoprene, selected compounds (Table II and III) were tested; the results are shown in Table IV. Two points were observed similar to those found in neoprene. The shatter points in all cases occurred at a higher temperature than the bend-brittle point. There is a range between the two points from 3-40° F. Since these stocks do not represent the best cold-resistant compounds of each type, their properties at low temperatures could definitely be improved by the addition of a freeze-depressant type of plasticizer.

TABLE III. POLYVINYL COMPOUNDS TESTED

Polyvinyl chloride-acetate	90.0	...
Calcium stearate	0.9	...
Dibutyl sebacate	37.2	...
Triercyl phosphate	22.8	...
Polyvinyl butyrate	..	100.0
Calcium silicate	..	100.0
Dibutyl phthalate	..	85.0
Paraffin	..	0.5

was practically identical with the bend-brittle test; therefore, the latter was used in place of the hand bend test in the following runs.

The cold box used was described by the du Pont Company (1). The temperature was lowered in steps of approximately 5° F. and kept at each interval for 15 minutes before testing. After each test the samples were examined for breaks while still in the cold box.

EFFECT OF VARIABLES

EFFECT OF PLASTICIZERS. To a Neoprene FR base compound equal amounts of various plasticizers were added and the compounds cured. The peak cures, as indicated by ten-

EFFECT OF TIME OF FREEZING. Rubber compounds exposed to low temperature have a higher brittle temperature due to progressive crystallization. Selected types of synthetics representing the butadiene-styrene, butadiene-acrylonitrile, chloroprene, and polysulfide rubbers were frozen for 24 hours at each temperature (Table IV). All of the samples tested broke at a higher temperature after 24 hours of freezing, and the shatter point was higher than the bend-brittle point. Since the samples were 0.0625 inch thick, it

TABLE IV. SHATTER AND BEND-BRITTLE POINTS OF ELASTOMERS

	—Frozen 15 Min.—		—Frozen 24 Hours—	
	Shatter point, ° F.	Bend-brittle point, ° F.	Shatter point, ° F.	Bend-brittle point, ° F.
Gum rubber (light load)	-58	-67
Buna S	-72	^a	-80
Butaprene NM	-31	-49	-11	-35
Butaprene NXM	-3	-6
Butyl B-1.5	-49	-6	-42
Hycar OR-15	-3	-6
Hycar OS-10	-6	-13
Hycar OS-20	-72	^a	-49	-55
Neoprene GN	-40	-49	-35	-45
Neoprene ILS	-3	-13
Noropol P-345-D	+10	-13
Thiokol FA	-40	-49	-35	-42
Thiokol RD	+20	+23
Plasticized polyvinyl chloride-acetate	-58	-67
Plasticized polyvinyl butyrate	-4	-49
Plasticized ethylcellulose	-22	-58

^a In good condition at -76° F.

^b In good condition at -50° F.

was felt that the shorter time gave a complete quick freeze without complete crystallization, and that the longer interval indicated a progressive condition if not crystallization. The greatest change, possibly due to crystallization, was found in the Hycar OS-20 compound. It is well known that the butadiene synthetics do not crystallize easily. However, there are some indications that at very low temperatures crystallization does take place to some extent.

EFFECT OF RATE OF BENDING. For the past two years this laboratory has recognized that the rate of bending varies the bend-brittle temperature. An instantaneous bend point was obtained in the same manner as the bend-brittle point except that the rod was given a hard, sharp push in an attempt to duplicate as rapid a blow as possible; however, the rod was always in contact with the sample. Table V indicates that the instantaneous bend gives a temperature that approaches the shatter point. If the rate was truly instantaneous, the bend test would be the same as the shatter point. A similar condition was noticed in the hand bend test when the sample was quickly bent back upon itself in contrast to a slow bend over a 1-1.5 second period. The same conclusions were made by Kemp and co-workers (8) in their studies of the brittle temperature of rubber under variable stress. The shatter point appears to be the true brittle temperature as the bend test varies with the rate, and approaches the shatter point as the rate of bending increases.

TABLE V. RATE OF BENDING AND BEND-BRITTLE POINT

	Bend-Brittle Point, ° F.		Shatter point, ° F.
	One-sec. bend	Instantaneous bend	
Butaprene NM	-49	-33	-31
Hycar OS-10	-13	-8	-6
Neoprene ILS	-13	-5	-3
Plasticized polyvinyl chloride-acetate	-67	-62	-58
Plasticized polyvinyl butyrate	-49	-8	-4

EFFECT OF HARDNESS THROUGH FILLERS. Harder stocks, as measured with the Shore durometer, appeared to have a more narrow range between the bend-brittle and shatter points, possibly due to lower percentage of rubberlike material in the compounds, and also to the dilution beyond the reinforcing range which decreases the cohesive bonds. Table VI shows this for three types of materials. Each compound of each type varied only in the semireinforcing carbon black content.

EFFECT OF DROPPING WEIGHT ON SHATTER POINT. As mentioned, Kohman and Peek (10) observed that the dimensions of the samples and the bending angle did not affect the brittle temperature, although a high rate of deformation was necessary to duplicate his results. The size of the sample did not seem to affect the bend-brittle or shatter points except that the dropping weight must be dropped from a height sufficient to produce a sharp blow without cutting the unfrozen sample. This, by experiment, determined the distance through which the weight fell. There is a definite minimum height for various stocks and hardnesses. Trial and error showed that, under 40 hardness in a Shore Type A durometer, a distance of 3.0 inches met these conditions. If the sample gave a shatter affect at a minimum height, dropping the weight through a greater distance did not raise the shatter point. The relation between the thickness of sample and height of dropping was not determined.

TABLE VI. EFFECT OF LOADING ON HARDNESS IN BEND-BRITTLE AND SHATTER POINT TESTS

	Hardness, Shore A	Bend Brittle, ° F.	Shatter Point, ° F.
Neoprene FR	40	-80	-75
	50	-78	-75
	60	-78	-75
	70	-77	-73
	85	-75	-72
Hycar OR-15	40	-38	-31
	50	-30	-23
	60	-25	-23
	70	-22	-20
Neoprene GN	40	-50	-39
	50	-48	-38
	60	-45	-36
	70	-42	-34
	80	-36	-33

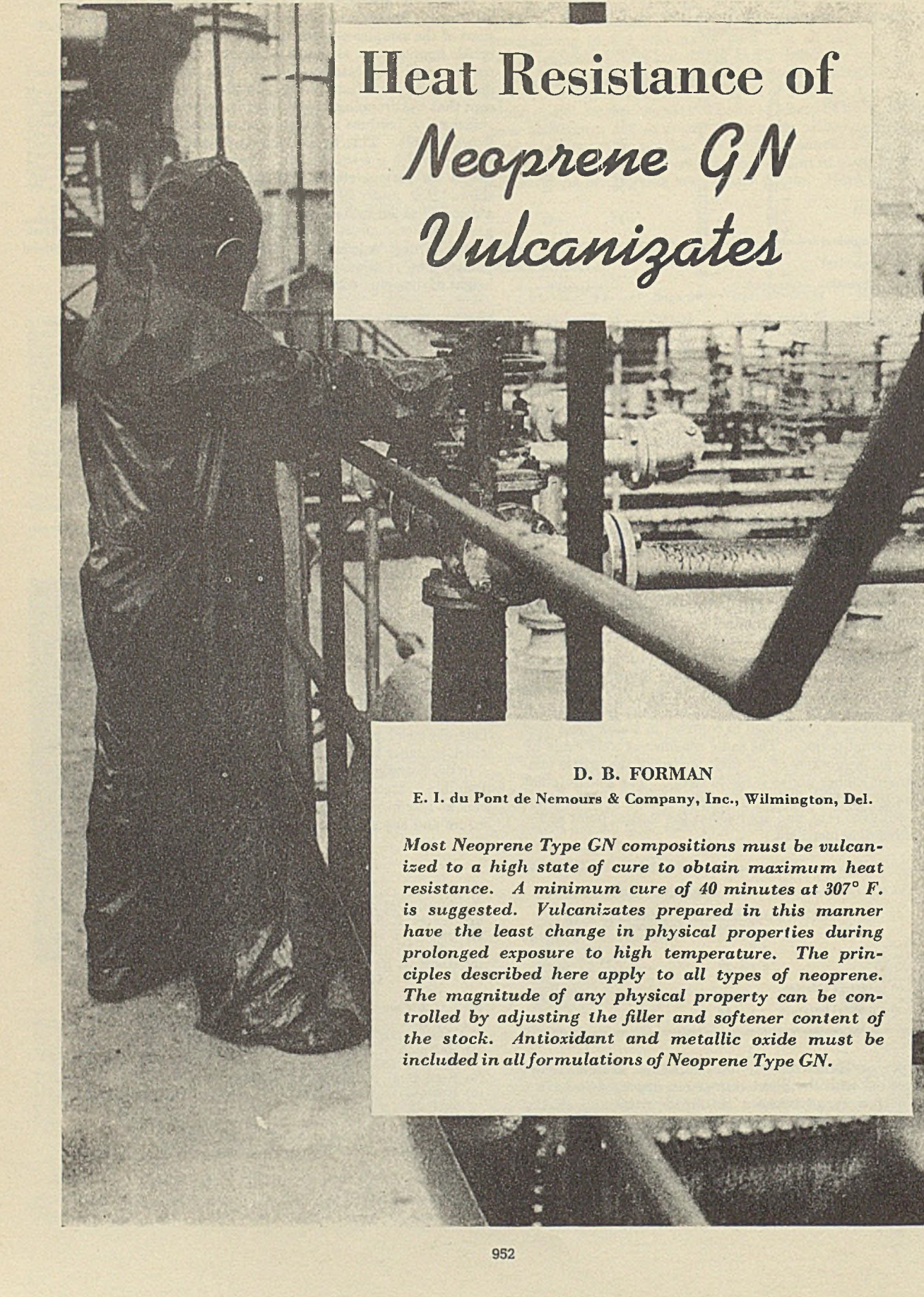
There is probably a relation between bend-brittle and shatter points. In most rubberlike materials a large number of variables would affect the results, such as type of material, loading, softeners, curing agents, and time and temperature of curing or processing. Fuoss (2) found that, in a sample of plasticized polyvinyl compound, there was a change in electrical properties several degrees higher than the brittle point. This electrical point may correspond to the shatter point, which is higher than the bend-brittle point.

In designing specifications for low-temperature testing, it is desirable to state the property or properties to be tested, the time and temperatures of test, the size of specimens, the procedure and apparatus to be used, and the rates of operation of the test.

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Heat Resistance of *Neoprene GN* *Vulcanizates*

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Most Neoprene Type GN compositions must be vulcanized to a high state of cure to obtain maximum heat resistance. A minimum cure of 40 minutes at 307° F. is suggested. Vulcanizates prepared in this manner have the least change in physical properties during prolonged exposure to high temperature. The principles described here apply to all types of neoprene. The magnitude of any physical property can be controlled by adjusting the filler and softener content of the stock. Antioxidant and metallic oxide must be included in all formulations of Neoprene Type GN.

CONTROL of heat deterioration is a continuous problem for the chemist. In the case of rubber and synthetic elastomers, the rubber chemist has charted the changes in the physical properties of vulcanized elastomers during heat aging. He has developed many methods for retarding the deterioration of rubber compounds by heat; but with the newer synthetic elastomers the development of methods of retarding deterioration by heat is now an active subject of investigation. The degree of deterioration is dependent upon the methods of compounding and curing the different elastomers as well as upon the conditions of aging. In general, continuous exposure to high temperatures softens natural rubber but hardens the synthetic elastomer.

Inherently neoprene has greater heat resistance than natural rubber (5). Many investigators have described the heat resistance of rubber vulcanizates, but only a few have reported on the heat resistance of neoprene vulcanizates and these reports have been primarily comparisons of given neoprene vulcanizates with one or more rubber stocks. The compounding of Neoprene Type GN for heat resistance was discussed by Catton, Fraser, and Forman (2). The oxygen bomb aging of Neoprene Types E and GN was compared with that of various rubber compositions by Neal, Bimmerman, and Vincent (4).

CRITICAL ANALYSIS OF HEAT AGING

In analyzing the changes in properties of heat-resisting rubber stocks during prolonged exposure to high temperature, a permanent and progressive decline in quality is observed. Tensile strength decreases slightly during the early stages of aging followed by a rapid drop to ultimate failure. Ultimate elongation usually follows the same trend as tensile strength while hardness increases slightly followed by a rapid decrease. During the heat aging of neoprene, a different pattern is apparent: (a) Tensile strength drops slightly in the early stages, but the loss seldom exceeds 35 per cent and thereafter little or no change is observed; (b) ultimate elongation decreases rapidly at first and declines slowly thereafter; and (c) hardness increases rapidly at first and then asymptotically approaches maximum hardness.

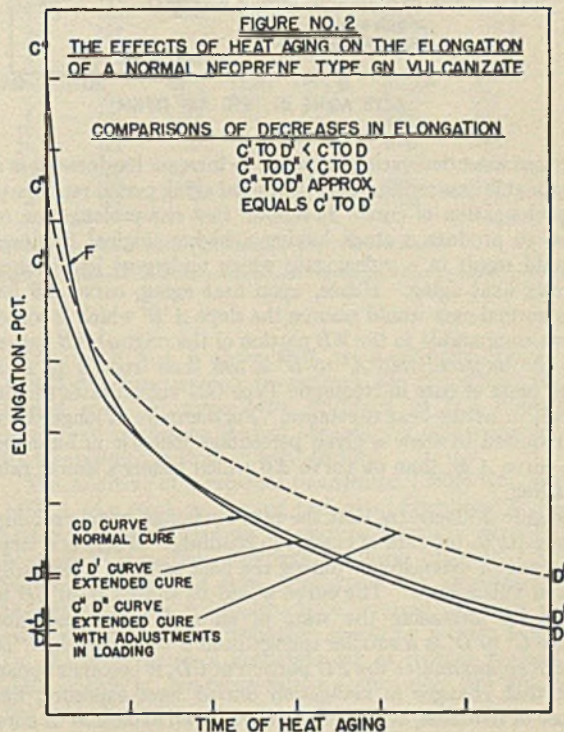
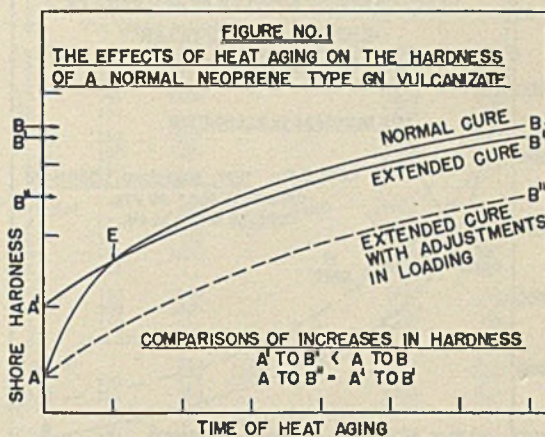
Since the tensile strength of practically all neoprene vulcanizates is not seriously reduced by severe aging conditions, this property is not a satisfactory criterion of age resistance. The magnitude of the changes in elongation and hardness under similar conditions, however, are generally larger; therefore these properties should be carefully studied in evaluating heat-resisting neoprene vulcanizates. Hardness is considered the more important because ultimate serviceability is often dependent upon it. Furthermore, the development of neoprene vulcanizates having satisfactory elasticity after heat exposure depends upon retarding their hardening during aging. The effects of heat on some physical properties must be considered separately because changes in elongation, hardness, and tensile strength cannot always be correlated with changes in resilience, flex resistance, electrical properties, and solvent resistance. However in this work only changes in elongation and hardness are considered.

Typical aging curves showing the changes in hardness and elongation of normal neoprene vulcanizates are reproduced in Figures 1 and 2; they are characteristic for all variations of high-temperature exposures. A normal neoprene compound is defined as one containing only the necessary curing ingredients, nominal filler loading but not special accelerators,

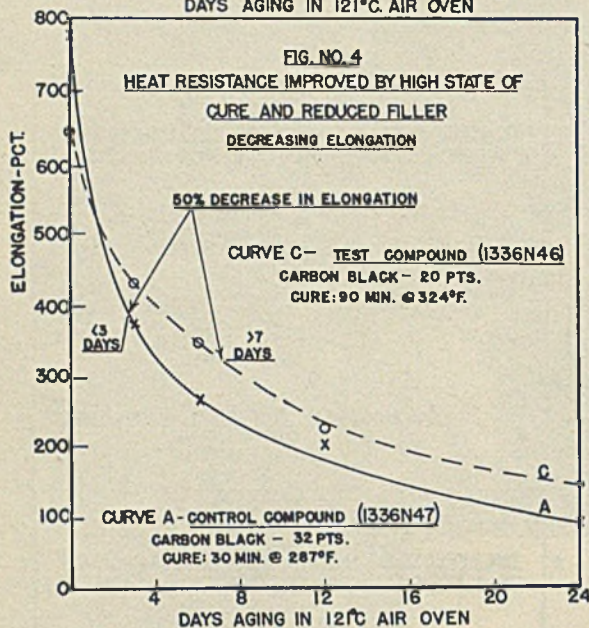
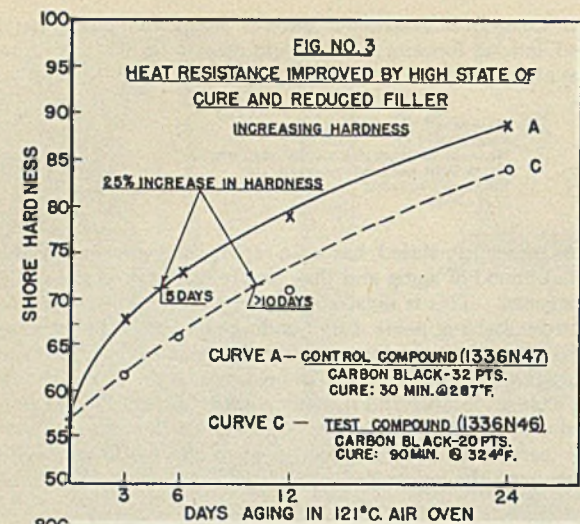
antioxidants, or retarders. Such a compound might have the following formula and it would usually be cured 30 minutes at 287° F.:

Neoprene Type GN	100.0
Stearic acid	0.5
Neozone A (phenyl- α -naphthylamine)	2.0
Extra light calcined magnesia	4.0
Filler and softener	As desired
Zinc oxide	5.0

As previously stated, hardness rapidly increases during the initial period of aging and then slowly increases as the aging progresses. This is illustrated by Figure 1. The difference between starting point A and ending point B is the increase in hardness during aging, and any reduction in this difference constitutes an improvement in heat resistance. Compounding changes in filler and softener content control the position of the curve on the scale but do not affect the magnitude of the increase in hardness except when the stock is heavily loaded and the vulcanizate approaches a maximum hardness.



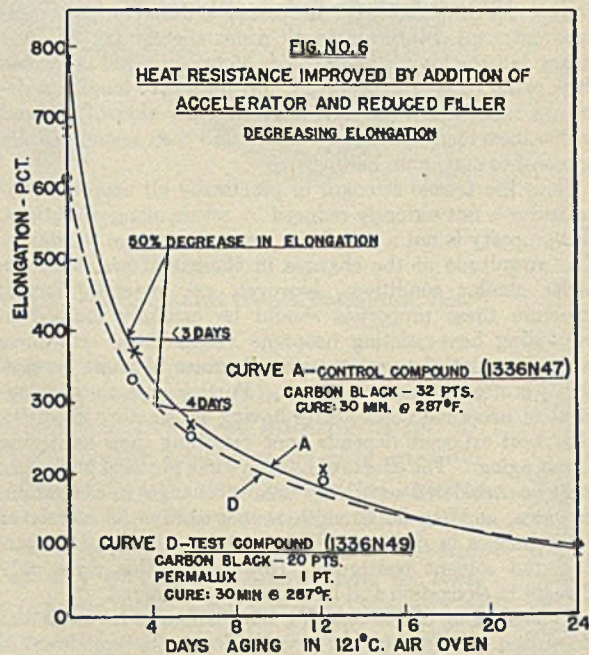
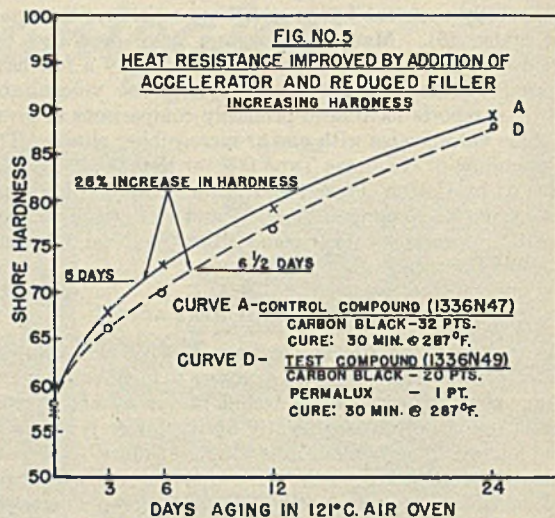
←
Neoprene Gloves, Hood, and Clothing Protect the Worker against Accidental Exposure to Chemicals



Since extended curing is known to increase hardness, it is a reasonable assumption that the initial aging period represents a prolongation of cure. It follows that the prolongation of cure to produce a stock having a higher original hardness should result in a vulcanizate which undergoes less change during heat aging. Hence, upon heat aging, curve *AB* for the normal cure would assume the slope *A'B'* which is somewhat comparable to the *EB* portion of the original *AB* curve. As the increase from *A'* to *B'* is less than from *A* to *B*, a high state of cure in Neoprene Type GN vulcanizates should result in better heat resistance. Furthermore, a longer time is required to show a given percentage increase in hardness on curve *A'B'* than on curve *AB* which means a slower rate of aging.

Figure 2 illustrates that the rate of change in extensibility is similar to the rate of change in hardness. There is a large decrease in extensibility during the heat aging of a normally cured vulcanizate. The curve would be shifted from *CD* to *C'D'* by increasing the state of cure of the vulcanizate. Since *C'* to *D'* is a smaller change than *C* to *D* and the *C'D'* curve approximates the *FD* portion of *CD*, it becomes apparent that changes in elongation during heat exposure, like those of hardness, should be reduced by an extension of cure.

The fact that a long cure results in a stiffer stock does not prevent the use of this method of improving heat resistance. If the elongation and hardness are outside of a specified or desired range, the filler and softener content can be adjusted to obtain the desired original properties. For example, if the desired hardness is *A* in Figure 1, a reduction in filler, increase in softener, or both would meet the requirements with a high state of cure. Curve *A'B'* would shift to *AB''* on the scale and the increase in hardness from *A* to *B''* would be the same as from *A'* to *B'*. This would result in a general increase in elongation as shown by curve *C'* to *D''* in Figure 2.



The effects of accelerators or retarders cannot be overlooked. Accelerators, by increasing the rate of cure, would be expected to affect the heat resistance in a manner similar to that of extending the cure. The use of accelerators has the added advantage of shortening vulcanization time. Retarders, by decreasing the rate of cure, would be expected to impair the heat resistance.

APPLICATION

In applying a test situation to the hypothesis just outlined, Neoprene Type GN was compounded in a heat-resisting formula. Thirty-two parts of semireinforcing carbon black were added, and the resulting stock was used as the control (1336N-47). The normal cure of this stock is 30 minutes at 287° F., and the original hardness obtained was 57. Reducing the carbon black to 20.0 parts produced a stock (1336N-46) having an original hardness of 52 with a normal cure. Increasing the carbon black to 43.0 parts (1336N-48) produced a stock having an original hardness of 63. The stock containing 20 parts carbon black was brought to an original hardness of 57 by two methods: (a) by extending the cure to 90 minutes at 324° F. (1336N-46), and (b) by the use of an accelerator, Permalux (di-*o*-tolylguanidine salt of dicatechol borate, 1336N-49). The original hardness of the stock containing 43.0 parts of carbon black was reduced to 59 by adding a retarder, MBTS (benzothiazyl disulfide, 1336N-50).

Standard test methods were used (1) with aging periods up to 24 days in the 121° C. air oven and up to 6 days in the 150° C. air oven. The physical properties of these compounds and the data obtained after aging are summarized in Table I.

These data provide the answer to the following questions arising from the hypothesis: For a given hardness does a stock with less filler having a high state of cure have better heat resistance? Does the addition of accelerator have the same effect as an extended cure? Does a compound having greater loading and added retarder for obtaining hardness have better heat resistance because the neoprene content would be less? Does heat resistance improve as the loading by filler increases? In discussing these questions, all references are made to curves showing the changes in elongation and hardness during aging in the 121° C. air oven. The results obtained in the 150° C. oven were similar except that the changes occurred in a much shorter time.

The curves in Figures 3 and 4 show that the simultaneous use of lower filler and longer cure to produce a given hardness results in greater heat resistance than the use of normal filler loading and normal cure. The original hardness of the two vulcanizates was 57. During aging in the 121° C. air oven, the highly cured vulcanizate increased 27 points in hardness compared with 32 points for the control stock. In addition, an analysis of the curve for compound 1336N-46 in Figure 3 shows that the rate of aging is lower for the highly cured vulcanizate because it must age a longer time to reach a given percentage increase in hardness. As expected, Figure 4 illustrates that the same composition changes least in elongation during aging. About 7 days were required for the highly cured stock to lose 50 per cent of its elongation compared with less than 3 days for the control vulcanizate. It is interesting to note that the elongation of the highly cured compound is greater after aging begins than the base stock. This is desirable, and it will be shown later that this is a function of loading rather than one of state of cure.

TABLE I. EFFECTS OF STATE OF CURE, QUANTITY OF FILLER, CHEMICAL ACCELERATOR, AND CHEMICAL RETARDER ON HEAT RESISTANCE

Compound No. 1336N-		46	47	48	49	50
Neoprene Type GN		100.0	100.0	100.0	100.0	100.0
Stearic acid		0.5	0.5	0.5	0.5	0.5
Neosone A		2.0	2.0	2.0	2.0	2.0
MUF ^a		1.0	1.0	1.0	1.0	1.0
Extra light calcined magnesia		4.0	4.0	4.0	4.0	4.0
Semireinforcing carbon black		20.0	32.0	43.0	20.0	43.0
Zinc oxide		10.0	10.0	10.0	10.0	10.0
Permalux		1.0	...
MBTS		1.5

Compound and Cure	Aging		Stress, Lb./Sq. In.			Tensile Strength, Lb./Sq. In.	Elongation at Break, %	Shore Hardness	
	Days	Temp., ° C.	100%	300%	500%				
1336N-46, 30 min. at 287° F.	Original		175	675	1350	3075	950	52	
	3	121	350	1475	...	2200	455	62	
	6	121	550	1875	...	2200	350	67	
	12	121	850	2075	235	74	
	24	121	2150	2325	115	85	
	0.75	150	575	1550	245	64	
	1.5	150	950	1475	160	70	
	3	150	1225	60	81	
	6	Too brittle to test							
	1336N-46, 90 min. at 324° F.	Original		250	1050	2050	2800	645	57
		3	121	350	1475	...	2250	430	62
		6	121	500	1900	...	2250	350	66
12		121	825	2050	230	71	
24		121	1825	2550	145	84	
0.75		150	475	1600	280	64	
1.5		150	800	1375	150	69	
3		150	1175	60	79	
6		Too brittle to test							
1336N-47, 30 min. at 287° F.		Original		300	1125	1850	2625	780	57
		3	121	650	2050	...	2350	370	68
		6	121	800	2350	270	73
	12	121	1400	2450	205	70	
	24	121	2400	90	89	
	0.75	150	725	1825	210	69	
	1.5	150	1425	1650	120	75	
	3	150	1475	60	85	
	6	Too brittle to test							
	1336N-48, 30 min. at 287° F.	Original		400	1500	2125	2250	620	63
		3	121	825	2450	...	2475	315	74
		6	121	1175	2450	215	79
12		121	1825	2400	130	83	
24		121	2800	80	94	
0.75		150	1125	1800	160	75	
1.5		150	1600	1600	100	81	
3		150	1200	20	90	
6		Too brittle to test							
1336N-49, 30 min. at 287° F.		Original		350	1150	2150	2625	605	58
		3	121	475	1900	...	2175	335	66
		6	121	650	2100	250	70
	12	121	1150	2100	185	77	
	24	121	2775	95	88	
	0.75	150	700	1650	220	69	
	1.5	150	1200	95	74	
	3	150	1100	30	85	
	6	Too brittle to test							
	1336N-50, 30 min. at 287° F.	Original		275	1250	1925	2200	730	59
		3	121	850	2275	...	2400	355	72
		6	121	1075	2550	265	77
12		121	1650	2575	180	81	
24		121	3000	90	91	
0.75		150	900	1975	200	73	
1.5		150	1650	1650	100	79	
3		150	1350	35	88	
6		Too brittle to test							

^a The antioxidant *N*-*p*-tolyl *N*'-*p*-tolyl sulfonyl *p*-phenylene diamine.

Figures 5 and 6 show that an accelerator (compound 1336N-49) can be used to approximate the effects of prolonged cure. However, the efficiency of this method is somewhat inferior to that of obtaining a high state of cure by increasing the time or temperature.

The addition of a retarder (compound 1336N-50), such as MBTS, to a stock containing additional filler slightly reduces rather than improves heat resistance (Figures 7 and 8). The conclusion regarding retarders must be qualified. MBTS reduces the state of cure throughout the complete range; therefore, if it is present, the time required to obtain a high state of cure for heat resistance would be greatly increased. On the other hand, a material such as sodium acetate (3), that retards at low-temperature cures only, will not affect the heat resistance.

Changes in filler loading have a significant effect on the absolute value of ultimate elongation or hardness both before and after aging but do not alter the magnitude of the changes that take place during heat exposure—i. e., the heat resistance. As shown by Figures 9 and 10, the rate of aging as based upon a 25 per cent increase in hardness or a 50 per cent decrease in elongation is the same for the stocks containing 20.0, 32.0, and 43.0 parts of semireinforcing carbon black.

The changes in elongation and hardness illustrated in Figures 3 to 10 show that a high state of cure would be essential for obtaining the maximum heat resistance in most applications. Since a 90-minute cure at 324° F. may be difficult to obtain, a suggested minimum cure for heat-resisting Neoprene Type GN stocks is 40 minutes at 307° F. (60 pounds per square inch steam pressure). With the minimum cure, a higher state of cure would be obtained by using a combination of accelerator, Permalux, and a selective retarder, sodium acetate. It is obvious that the absolute values of hardness depend upon the thickness of the slab. Tests on specimens 0.250 inch instead of 0.090 inch thick show the same general effects

TABLE II. HEAT RESISTANCE OF NEOPRENE TYPE GN COMPOUNDS

Compound 1336N-	58	59	60	61	62	63	64
Neoprene Type GN	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Stearic acid	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Neozone A	2.0	...	2.0	2.0	2.0	2.0	2.0
MUF	...	4.0	1.0	1.9	...
Extra light calcined magnesia	4.0	4.0	4.0	...
Semireinforcing carbon black	28.8	28.8	28.8	28.8	28.8	28.8	28.8
FF wood rosin	10.0	...
Zinc oxide	...	10.0	10.0	10.0	10.0	10.0	10.0
Litharge	20.0

STRESS-STRAIN RESULTS (ALL STOCKS CURED 30 MINUTES AT 287° F.)

Original							
Stress at 300%, lb./sq. in.	800	1225	600	1100	1075	1000	1025
Tensile strength, lb./sq. in.	2575	2650	2875	2825	2700	2775	2700
Elongation at break, %	695	675	900	740	720	800	685
Shore hardness	52	59	53	59	60	59	58
After 7-day exposure in 121° C. oven							
Tensile strength, lb./sq. in.	375	1650	1725	2050	2150	2100	1300
Elongation at break, %	40	110	225	200	280	370	155
Shore hardness	75	79	72	77	77	75	71
Retained tensile strength, %	14.6	62.3	60.0	72.6	79.6	75.9	48.2
Retained elongation, %	5.8	16.3	25.0	27.1	38.9	46.2	22.3
After 21 days in oxygen bomb (70° C. at 300 lb./sq. in.)							
Stress at 300%, lb./sq. in.	Failed	1525	1050	1500	1525	1000	1300
Tensile strength, lb./sq. in.	Failed	1525	2375	2050	1925	1875	2150
Elongation at break, %	in	200	780	520	520	485	620
Shore hardness	14	81	61	68	70	72	65
Retained tensile strength, % days	57.5	82.6	72.6	71.4	67.6	79.3	68
Retained elongation, %	20.7	84.5	70.3	72.2	60.6	90.8	60.8

but give absolute hardness values ranging from 2 to 7 points lower. The data in Table I show that when the aging is carried out at 150° instead of 121° C., the same relations exist between the compounds. At the higher temperature, changes in elongation are obtained approximately eight times faster and changes in hardness are obtained approximately five times faster.

TENSILE STRENGTH

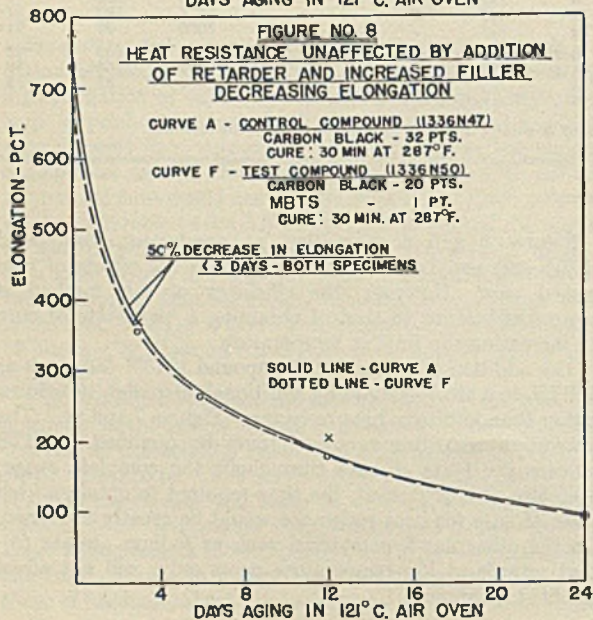
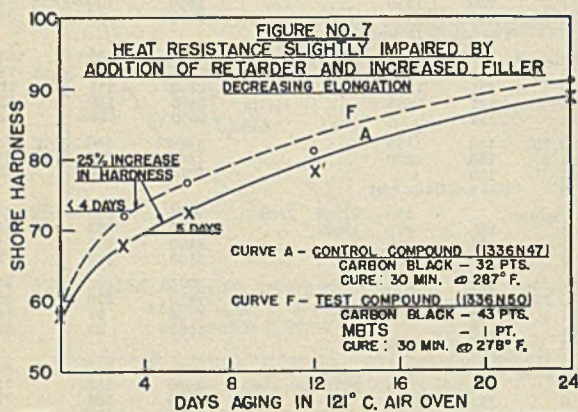
As previously stated, tensile strength deterioration is not considered a good criterion for evaluating heat resistance. This is illustrated by comparing the tensile strength curves in Figures 11 and 12 with the elongation and hardness curves in Figures 3 to 10, inclusive. The absolute tensile strength values are above a serviceable minimum, but the specimens have hardened to a point where they are no longer serviceable.

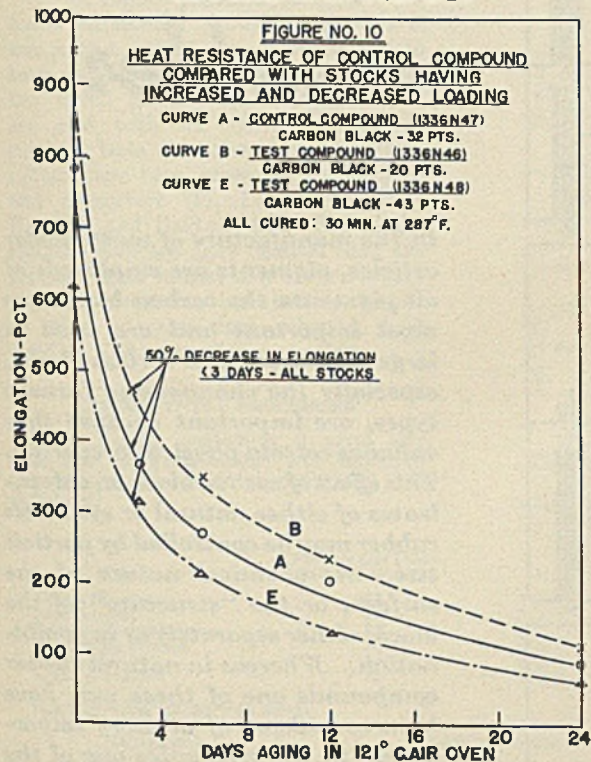
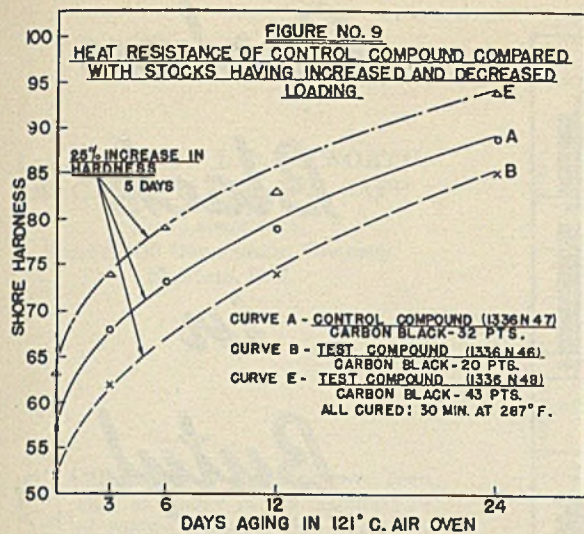
COMPOUNDING AND PRACTICAL APPLICATION

The previously described base formula for heat-resisting Neoprene Type GN vulcanizates contains all ingredients necessary for heat or natural aging. Antioxidant and zinc oxide are essential. The former is not added to Neoprene Type GN during manufacture and must be included in all compositions. Zinc oxide is required for good natural aging and significantly improves heat aging. Magnesia is included to balance the physical properties of the vulcanizate, and stearic acid is included for processing. The general use of these materials was discussed previously (2).

The data in Table II show that the base formula (1336N-62) used to study the effect of state of cure is not the only Neoprene Type GN composition that has good heat resistance or has extremely long life during natural aging. However, extensive laboratory tests and practical experience have shown that this combination is preferred because of general excellent physical properties after vulcanization. The data on compounds 1336N-58 and 59 show the necessity of including antioxidant and metallic oxide. Compounds 1336N-60, 61, and 64 illustrate the effects of the metallic oxides:

1. Magnesia stiffens vulcanizates before and after aging but imparts a greater retention of tensile strength after heat aging.
2. Zinc oxide improves the elasticity and thereby helps to limit stiffening before or after aging.

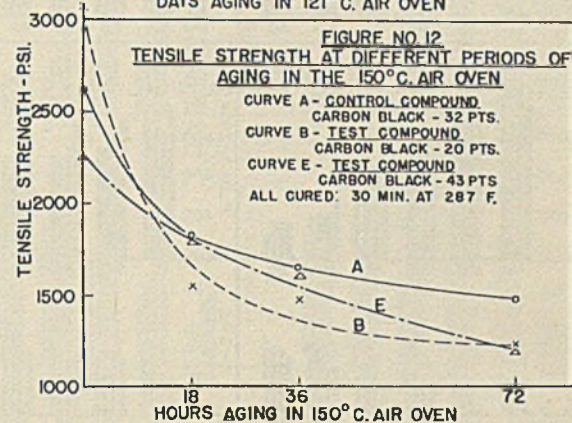
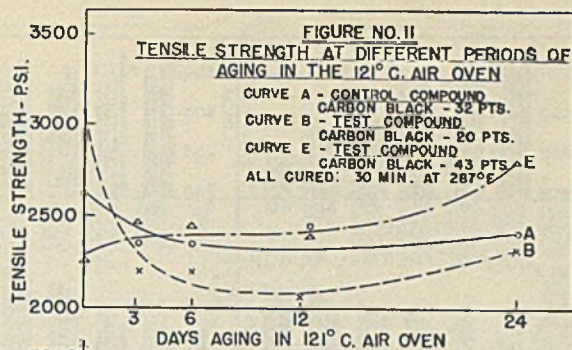




3. Lead oxide greatly limits hardening during heat exposure, but vulcanizates containing it do not retain tensile strength or extensibility as well as others.

A comparison of compounds 1336N-61 and 62 shows the improved extensibility after aging caused by the addition of MUF. This effect is even more pronounced than the figures indicate. Finally, from the standpoint of heat resistance exclusively, the base stock plus FF wood rosin (compound 1336N-63) gives the best heat service. Greater extensibility before and after aging is obtained by the use of rosin. The general use of FF wood rosin is slightly limited because it tends to activate low-temperature curves and increases heat generation during flexing.

Inert fillers and softeners must be used for loading practical stocks. The softeners must be carefully selected on a basis



of heat stability and volatility. The over-all physical properties of the unaged vulcanizates must be considered and the action of heat upon them is a factor.

Table III summarizes the changes usually observed in many of the physical and chemical properties of Neoprene Type GN vulcanizates during aging. As previously indicated, some properties can be correlated with changes in stress-strain properties.

TABLE III. USUAL CHANGES IN PROPERTIES DURING HEAT SERVICE

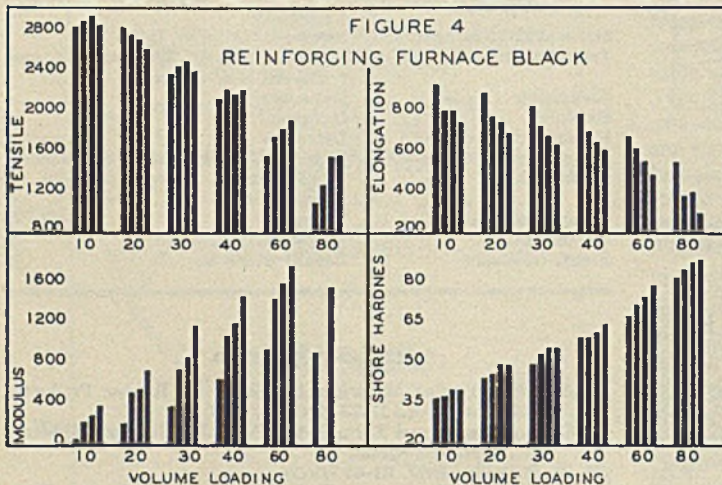
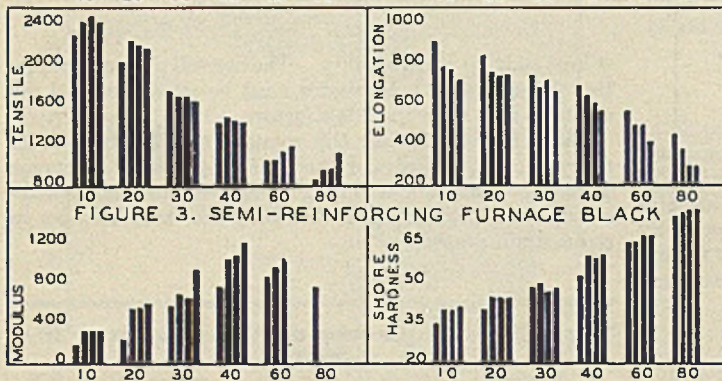
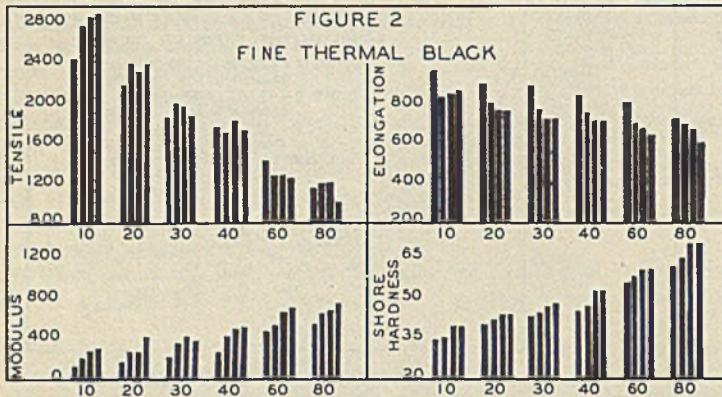
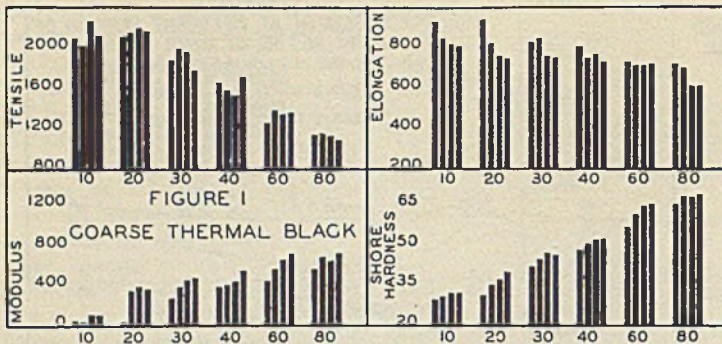
Property	Effect
Stress at given elongation	Increases
Tensile strength	Dependent upon filler content and method of compounding
Elongation	Decreases
Hardness	Increases
Resilience	Decreases
% compression set, methods A and B	Increase when aged during compression but decrease when aged prior to compression
Water absorption	Increases
Oil absorption	Decreases
Freeze resistance	Usually decreases

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Carbon Black in Butyl Rubber



Figures 1 to 4. Stress-Strain Properties of Compounds Containing Different Loadings of Carbon Blacks

Cured at 307° F. for 20, 40, 60, and 120 minutes. Tensile strengths in pounds per square inch; modulus at 400 per cent elongation; elongation in per cent.

In the manufacture of most rubber articles, pigments are employed; of all pigments the carbon blacks are most important and are used in large volumes. The carbon blacks, especially the channel and furnace types, are important because they enhance certain physical properties. This effect of carbon black on vulcanizates of either natural or synthetic rubber may be controlled by particle size, the chemical nature of the surface, or the "structure" of the black, either separately or in combination. Whereas in natural rubber compounds one of these may have been considered of primary importance, in the synthetics one of the others may be more important. Since natural rubber is now being replaced by synthetics, it is desirable to know how they respond to different types of carbon black. This paper presents data obtained on Butyl rubber by varying the type and concentration of the black. The relation of the results to particle size and chemical nature of the surface of the different blacks is discussed.

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CARBON black pigments have been used so widely in the manufacture of rubber products that their behavior in natural rubber compounds is well known. Now it is desirable also to have available information on the properties which result when these pigments are used with the synthetic types of rubber. Data on carbon blacks in Butyl rubber have been presented by Thomas and co-workers (8), Drogin (9), and Haworth and Baldwin (5). The results reported here are more detailed than the previous work in that they cover not only physical properties but include results on effect of cure time, rebound, heat build-up, and on two types of aging.

EXPERIMENTAL PROCEDURE

Butyl B-1.45, containing 5 parts zinc oxide and 1.5 parts sulfur, was employed throughout; the carbon pigments used were as follows:

Type	Particle Size Diam., Millimicrons (10)	pH (9)
Coarse thermal	274	7.2
Fine thermal	74	7.4
Semireinforcing furnace	31	9.8
Reinforcing furnace	35	9.8
Coarse channel	30	4.0-4.5
Medium channel	28	4.0-4.5

The following recipe was used:

Ingredients	Parts by Weight
Butyl B-1.45	100.0
Zinc oxide	5.0
Stearic acid	3.0
Sulfur	1.5
Tetramethylthiuram disulfide	1.0
Carbon pigment	10-80 volumes

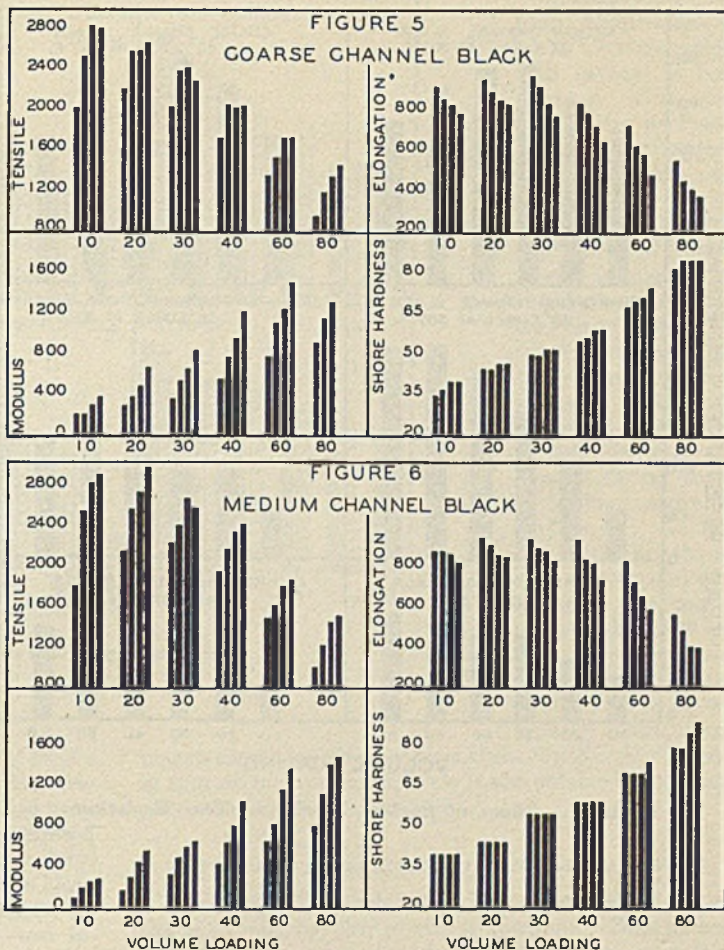
Mixing was carried out on a 6 × 12 inch laboratory mill with a mill roll temperature of 110-120° F. The mixing specification was as follows: The polymer was sheeted on the mill; black and stearic acid were added together; the accelerator was added after the black had been worked in; and the stock was batched out by A. S. T. M. method.

METHODS OF TEST. Stress-strain measurements were made by the A. S. T. M. procedure (1) at 72° F. and a relative humidity of 35 per cent. The cures were 20, 40, 60, and 120 minutes at 307° F.

Durometer hardness was measured by a type A Shore durometer on a double thickness of a 0.075-inch sheet cured 20, 40, 60, and 120 minutes at 307° F.

Rebound was measured with the Goodyear-Healy pendulum machine (4), using a 15° arc on specimens 2 × 1 × 1 inch, cured 60 and 120 minutes at 307° F.

Heat build-up was determined on the Goodrich flexometer (6) on pellets 0.7 inch in diameter, cut from blocks 2 × 1 × 1 and



Figures 5 and 6. Stress-Strain Properties of Compounds Containing Different Loadings of Carbon Blacks

Cured at 307° F. for 20, 40, 60, and 120 minutes. Tensile strengths in pounds per square inch; modulus at 400 per cent elongation; elongation in per cent.

cured 60 and 120 minutes at 307° F. The stroke was 12.5 per cent and the load was 148 pounds per square inch. The temperature of the test was 78° F.

Tear resistance was determined by the A. S. T. M. procedure, using five nicks in specimens cured 60 minutes at 307° F. (2).

Permanent set was determined by the A. S. T. M. procedure (1), using specimens cured 60 minutes at 307° F.

Oven aging was run in the air oven for 48 hours at 250° F., using the 60-minute cure at 307° F.

Oxygen bomb aging was run for 14 days at 300 pounds per square inch oxygen pressure and 158° F., using the 60-minute cure at 307° F.

EFFECT OF CARBON BLACKS

STRESS-STRAIN. The stress-strain properties of compounds containing the different blacks as the load is varied from 10 to 80 volumes cured 20, 40, 60, and 120 minutes at 307° F. are shown in Figures 1 to 6. It has already been reported (5, 8) that the addition of the reinforcing blacks does not result in the enhancement of tensile strength for this type of Butyl rubber; this finding is confirmed by the results reported here. The highest tensiles, however, are obtained with the reinforcing types. This is especially evident at pigment contents above 10 volumes. The semireinforcing furnace black is intermediate between the reinforcing and thermal blacks. In this respect the different blacks follow the pattern exhibited by them in natural rubber.

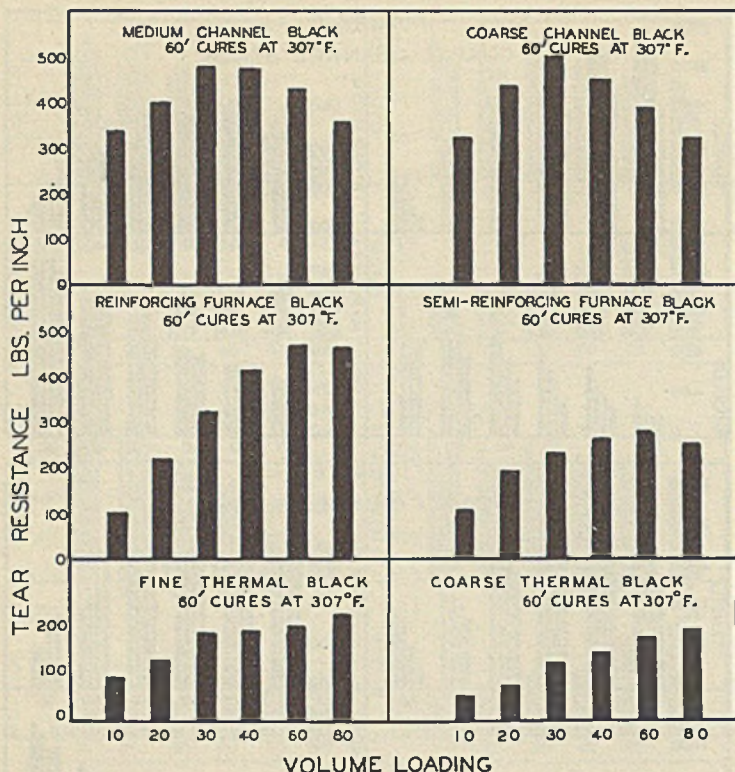


Figure 7. Effect of Carbon Blacks on Tear Resistance

higher elongations than those containing either furnace or thermal types. The concentration also seems to be more effective in reducing elongation in the case of the semireinforcing and thermal blacks than for the reinforcing types.

CURE RATE. As to the effect of black type and concentration on cure rate, it is evident that the channel type requires the longest time to reach optimum tensile. As would be expected, this is also generally true with respect to modulus. The concentration of any type behaves about the same throughout the concentration range. With respect to curing characteristics, the reinforcing furnace black gives results which would be expected from this type.

SHORE HARDNESS. Increasing concentration of any type of black produces a progressive increase in hardness (Figures 1 to 6). The rate of increase with increase in concentration is greatest with the reinforcing types. As would be expected, the reinforcing types also provide the hardest compounds; the semireinforcing furnace black is intermediate and the thermal blacks are lowest. With respect to the effect of cure time on a given concentration of any type, it can generally be said that there is very little change over the range.

An increase in concentration of all the blacks produces an increase in modulus. The best moduli are obtained with the reinforcing types; the semireinforcing and thermal blacks come next in order. The moduli of the compounds containing the reinforcing furnace black are worthy of attention. This black consistently gives higher moduli than either of the channel blacks. It may be that this is the result of the type of surface since the particle size of the three blacks is not widely different, but the type of surface is believed to be of considerable importance and is now under active investigation.

Compounds containing the channel blacks give consistently

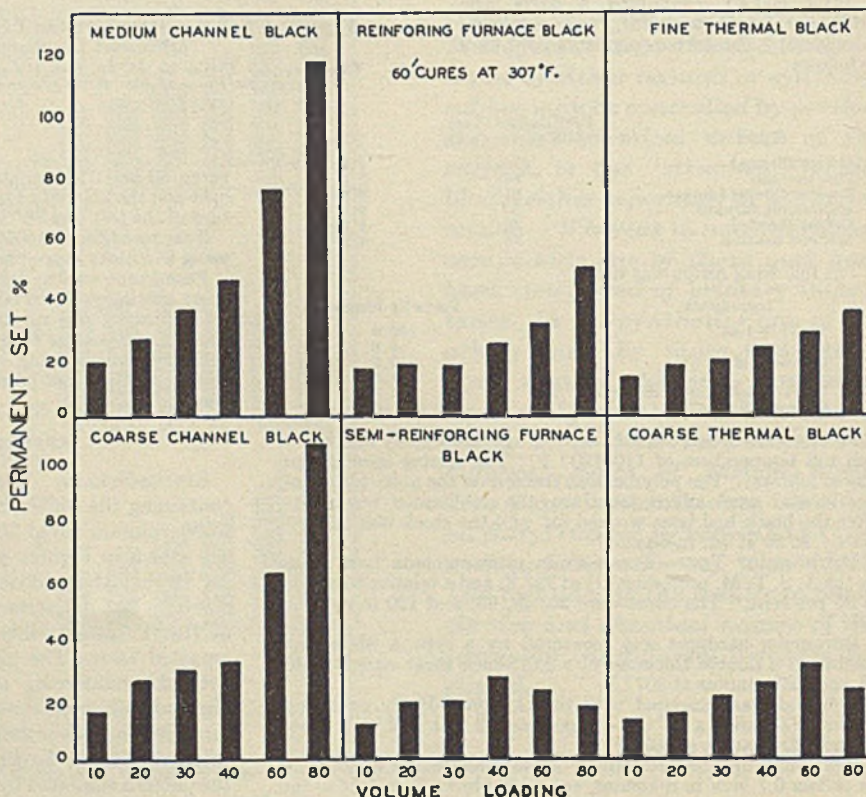


Figure 8. Effect of Carbon Blacks on Permanent Set

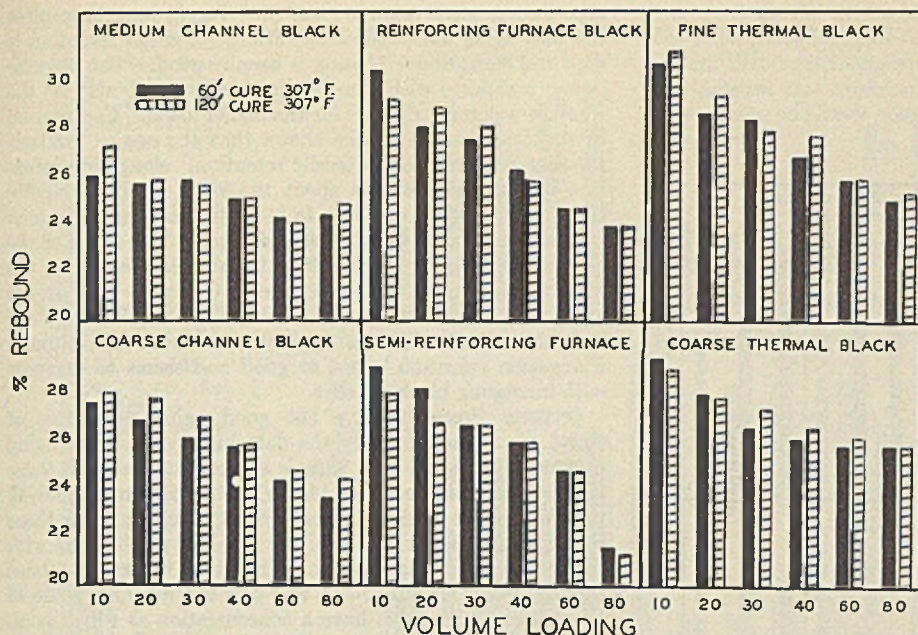


Figure 9. Effect of Carbon Blacks on Rebound

TEAR RESISTANCE. Increase in tear resistance by carbon black addition is usually considered evidence of reinforcement. In natural rubber all the types of black studied here, except the coarse thermal, reinforce as shown by the increased tear resistance of compounds containing them. In Butyl B-1.45 the channel blacks and the reinforcing furnace black are quite effective in improving tear resistance (Figure 7). As the concentration of these blacks is increased, tear resistance increases to a maximum and then decreases. The concentration of black for optimum reinforcement is in the vicinity of 30 volumes for the two channels and near 60 volumes for the reinforcing furnace type. The effect of the other three blacks is much less than that of the true reinforcing types. The semireinforcing furnace type produces the best result; the fine thermal comes next, and the coarse thermal type has the least effect. The semireinforcing furnace black shows a maximum effect at about 60 volumes while improvement is still being obtained even at 80 volumes concentration with the two thermal grades.

PERMANENT SET. Data on permanent set are presented in Figure 8. They show that for low permanent set the thermal and the semireinforcing furnace blacks should be used. Results obtained with the coarse thermal black and the semireinforcing furnace black are similar in that permanent set increases as the loading is increased and then decreases. Medium channel black compounds have the highest set, followed closely by the coarse channel. The reinforcing furnace type gives results which are similar to those obtained by the use of fine thermal black except that they are somewhat higher at the higher loadings.

REBOUND. Data on rebound at room temperature were obtained on two cures (Figure 9). Generally rebound is low. As the black content is increased, rebound decreases. The best results are obtained with the thermal blacks. Up to 30 volumes the fine thermal type gives better results. The two furnace types are comparable, while the coarse channel compounds are more resilient than those containing the medium grade. Although there seem to be a few exceptions, increasing the cure time improves resilience.

Although rebound at room temperature is low, it increases rapidly with increase in temperature. This effect is illustrated by Figure 10 for the semireinforcing furnace black compounds cured 60 minutes at 307° F. At 212° F. the rebound is greatly increased. As the pigment concentration is increased, the rebound values follow the same general pattern as that obtained at room temperature in that the greatest change comes at loadings above 30 volumes. At the higher loadings the increase of rebound with increased temperature is considerably less than for the lower loadings. Although data are shown for one type of black, com-

pounds containing the other blacks behave in a similar manner in that an increase in resilience is also obtained as the temperature of the test is increased.

EFFECT OF TEMPERATURE ON PHYSICAL PROPERTIES

Frequently it is desirable to know how the physical properties of a compound change with temperature. Data on tensile strength, elongation, and tear resistance at room temperature and at 212° F. for compounds containing 20 and 30 volumes of different blacks, respectively, are shown in Figure 11.

Tensile retention is good for all of the carbons, being best for the reinforcing types. Elongation retention is outstanding since little of the original elongation is lost at the higher temperature.

Tear resistance at elevated temperature is retained to a satisfactory degree. The reinforcing types of carbon give

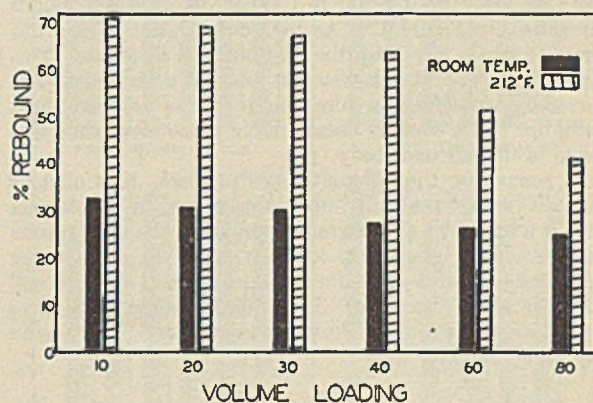


Figure 10. Temperature Rebound Characteristics of Semireinforcing Furnace Black Compounds Cured 60 Minutes at 307° F.

compounds which have the highest tear strength at the higher temperature. On a per cent retained basis, all of the types are about equal. From the results it is evident that in applications where good high-temperature tear resistance is desired, the reinforcing types of carbon should be used.

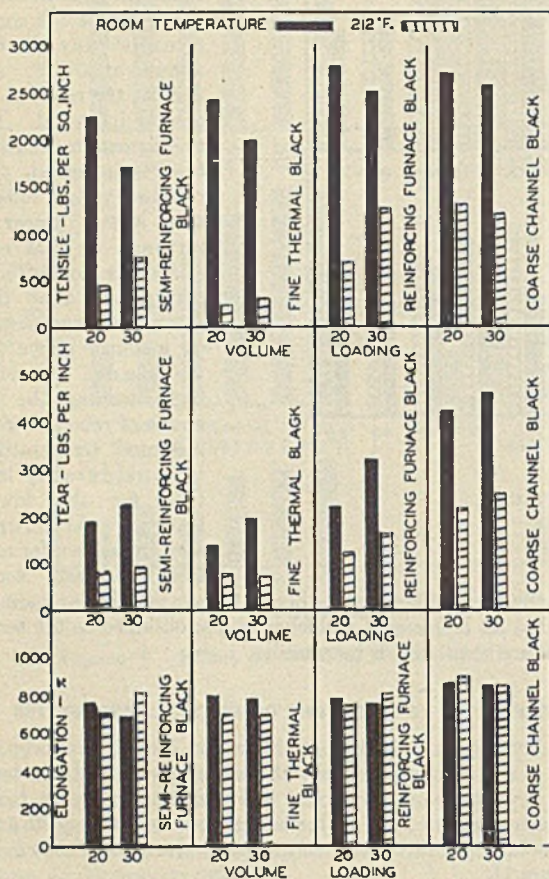


Figure 11. Hot Temperature Properties of Stocks Cured 60 Minutes at 307° F.

HEAT BUILD-UP. The Goodrich flexometer has been frequently used to study the hysteresis properties of rubber compounds as indicated by heat build-up during dynamic flexure. Data on the various Butyl B-1.45 carbon black compounds are shown in Figure 12. As the concentration of the different blacks is increased, the heat build-up increases. This corresponds with the decrease in rebound described above. Generally an increase in cure time results in decreased heat build-up. This effect is usually more pronounced than was found in the rebound study.

In comparing the different types of black, it is obvious that the highest heat build-up is obtained when the channel type is used. The coarse grade gives about the same results as the medium grade. In loadings up to 30 volumes the heat build-up of the reinforcing furnace and the thermal blacks is about the same. The semireinforcing black gives results which are lower. Presently there does not seem to be any explanation for this.

AGING PROPERTIES

HEAT AGING. Butyl B-1.45 has good aging properties. Figure 13 presents data on heat aging at 250° F. as the black

type and concentration are varied. The furnace type gives the best aging under these conditions. Tensile retention is high and elongation retention is usually good. The increase in age resistance with increase in black content may be the result of a slight undercure for the higher loads. Comparison of the two thermal blacks shows that the coarse grade is superior with respect to tensile retention; elongation retention is very good and is about the same for both blacks. Here again there is evidence to indicate that increasing load results in increased oven-aging resistance. The aging of the channel black compounds differs from those containing the other types in three main categories. Generally they do not age so well, at least up to 60-volume loads. Further, age resistance seems to be a minimum at about 30 volumes. Elongation retention is not so good and seems to decrease with increasing black content.

OXYGEN BOMB AGING. The good aging properties of Butyl are again shown by the data on oxygen bomb aging presented in Figure 14. This is especially true since these results were obtained after 14-day exposure. In comparing the effect of the different types of black on aging under these conditions, it seems that the best results are obtained with the reinforcing furnace black. The other blacks are about equal, and all are good. In this test the medium grade of channel black seems to have a concentration at which minimum age resistance results. There is some indication that a similar result is obtained with the semireinforcing furnace black. The age resistance of the coarse channel compounds seems to decrease slightly as the concentration is increased. All of these effects can be classed as indications and can be fully established only by further work.

CONCLUSIONS

If tensile strength alone is considered, carbon pigments which reinforce natural rubber do not reinforce Butyl. However, when the enhancement of other physical properties, such as modulus and tear resistance, associated with reinforcement are considered, it can be said that the types which reinforce natural rubber also reinforce Butyl. The results obtained when the other types of carbon are used in Butyl are in line with the general performance of these carbons in rubber compounds.

As to the effect of particle size, over the wide range studied for the thermal and over the narrow range for the channel types the change in this property does not produce any substantial change in physical properties. The reinforcing furnace black shows a decided improvement when particle size is reduced. Further, by the use of this black a higher modulus results than is obtained by using a channel black of about the same particle size. As already indicated, this may be due to the difference in chemical nature of the surface as shown by the difference in pH. On the other hand, it may be the result of a difference in the "structure" (?) of the different types. In order to clear up this question additional work is being done.

The hysteresis properties as shown by rebound and heat build-up are influenced by carbon type and concentration in a manner similar to that observed for natural rubber compounds. Although rebound at room temperature is low, an increase in temperature greatly increases it. From this it would be expected that Butyl would heat up quickly under flexure but that equilibrium temperature would not be excessive except in severe applications. For a balance of physical properties with low heat build-up, the furnace type carbons are suggested.

The aging of carbon black compounds of Butyl is good. For best aging here again the use of the furnace blacks is indicated.

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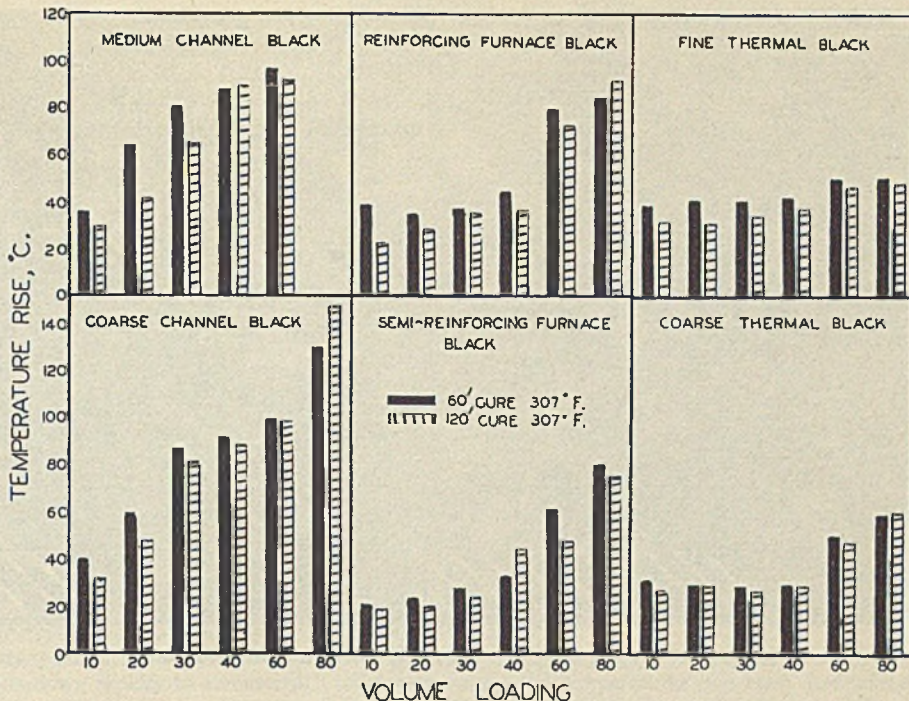


Figure 12. Effect of Carbon Black on Heat Build-up in a Goodrich Flexometer
Applied load, 148 pounds per square inch; compression stroke, 1/8 inch; room temperature.

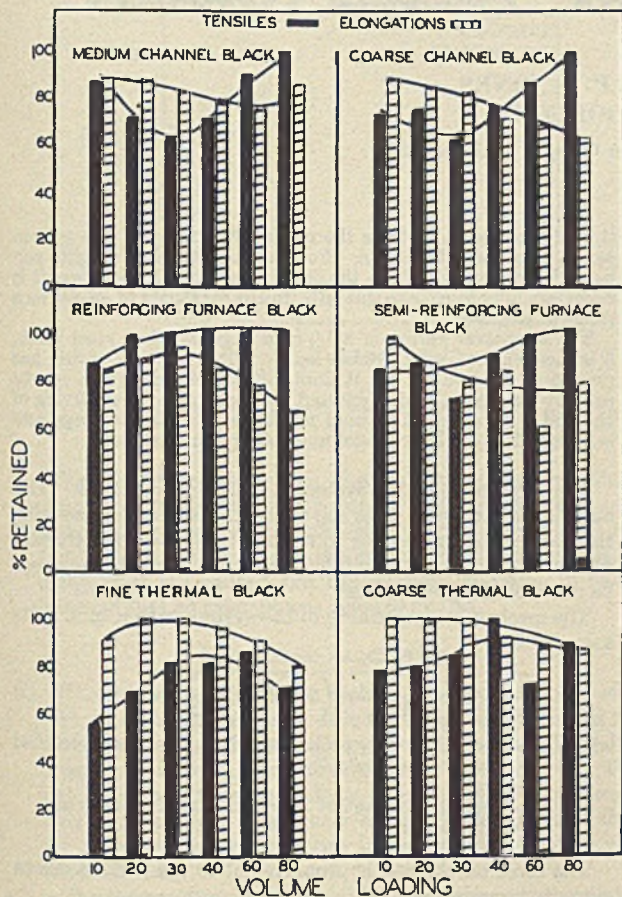


Figure 13. Effect of 48-Hour Heat Aging at 250° F. on Stocks Cured 60 Minutes at 307° F.

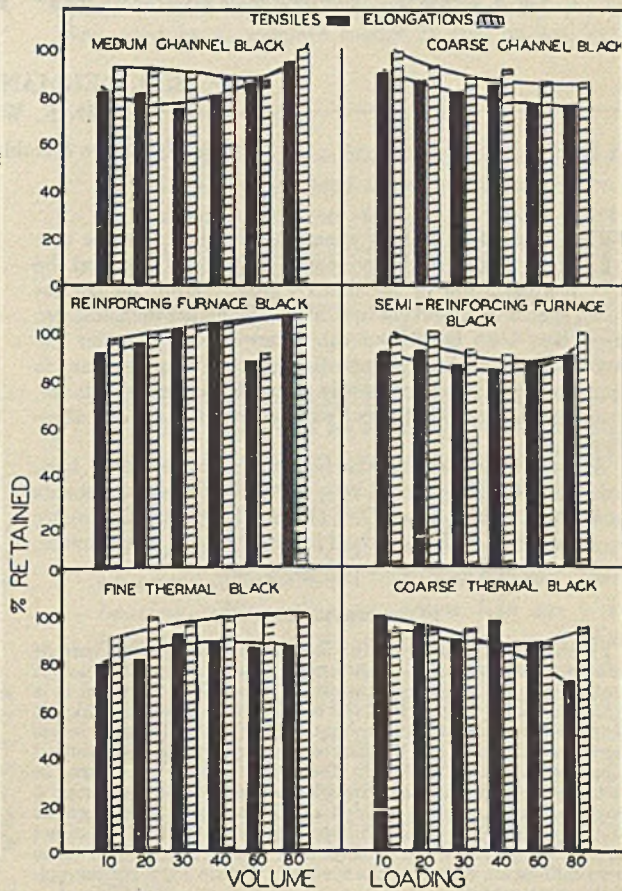


Figure 14. Effect of Oxygen 11-Day Bomb Aging at 158° F. under 300 Pound, of Stocks Cured 60 Minutes at 307° F.

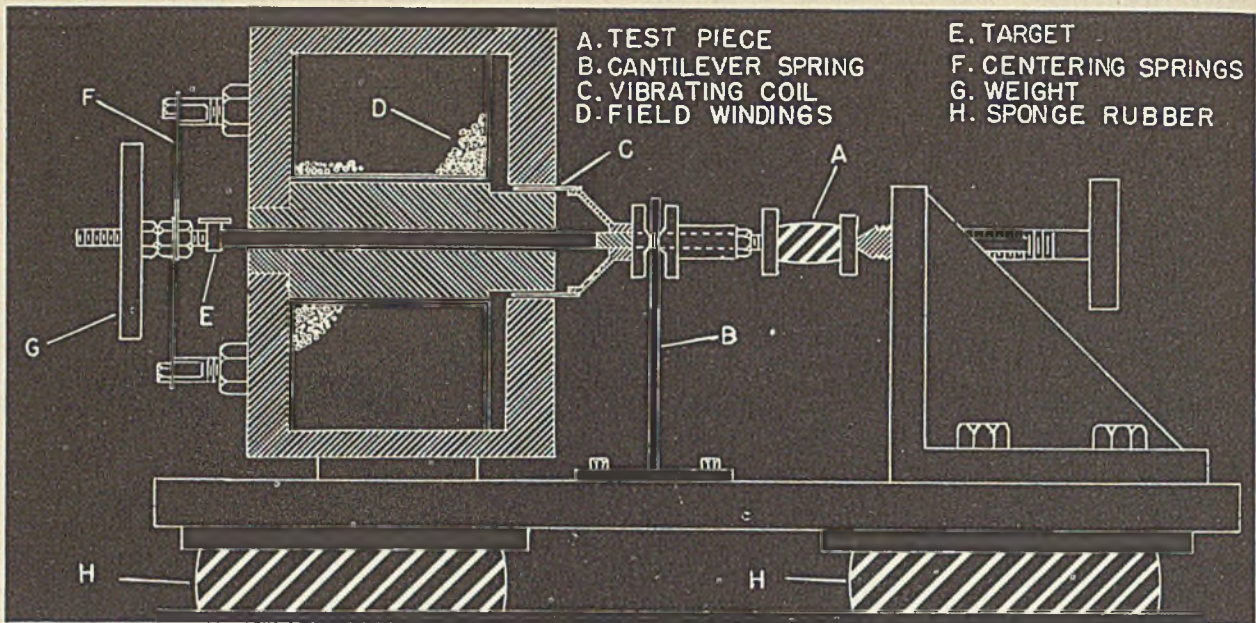


Figure 1. Drawing of Flexometer

Heat Generation in Flexed Rubber

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THE problem of heat generation in tires assumes new importance with the advent of synthetic rubber and the increased use of reclaimed rubber. Even though reduced speeds may prevent heat blowouts, higher temperatures mean that both fabric and rubber are operating under unfavorable conditions. Synthetic rubber, in particular, is then working at reduced tensile strength and tear resistance. It is more susceptible to heat embrittlement, cuts, and abrasion.

A number of flexometers for rubber testing have been described (1, 3, 10, 12, 17, 20); some of these instruments have been widely used (11, 13, 18, 29). The flexometer here described is characterized by simplicity of construction, high speed, and convenience of operation.

FLEXOMETER DESIGN

Figure 1 is a drawing of the flexometer. Sixty-cycle current from a 12-volt filament transformer, the primary of which is controlled by a variable transformer, is supplied to a coil in a radial magnetic field so that the coil and the system to which it is attached vibrate with this frequency. The coil has an inside diameter of 3 inches and consists of two layers of No. 18 enameled copper wire wound on a thin fiber tube, twenty-three turns in each layer. The current through the coil is usually about 5 amperes, but it may be as high as 15 amperes. The magnetic field is produced by a field coil operated from the 110-volt direct current line and is about 8000 gauss. Figure 2 shows the static force calibration curve for the system. Figure 3 is a photograph of the instrument.

Since the central system of rod, coil, cantilever spring, and rubber test piece is driven at a frequency of 60 cycles per second,

it is advantageous to have the natural frequency of the system somewhere near this value. For this adjustment, weights can be added or removed from the end of the rod. In practice, it is necessary only to change this adjustment for stocks of an extreme range of stiffness.

The cantilever spring is a $\frac{1}{4}$ -inch gage stainless steel plate, 3 inches wide and $7\frac{1}{4}$ inches long. The cantilever spring has proved to be durable, but it limits the amplitude which can be used by its action, when deflected, of disturbing the centering of the coil. A coil spring would not have this disadvantage and is designed into a later model now under construction.

The impedance of the system is rather complicated. The electrical impedance of the coil at rest must be combined with the mechanical impedance to secure the over-all impedance. Morse (21) gives the equations for a loud-speaker which can be used for the present case.

The mechanical impedance of the system with c. g. s. units assumed is:

$$Z = \sqrt{R^2 + \left(2\pi\nu M - \frac{K}{2\pi\nu}\right)^2} \quad (1)$$

where R = constant of proportionality between frictional force and velocity

M = mass

K = spring constant or force per unit displacement

ν = frequency

The force on the coil is proportional to the instantaneous current through it so that

$$F = DI \quad (2)$$

where F = force, dynes
 I = current, amperes
 D = constant of proportionality

The total impedance of the coil is given by

$$Z_E = \left\{ \left[R_c + \frac{GR}{Z^2} \right]^2 + \left[2\pi\nu L_c + \frac{KG}{2\pi\nu Z^2} - \frac{2\pi\nu MG}{Z^2} \right]^2 \right\}^{1/2} \quad (3)$$

where R_c = resistance of coil
 $G = D^2 \times 10^{-7}$
 L_c = self-induction of coil

The amplitude of the motion for an applied alternating voltage of maximum value E is:

$$A = \frac{DE}{2\pi\nu Z Z_E} \quad (4)$$

Some of the values for the system can be given. The d. c. resistance of the coil is 0.26 ohm. Its self-induction, L_c , is 217 microhenrys; hence its static impedance at 60 cycles is 0.27 ohm. From Figure 2, D can be determined as 931,000 and G as 8.67×10^4 . The constants for the mechanical system will depend upon the rubber test piece. Under suitable operating conditions, the impedance measured when running with a gum stock was 0.35 ohm and for a GR-S tread stock, 0.75 ohm. As the test piece heats up, the impedance changes somewhat and an adjustment must be made in the coil current to maintain a constant amplitude. But the system is stable and tends to settle down rapidly to a constant amplitude.

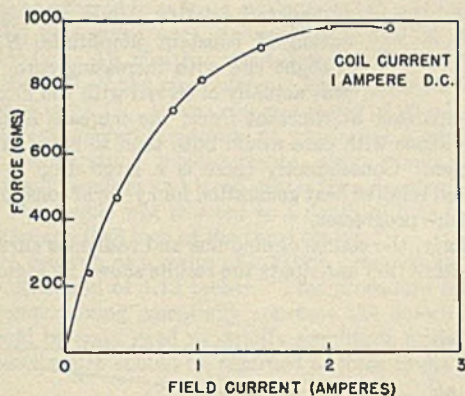


Figure 2. Force Calibration Curve

The impedance of the coil, when the flexometer is running, can readily be determined by measuring the voltage and current. It is possible that some technique might be worked out to use this measurement in the evaluation of the stiffness or damping of the rubber, but the relations appeared to be so involved that no attempt was made to do this.

TESTING PROCEDURE

The rubber test piece is a rectangular block 2 inches long with a 1-inch square base. It is the same test piece used for the Goodyear pendulum rebound test. It is mounted between metal plates containing recessed fiber inserts. The test piece is put under a static compression of 6 per cent. This is determined by a spacer block. Figure 4 shows that the observed temperature rise is rather insensitive to this compression.

The temperature in the middle of the block is measured by a needle thermocouple and a Leeds & Northrup tempera-

ture indicator. The needle thermocouple was made by running a silk-insulated constantan wire through a hypodermic needle and soldering the wire to the needle at the point.

The temperature of the block is measured at the start of the test and after running for 10 minutes at a fixed amplitude. The difference in these readings and the calibration of the thermocouple determine the temperature rise due to flexing. Figure 5 shows that after 10 minutes the temperature of the test piece approximates the equilibrium temperature. The test piece is enclosed in a jacket during the test, the temperature of which is controlled at 35° C. A small fan is provided to circulate the air.

The amplitude is determined by the visual observation of a suitable target through a magnifying lens. The target consists of a solid black arrowhead pointing at a broad black line on a white background. In vibration the arrowhead and the line are spread out or blurred due to the persistence of vision. The current through the coil is set so that the point of the blurred arrow just touches the edge of the blurred line. The amplitude is then one half of the distance between the arrowhead and the edge of the line when at rest. For different amplitudes one target can be readily replaced by another.

The compounds here reported were accelerated with Captax (mercaptobenzothiazole) in conventional formulas published previously (7).

Figure 6 shows the cooling curve for a test piece mounted in the flexometer; the temperatures had been determined for various elapsed times with the needle thermocouple. The rate of cooling at the start is about 7° C. per minute, which corresponds to the cooling rate to be expected while a reading is being taken after a test piece is run. As the reading is obtained within about 10 seconds after stopping, the technique used seems accurate enough in this respect for the

A flexometer is described which is adapted for the accurate and rapid determination of the temperature rise in a rubber test piece due to flexing in compression. Curves illustrate the effect of amplitude, cure, pigment loading, and other factors on the temperature rise for Hevea and GR-S stocks. Results of resiliometer tests indicate that about half the temperature rise in a tire tread can be ascribed to deformation cycles, such as bending, for which the amplitude is independent of the stiffness of the stock, and half to cycles, such as compression, for which the amplitude is inversely proportional to the stiffness. The bearing which this situation has on the interpretation of flexometer tests and the methods of running the tests are discussed. The principles involved in heat generation by flexed rubber and synthetics as revealed by flexometer data and other vibration tests are examined with a view to understanding something of the fundamental molecular or structural mechanisms involved.

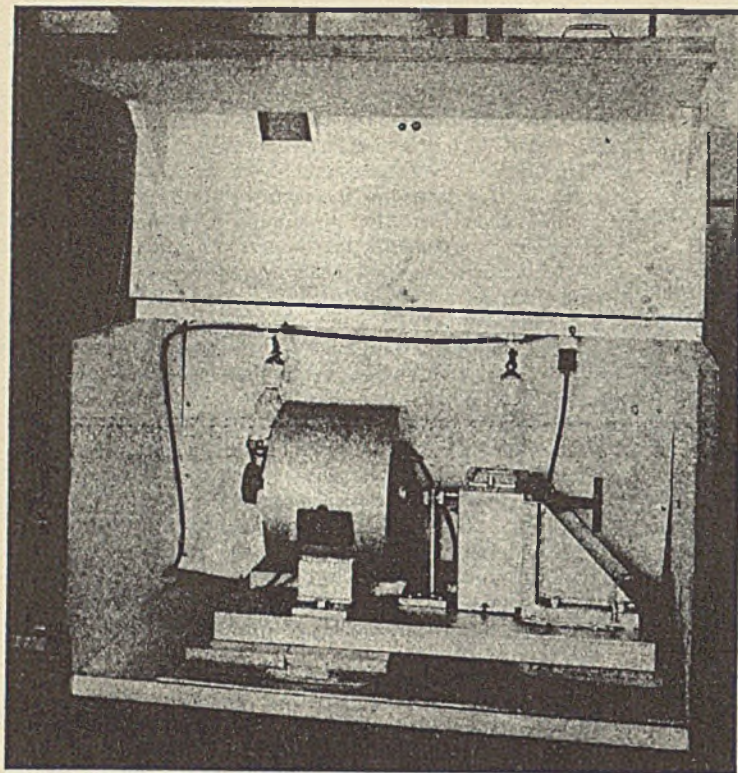


Figure 3. Photograph of Flexometer

comparison of rubber compounds. Insertion of the needle at the end of the test, without stopping the flexometer, also gives accurate results.

Figure 7 illustrates the temperature gradient along the test piece after running. The maximum temperature occurs in the mid-plane of the test piece where the alternating strain is greatest and the heat losses are a minimum. The curve shows some advantage in the technique of measuring the temperature of the test piece in the middle rather than at the end even if this precludes the possibility of a continuous temperature record. It is noteworthy that the temperature at the moving end is somewhat lower than that at the stationary end, probably due to a fanning action of the air on the moving end.

Figure 8 shows the effect of amplitude of vibration on heat generation. Theoretically the heat generation increases with the square of the amplitude; but as the temperature rises, the resilience increases, the modulus decreases, and the heat losses increase so that actually the relation between heat generation and amplitude is approximately linear.

Figure 9 gives some curves relating the observed temperature rise to various pigment loadings in Captax-accelerated stocks. The higher heat generation in GR-S as compared to natural rubber is emphasized.

Figure 10 illustrates the effect of the initial uniform temperature of the test piece upon the ensuing temperature rise. The jacket temperature was adjusted to be equal to the initial temperature in each case. When a test piece is run in the flexometer, the final temperature reached represents an equilibrium value between heat generation and heat losses. These curves show that the rate of heat generation is not constant but falls off at the higher ambient temperatures so that equilibrium is reached sooner and with a lower temperature rise than would otherwise be the case.

The data in Figure 11 bring out the facts that the temperature rise for GR-S is relatively independent of cure in the technically useful range and that the sensitivity of the equipment for differentiating between small variations in heat generation is best at higher amplitudes. Figure 12 represents a further study of the effect of cure on heat generation for both natural rubber and GR-S tread stocks.

FLEXOMETER RESULTS

Although from a practical standpoint these flexometer measurements are comparatively straightforward, the measured temperature rise actually represents a composite result from many interrelated factors, the ultimate analysis of which would go back to the molecular structure of the rubber. For many purposes it is sufficient for a better understanding of the results to consider the vibration properties of the rubber as determined by suitable vibration tests (7, 27).

The small effect of cure on temperature rise (Figures 11 and 12) results from the fact that for these stocks both modulus and resilience increase with cure and have opposite effects on the heat generation at constant amplitude. Figure 13 shows the course of the curves from the vibration test. Calculated relative values of heat generation at constant amplitude, H_s , show a slight rise with increasing cure, such as was actually observed with the flexometer.

For comparison at constant force, the increase in modulus and resilience with cure would both tend to reduce the heat generation. Consequently there is a large drop in H_s , the calculated relative heat generation for cycles of constant force, as the cure progresses.

Similarly, the course of modulus and resilience curves with temperature (27) anticipate the results shown in Figure 10.

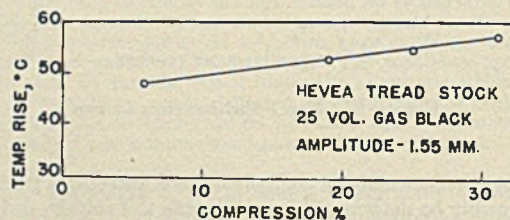


Figure 4. Temperature Rise vs. Static Compression

In any given comparison in this work, all of the rubber compounds were flexed at the same amplitude. It is well recognized that conditions of deformation in a pneumatic tire tread are complicated and cannot be simulated exactly by a constant amplitude comparison. In a general way, bending of the tread due to the tire deflection is an amplitude cycle relatively independent of the stiffness of the stock. On the other hand, the pressure between the rubber and the road brings into play a force cycle for which the deformation will vary inversely with the stiffness of the stock. For the correct interpretation of the flexometer results, it is important to know the relative proportion of the heat generation which

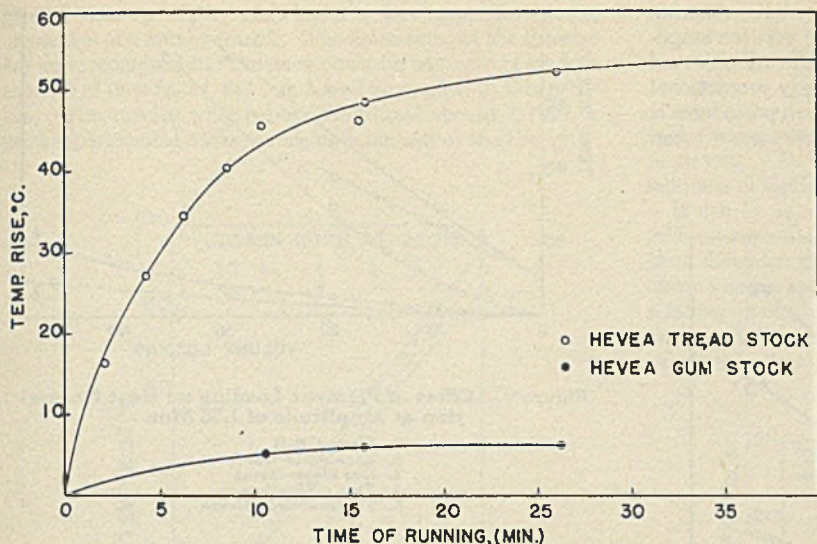


Figure 5. Dependence of Temperature Rise on Time

occurs under these two conditions. A resiliometer test was run to secure some information on this point and to try to separate the two effects.

Two tread stocks of WPB qualities A and C were compared in a tire test on the resiliometer. For brevity the stocks will be referred to as tread stocks A and C, respectively. The results here given were obtained for a 9.00 × 20 tire with a Goodyear All Weather tread design. The tire had a two-way tread, half the circumference being of stock A, the other half of stock C. It was run at a speed of 30 miles per hour on a resiliometer, the wheel of which was 7 feet in diameter. Temperature measurements after running were made at tread shoulder and tread center by a needle thermocouple. The needle was inserted to a depth of 0.54 inch at the shoulder and 0.43 inch at the tread center.

The tire was run at a series of inflation pressures but at a constant deflection of 1.12 inches. This procedure had the effect of maintaining essentially constant the deformations which could be considered as strictly amplitude cycles; the deformations which should be regarded as force cycles varied

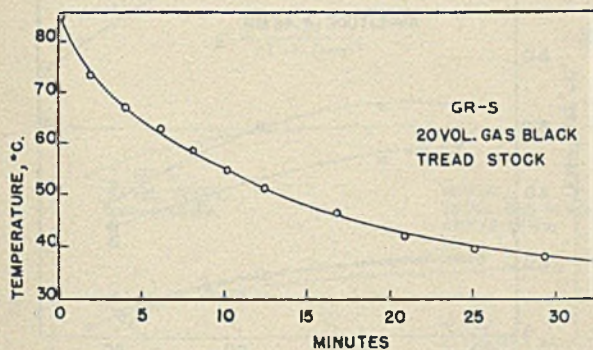


Figure 6. Cooling Curve

with the inflation pressure. The results of the test are shown in Figure 14 where the temperature rise is plotted against the inflation pressure. Smooth curves were obtained which have definite intercepts on the temperature rise axis. For the

tread center, for both stocks, this intercept is about 40 per cent of the temperature rise at 65 pounds per square inch inflation, the normal inflation pressure. For the shoulder the intercept is about 60 per cent of the total rise. Presumably the intercept represents the temperature rise that can be attributed to amplitude cycles which are independent of the inflation pressure. The deformations involved are controlled by the change in shape of the deflected carcass and are independent of the stiffness of the stock. The above analysis is an "averaging type" with obvious limitations in precision. The effect on the tread temperature of the heat developed in the carcass is assumed to be negligible. In spite of these limitations, it is felt that the experiment gives a picture of the mechanism of heat generation in tire treads which is essentially correct.

The average ratio of the temperature rise for stock C to that for stock A in the resiliometer test was 1.17. A flexometer comparison of the stocks showed a ratio of 1.27. In general, flexometer comparisons at cycles of the same ampli-

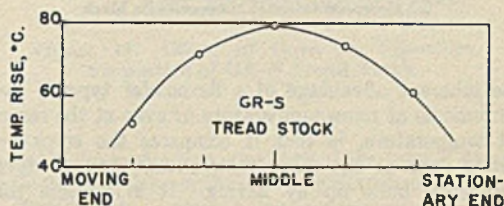


Figure 7. Temperature Gradient along Test Piece after Running

tude can be expected to rate stocks in the correct order for tire tread temperature rise but to exaggerate the differences between the stocks, because about half of the tread temperature rise occurs under conditions corresponding to constant force cycles. This same tendency is shown in results of an experiment reported by Mackey, Anderson, and Gardner (18) in which two stocks containing different amounts of carbon black were compared. Flexometer tests at the same amplitude showed temperature rises of 110° and 92° F. for the high-black and low-black stock, respectively. In a resiliometer test, tread temperatures of 146° and 140° F., respectively were observed.

As long as this characteristic of the flexometer results is kept in mind, it is not a serious disadvantage for laboratory testing since it tends to emphasize trends and differences. For a more precise evaluation of the heat generation of rubber compounds in tire treads, more attention should be given to some means of also taking into account the heat generation of the stocks under cycles of the same force. For solid tires the constant force comparison would have much more significance than the constant amplitude comparison.

If it is desired to compare rubber stocks when subjected to cycles of the same force, it is necessary to determine the dynamic moduli of the compounds by an independent test (7) and then to run them in the flexometer at amplitudes

which are inversely proportional to the moduli. Alternatively, use may be made of the linear relation between amplitude and temperature rise (Figure 8) to correct observed temperature rises to values which are inversely proportional to the moduli. One of the difficulties with such procedures is that the variation of modulus with temperature is not taken into account.

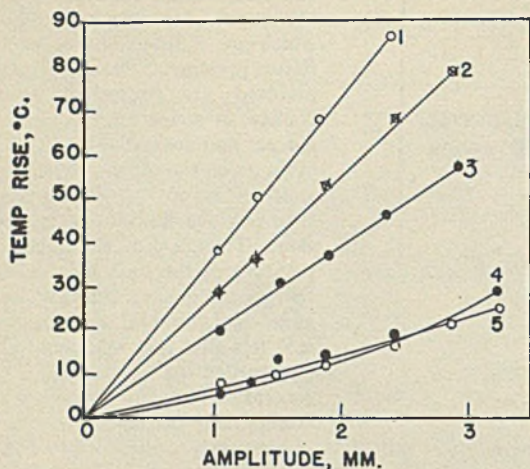


Figure 8. Effect of Amplitude on Heat Generation

1. GR-S-20 volumes gas black
2. Hevea-25 volumes gas black
3. Hevea-20 volumes gas black
4. Hevea-20 volumes zinc oxide
5. Hevea-20 volumes thermatomic black

The inherent advantage of a flexometer type of test to measurements at room temperature or even at the same elevated temperature, is that it compares the stocks when operating, not at the same temperature, but at different temperatures built up by flexing. It is possible that a flexometer comparison of rubber stocks can be devised which will simulate more closely conditions in a tire tread than anything yet reported. It seems worth while to suggest that, in a flexometer of the type described, the test piece could be loaded against a dynamometer, the relatively small vibrations of which would be proportional to the alternating force. By suitable magnification of the motion of the dynamometer, the force amplitude could be observed and set at a constant value for a series of stocks. The average rating from the constant force and constant amplitude comparison should then give a precise rating of the stocks in respect to their heat generation as tire treads.

RELATION OF HEAT GENERATION TO RUBBER STRUCTURE

The transformation of mechanical energy into heat, which occurs in the flexing of rubber, is naturally thought of as due to (a) some process similar to the frictional development of heat during the flow of a viscous liquid, or (b) solid friction such as is responsible for vibration damping for metals and other solids (16, 25). A dilute solution of rubber in an organic solvent will approximate a pure liquid in viscous behavior. As the concentration is increased, the phenomena become more complicated and the flow properties depend on the rate of shear. This is due to the interaction of the dissolved molecules or a tendency to assume equilibrium positions with respect to one another. In other words, it represents the appearance of a rudimentary type of elasticity. Such systems are called elasto-viscous. In the case of rubber, the elastic nature of the solution will become more

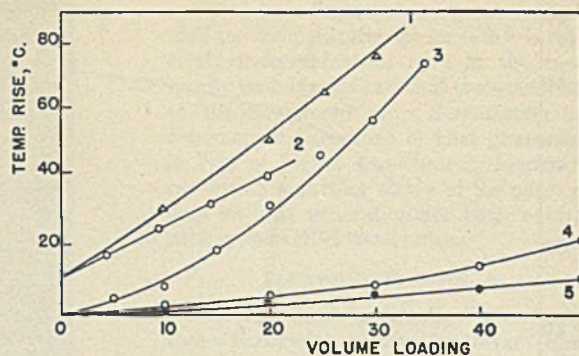


Figure 9. Effect of Pigment Loading on Heat Generation at Amplitude of 1.55 Mm.

1. Wyex-GR-S
2. Zinc oxide-GR-S
3. Gas black-Hevea
4. Zinc oxide-Hevea
5. Theratomic-Hevea

and more pronounced as the concentration is increased; correspondingly, the viscous nature will be suppressed. Consequently, raw rubber may be thought of as being at the end of such an elasto-viscous system. Vulcanization further enhances the elastic character at the expense of the plastic or viscous nature. But it is not unexpected that both aspects of the structure should be evident in the heat generation phenomena.

It is customary to think of elasto-viscous systems in terms of mechanical models (2, 9, 14, 19). The mechanical model for an elasto-viscous material represents the elastic and viscous elements as a spring connected in series with a piston which moves in a viscous liquid. Equations for such a system were first provided by Maxwell's relaxation theory. Since that time considerable work has been published on such systems both from the experimental and theoretical side. Reasonable success has been achieved in explaining the

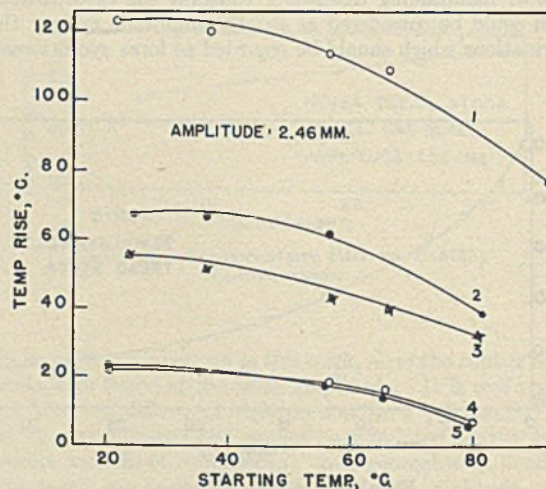


Figure 10. Effect of Temperature on Heat Generation at Amplitude of 2.46 Mm.

1. GR-S-25 volumes gas black
2. Hevea-25 volumes gas black
3. GR-S-20 volumes zinc oxide
4. Hevea-20 volumes zinc oxide
5. Hevea-20 volumes thermatomic black

general pattern of the phenomenon, but quantitative discrepancies are usually found. The limitations of the theories are well recognized and the more powerful concepts of modern theories of flow (4, 24, 28) might well be applied to this problem. The results with rubber vibrations should furnish a good experimental background for extension of the theory.

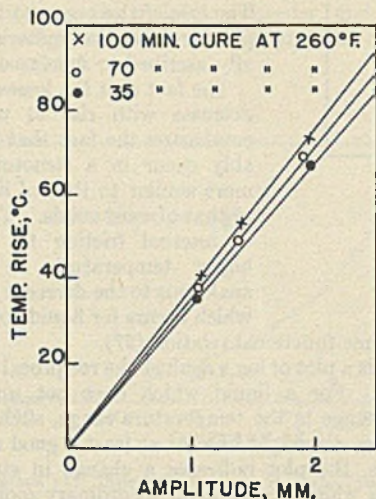


Figure 11. Effect of Amplitude and Cure on Heat Generation of GR-S-20 Volumes Gas Black

The quantity η which has been used in previous publications (6, 7, 27) to denote the internal friction for rubber vibrations has usually been called the "equivalent viscosity" (8, 16). It is not the same, by definition, as the coefficient of viscosity of a liquid. It is the frictional stress per unit of strain velocity. But it has the same dimensions as the coefficient of viscosity and can be thought of as arising from gradients of shear velocity. Its similarity to an ordinary viscosity coefficient will be emphasized in the following discussion.

Philippoff (23), making use of the theories of Hencky and Weissenberg and the Maxwell model, introduced a quantity called the "dynamic viscosity", η' , to show the effect of frequency. He deduced the relationship:

$$\eta' = \frac{\eta_0}{1 + (\omega\tau_0)^2} \quad (5)$$

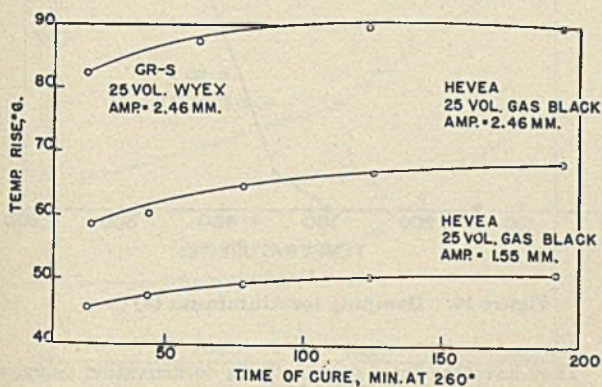


Figure 12. Effect of Cure on Temperature Rise

where η_0 = viscosity for small stresses

ϵ = $2\pi \times$ frequency

τ_0 = time constant of relaxation = time required for an applied stress to drop to the fraction $1/e$ of its value

τ_0 gives the order of magnitude of the time required for flow to develop. It is equal to the ratio η_0/S_0 , where S_0 is the modulus of rigidity.

It can be shown that the internal friction, η , for rubber, follows essentially this same frequency dependence and thus simulates the functional dependence of the viscosity of elasto-viscous systems on the frequency. Equation 5 shows a falling off of η' as the frequency increases. A transition between elastic and viscous behavior occurs when $\omega\tau_0$ approaches unity.

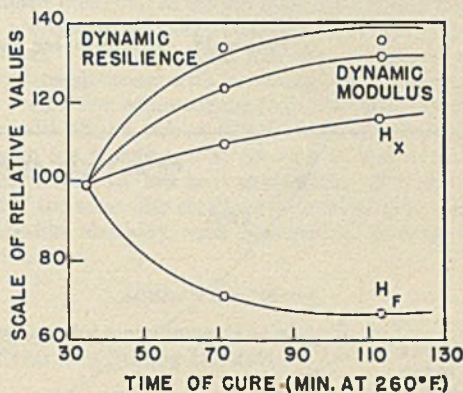


Figure 13. Effect of Cure on Vibration Properties of GR-S Tread Stock

Figure 15 illustrates how equations of the type of Equation 5 can be fitted to experimental data of Stambaugh for rubber (27). The points represent the experimental data; the curves are plots of the following equations:

For GR-S tread stock:

$$\eta = \frac{1.67 \times 10^5}{1 + (0.0036 \omega)^2} \quad (6)$$

For Hevea tread stock at 110° C.:

$$\eta = \frac{1.4 \times 10^5}{1 + (0.0097 \omega)^2} \quad (7)$$

For Hevea tread stock at room temperature:

$$\eta = \frac{7.4 \times 10^4}{1 + (0.0034 \omega)^2} \quad (8)$$

Aside from the formal difference between η and η' , it is doubtful whether much significance can be given to τ_0 as a relaxation time. It has been generally realized that a single relaxation time is inadequate to describe the elasto-viscous nature of rubber. Although the equation should be used with much caution in this respect to secure insight into the structure of rubber, it does serve to classify the friction-frequency phenomena for rubber vibrations as being elasto-viscous in nature; and the load is alternately supported by elastic and viscous elements of the structure. The molecular equilibrium positions when under stress are evidently always somewhat displaced with reference to the unstressed equilibrium positions. There is not only an accommodation to the stress by displacement about the unstressed equilibrium

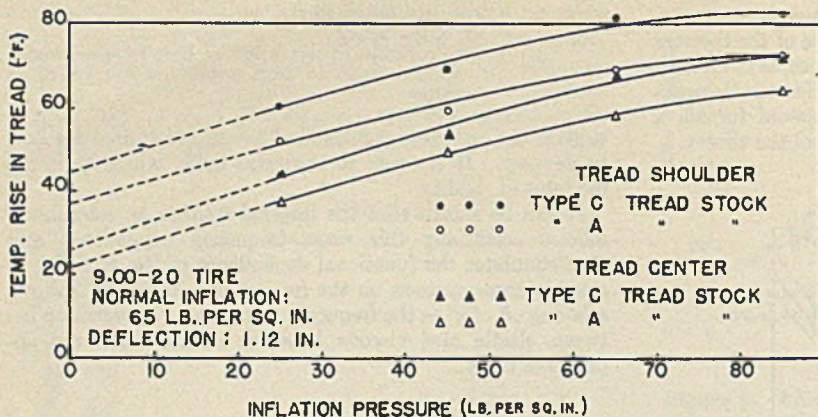


Figure 14. Resiliometer Results

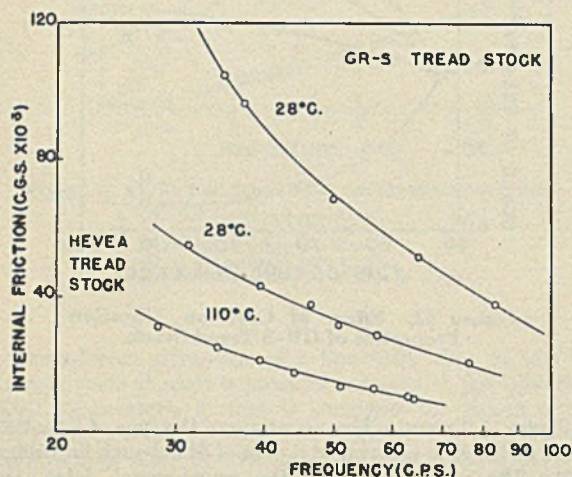


Figure 15. Dependence of Internal Friction on Frequency

positions, but also a rearrangement of the equilibrium positions which requires time. Furthermore, the range of mechanical vibrations appears to be in the transition region where $\omega\tau_0$ approaches unity.

The dependence of the internal friction for rubber upon temperature is more illuminating in regard to structure. It can be shown that this dependence is abnormal in comparison to that of metals and most other solids. Figure 16 gives a curve for the damping for aluminum at various temperatures as determined by Förster and Köster (5). "Damping" here means the logarithmic decrement or the logarithm of the ratio of the amplitudes of two successive free vibrations. The rise in the damping curve with increase in temperature is characteristic of metal, glass, most plastics, and similar materials. With rubber, on the other hand, the resilience improves at higher temperatures.

Figure 17 shows the specific loss for Lucite as a function of temperature, as measured by Rinehart (26). The specific loss is the loss of energy per cycle expressed as a fraction of the total

vibrational energy. The specific loss is twice the logarithmic decrement.

The scale of the curves for aluminum and Lucite shows that the energy loss for the metal is of a smaller order of magnitude, but for Lucite it is the same order of magnitude as that encountered with rubber vibrations. The rise of the curve at higher temperatures for these materials is generally ascribed to increased plasticity.

The fact that the losses for rubber decrease with rise of temperature emphasizes the fact that they probably occur in a structure which is more similar to that of liquids than to that of most solids. The decrease of internal friction for rubber at higher temperatures is not only analogous to the decrease in viscosity which occurs for liquids but actually

shows the same functional relation (27).

Figure 18 is a plot of $\log \eta$ against the reciprocal of absolute temperature. For a liquid which does not undergo any structural change in the temperature range, such a plot for viscosity gives a straight line (or at least a good approximation). Thus, the plot indicates a change in structure for GR-S rubber which occurs at about ordinary room temperatures. For natural rubber, on the other hand, this transition point is at a lower temperature (27). The temperature at which this change of structure occurs appears to be insensitive to cure in the technical range and, as shown, is also relatively insensitive to pigment loading. It is therefore reasonable to suppose that this change of structure is associated with localized and intimate molecular groupings rather than with a larger network structure.

Activation energies can be calculated from the equation:

$$\eta = A e^{\frac{E_a}{RT}} \quad (9)$$

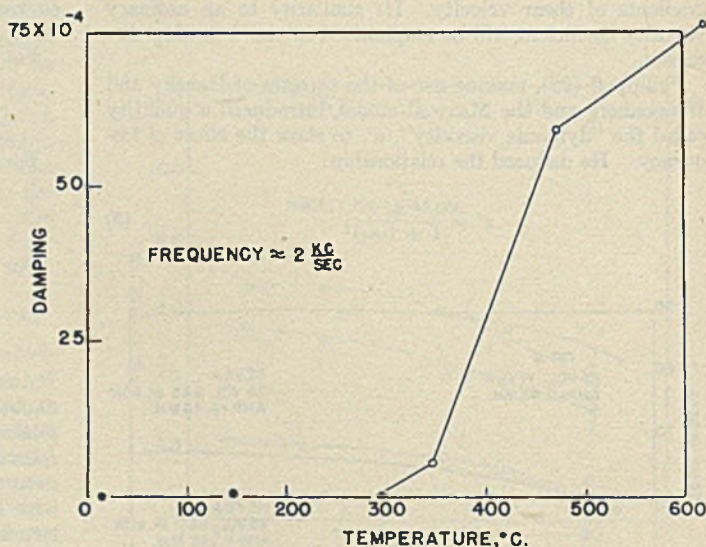


Figure 16. Damping for Aluminum (5)

They have the same magnitude as do activation energies of organic liquid viscosities. For octane the value is 2.18 (15). The values follow:

	E _v , Kg.-Cal./Mole	
	Low temp.	High temp.
Hevea tread stock	7.10	2.06
GR-S tread stock	5.80	2.43
GR-S gum stock	4.83	0.36

The picture obtained from this experimental evidence and line of thinking is that heat generation in flexed rubber arises from the disturbance of equilibrium molecular configurations. The stress increases the molecular disorder, and when new equilibrium configurations are established, some of the work done appears as heat.

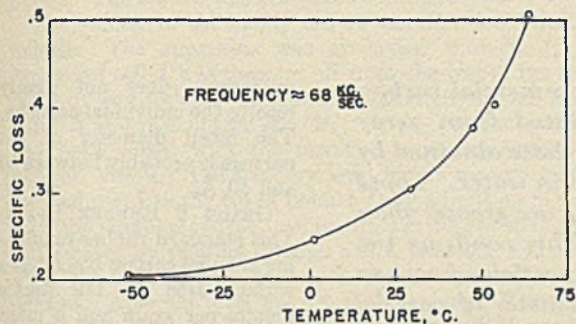


Figure 17. Specific Loss in Lucite (26)

What effect various molecular structures in polymers might have on the internal friction is a complicated question. In the first place, the constitution of the monomers should probably be considered. A great deal of work has been done on the effect of constitution on the viscosity of liquids (15). Some generalizations have been reached but they are not satisfactory, and certainly nothing appears from them which could be carried over directly to polymer structure. Nissan, Clark, and Nash (22) made a thorough study of the effect of constitution on the viscosity of liquids. By relating the viscosities to the ratio of the absolute temperature of measurement and the boiling point, they were led to the conclusion that the molecular shape was the chief variable affecting their curves. Dipole moments and the nature of the atoms of the molecule were found to be relatively immaterial as compared to the shape of the equipotential surfaces surrounding the molecule. A spheroidal shape gave the highest viscosity for a given temperature ratio.

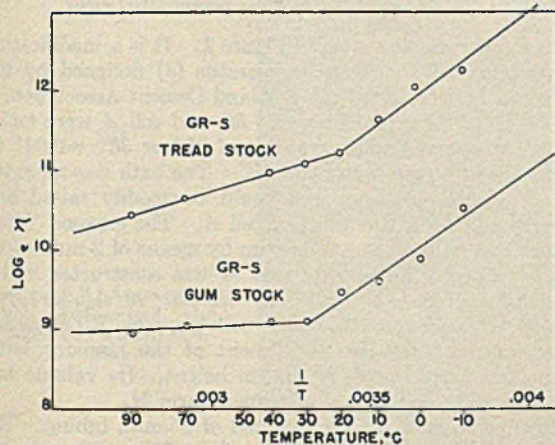


Figure 18. Temperature-Internal Friction Relation

It seems doubtful that the shape of the monomer molecule could be of compelling influence on the internal friction of a polymer. The chain shape and structure should be more important, particularly the size and shape of the chain segments which act as kinetic units and serve to build up a structure with configurational energy. The chain length and extent of cross linkages are other features which enter into the picture although their influence may be rather indirect.

Just what characteristic of the molecular structure of synthetic rubber is responsible for its higher heat generation is difficult to say. The low resilience of all synthetic rubbers to date as compared to natural rubber leads us to look for the explanation in unique characteristics of the natural rubber structure rather than to specific features of the molecular structure of any one synthetic rubber. In the natural rubber structure we feel reasonably certain of such characteristics as long linear molecules of *cis* form, regular in structure and with the property of aligning themselves readily in the direction of stress. It is well known that the viscosity of elasto-viscous systems decreases with increasing stress, in correlation with the orientation of the structure in the direction of flow. Similarly, with natural rubber this "streamlining" of the long molecules in the direction of stress may be one of the most important reasons for low heat generation. But until more is known of the molecular configurations existing in materials with rubberlike elasticity, such conclusions are only reasonable speculations.

ACKNOWLEDGMENT

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Density of Carbon Black

BY HELIUM DISPLACEMENT

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FROM recent x-ray diffraction data (2), it is possible to calculate a limiting density value for a few commercial carbon blacks. The values thus obtained are considerably higher than those generally accepted (4). The experimental values have, for the most part, been determined with the liquid pycnometer. Densities so obtained have been regarded with some suspicion due to the possibility of incomplete wetting of the solid by the immersion liquid (3, 6, 7, 8).

In the present investigation helium was used as the immersion fluid. The general procedure was described by Howard and co-workers (5, 8). The use of helium removes many of the uncertainties associated with incomplete wetting and, accordingly, should permit a more reliable comparison with densities calculated from the diffraction data.

There has been some tendency to the belief that the ability of carbon black to reinforce rubber is associated with its structure, and that this ability decreases as the structure approaches more closely that of graphite. One object of the present investigation was to observe whether a relation between structure, density, and value as a reinforcing pigment could be observed.

DESCRIPTION OF CARBONS

The carbon samples were identical with those employed by Biscoe and Warren (2) in their x-ray diffraction study. The blacks were taken from standard commercial samples. The surface of the channel carbon blacks is partially covered with chemisorbed oxygen. In the case of Carbolac 1 this oxygen amounts to about 10 per cent while for Grade 6 it is around 3 per cent by weight of the sample. In addition they also contain some 0.8 per cent by weight of hydrogen. The volatile content of acetylene black is less than 1 per cent by weight and consists chiefly of hydrogen.

GRAPHITE. A sample of carefully selected Ceylon graphite was extracted with acetone for 6 hours and dried in vacuum for 2 hours at 200° C. The ash was less than 0.8 per cent.

CARBOLAC 1. This extremely fine particle channel black is used in the paint and lacquer industry. It has a surface area of around 900 square meters per gram. The electron

The densities of three commercial carbon blacks have been calculated from x-ray data and compared with those obtained by immersion in helium and in water. Those calculated from x-ray data are greater than the immersion values. This confirms the structure of the working particle of carbon black as consisting of a cluster of parallel layer groups. By comparing the density of the parallel layer groups as determined from x-ray data with the helium immersion density of the cluster, the porosity of free space within the particle can be evaluated. In the case of acetylene black, this free space is accessible to helium and is evidenced by a pronounced drift in the helium density value. In the case of channel blacks, the separation between parallel layer groups is too small to permit penetration by helium.

microscope does not clearly resolve the individual particles. The mean diameter of the particle is probably between 30 and 50 Å.

GRADE 6 RUBBER BLACK. This standard rubber-reinforcing channel carbon black has a surface area of 110 square meters per gram and a mean diameter from electron microscope measurements of 236 Å.

SHAWINIGAN ACETYLENE BLACK. Prepared by the thermal decomposition of acetylene, this is generally classified as a semireinforcing carbon. It displays a high electrical conductance, both in the dry state and in compounded rubber stocks. It has a measured surface area of 64 square meters per gram and from electron microscope measurements, a mean diameter of 426 Å.

HELIUM. For the density measurements helium was supplied in one-liter Pyrex flasks and was used without further purification. Density measurements made on a sample of Grade 6 carbon black at 0° and 100° C. agreed within 0.3 per cent, well within the experimental error, which indicated the absence of any measurable amount of adsorbable impurity.

APPARATUS FOR DENSITY DETERMINATION

The apparatus is shown in Figure 1. It is a modification of the Howard and Hulett apparatus (5) designed by the Research Laboratory of the Portland Cement Association.

The buret *B*, manometer arm *M*, and cell *A* were maintained at operating temperatures of 25° or 30° ± 0.02° C. by means of a glass water bath *W*. The bath was mounted on an adjustable stand and could be readily raised and lowered to permit the filling of cell *A*. The exposed "dead space" was reduced to a minimum by means of 2-mm. capillary as shown. Manometer arm *M* was constructed of 15-mm. tubing to avoid capillary effects. A slender glass pointer, *D*, sealed to the inner wall, provided a permanent reference mark for the adjustment of the mercury level. Manometer arm *G* was 80 cm. in height. Its volume was adjusted to exceed that of manometer arm *M*.

Helium buret *B* was constructed of 25-mm. tubing. The combined volume of *B* and *M* was about 75 cc. Density cell *A*, about 40 cc. in volume, was connected to the apparatus by

a lightly greased 14/35 \overline{f} ground joint. Mercury weighing bottle *R* had a capacity of about 75 cc. and was connected to the apparatus by a dry, spherically ground joint. Stopcock *E*, connected to pressure and vacuum, permitted transfer of mercury from the weighing bottle to buret *B*. The three-way 2-mm. stopcock *F* was specially ground and was fitted with an extra heavy plug measuring 23 mm. at the bores; a large extent of sealing surface was thus provided between the ports. The high rate of diffusion of helium made it imperative that all stopcocks in the apparatus be specially selected for excellence in grinding. Helium was introduced to the buret and manometer through *H* by means of a Toepler pump. The system was evacuated through *J*.

The volume of the empty cell *A* was first determined as follows: The apparatus was evacuated through *J*, and evacuated cell *A* was then cut off from the rest of the apparatus by stopcock *F*. Helium was admitted through *H* into buret *B* and manometer arm *M*. To this point stopcock *K* had been closed with the mercury in approximately the position shown. The mercury level in the manometer was then adjusted to the tip of pointer *D* by admitting mercury from the weighing bottle. An accurate setting of the pointer was assured by sighting through a 20X telescope and noting when the tip and its reflection in the mercury surface just merged. After the level was set, mercury bottle *R* was carefully weighed and replaced. The evacuated cell *A* was then opened to the buret and manometer through stopcock *F* and filled with helium. The level in *D* was once again adjusted by admitting mercury from *R*. After this setting, bottle *R* was again reweighed. From the difference in weight the amount of mercury required to displace the helium to fill cell *A*, and hence the volume of the cell, was readily calculated. The density of a carefully weighed sample of carbon black was obtained by measuring the difference in volume between the cell when empty and when filled with black. Approximately 10 grams of black were used in each measurement. The sample was evacuated in cell *A* while

being heated to 110° C. by a small electric furnace. When a flat gage was obtained, the furnace was removed, water bath *W* raised in position, and the apparatus permitted to come to working temperature.

In the early part of the work the bath was maintained at 25° ± 0.02° C. As the work progressed into warm weather, 30° ± 0.02° was adopted as a more convenient temperature. No significant change in density of a given carbon black could be observed at these two temperatures. Seventeen separate determinations of the empty cell volume showed a maximum deviation of 0.03 per cent. The volume of the carbon black used in a run was only 10 per cent that of the empty cell. Since this volume was obtained by difference, the maximum accuracy of the final density was 0.3 per cent. Over the period of an hour, the final pressure setting was unchanged.

However, after the sample of carbon black was allowed to remain immersed in helium overnight, a slight decrease in pressure was noted. This was most marked in the case of acetylene black. To follow this drift, a new apparatus was designed in which the helium and carbon black could be confined between two mercury levels, and the uncertainties associated with stopcocks could thus be eliminated. With this apparatus it was possible to follow the drift in the density value over a period of several weeks. The apparatus is shown in Figure 2.

A narrow constriction lightly plugged with glass wool separated the cell into two compartments, *A* and *A'*. The black sample was thus suspended in *A* with *A'* serving as a buret in which the mercury level could be set by means of glass pointer *D*₁ as previously described. A second internal pointer, *D*, permitted adjustment of the mercury level in the manometer arm. The cell *AA'* was cut out of the apparatus below *D* and *D*₁. A weighed sample of carbon black was then introduced into *A*, and the cell was sealed back into the line. By means of stopcock *F* mercury was transferred from *R*₁ and sealed the cell off at *D*₁. The mercury level in manometer arm *M* was drawn below the U by *R*₂.

Figure 1. Apparatus for Density Determination by Helium Displacement

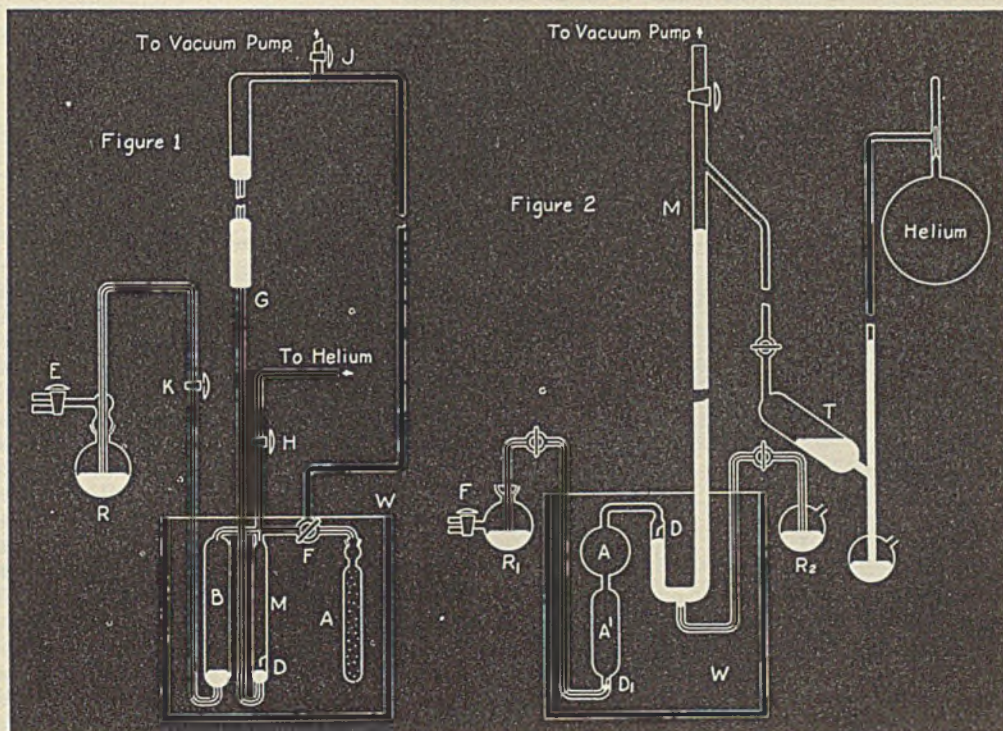


Figure 2. Apparatus for Following the Drift in Helium Density

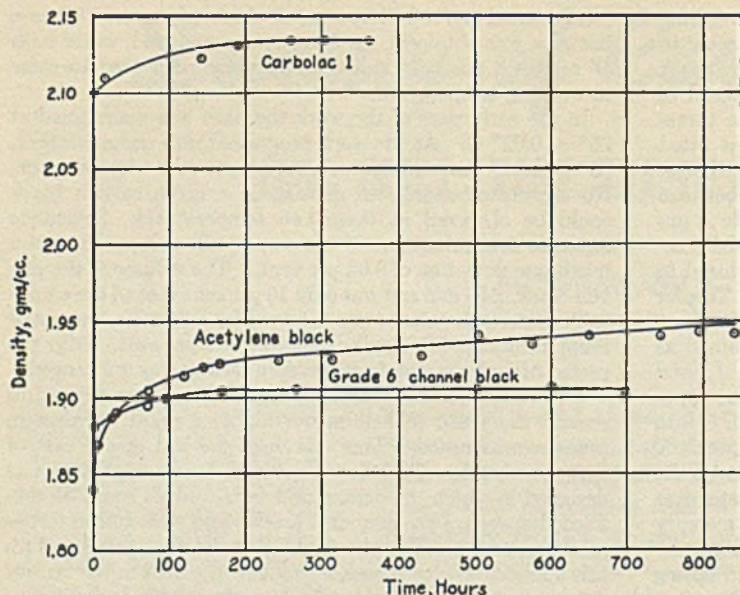


Figure 3. Drift in Helium Density for Three Commercial Carbon Blacks

The cell and sample were evacuated through *M*. Helium was then admitted to the cell through *M* by means of Toepfer pump *T*. Mercury was introduced into the manometer from *R*₂, and the top of the manometer was opened to the vacuum pumps. The mercury levels at *D*₁ and *D* were then accurately adjusted, and mercury weighing bottle *R*₁ was carefully weighed.

In following the drift, the pressure in *AA'* slowly decreased. The decrease was measured by admitting sufficient mercury into *A'* to maintain the mercury level at *D*. From the difference between the original weight of mercury in *R*₁ and that of any given time, the volume of helium diffusing into the black, and hence the change in density, could be readily calculated. The cell volumes necessary for an absolute density value can be obtained in this apparatus only by means of the pressure-volume relation. Since it was not possible to make pressure readings on mercury manometer *M* with sufficient accuracy, the absolute density values obtained with this apparatus do not compare in accuracy with those obtained with the equipment shown in Figure 1. Consequently the drift data in Figure 3 were corrected to an accurate absolute density by adjusting the hour value to that previously obtained with the first apparatus.

The drift in the helium density value was followed for about a month on Carbolac 1, Grade 6, and acetylene black. After about 300 hours, the rate of disappearance of helium for the first two blacks was nearly identical with that observed with the empty cell:

Sample	Helium Lost, Cc./Hr.
Empty cell	3.54×10^{-4}
Carbolac 1	3.38×10^{-4}
Grade 6	3.00×10^{-4}
Acetylene black	4.24×10^{-4}

The rate of diffusion of helium through the empty glass cell corresponds to 9.8×10^{-10} cc. per second per sq. cm. per mm. of wall thickness. This value is in agreement with Baxter's figure of 6.8×10^{-10} cc. for the diffusion of helium through Pyrex (1). The curves in Figure 3 were corrected for this loss of helium.

A standard pycnometer bottle, with a ground-in thermometer, was used in determining the water densities. In all cases the carbon black samples were dried at 110° C. before weighing. After the sample and distilled water were introduced, the water was boiled for 15 minutes to expel occluded air completely. The pycnometer was then tempered to 25° C. and the water volume adjusted before weighing.

DIFFRACTION AND DENSITY DATA

Table I gives Biscoe and Warren's diffraction data (2) on the three carbon blacks studied. *L*_a is the effective dimension of the graphite layer in the plane of the layer and *L*_c is the dimension of the group perpendicular to the layer. These are the effective dimensions of the parallel layer groups, clusters of which make up the "working particles". Using the hexagonal axes of graphite, *a* and *c* are the dimensions of repetition within and normal to the layer, respectively. Comparison of these axial dimensions with the corresponding values for graphite demonstrates that the density of the carbon blacks will stand in the same ratio to that of graphite as the corresponding values of *c*, since the values of *a* are identical within experimental error. Also included in Table I are the "mean" diameters of the working particle, as obtained from electron microscope measurements. Carbolac 1 particles were not sufficiently resolved to permit an actual count of the plate. From this fact and a surface area value of approximately 900 square meters per gram, a diameter of around 50 Å. is deduced.

TABLE I. DIFFRACTION DATA OF WARREN AND BISCOE

Sample	<i>a</i> , Å.	<i>c</i> , Å.	<i>L</i> _c , Å.	<i>L</i> _a , Å.	Mean Particle Diam., Å.
Graphite	2.456	6.697 ^a	13.1	18.6	50
Carbolac 1	2.46	6.95	12.7	20.0	285
Grade 6	2.45	7.10	26.6	47.5	440
Acetylene black	2.42	7.0			

^a Calculated from (002) reflection.

The values in the second column of Table II were obtained with the apparatus shown in Figure 1 and, with the exception of acetylene black, were reproducible over a period of an hour; they are referred to as immediate values. The "final" values were obtained after several weeks' immersion in helium in the apparatus shown in Figure 2.

While the immediate helium density values of the carbon blacks are around 5 per cent greater than those obtained by water immersion, the same relative differences exist between densities. In all cases the measured densities are considerably less than those calculated from the diffraction data. Since the latter are substantially the same for each carbon black studied, it must be concluded that values obtained by immersion methods cannot be interpreted as true density in the strict sense of the word. The true density of carbon black can be obtained only from diffraction data. The present experimental values must be interpreted as a measure of the closeness with which the parallel layer groups are packed within the working particle, or of the extent of "free space" within each particle.

TABLE II. DENSITY VALUES

Sample	Immediate Helium Density	Final Helium Density	H ₂ O Density	Density Calcd. from c
Graphite	2.26 ± 0.01	2.26	2.26	2.262
Carbolac 1	2.10	2.13	1.99	2.18
Grade 6	1.88	1.90	1.82	2.13
Acetylene black	1.84	1.95	1.79	2.16

Table I indicates that Carbolac 1, with the highest measured density, is composed of working particles around 50 Å. in diameter. However, the size of the parallel layer groups composing the working particle is about the same as those composing the much coarser Grade 6 black. From the dimensions of the parallel layer groups (L_c and L_g) and the ratio of the diffraction density to the immediate helium density the free space in a Carbolac 1 particle is found to be around 170 cubic Å., while a similar calculation for the Grade 6 black gives a free space value of 675 cubic Å.; in effect this is merely another way of saying that Carbolac 1 is more dense than Grade 6. The extent of drift in these two cases is not very marked; accordingly it can be assumed that there is little tendency for helium to diffuse into the working particle. The reason becomes more obvious if we calculate the separation between the parallel layer groups within the working particle. In this calculation we assume each parallel layer group to be a regular hexahedron. Around each hexahedron there is a shell, the volume of which corresponds to the free space. From the dimensions of the hexahedra as given in Table I, the thickness of the shell can be calculated. In the case of Carbolac 1, this is found to be of the order of 0.10 Å. Thus the separation between groups in the Carbolac 1 particle is only some 0.2 Å. greater than any of the dimensions within the parallel layer group itself. In the case of Grade 6 carbon, a value of 0.8 Å. is obtained. Accordingly, there can be little penetration of the helium atom into the working particles of these two carbon blacks. This is evidenced by the slight drift and a close correspondence between the immediate and final density values.

Acetylene black offers an interesting contrast. In this case a low initial density is observed. The drift is pronounced, and after immersion for a month in helium, the density was still slowly increasing. The dimensions of the parallel layer groups in acetylene black are more than twice those of the channel blacks. A calculation of the free space within the working particle shows it to be of the order of 9500 cubic Å., more than ten times that found in Carbolac 1 and Grade 6. From the electron microscope diameter, the number of parallel layer groups in a working particle is only 1000 compared to 3000 for Grade 6. This porous internal structure is reflected in the low initial density. By the method indicated above, it is found that the parallel layer groups within the working particle of acetylene black may be separated by as much as 6 Å. In this instance it is possible for helium to diffuse into the working particle, resulting in the steady increase in density indicated by the drift curve in Figure 3, even after several weeks' immersion.

The development of an internal porosity and a subsequent decrease in measured density was strikingly illustrated in the following experiments: A sample of Carbolac 1

was heated in the absence of air for 2 hours at 2200° C. Figure 4 shows the diffraction patterns before and after treatment. The pattern of the latter indicates a definite growth of the parallel layer groups and a more orderly arrangement. From the diffraction pattern, a density approaching graphite was anticipated. However, the helium density was found to have decreased from 2.10 to 1.48. The water density value also decreased from 1.99 to 1.42. The surface area as determined by the low-temperature nitrogen adsorption method also decreased sharply from 900 to 240 square meters per gram. Heat treatment evidently causes a sintering together of working particles. Since the Carbolac 1 particle has a diameter of only 50 Å., it cannot contain more than ten to fifteen parallel layer groups. It is probable that this sintering occurs between the working particles. The large free space in the interior of these clusters, not available to helium, accounts for the low density of the material after heat treatment. These results lend support to the structure of acetylene black suggested above.

This decrease in helium density on heat treatment is apparent only with fine-particle carbon blacks. Grade 6 carbon black, with a diameter of 285 Å., has a helium density of 1.88, a water density of 1.82, and a surface area of 110 square meters per gram. After heating for 10 hours at 2000° C., the helium density had increased slightly to 1.92 and the water value to 1.89; the surface area after heating was 95 square meters per gram.

CONCLUSIONS

It is apparent that density values of carbon black, in the strict sense of the term, may be obtained only from diffraction data. Immersion methods yield only an apparent density which, in effect, is a measure of the free space within the working particle. Since, however, it is well established that the entity of the working particle of carbon black is preserved in all practical applications, the immersion values are the proper ones to employ in such instances. Whether helium or water is the better immersion fluid again depends upon the

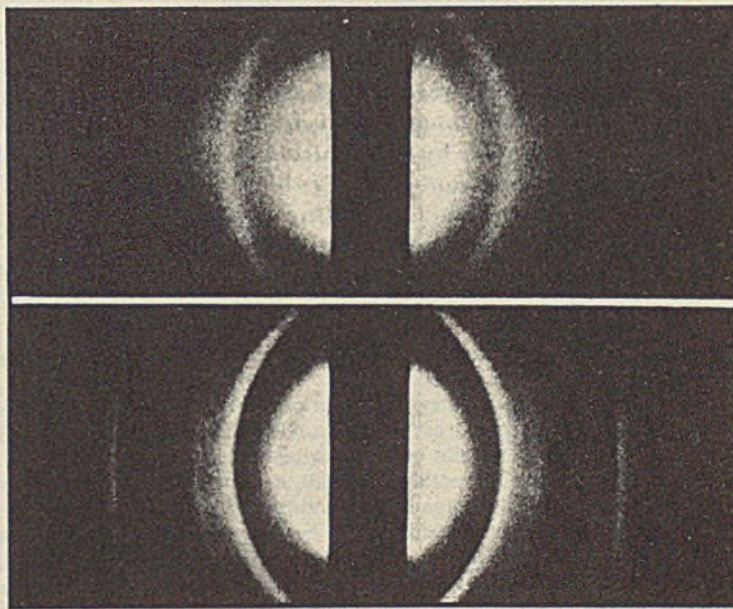


Figure 4. X-Ray Diffraction Patterns of Carbolac 1 before (above) and after Heating for 2 Hours at 2200° C.

application. In surface area determinations, the helium value is obviously to be preferred. In ink and rubber compounding, the water values are undoubtedly adequate.

Since, as pointed out above, the carbon black particle retains its entity in all applications, the properties manifested in these applications are primarily due to surface phenomena. Accordingly, the density of the particle is associated only in a secondary manner with such phenomena as reinforcement, color, and flow. It is interesting, however, that acetylene black, which in many ways is unique in its properties, is composed of very porous particles. This rather "loose" association between parallel layer groups in the working particle may be reflected in residual forces at the surface of the particle. If these forces are sufficient to induce a secondary association or agglomeration between working particles, then they may offer a satisfactory explanation for the high

liquid retention and excellent electrical conductivity of acetylene black.

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SIMPLE VULCANIZATES OF

Buna S and Sulfur

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Physical and Chemical Properties

Physical and chemical data are presented for a series of Buna S-sulfur vulcanizates, covering the range from soft to hard rubber-like products. The data indicate that Buna S-sulfur "ebonites" resemble those of rubber, that combination of 10 per cent or more of sulfur takes place by substitution as well as addition, and that unlike rubber, the products of intermediate sulfur content possess intermediate tensile strength and elongation.

THE earliest vulcanizates of rubber consisted of only two ingredients, rubber and sulfur. Actually, at least one other ingredient, fatty acid, was probably present in the so-called acetone extract of the rubber. However, it was not long before the use of other compounding ingredients, especially inorganic accelerators, was developed.

After the introduction of organic accelerators (20, 29, 30), most rubber goods were compounded to contain them, together with various activators. The simple products containing only rubber and sulfur were practically forgotten. Those in the ebonite range, however, were found to possess interesting properties and were studied in more detail (11, 13, 17, 18, 21, 32, 40).

The only studies of the simple rubber-sulfur system over the entire range from soft to hard rubber have been those concerned chiefly with the mechanism of vulcanization. Houwink (21) gives a graphical presentation of the variation of stress-strain properties with sulfur content. Blake (4) and Jessup and Cummings (23) present data for such a series, although their samples were vulcanized to the absence of significant sulfur in the free state.

Most of the reported work on the compounding of Buna S has, under the pressure of wartime necessity, been concerned with the substitution of this polymer in accelerated formulas which could be processed and handled in conventional rubber equipment and which would involve little change in operating technique (5, 14, 16, 37, 38).

A few investigators have published isolated bits of information concerning ebonites prepared from the various butadiene polymers (15, 19, 25, 26, 33, 34, 36). Klebsattel (25) mentions some characteristics of Perbunan vulcanizates containing intermediate sulfur contents (10-15 per cent on the polymer) and indicates them to be superior to the corresponding rubber products. Most of these data were obtained on accelerated stocks and consequently provide little direct information on the simpler combination between Buna S and sulfur in the absence of other compounding ingredients.

This investigation was undertaken to obtain information on the simpler system and to attempt to fill in a few of the many gaps in the existing knowledge of Buna S vulcanization. It seemed possible that such data might also provide additional

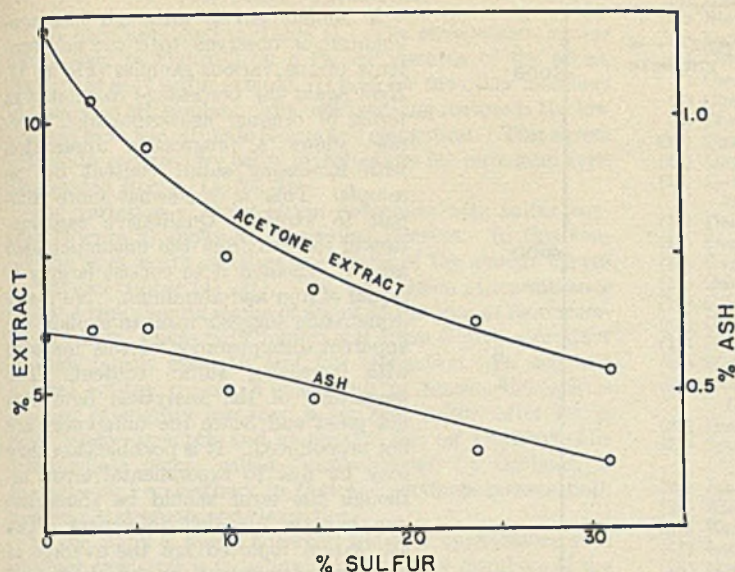


Figure 1. Analytical Data on 6.5-Hour Cures

TABLE I. ANALYTICAL DATA ON 6.5-HOUR CURES

% sulfur, as compounded	0	2.5	5	10	15	25	35
Acetone ext. (calcd. on original polymer)	11.91	10.31	9.30	7.45	6.78	6.30	5.12
Ash (calcd. on original polymer)	0.64	0.65	0.65	0.50	0.49	0.38	0.37
Free sulfur	0.22	0.17	0.20	0.19	0.14	0.19	0.58
Combined sulfur	0.74	2.70	5.37	9.88	14.72	23.65	31.04
Density, measured	0.930	0.943	0.971	0.971	1.003	1.090	1.170
Density, calcd.	...	0.944	0.966	0.983	1.012	1.078	1.152

evidence toward an elucidation of the mechanism of vulcanization in general.

The problem is divided into two parts: (a) a study of the physical and chemical properties of the vulcanizates containing various percentages of combined sulfur and (b) measurement of the heats of combustion of these vulcanizates to provide data on the thermal relations involved in the vulcanization. The thermal measurements will be the subject of a second paper. Some of the data in this section are not so complete as might have been desired because the same set of samples had to be used for both series of measurements.

EXPERIMENTAL PROCEDURE

The major portion of the experimental work was performed at the University of Akron; owing to the departure of both authors from the university, some of the information which might have aided in creating a more complete picture of this system was not obtained. It is believed, however, that the data are of sufficient interest to warrant their presentation, if only for the reason that data on such relatively simple systems are lacking in the technical literature.

The Buna S used was a typical batch of American factory production, supplied by The Firestone Tire & Rubber Company in February, 1942. It was compounded, as received, with the desired amount of sulfur, and the uncured stocks were stored between sheets of heavy parchment paper until used. Stocks were compounded to contain 2.5, 5.0, 10.0, 15.0, 25.0, and 35.0 per cent sulfur. These correspond to "coefficients of vulcanization" (40) of 2.57, 5.26, 11.11, 17.65, 33.33, and 53.85, respectively.

Press cures were carried out by the recommended A. S. T. M. procedures (1) for 2, 4, 6.5, and 10 hours at 315° F. In the samples containing 15 per cent or more of sulfur, vigorous evolution of hydrogen sulfide was observed during the cures; this was most pronounced in the 35 per cent sample.

Stress-strain properties were measured by the A. S. T. M. procedure (3). Hardness was determined by the method of Cooper (10), with a Shore durometer calibrated by the method of Larrick (27). Densities were measured by an adaptation of the hydrostatic method of Wood *et al.* (41), using a Saran filament for suspension of the sample and sinker.

"Free" sulfur was determined in the acetone extract by the A. S. T. M. bromine oxidation method (2). This value actually represents not only free sulfur, but also that in any form of combination which is acetone soluble. Combined sulfur was determined on the extracted samples by the method of Cheyney (9); this value is likewise a function of solubility relations. Nevertheless, these extracted samples were employed for some of the thermal measurements, and it was desirable to obtain the analytical data for the same samples.

The extractions were carried out for 72 hours in order to eliminate any differences existing between the soft and hard samples because of different degrees of extraction. The extracts obtained with all samples increased on continued extraction but tended to approach a constant value after about 60 hours. Several samples were also extracted exhaustively with ethanol, and the extract values in all cases were somewhat lower than those obtained with acetone. It is believed that the acetone may be exerting a solvent action upon certain of the hydrocarbon fractions, similar to the effect noted with methyl ethyl ketone on natural rubber (8). It is also believed that ethanol is, in general, a somewhat safer solvent to employ for extraction of this type of polymer, as it seems to have no solvent action on the polymer itself.

The ash determinations were made by the A. S. T. M. procedure without variation.

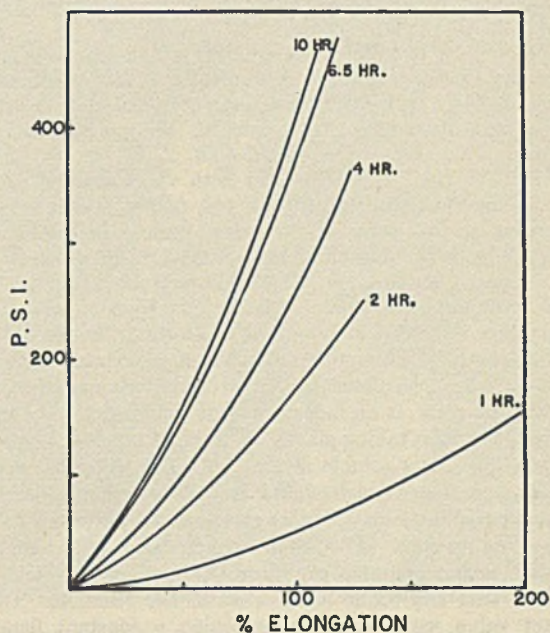


Figure 2. Stress-Strain Curves for 10 Per Cent Sulfur Sample

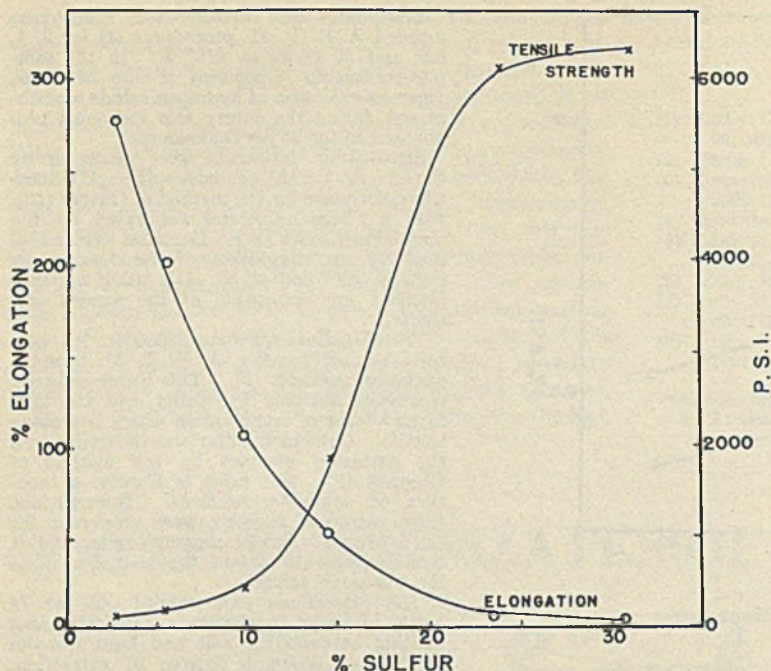


Figure 3. Variation of Stress-Strain Properties with Sulfur Content

ANALYTICAL DATA

Table I and Figure 1 give the analytical data which are the averages of several determinations in each case. The actual percentage of combined sulfur in the extracted samples shows good agreement with that compounded, except in the 35 per cent sample. Here a considerable amount of substitution must have taken place, with the liberation of a large amount of hydrogen sulfide. However, all of the samples containing more than 5 per cent sulfur give analytical figures less than the calculated values, especially when one adds to the as-compounded sulfur the value of the blank in the original sample.

The presence of sulfur in the original sample is interesting, especially since a portion of it is in the acetone-insoluble or "combined" state. This presumably originated from the use of sulfur-containing materials in the polymerization process. This is not new practice (6, 7, 28, 31, 35, 39). Olefins have been shown to react with various sulfur compounds and even with sulfur itself (22, 24), so that it is not surprising to find some of the sulfur present in combined form. The determination of the actual form in which it is present would be the subject of a separate problem and would require the use of considerably larger quantities of material. Probably it is present in more than one form of combination.

The progressive diminution of the acetone extract (Figure 1), even when calculated in terms of the original as-compounded polymer, is an indication that some reaction of the soluble material is taking place. This might involve polymer fractions originally soluble in acetone which could be combining with sulfur or which might merely be undergoing further thermal polymerization. Either reaction could give rise to a less soluble product. The progressive character of the effect with increasing amounts of sulfur tends to favor the hypothesis that the sulfur is involved in the reaction. The extract value seems to be approaching a constant figure of 5-6 per cent which is presumed to represent nonpolymer material originally present.

A similar effect, although less pronounced, is observed with the ash contents of the various samples (Figure 1). Here again the percentage calculated in terms of original as-compounded polymer shows a progressive diminution with increasing sulfur content of the sample. This is somewhat more difficult to explain. Qualitative examination of the ash from the uncomounded sample indicated it to consist largely of oxides of iron and aluminum. No ready explanation suggests itself to explain the apparent disappearance of this material with increasing sulfur content. The magnitude of the analytical figures is not great and hence the differences are not pronounced. It is possible that they may be due to experimental error, although the error should be somewhat less than the recorded differences. The ash values reported are the average of duplicate determinations, which showed reasonably good agreement. However, the reported values do not fall so readily on a smooth curve as do those of the extracts, nor is the accuracy so great. No real significance can therefore be justifiably attached to this variation. One possibility is a variable conversion to sulfates during the ash-

ing procedure, even though the latter was supposedly carried out under constant conditions. Insufficient sample was available to investigate this question to any greater extent.

The densities of the vulcanized samples showed reasonable agreement with those of the unvulcanized which, in turn, agreed with the calculated values. Two generalizations are evident: (a) There is no appreciable change in density on vulcanization; (b) no discontinuity is evident in the density curve, such as might be produced by major changes in structure of the polymer during some stage of the vulcanization.

TABLE II. PHYSICAL PROPERTIES OF CURED STOCKS

Sulfur Content, %	Time of Cure, Hr.	Tensile Strength, Lb./Sq. In.	Elongation, %	Tensile Product $\times 10^{-4}$	Shore Hardness
2.5	1	140	400	5.60	34
	2	148	385	5.70	38
	4	200	260	5.22	45
	6.5	175	210	4.80	50
	10	240	200	3.68	52
5	1	120	325	3.88	36
	2	160	325	5.20	45
	4	180	265	5.04	53
	6.5	200	260	5.00	69
	10	212	204	4.32	63
10	1	155	200	3.10	43
	2	250	130	3.25	55
	4	360	125	4.51	67
	6.5	480	120	5.75	70
	10	465	110	5.12	72
15	1	200	175	3.50	49
	2	375	150	5.62	65
	4	1680	125	21.0	98
	6.5	1860	60	11.5	100
	10	2960	20	5.92	100
25	1	200	175	3.50	55
	2	1680	75	12.00	100
	6.5	6077	9	5.35	100
35	6.5	6182	8	5.25	100

PHYSICAL PROPERTIES

The data are listed in Table II. The stress-strain curves are plotted in Figure 2 for a typical member of the series, the 10 per cent sulfur sample. Those for the other members of the series are similar. The most striking feature is the low value of both the ultimate tensile and elongation. This agrees with data reported by other investigators for pure gum type accelerated stocks (14, 37, 38).

The variation of stress-strain properties with sulfur content (Figure 3) shows an interesting relation. In this connection it is worth recalling the shape of the similar curves for natural rubber (18, 21). The only region of resemblance is in the true ebonite region of about 25 per cent or more combined sulfur, where both rubber and Buna S give a product of high tensile strength and low elongation. In the soft natural rubber region, a maximum in tensile strength is reached at slightly less than 6 per cent sulfur, after which both tensile strength and elongation fall off rapidly. The intermediate stage, called "semi-ebonite" by Gibbons, is characterized as leathery in that the products possess both low tensile strength and elongation.

In the Buna S series, however, the only resemblance to a leathery character is to be found in the early members of the series, which possess low tensile strength coupled with moderate elongation. The tensile strength increases concurrently with a progressive decrease in elongation as the sulfur content increases. The trend of elongation is somewhat similar to that of the rubber series, although at no time are elongations approaching those of the rubber samples obtained. It should be noted that the stress-strain data of Houwink (21) are calculated in terms of final rather than original cross section. The general character of the curve for rubber is not altered significantly by this difference.

The trend of the property known as tensile product bears a direct relation to the ultimate tensile strength, expressed in terms of breaking cross section (12). Since a limited series of cures was available for the hard samples, it cannot be assumed that the maximum tensile product was obtained in all cases. The maximum tensile product for the 15 per cent sulfur sample was for a cure still definitely in the soft rubber stage. As the sample hardens, the elongation decreases more rapidly than the tensile strength increases, with a consequent drop in tensile product.

In general, the hardness values show the same trend as those of tensile strength. Modulus of elasticity figures are of little value over a wide range of properties such as these samples exhibit and since, like natural rubber, Buna S apparently does not follow Hooke's law, no further interest in this property was manifested.

This study leaves questions unanswered on other physical properties, such as cold flow, brittle point, aging properties, etc. Additional analytical data on some of the samples would be desirable. It should be emphasized that these data were all obtained with a single batch of polymer and that considerable variation could be expected in any work with other batches.

ACKNOWLEDGMENT

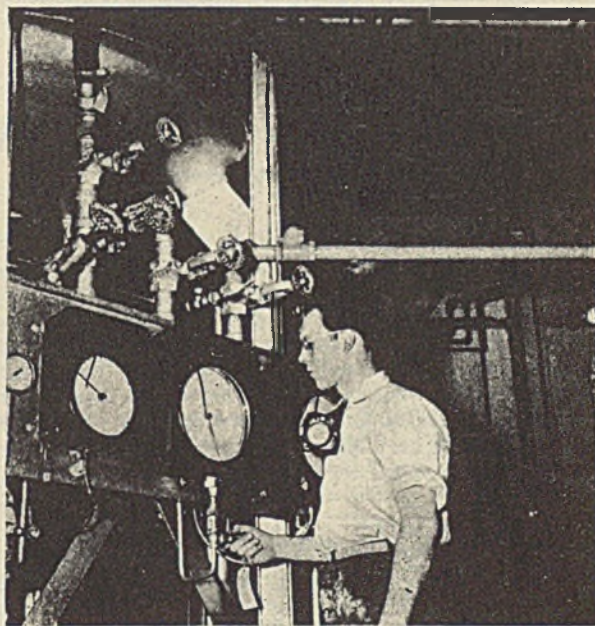
The authors are grateful to The Firestone Tire & Rubber Company for supplying the polymer used in this study. Some of the data were obtained by Carl E. Snyder and Max H. Keck, to whom thanks are due. Acknowledgment is also made to H. J. Osterhof for suggestions and criticisms of this manuscript.

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Checking Controls for One of the Chemical Reactions Leading to the Manufacture of Goodyear's Synthetic Rubber, Chemigum

Molecular Weights of High Polymers

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Methods for the estimation of molecular weights of high polymers from data on properties of their dilute solutions are critically discussed. Specific recommendations are made regarding future procedure.

THE molecular weights of small molecules can readily be determined, either from measurements of certain of their properties in the gaseous state or from measurements of certain properties (osmotic pressure, freezing point depression, etc.) of their dilute solutions. The molecular weights of very large molecules, however, cannot be determined from gaseous state data because of their very low vapor pressures. Moreover, the application of the usual equations relating osmotic pressure and similar properties of a solution to the determination of molecular weights of very large solute molecules leads, in general, to large errors. These equations are, theoretically and experimentally, truly applicable only to infinitely dilute solutions. If they are incorrectly used for solutions of finite concentration, an error is introduced, both for small-molecule and for large-molecule solutes. Comparing measurements for two solutes which are similar except for their size, in the same solvent and at the same concentration and temperature, the magnitude of the error in the calculated reciprocal of the molecular weight ($1/M_2$) is about the same in the two cases. This leads to a much greater error in the molecular weight in the case of a macromolecular solute than in the case of a small-molecule solute. This may be illustrated by Figure 1, which shows the relation between osmotic pressure (Π , in atmospheres) and concentration (C_2 , in grams of solute per cc. of solution), for solutions in dioxane of two fractions of chlorinated polyvinyl chloride.

The equation,

$$\frac{\Pi}{C_2} = \frac{RT}{M_2} \quad (1)$$

where R = gas constant, cc. atm./degree mole
 T = absolute temperature

is thermodynamically correct at infinite dilution. Extrapolation of the experimental data, plotted in Figure 1, to infinite dilution ($C_2 = 0$) gives intercepts indicating, according to Equation 1, molecular weights of 48,000 and 242,000 for the two fractions. If, however, one (incorrectly) substitutes the observed Π/C_2 values into Equation 1, "molecular weights" ranging from 35,000 to 49,000 for one sample and from 82,000 to 172,000 for the other are deduced. The error resulting from the use of Equation 1 for solutions of finite concentration (in the usual experimental range) is thus far from negligible and is greater, the larger the molecular weight (other things being equal).

The difficulty is aggravated by the fact that accurately measurable values of the osmotic pressure of high polymer solutions are not readily obtained in very dilute solutions.

Although still neglected by some workers (17, 18, 19) these facts have been recognized by others (24, 26). It has been found empirically that graphs of Π/C_2 (or ϑ/C_2 , if the data are measurements of freezing point depressions, ϑ)

against C_2 show an approximately rectilinear relation (Figure 1). Such graphs are useful, therefore, in extrapolating to $C_2 = 0$ to obtain limiting values of Π/C_2 (or ϑ/C_2) which can properly be substituted into Equation 1 (or into the corresponding equation relating the freezing point depression to the molecular weight).

A THEORETICAL explanation for the approximate rectilinear relation between Π/C_2 (or ϑ/C_2) and C_2 was furnished by the statistical treatment of the thermodynamic properties of long-chain molecules, developed independently by Flory (5, 6) and the writer (7, 8, 9, 12, 15). This theoretical treatment also explains the different slopes of the lines obtained for different systems in terms of molecular properties and accounts for the deviations from the straight-line relation which occur at higher concentrations.

The new theoretical equation, for the osmotic pressure case, may be written

$$\frac{\Pi}{C_2} - \frac{RTd_1C_2^2}{3M_1d_2^2} - \dots = \frac{RT}{M_2} + \frac{RTd_1}{M_1d_2^2} \left(\frac{1}{2} - \mu_1 \right) C_2 \quad (2)$$

where d_1, d_2 = densities of solvent and solute, respectively
 M_1, M_2 = molecular weights of solvent and solute, respectively
 μ_1 = a constant depending on nature of solvent and solute, but not on molecular weight of the latter

The second term on the left in Equation 2 is negligible for many osmotic pressure studies. This is also true of the terms involving higher powers of C_2 , represented in the equation by dots. Inclusion of this second term would lower the points at highest C_2 values (Figure 1) only about 0.004, approximately the width of the straight lines in the graph.

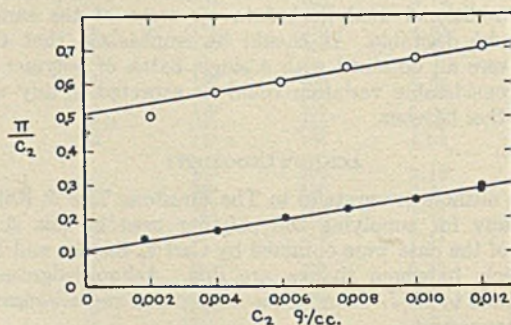


Figure 1. Dependence of Osmotic Pressure on Concentration for Solutions of Two Fractions of Chlorinated Polyvinyl Chloride (Per Cent Cl \approx 66) in Dioxane at 27° C.

Data by Staudinger and Schnelders (35); $\mu_1 = 0.38$

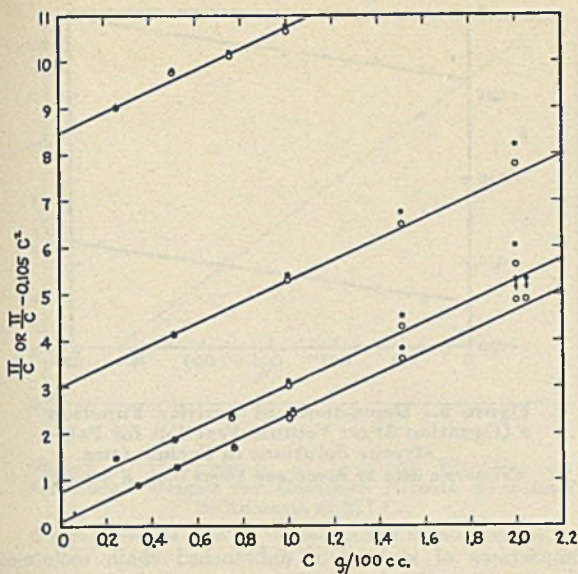


Figure 2. Dependence of Osmotic Pressure on Concentration for Solutions of Polyisobutylene in Cyclohexane at 25° C.

Data by Flory (4). The ordinates are Π/c for the filled circles, $\frac{\Pi}{c} - \frac{RTd^2c^2}{355d^2}$ for the open circles; Π is in grams/sq. cm.; c is in grams/100 cc. of solution.

Flory's recent study (4) of osmotic pressures of solutions of polyisobutylene in cyclohexane may be cited as an example of an instance in which the second term of Equation 2 is not negligible. (Contrary to Flory's statements in this paper, his experimental results are in entire agreement with the theoretical conclusions published by the writer.) As Figure 2 shows, much of the curvature obtained when the ratio of osmotic pressure to concentration is plotted against concentration is removed when the additional term is included. (The remaining curvature, if real, can be attributed to a slight dependence of μ_1 on concentration, a change from $\mu_1 \approx 0.42$ at $c = 0$, to $\mu_1 \approx 0.41$ at $c = 2$ grams per 100 cc.)

An alternative method of plotting osmotic pressure, cryoscopic, or other similar data is shown in Figures 3, 4, and 5. This method is based on the theoretical equation (7):

$$\phi \equiv \frac{\ln a_1 - \ln V_1}{V_2} - 1 = -\frac{\bar{V}_1}{V_2} + \mu_1 V_2 \quad (3)$$

where V_1, V_2 = volume fractions of components

\bar{V}_1, \bar{V}_2 = partial molal volumes of components

$$\bar{V}_1 \approx V_1 = M_1/d_1 \quad (4)$$

$$\bar{V}_2 \approx V_2 = M_2/d_2 \quad (5)$$

and a_1 = activity of solvent

a_1 is related to the osmotic pressure by the equation,

$$\ln a_1 = -\frac{\Pi \bar{V}_1}{RT} \quad (6)$$

and to the freezing point lowering by a similar equation. Plotting ϕ against V_2 , the experimental points for a given polymer sample obey a straight-line relation within the probable experimental error. The intercept of this straight line with the ordinate axis gives $-\bar{V}_1/V_2$, from which, by Equations 4 and 5, M_2 can be computed.

This method of plotting has the advantage of being applicable to relatively high concentrations (provided μ_1 re-

mains constant) without the introduction of additional terms. It also gives the constant μ_1 directly, as the slope of the straight line obtained. Once μ_1 is known for a given polymer-solvent combination, a single good osmotic pressure or cryoscopic measurement suffices to determine the molecular weight of the solute. (Of course one must not assume the same value of μ_1 for two copolymers consisting of the same monomeric units but in different proportions, or for two polymers which are otherwise chemically different.) The apparent slight variation of μ_1 with average molecular weight, (Figure 6) for polymethylmethacrylate fractions in acetone is probably the result of slight chemical differences between the average molecules of the different fractions or of the presence of small amounts of impurities, rather than a true dependence on the molecular weight of the polymer.

SAMPLES of high polymers, as normally obtained, are always mixtures of chains of different length and, hence, of different molecular weight. The molecular weights obtained from osmotic or cryoscopic data by either of the procedures just outlined are averages; these are ordinary number averages, defined as the total weight of the molecules (in molecular weight units) divided by the number of molecules (N):

$$\bar{M} = \frac{\sum_{i=1}^N M_i}{N} \quad (7)$$

A small percentage (by weight) of small molecules (or ions) in a high polymer has a large effect on the number-average molecular weight. For instance, 1 per cent of a compound of molecular weight 100 in a polymer of molecular weight 100,000 reduces the average molecular weight to about 10,000. Great care should therefore be exercised in interpreting average molecular weights, obtained from osmotic or cryoscopic data on high polymeric materials which may also contain molecules of low molecular weight.

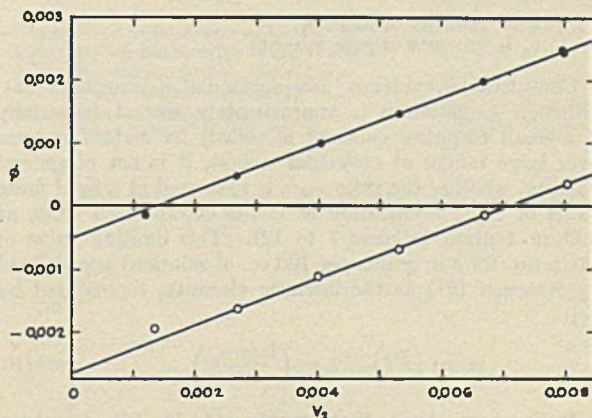


Figure 3. Alternative Method of Showing Dependence of Osmotic Pressure on Concentration (Equation 3) Same data as for Figure 1; $\mu_1 = 0.38$.

Much use has been made of a relation (30) known as Staudinger's law or Staudinger's rule, an assumed proportionality between the ratio of specific viscosity (η_{sp}) to concentration (in any of various units) and the average molecular weight:

$$\left(\frac{\eta_{sp}}{c}\right)_a = K\bar{M} \quad (8)$$

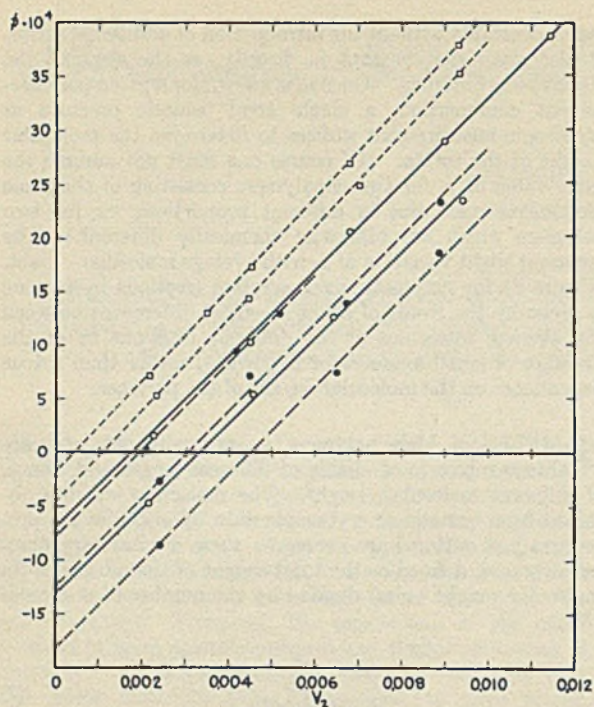


Figure 4. Dependence of Osmotic Pressure on Concentration for Solutions of Polybutadiene Fractions in Toluene at 27° C.

Data by Staudinger and Fischer (32):
 —○— Sodium polymer, B 85
 —●— Emulsion polymer, polymerized with much controlling agent
 —□— Emulsion polymer, polymerized with little controlling agent

The specific viscosity is defined by the equation,

$$\eta_{sp} \equiv \frac{\eta}{\eta_0} - 1 \quad (9)$$

where η = viscosity of solution
 η_0 = viscosity of pure solvent

Considerable evidence has accumulated showing that, although Equation 8 is approximately correct (especially if a small empirical constant is added) for certain systems over large ranges of molecular weight, it is not of general validity, whether the ratio η_{sp}/c is measured at a fixed finite value of the concentration or is the extrapolated value at infinite dilution (Figures 7 to 12). This limiting value of the ratio (for c in grams per 100 cc. of solution) was defined by Kraemer (21) as the intrinsic viscosity, represented by $[\eta]$:

$$[\eta] \equiv \left(\frac{\eta_{sp}}{c}\right)_{c=0} \equiv \left(\frac{\ln(\eta/\eta_0)}{c}\right)_{c=0} \quad (10)$$

It has been shown theoretically (11, 13, 14), moreover, that Equation 8 should not be generally valid. Plots of $[\eta]$ against \bar{M} , or of $(\eta_{sp}/c)_c$ against \bar{M} , should and do deviate from rectilinearity, often markedly; the deviations depend, according to the theory, on tightness or looseness of coiling of the kinked double-chain molecules and on other factors. Measurements of the viscosity of solutions of polymers can validly be used to estimate molecular weights only if the course of the (intrinsic) viscosity vs. molecular weight curve is known.

It may be noted in passing that deviations from Staudinger's rule furnish no justification for assuming that the polymer chains are branched (31, 32). It is equally reasonable to assume that these deviations result from variations in the

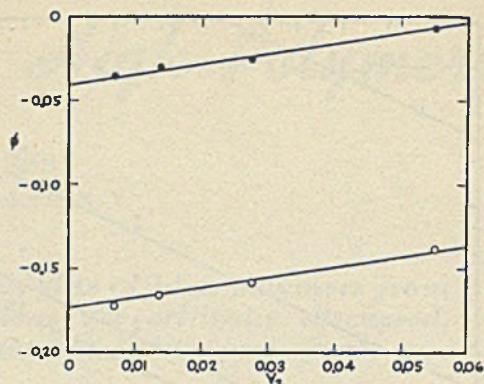


Figure 5. Dependence of Activity Function ϕ (Equation 3) on Volume Fraction for Polystyrene Solutions in Cyclohexane
 Cryoscopic data by Kemp and Peters (15); $\mu_1 = 0.62$

compactness of kinking of unbranched chain molecules; such an assumption is in better agreement (in certain cases, at least) with other facts, such as the differences in the viscosity-molecular weight relation in different solvents. Doubtless the chains are branched in some materials of high molecular weight, but deviations from Staudinger's rule cannot justifiably be cited as pertinent evidence.

The use of $[\eta]$, rather than $(\eta_{sp}/c)_c$ or $\left(\frac{\ln(\eta/\eta_0)}{c}\right)_c$ at some arbitrary concentration other than zero, is to be recommended, both because of the simpler theoretical interpretation and for convenience in comparing viscosity data obtained at different concentrations. From measurements at finite concentrations, $[\eta]$ is easily obtained by means of the relation (10, 28),

$$\frac{\eta_{sp}}{c} = [\eta] + k'[\eta]\eta_{sp} \quad (11)$$

which may also be written:

$$[\eta] = \frac{\eta_{sp}}{c} \quad (12)$$

Like μ_1 , k' depends on the type of polymer, on the solvent, and on the temperature, but only slightly or not at all on the molecular weight of the polymer.

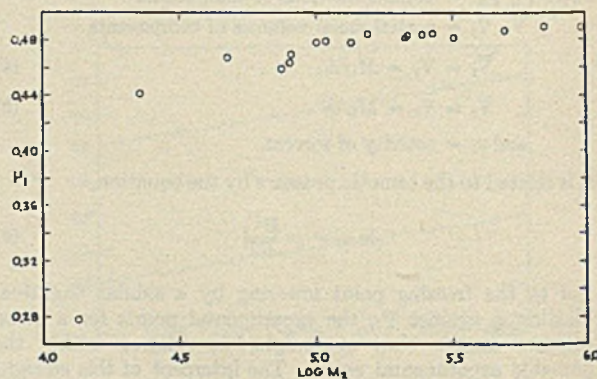


Figure 6. Apparent Variation of μ_1 with Number-Average Molecular Weight, for Polymethylmethacrylate Fractions in Acetone at 27° C.

Osmotic pressure data by Schulz and Dinglinger (29)

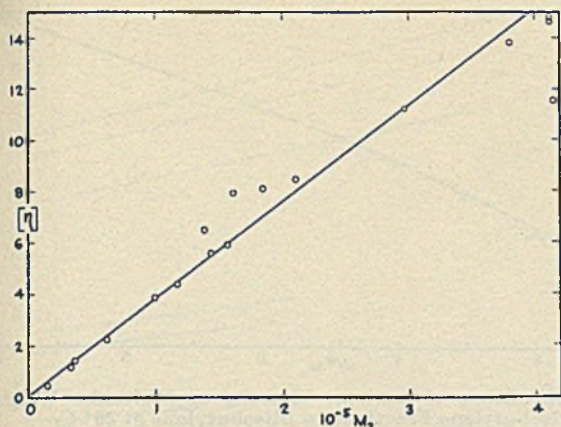


Figure 7. Dependence of Intrinsic Viscosity on Molecular Weight for Cellulose Nitrate Fractions in Acetone at 27° C.

Osmotic pressure data by Husemann and Schulz (16); $[\eta] = 3.8 \times 10^{-4} M_z$

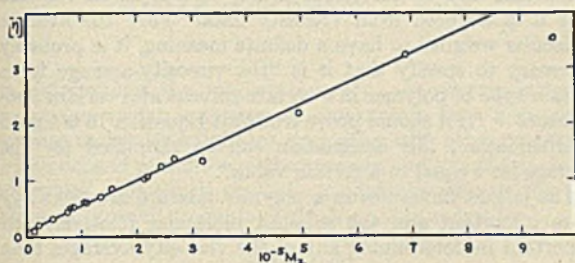


Figure 8. Dependence of Intrinsic Viscosity on Molecular Weight for Polymethylmethacrylate Fractions in Chloroform at 20° C.

Data by Schulz and Dinglinger (29); $[\eta] = 0.1 + 4.5 \times 10^{-5} M_z$

This relation has a sound theoretical basis and has been amply verified experimentally (Figures 13 to 15). The value of k' for a given polymer-solvent combination can be deduced from a series of measurements on a polymer sample at different concentrations. For this purpose the polymer need not be homogeneous, as regards molecular weight. A convenient procedure is to plot η_{sp}/c against η_{sp} and to draw the best straight line through the experimental points. The ratio of the slope to the intercept (at $c = 0$) is k' . Once this constant has been determined, a single viscosity measurement suffices to determine $[\eta]$ and, hence, the molecular weight if the $[\eta]$ vs. M curve is also known. Alternatively, one may plot η_{sp}/c or $\frac{\ln(\eta/\eta_0)}{c}$ against c . The limiting slope, assuming Equation 11 to hold, is then $k'[\eta]^2$ or $(k' - 1/2)[\eta]^2$.

A "MOLECULAR weight" obtained in this manner for a polymer sample consisting of a mixture of molecules of various sizes is not the ordinary number average (3, 20, 22, 27). This becomes obvious on consideration of the following approximate theoretical equations (11, 13, 14) for the viscosities of dilute solutions of long-chain molecules.

For rodlike chain molecules,

$$[\eta] \approx K_1 \frac{\sum M_i^2}{\sum M_i} \quad (13)$$

For randomly kinked chain molecules,

$$[\eta] \approx K_1 \frac{\sum M_i^2}{\sum M_i} \quad (14)$$

For comparison, Einstein's theoretical equation (2) for large spherical molecules may be written:

$$[\eta] \approx K_0 = K_0 \frac{\sum M_i}{\sum M_i} \quad (15)$$

One may guess that, for solutions of actual chain polymers, the following more general relation will be found to hold:

$$[\eta] \approx K \frac{\sum M_i^{\nu+1}}{\sum M_i} \quad (16)$$

where ν denotes a number, not necessarily integral, between 0 and 2, its value depending on the nature of the solute and solvent molecules and on the temperature. Usually, ν should be less than one.

For molecularly homogeneous samples, Equation 16 reduces to

$$[\eta] \approx KM^\nu \quad (17)$$

This form of equation has been proposed by various authors, probably first by Mark (23).

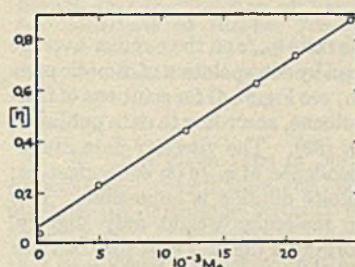


Figure 9. Dependence of Intrinsic Viscosity on Molecular Weight for ω -Hydroxyundecanoic Self-Polyesters in Chloroform at 25° C.

Data by Baker, Fuller, and Heiss, Jr. (1); $[\eta] = 0.06 + 3.2 \times 10^{-5} M_z$

There are few satisfactory data in the literature, on sufficiently well-fractionated polymer samples of accurately determined molecular weight, for testing the accuracy of this relation. Such data as are available, however, suggest its approximate validity. For example, Figure 11

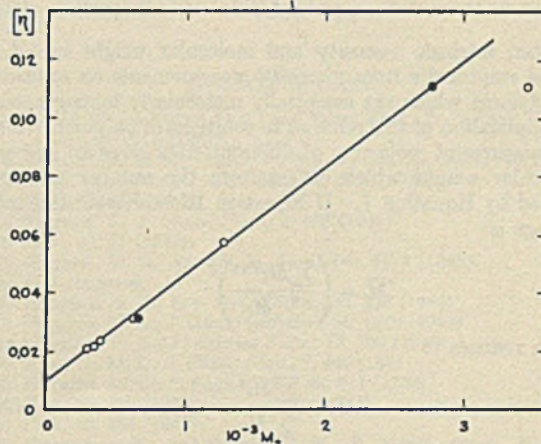


Figure 10. Dependence of Intrinsic Viscosity on Molecular Weight for Polystyrene Fractions in Benzene (at 25° C.)

Data by Kemp and Peters (18); $[\eta] = 0.01 + 3.55 \times 10^{-4} M_z$

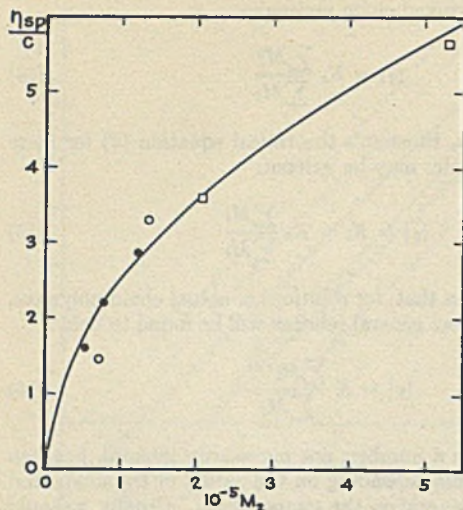


Figure 11. Dependence of η_{sp}/c (Measured at c Values between 0.04 and 0.1 Gram/100 Cc.) on the Number-Average Molecular Weight for Solutions of Butadiene Polymer Fractions in Toluene at 20° C.

The curve corresponds to Equation 17, with $k = 0.008$ and $\nu = 0.5$, and assuming M to equal the number-average molecular weight. Data by Staudinger and Fischer (32). The polymers are distinguished in the same manner as in Figure 4.

shows the dependence of the ratio η_{sp}/c on the number-average molecular weight (determined by extrapolation of osmotic pressure data to infinite dilution; see Figure 4) for solutions of fractions of polybutadiene in toluene, according to data published by Staudinger and Fischer (32). The viscosity data are insufficient to show the dependence of η_{sp}/c on concentration; hence, extrapolation to infinite dilution is impossible. This affects the dependence on molecular weight only slightly, however; much more important is the fact that the fractions used for the viscosity measurements were far from homogeneous, as regards molecular weight. Similar results, obtained by Flory (4) from solutions of polyisobutylene fractions of greater probable homogeneity, are shown in Figure 12.

IF A RELATION (graphical or analytical)

$$[\eta] = f(M) \quad (18)$$

between intrinsic viscosity and molecular weight is determined empirically from viscosity measurements on solutions of polymers which are essentially molecularly homogeneous, the application of this relation to solutions of polymers which are mixtures of molecules of different sizes gives an average molecular weight which differs from the number average, defined by Equation 7. If Equation 16 is obeyed, this new average is

$$\bar{M} = \left(\frac{\sum M_i^{\nu+1}}{\sum M_i} \right)^{\frac{1}{\nu}} \quad (19)$$

which reduces to

$$\bar{M} = \frac{\sum M_i^2}{\sum M_i} \quad (20)$$

the equation for the weight average of Kraemer and Lansing (22), if Staudinger's rule is obeyed; i. e., if $\nu = 1$.

Flory (4) suggested that the average molecular weight obtained from properly interpreted viscosity measurements be

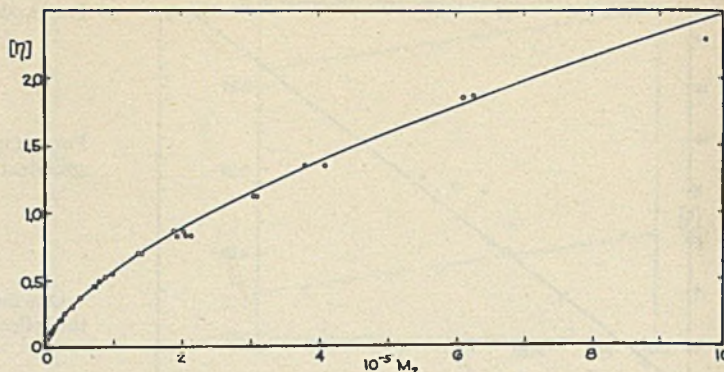


Figure 12. Dependence of Intrinsic Viscosity on Molecular Weight [for Polyisobutylene Fractions in Diisobutylene at 20° C. Data by Flory (4); $[\eta] = 3.60 \times 10^{-4} M_z^{0.44}$. (Two experimental points, for $M_z > 10^6$, are omitted.)

termed a "viscosity-average" molecular weight. This is insufficient identification, however, since the equation defining the type of average depends on the nature of both solvent and solute and on the temperature, as well as on the fact that it is deduced from viscosity data. For "the average molecular weight" to have a definite meaning, it is probably necessary to specify that it is "the viscosity-average for a certain type of polymer in a certain solvent at a certain temperature". If it should prove true that Equation 16 is a good approximation, this designation can be simplified to "the average for ν equal to a certain value".

The largest molecules in a polymer mixture are relatively more important and the smallest molecules relatively less important in determining any of the viscosity averages than

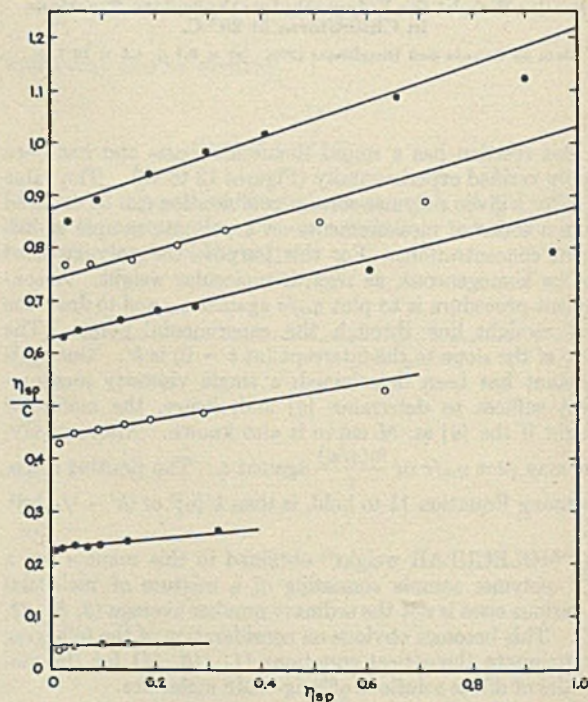


Figure 13. Dependence of Viscosity on Concentration (Equation 11) for Solutions of ω -Hydroxyundecanoic Self-Polyesters in Chloroform at 25° C.

Data by Baker, Fuller, and Heiss (1); $k' = 0.395$.

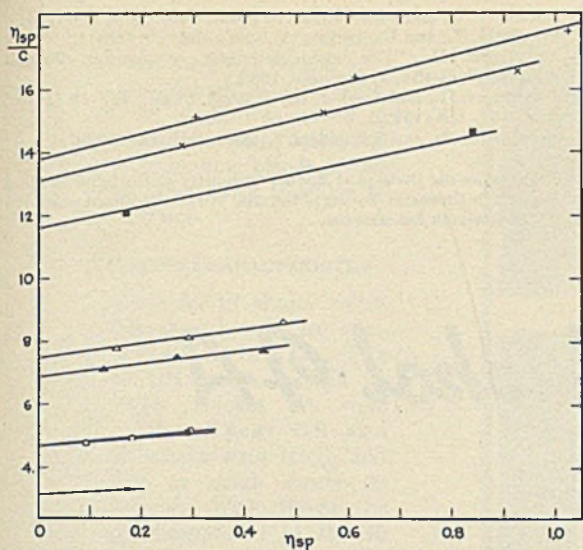


Figure 14. Dependence of Viscosity on Concentration for Solutions of Polyvinyl Chloride in Cyclohexanone at 25° C.

Data by Mead and Fuoss (25); $k' = 0.32$.

in determining the number average. A viscosity-average molecular weight is thus more appropriate than a number-average molecular weight for correlation with other properties which depend primarily on the presence and size of very large molecules, and which are only incidentally affected by the presence of small amounts of much smaller molecules.

SUMMARY

1. The equations generally used for the calculation of molecular weights from osmotic pressure or cryoscopic data are valid only at infinite dilution; their use with data obtained at finite concentrations (without extrapolation to infinite dilution) leads to very large errors, if the solute molecules are large.

2. In extrapolating osmotic or cryoscopic data to infinite dilution, graphs of Π/c (or ∂/c) against c are useful and show a rectilinear relationship. At concentrations which are not very low, a correction term should be subtracted, or the quantity $\ln a_1 - \ln V_1/V_2 - 1$ should be plotted against V_2 . For both types of graph the slope is characteristic of the solute-solvent system and the temperature, but is independent of molecular weight.

3. The use of Staudinger's rule to obtain molecular weights of high polymers is, theoretically and experimentally, unjustifiable, for most polymer-solvent systems at least. The more general relationship,

$$[\eta] \equiv \left(\frac{\eta_{sp}}{c} \right)_{c=0} = KM^{\nu}$$

where K and ν are constants to be determined empirically, is certainly more satisfactory, but whether or not this form of equation is really adequate remains to be proved. At present, empirical $[\eta]$ vs. M curves must be determined, using polymer samples which are molecularly homogeneous, before true molecular weights can be deduced from viscosity data.

4. Theoretically and experimentally it is preferable to relate the molecular weight to $[\eta]$, rather than to η_{sp}/c or $\ln(\eta/\eta_0)/c$ at some finite concentration. Extrapolation to infinite dilution is readily accomplished by means of graphs of η_{sp}/c vs. η_{sp} . The ratio of the slope of the straight line ob-

tained to its intercept depends on the type of solute and solvent and on the temperature but not on the molecular weight of the solute.

5. Osmotic pressure and cryoscopic measurements yield ordinary number-average molecular weights. Viscosity data, properly interpreted, yield another sort of average, in which the heavier molecules are relatively more important. The exact nature of this average depends on the $[\eta]$ vs. M curve (or on the value of ν in the equation $[\eta] = KM^{\nu}$).

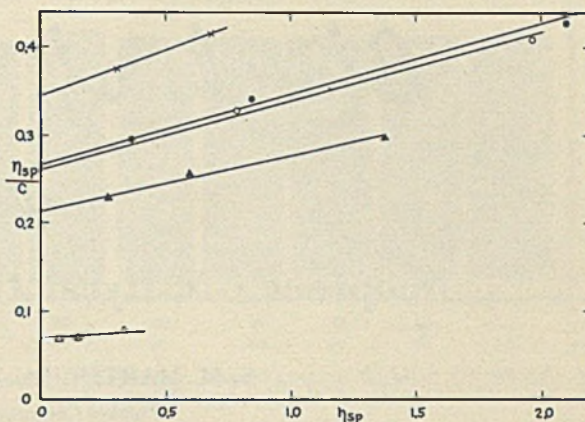


Figure 15. Dependence of Viscosity on Concentration for Solutions of Rubber Fractions in Cyclohexane at 25° C.

Data by Kemp and Peters (17); $k' = 0.30$.

6. If, for a given type of polymer, one knows (1) the constant (μ_1) determining the dependence of the osmotic pressure (in a suitable solvent) on concentration, (2) the constant (k') determining the dependence of the viscosity (in a suitable solvent) on concentration, and (3) the constants (K and ν) determining the dependence of the intrinsic viscosity on molecular weight (or an empirical curve showing this dependence); then a single osmotic pressure measurement and a single viscosity measurement on a given sample suffice to give the number-average molecular weight and a viscosity-average molecular weight (the meaning of which depends on the magnitude of ν). These two together give a better characterization of the polymer sample than either alone.

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Blends of Thiokol FA

with

Neoprene GN, Hycar OR-15, and Perbunan 26

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THE use of blends of the various synthetic rubbers in the compounding of stocks is increasing. The purpose is to get better processing stocks, to obtain specific properties in the cured composition, and to extend the supply of any one that might be momentarily short. Thiokol FA¹ is being successfully used in combination with other synthetic rubbers. In some of the stocks Thiokol FA is the predominant phase; in others, some other synthetic is the principal constituent of the rubber phase and Thiokol FA is used to impart specific properties to the compound.

The purpose of this study was to obtain basic information on the properties of Thiokol FA blends with Neoprene GN, Hycar OR-15, and Perbunan 26. It is felt that the data will show general characteristics which prevail in blends even though any specific property can be varied within certain limits by formulation changes.

A typical FA stock of 70 durometer hardness was selected for one part of each series of blends. The other portion was made up of typical compounds of Neoprene GN, Hycar OR-15, and Perbunan 26. These latter stocks had the same hardness as the Thiokol FA compound but contained no extractable plasticizers; the latter were purposely omitted to simplify the interpretation of the data.

When stocks are being compounded for blending with Thiokol FA, it is important that accelerators be selected

¹ The trade name "Thiokol" used throughout this article is registered in the U. S. Patent Office.

The properties of Thiokol FA blends with Neoprene GN, Hycar OR-15, and Perbunan 26 have been studied. Thiokol FA is compatible with these synthetics in all proportions, but properties of the blends do not show a change which is proportional to the amount of each synthetic in the stock for all properties measured. Consequently, since a number of the properties of the blends do not vary as a linear function of the composition, it was necessary to establish trends for blends of each of the several synthetics. Data of a basic nature are presented which should prove useful even though any specific property can be modified to some extent by compounding variations.

which will not adversely affect the rate of cure of Thiokol FA. Thus, in the Hycar OR-15 and Perbunan 26 compounds, benzothiazyl disulfide and DPG (diphenylguanidine) were used for acceleration. Formulas of the base stocks and a summary of their physical characteristics are shown in Table I. The stocks were mill-blended so that the crude synthetic content of each blend was that shown in Table II.

In the discussion all mention of blends refers to the crude synthetic content and not to parts of compounded stock. The stocks blended easily in all proportions. In all cases the Thiokol FA stock was first mill-warmed by six passes through

TABLE I. FORMULAS OF BASE STOCKS

Thiokol FA	100
Neoprene GN	..	100
Hycar OR-15	100	..
Perbunan 26	100
Zinc oxide	10	..	5	5
Semireinforcing black	60	50	50	60
Stearic acid	0.5	1	1	1
Benzothiazyl disulfide	0.3	..	1	1
Diphenylguanidine	0.1	0.2
Phenyl- α -naphthylamine	..	2
Extra light calcined magnesia	..	4
Sulfur	1.5	1.5

Physical Properties of Sheets Cured 60 Min. at 298° F.

Tensile, lb./sq. in.	1290	2820	3000	2760
Elongation, %	410	430	450	310

the mill. The other synthetic stocks were then put on the mill, and when each had formed a sheet, Thiokol FA stock was added in small increments with occasional cutting. In making blends of this type, the softer stock is added to the tougher one.

CALENDERING CHARACTERISTICS

The character of sheets calendered from these blends are summarized in Table III. The Neoprene GN stocks and all its blends with Thiokol FA were smooth. The Hycar OR and Perbunan stocks were tough and gave wavy or rough sheets on calendering. With Hycar the roughness disappeared in the 40 Thiokol-60 Hycar blend. With Perbunan a smaller amount of Thiokol gave a smooth sheet. In a sense the Thiokol acted as a plasticizer for the Hycar and Perbunan. Since Thiokol FA is highly resistant to solvents and is nonextractable, it offers possibilities as a nonextractable plasticizer for these synthetic rubbers. Calendered sheets of Thiokol FA-Hycar OR blends and Thiokol FA-Perbunan blends are shown in Figure 1.

DIFFUSION OF AROMATIC-BLENDED FUEL

The rate at which aromatic-blended gasoline diffuses through Thiokol FA, the other synthetic rubbers, and blends of Thiokol with the other synthetics is shown in Figure 2. The data show cumulative losses; and the solvent used, designated as 813 fuel, is a mixture of the following ingredients:

100-octane aviation gasoline	00%
Toluene	20
Xylene	15
Benzene	5

The diffusion was measured by putting 74 ml. of fuel in a half-pint Mason jar equipped with a Kerr top. A disk cut from sheets 0.062 inch thick (cured 40 minutes at 298° F.) was inserted into the top, replacing the regular metal disk of the Kerr top. The jars were stored in an inverted position in a constant-temperature room (80° F.) with free circulation of air across the surface of the disk and were weighed on a balance sensitive to 0.02 gram.

Diffusion through the straight Thiokol FA stock is fairly low and increases slightly on addition of small amounts of another synthetic. Blends containing more than 20 per cent Neoprene GN and Perbunan show rapid increase in diffusion as the proportion of either of these synthetics in the blends is raised. With Hycar OR the same general characteristics prevail, but diffusion losses are lower than for Neoprene GN and Perbunan blends.

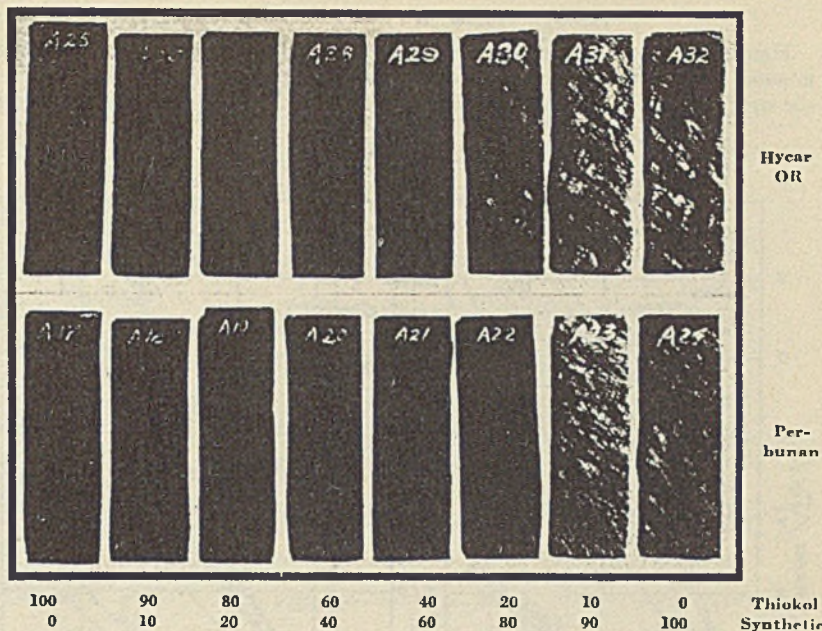


Figure 1. Calendered Surface Appearance of Thiokol FA Blends with Hycar OR and with Perbunan

VOLUME SWELL IN AROMATIC-BLENDED FUEL

Another series of curves (Figure 3) shows the volume swell of the various blends in 813 fuel. The increase in length of strips $4 \times \frac{1}{4} \times \frac{1}{16}$ inch cut from press-cured sheets was measured and the volume swell calculated from the increase in length. The data plotted are for 7-day immersion at room temperature for the 60-minute cure at 298° F. In this time the strips had attained maximum swell, and since no extractable plasticizers were present, there was no tendency toward shrinkage on further aging. In all cases the percentage swell increases linearly from the low swell of Thiokol FA on one extreme and the higher swell of the other synthetic rubbers on the other extreme.

TABLE II. CRUDE SYNTHETIC COMPOSITION OF BLENDED STOCKS

Stock No.	1	2	3	4	5	6	7	8
Per Cent by Weight								
Thiokol FA	100	90	80	60	40	20	10	0
Other synthetic	0	10	20	40	60	80	90	100
Per Cent by Volume								
Thiokol FA	100	89.3	78.9	58.3	38.3	18.9	9.4	0
Neoprene GN	0	10.7	21.1	41.7	61.7	81.1	90.6	100
Thiokol FA	100	87.1	74.9	52.8	33.2	15.9	7.7	0
Hycar OR	0	12.9	25.1	47.2	66.8	84.1	92.3	100
Thiokol FA	100	86.5	74.1	51.8	32.3	15.2	7.4	0
Perbunan	0	13.5	25.9	48.2	67.7	84.8	92.6	100

TABLE III. SURFACE APPEARANCE OF CALENDERED SHEETS^a

Parts Thiokol FA	100	90	80	60	40	20	10	0
Parts other synthetic	0	10	20	40	60	80	90	100
Neoprene GN	Sm	Sm	Sm	Sm	Sm	Sm	Sm	Sm
Hycar OR	Sm	Sm	Sm	Sm	V SI W	W	W	W
Perbunan	Sm	Sm	Sm	Sm	Sm	V SI W	SI W	W

^a Sm = smooth; W = wavy, SI W = slightly wavy; V SI W = very slightly wavy.

TENSILE STRENGTH

Figure 3 also shows tensile strength curves for the 60-minute press cure at 298° F. for the various stocks. The tensile strength was determined according to A. S. T. M. proce-

give better processing stocks than straight Thiokol. Here again it is sometimes better to sacrifice slightly in solvent resistance to gain better working characteristics even though the tensile strength of the blend is not materially increased

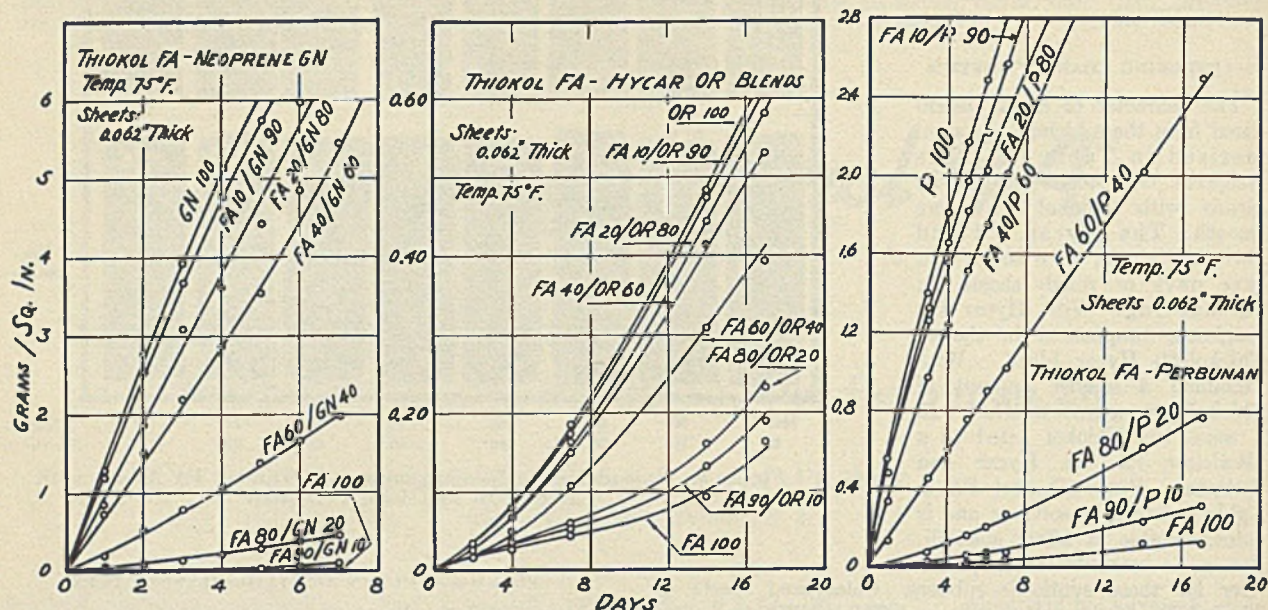


Figure 2. Diffusion of 813 Fuel through Thiokol FA Blends with Thiokol FA, Hycar OR, and Perbunan

dures (2) for testing vulcanized rubber. The volume swell of the stocks increases more rapidly with addition of other synthetics to Thiokol FA than does tensile strength. At the same time the tensile strength of the other synthetics decreases to a greater extent with the addition of Thiokol FA than does volume swell. However, it may sometimes be advantageous to sacrifice tensile strength to gain better working characteristics even though the volume swell is only slightly improved through blending. On the other hand, 10 to 20 per cent of the other synthetic rubbers blended with Thiokol FA

over that of the original Thiokol compound. It should be pointed out that Neoprene GN-Thiokol FA blends do not cure satisfactorily in open steam. Both the Thiokol FA and the Neoprene GN stocks alone cure well under the same conditions.

TEAR RESISTANCE

Tear was determined on five strips at each cure and all values falling within 20 per cent of the highest value were averaged (3). Data were obtained on three separate stock mixes, and tear values for the three mixes checked one another within 20 per cent. Table IV summarizes tear resistance of all stocks; and for the purpose of establishing trends, tear values for the three cures were averaged.

Blends of Thiokol FA-Neoprene GN show a decided dip in tear in the middle of the range. Small additions of Neoprene GN to Thiokol FA or of Thiokol FA to Neoprene GN do not affect the tear of either control stock. The reason for the low tear values in the middle of the range is not immediately apparent. It is possible that some constituent present in the crudes may exert this undesirable effect. Since the dip appears in repeated tests, it signifies an actual trend.

The tear resistance of Hycar OR shows great improvement with small additions of Thiokol FA, and the average tear across the whole range of the Thiokol FA-Hycar OR blends is comparatively high. This improvement in tear resistance of the Hycar OR stock by the addition of Thiokol FA has been demonstrated on a number of mixes. Such blends offer possibilities for obtaining better tear-resisting Hycar compounds.

Blends of Thiokol FA and Perbunan show practically a linear increase as the amount of Thiokol FA increases beyond 10 parts.

TABLE IV. TEAR RESISTANCE DATA

Cure at 298° F., Min.	Parts Thiokol FA										
	100	90	80	60	40	20	10	0	Parts Other Synthetic		
	0	10	20	40	60	80	90	100			
Thiokol FA-Neoprene GN Blends											
20	301	299	244	211	221	350	368	370			
40	286	305	264	210	253	316	353	323			
60	290	289	205	199	181	277	300	296			
Av.	292	291	238	207	218	314	340	330			
Thiokol FA-Hycar OR-16 Blends											
20	308	289	246	253	258	351	360	247			
40	305	328	311	309	301	295	284	186			
60	295	335	340	270	285	262	227	181			
Av.	303	311	299	277	281	303	290	205			
Thiokol FA-Perbunan 26 Blends											
20	280	243	224	203	222	208	195	193			
40	277	298	262	254	238	181	165	173			
60	278	240	243	228	189	171	155	157			
Av.	278	260	243	228	216	187	172	174			

TABLE V. PROPERTIES OF THIOKOL FA-NEOPRENE GN BLENDS

Thiokol FA, Parts	Neoprene GN, Parts	Cure at 298° F., Min.	Plasticity Index ^a	Raw Stock Elongation, %	Modulus at 300% Elongation, Lb./Sq. In.	Tensile, Lb./Sq. In.	Elongation, %	Shore Hardness	Compression Set, %	Lap Rebound	Open Steam Cure (50 Min., 50 Lb.)			Aviation gas	813 fuel	Volume Swell ^b		Ethyl acetate	CCl ₄	Swell Hardness	Process Oil/ Swell	70 Hr. at 212° F. in Circu Light
											Tensile strength	Elongation	Hardness			Acetone	CCl ₄					
100	0	20	0.121	640	700	1075	650	69	100	47.8	1110	10.0	18.5	17.0	10.0	18.0	37.0	6.5	75			
		40			1005	1240	480	71	100	47.0		1.0	17.0	17.0	10.0	38.0		7.0	78			
		60			1090	1220	380	71	100	44.0		1.0	14.5	16.5	9.0	34.5		7.0	77			
90	10	20	0.121	960	1025	1320	460	70	98.4	44.0		2.0	15.5	20.0	15.5	53.5		6.5	75			
		40			1255	1430	370	72	99.2	41.0	375	2.0	20.0	22.5	13.5	47.5		3.5	76			
		60			1395	1425	310	74	98.8	40.0		2.0	21.5	21.5	13.5	44.5		6.5	76			
80	20	20	0.125	1080	1145	1375	410	71	98.8	42.0		4.0	21.5	27.0	24.0	68.0		5.0	64			
		40			1340	1350	270	73	97.8	40.8	395	4.0	20.0	20.0	25.0	58.0		5.5	67			
		60			...	1425	280	73	95.5	40.0		4.0	21.5	28.0	24.0	57.5		6.0	68			
60	40	20	0.134	1000	1230	1310	350	70	91.2	41.0		10.0	25.0	37.0	112.5	38.0	34					
		40			1365	1430	340	71	91.1	39.0	715	10.0	24.0	35.0	42.5	96.0	41					
		60			1430	1500	340	71	89.7	37.0		10.0	24.0	34.5	42.0	92.5	44					
40	60	20	0.142	980	1375	1660	420	70	85.9	39.4		16.5	29.0	46.5	147.5	23						
		40			1600	1825	310	70	85.3	38.0	1235	16.3	28.0	43.5	137.5	68.0	24					
		60			1615	1790	370	70	81.8	38.0		16.3	28.0	43.5	139.0	64.0	23					
20	80	20	0.142	960	1505	2150	540	68	83.3	42.0		21.5	31.5	56.5	178.0	14						
		40			1880	2300	490	69	80.6	41.0	1975	20.5	30.5	54.5	165.0	19						
		60			1800	2245	420	70	74.0	42.0		20.5	34.5	58.5	183.0	11						
10	90	20	0.128	1000	1525	2290	610	67	83.0	43.0		24.0	33.0	64.5	233.5	11						
		40			1730	2470	520	68	79.6	44.0	2300	23.5	35.0	60.5	181.5	16						
		60			1875	2580	430	69	73.0	44.0		22.5	31.5	58.5	193.5	21						
0	100	20	0.125	1020	1760	2500	540	69	51.5	45.0		27.0	34.5	65.5	205.5	22						
		40			2130	2820	490	71	38.3	44.0		25.0	33.0	60.5	180.5	31						
		60			2300	2840	430	72	28.8	45.0		26.0	33.0	60.5	171.5	40						

^a Modified Williams plasticity. Height of 2-cc. pellet in inches after 10 minutes in plastometer at 158° F. ^b Elongation of tensile test strip cut from uncured stock. ^c 25 per cent original compression. ^d Determined on compression plug, 1 1/8 inches in diameter and 1/8 inch thick. ^e Calculated from linear swell of strips 4 x 1/8 x 1/16 inch after 1 week immersion at room temperature. ^f The oil used in these tests has an aniline point of 157 ± 3° F. and a Saybolt Universal viscosity of 160 to 160 seconds.

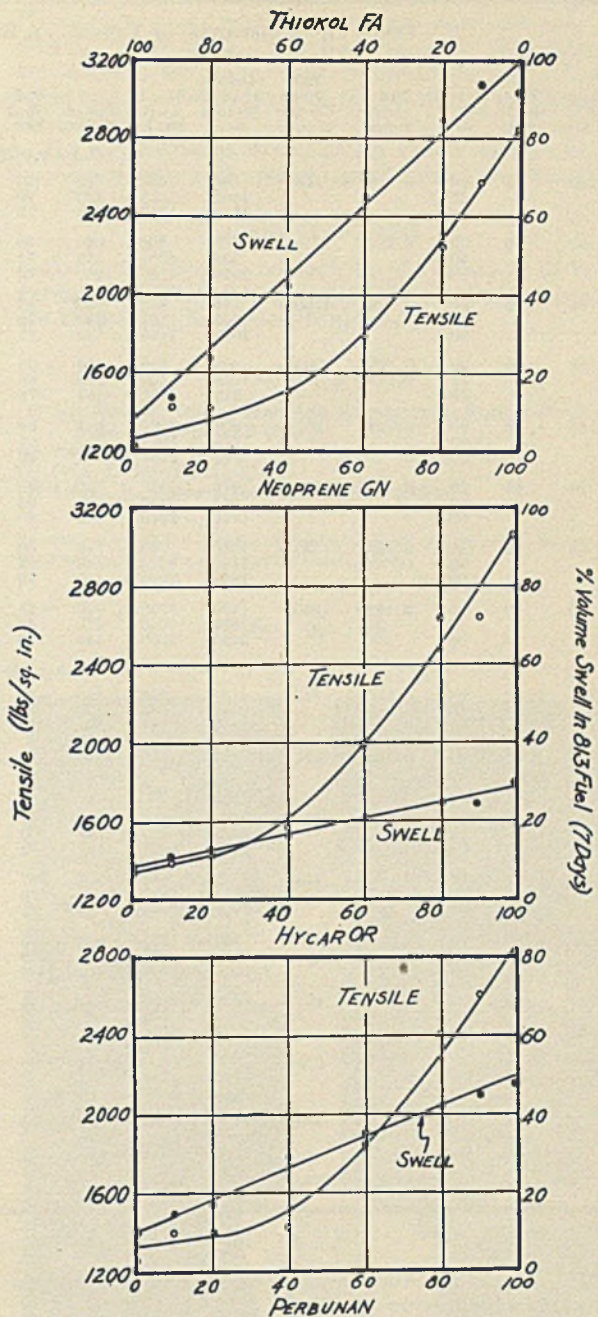


Figure 3. Swell (in 813 Fuel) and Tensile Strength of Thiokol FA Blends with Neoprene GN, Hycar OR, and Perbunan (Cured 60 Minutes at 298° F.)

COMPRESSION SET

Tables V and VI summarize data on the resilience and compression set of the various stocks. Under momentary distortion as measured by rebound, Thiokol FA shows a relatively high degree of recovery. However, under sustained compression it tends toward high set.

Compression set measurements were run by A. S. T. M. method B (1) under constant deflection using plugs 1 1/8 inches in diameter and 1/2 inch thick. A compression of 25 per cent was used and the test assembly was aged 22 hours at 158° F.

TABLE VI. PROPERTIES^a OF THIOKOL FA BLENDS WITH HYCAR OR-15 AND WITH PERBUNAN

Thiokol FA, Parts	Synthetic, Parts	Cure at 298° F., Min.	Plasticity Index	Raw Stock Elongation, %	Modulus at 300% Elongation	Tensile, Lb./Sq. In.	Elongation, %	Shore Hardness	Compression Set	Lupke Rebound	Volume Swell				70 Hr. at 212° F. in Circlo Light Process Oil		
											Aviation gas	813 fuel	Acetone	Ethyl acetate	CCl ₄	Swell	Hardness
Thiokol FA-Hycar OR-15 Blends																	
100	0	20	0.118	450	665	1050	660	66	100	47.5	1.0	11.0	20.0	23.0	38.0	-0.0	74
		40			1005	1315	490	70	100	46.5	1.0	10.0	20.8	20.0	36.0	-0.0	75
		60			1130	1340	420	72	100	44.0	1.5	8.5	20.8	18.5	33.0	-6.5	77
90	10	20	0.122	450	565	960	660	69	100	36.5	1.0	12.5	75.0	42.0	38.0	-7.5	70
		40			930	1285	530	71	100	36.5	1.5	11.0	60.2	32.0	33.0	-2.0	72
		60			1090	1380	460	72	100	35.5	1.5	11.0	48.2	30.5	36.0	-1.5	76
80	20	20	0.126	1100	535	875	780	68	100	31.5	1.0	12.5	122.2	57.0	38.5	-4.0	70
		40			805	1255	640	70	100	31.5	1.0	12.5	107.2	44.5	35.0	-0.3	73
		60			1030	1420	530	71	100	32.0	1.5	12.5	82.7	40.0	33.0	-0.3	74
60	40	20	0.136	1200+	460	945	970	60	100	26.0	1.0	18.0	240.9	96.0	39.0	-2.0	70
		40			775	1400	710	69	97.5	26.5	1.0	18.0	229.0	76.0	36.5	-2.0	70
		60			935	1560	650	71	96.5	27.0	1.0	16.5	197.0	66.0	36.0	-0.3	70
40	60	20	0.148	1200+	500	1235	980	66	95.2	22.5	2.0	23.0	339.0	111.5	39.0	2.0	68
		40			775	1860	780	69	86.2	23.5	1.5	21.5	281.5	132.0	40.0	3.5	69
		60			945	1985	680	70	84.5	25.0	1.5	21.5	220.8	91.0	38.0	4.0	70
20	80	20	0.167	1200+	675	2120	880	65	79.6	20.0	1.5	26.0	413.3	145.5	44.0	5.0	67
		40			1045	2550	700	68	67.6	20.5	2.0	27.0	300.1	127.0	42.0	5.6	67
		60			1270	2630	630	69	60.1	21.0	1.5	25.0	259.9	105.0	42.0	5.5	70
10	90	20	0.162	1200+	1010	2760	740	66	58.2	18.0	1.5	29.5	369.9	146	40.5	5.5	66
		40			1440	2770	560	69	54.9	19.0	1.5	27.5	259.9	123.5	39.0	6.5	69
		60			1885	2620	430	70	42.0	18.5	1.5	24.0	220.9	107.0	38.0	8.5	70
0	100	20	0.158	1200+	1460	3060	620	67	31.6	16.5	1.5	30.5	254.7	142	42.0	8.0	68
		40			1930	2940	470	69	23.1	15.5	2.0	29.5	189.3	116	39.0	8.5	69
		60			2250	3050	440	70	17.7	14.5	1.5	30.5	167.2	107.0	38.0	7.0	70
Thiokol FA-Perbunan Blends																	
100	0	20	0.117	345	485	835	660	67	100	47.5	1.5	10.0	21	23.0	38.0	-5.5	73
		40			935	1180	500	70	100	47.5	1.5	11.0	21	20.0	37.0	-6.0	74
		60			1140	1265	370	72	100	46.0	1.5	10.0	20	18.0	33.0	-7.0	76
90	10	20	0.122	325	485	800	680	65	100	43.0	2.0	17.0	50	46.0	48.5	-4.0	71
		40			950	1285	492	71	100	42.5	1.5	17.0	46	35.0	44.0	-0.3	70
		60			1190	1405	420	72	100	40.0	1.5	14.5	34	30.5	41.0	0	75
80	20	20	0.144	390	510	810	660	66	100	41	2.5	20.5	76	64.5	60.0	-2.5	66
		40			895	1200	480	70	100	41	2.5	21.5	59	47.5	48.5	-3.0	70
		60			1145	1400	410	72	100	40+	2.5	17.0	50	41.5	47.5	+0.3	74
60	40	20	0.174	410	585	885	580	67	92.8	40	5.5	35.0	115	106.5	77.0	5.0	64
		40			890	1175	440	70	93.1	40	4.0	30.5	106	81.0	68.0	5.5	65
		60			1135	1420	410	71	91.4	40.5	5.0	29.0	99	70.5	66.5	5.0	65
40	60	20	0.140	375	900	1335	480	66	84.5	40	7.5	40.0	134	114.5	84.0	8.0	63
		40			1270	1770	450	69	72.8	41	6.5	35.0	122	102.0	77.5	7.5	64
		60			1465	1905	420	70	72.6	41	6.5	32.0	112	90.5	72.5	8.5	65
20	80	20	0.213	405	1450	2145	460	68	62.8	41	10.0	44.5	142	121.0	89.0	13.5	65
		40			1950	2460	400	69	48.6	42	10.0	41.5	118	102.0	75.0	13.5	66
		60			2100	2405	350	70	41.7	41.5	10.0	41.5	109	91.5	74.0	13.5	67
10	90	20	0.220	345	1980	2600	410	69	49.4	41.5	11.0	46.5	112	119.5	81.0	11.0	67
		40			2420	2620	330	70	37.3	42.0	10.0	44.0	109	99.0	77.5	12.5	68
		60			2480	2600	320	71	32.6	41.5	10.0	44.0	107	98.0	74.5	13.5	69
0	100	20	0.236	260	2280	2500	330	69	24.7	39.0	11.0	51.5	118	118.0	89.0	18.5	69
		40			2760	2800	310	70	14.0	40.0	12.0	48.5	112	121.5	83.0	18.5	69
		60			2740	2820	310	71	12.1	41.5	10.5	46.5	112	103.0	83.0	20.5	70

^a See Table V for explanatory notes.

(70° C.). Resilience or percentage rebound was measured on the Lupke resiliometer (4).

The compression set of Thiokol FA is improved by blending with the other synthetic rubbers. The amount required to effect a noticeable change varies with the different synthetics. In a great many applications this high permanent set does not detract from serviceability. Where greater resistance to set is required, it can be obtained by the use of blends without sacrificing too much in solvent resistance. Thiokol FA is not generally recommended where resistance to compression set is a primary consideration in use.

FREEZE RESISTANCE

In stocks containing no plasticizers, Thiokol FA shows better low temperature flexibility than Neoprene GN, Hycar OR-15, or Perbunan 26. The low temperature flexibility of Hycar OR-15 and Perbunan 26 is improved by blending with Thiokol FA.

A summary of the low temperature characteristics of these blends is shown in Table VII. The flexibility was determined by mounting strips $4 \times \frac{1}{4} \times \frac{1}{16}$ inch on sticks $\frac{3}{4} \times \frac{3}{4}$ inch in cross section, aging in dry air at the temperatures shown, and pinching the samples with a gloved hand. This method gives a good qualitative index of the rate of stiffening of each stock.

OTHER PROPERTIES

Tables V and VI include supplementary data on various properties for a series of cures. These data are included to give as complete a picture as possible of the properties of the blends.

SUMMARY

PROCESSING. The addition of Thiokol FA to Hycar and Perbunan improves processing. Since Neoprene GN requires no additive to get smooth running stocks, no marked improvement was noticed in processing through the use of

TABLE VII. FREEZE RESISTANCE DATA

Parts Thiokol FA	100	90	80	60	40	20	10	0
Parts other synthetic	0	10	20	40	60	80	90	100
Hycar OR-15								
Flexible point, ° F.	-40	-35	-15	-10	-5	+5	+5	+10
Stiff point, ° F.	-50	-45	-40	-15	-15	-5	-5	0
Break point, ° F.	-60	-60	-50	-45	-30	-15	-15	-10
Perbunan 20								
Flexible point, ° F.	-40	-35	-30	-25	-25	-20	-5	0
Stiff point, ° F.	-50	-50	-45	-45	-35	-30	-25	-20
Break point, ° F.	-60	-60	-60	-50	-40	-40	-40	-30
Neoprene GN								
Flexible point, ° F.	-40	-30	-30	-30	-30	-30	-30	-30
Stiff point, ° F.	-50	-45	-40	-40	-40	-40	-40	-40
Break point, ° F.	-60	-60	-60	-60	-60	-55	-55	-55

blends. The addition of Neoprene, Hycar, or Perbunan to Thiokol gives a tougher uncured stock which is an advantage for many processing operations.

DIFFUSION. The diffusion of aromatic-blended gasoline through blends of Thiokol FA and other synthetics, expressed in grams per square inch per day, does not increase linearly with the percentage composition of the blends. Small amounts of the other synthetics added to Thiokol do not increase the diffusion as much as if the increase were linear. Likewise, the addition of smaller amounts of Thiokol to the other synthetics does not lower the diffusion as much as would be expected from a linear relation.

SWELL IN SOLVENTS. For blends of Thiokol FA and Neoprene GN, the linear relation holds for percentage swell in 813 fuel, acetone, ethyl acetate, and carbon tetrachloride at room temperature and in Circo light process oil at 212° F. The volume swell of Thiokol-Hycar blends in 813 fuel and carbon tetrachloride, at room temperature and in Circo light oil at 212° F., increases linearly as the percentage of Hycar is increased. In acetone and ethyl acetate the percentage swell increases linearly with increase in Hycar content until the 80 Hycar-20 Thiokol proportion is reached, where the swell holds constant or perhaps decreases. This is probably due to the state of cure of the Hycar phase in the blend.

The volume swell of Thiokol-Perbunan blends increases linearly with increased percentages of Perbunan in 813 fuel at room temperature and Circo light oil at 212° F. The volume swell of these blends in acetone, ethyl acetate, and carbon tetrachloride does not follow a linear relation. The percentage swell of the blends is greater than would be expected if the relation were linear.

It should be pointed out that in the case of Neoprene GN-Thiokol FA blends, where the swell relation is practically linear in all solvents, the difference in volume swell for different cures on any one blend is relatively small. In the case of the Hycar OR and Perbunan blends with Thiokol FA where the relation is not linear, there is a relatively large difference in the volume swell between different cures of the same blend. This leads to the belief that, in blends which swell more than would be expected, that one phase has not reached a good state of cure.

TENSILE STRENGTH. The tensile strength of the blends do not change linearly with the composition. In all cases the tensile strength was lower than would be expected from the tensile strength of the stocks blended.

FREEZE RESISTANCE. The freeze resistance of the blends bears practically a linear relation to the composition and the freeze resistance of the synthetic blended.

TEAR RESISTANCE. In Neoprene GN-Thiokol FA blends the tear resistance decreases with the addition of Thiokol to Neoprene and with the addition of Neoprene to Thiokol. The curve goes through a minimum in blends that are approximately 50 per cent Neoprene and 50 per cent Thiokol

by weight. The addition of small amounts of Thiokol to Hycar gives stocks with improved tear resistance over the original Hycar stock. The tear resistance approaches a maximum in the 90 per cent Hycar-10 per cent Thiokol blend and remains constant as the percentage of Thiokol is increased.

The tear resistance of Thiokol FA blends with Perbunan increases linearly as the percentage of Thiokol is increased.

ACKNOWLEDGMENT

The authors wish to acknowledge the assistance of V. H. Perrine of the Thiokol Corporation, who supplied the data for the Thiokol FA-Neoprene GN blends.

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PRESENTED before the Division of Rubber Chemistry at the 105th Meeting of the AMERICAN CHEMICAL SOCIETY, Detroit, Mich.



Thiokol Emerges from the Storage Tank, in a Water Carrier, in the Form of Floc; Water Seeps from the Bag Leaving the Floc Ready for the Next Process

PREPARATION OF CYCLOPENTANE

From an Oklahoma Natural Gasoline

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The application of precise fractionation to a pentane-hexane fraction of natural gasoline from the Burbank field has led to the isolation and testing of cyclopentane in high concentration. The best sample contained 95 per cent cyclopentane; a 44-gallon composite contained 91 per cent. The amount of cyclopentane in the original pentane-hexane stock is estimated to be 5.7 per cent, in the 12-pound Reid vapor pressure natural gasoline, 2.4 per cent.

CERTAIN hydrocarbon oils have long been known to contain small amounts of cyclopentane. Brown and Carr (1) in 1926 found an indication of cyclopentane in several gasolines. In 1938 Tongberg, Fenske, and Sweeney (5) cited the presence of cyclopentane in practically all of twenty naphthas investigated by them. They further mentioned the possibility of obtaining fractions (5 or more volume per cent of over-all naphtha) of 50 per cent of a particular hydrocarbon by applying efficient fractionation. Cyclopentane was listed as one of the definite possibilities from virgin naphthas. Rossini, Mair, Forziati, Glasgow, and Willingham (4) in 1942 showed the presence of cyclopentane in the paraffin-naphthene portion of an East Texas naphtha as a result of one distillation. Although these investigators and others have recognized the presence of cyclopentane in hydrocarbon oils, no one appears to have reported the actual isolation and testing of the material in high concentration. The purpose of this paper is to report a method for preparing cyclopentane from a natural gasoline.

Appreciable quantities of cyclopentane in natural gasoline produced in the Burbank, Okla., field were first suspected when kettle products from the fractionation of normal pentane from this source were observed to possess unusually low A. P. I. gravities. This was attributed to the presence of a cyclic hydrocarbon and, since it possessed a boiling point between normal *n*-pentane and *n*-hexane, was thought to be cyclopentane. A systematic effort was made to obtain the cyclopentane by precise fractional distillation.

FRACTIONATION

ORIGINAL STOCK. A pentane-hexane fraction from natural gasoline was used. The A. S. T. M. distillation and A. P. I. gravity follow:

Initial b. p. 88° F.	40% over 99° F.	90% over 113° F.
5% over 96	50% 99	95 135
10% 96	60% 100	End point 210
20% 98	70% 101	
30% 99	80% 104	° A. P. I. 89.5

EQUIPMENT. The fractionation equipment consisted of two steel batch-type packed columns. The first column or that used for the initial fractionation was 6 inches in diameter and had an over-all height of 20 feet 3 inches. It was packed with 1/2-inch steel Lessing rings for a total depth of 17 feet 5

inches. Reflux was provided by an internal water-cooled coil so that the column operated under partial condensation. Product removal was from the head as a vapor and condensed in a separate water-cooled product condenser. The still had a 250-gallon kettle and was heated by steam.

The second column (used for the final fractionation) was 6 inches in diameter and had an over-all height of 22 feet 9 inches. It was packed with 1/2-inch stoneware Raschig rings for a total depth of 18 feet 11 inches. The reflux arrangement and vapor take-off assembly were the same as that for the first column. This kettle had a 100-gallon capacity and was also heated by steam.

PROCEDURE. For the preliminary fractionation the still was operated at an average pressure of 47 pounds per square inch gage, a vapor temperature of 181° F., and a kettle temperature of 205° F.

The original stock was charged in six batches of approximately 225 gallons each for a total charge of 1350 gallons. For each batch the still was brought up to temperature and allowed to come to equilibrium under total reflux. When this had been accomplished, vapor was removed from the head of the column and condensed at the rate of about 5 pounds per hour and a reflux ratio of about 25 to 1 until nearly all of the *n*-pentane had been removed. At this point the vapor removal rate was reduced to 2 pounds per hour at a reflux ratio of about 50 to 1. Fractionation was continued until all the material boiling between 110° and 130° F. had been taken overhead. The fractions of the distillate boiling below 110° and above 130° F. were discarded.

From time to time during the fractionation, samples of the distillate were examined for A. P. I. gravity and boiling range. Boiling points and ranges were determined by a modified Cottrell boiling apparatus as developed by Quiggle, Tongberg, and Fenske (3). A typical boiling range-gravity curve showing concentration of the cyclopentane is given in Figure 1. All boiling points and ranges were obtained under controlled pressure of 760 mm. of mercury with a certified mercury thermometer. Stem corrections were also applied.

From the six preliminary fractionations, 108 gallons of cyclopentane concentrate were accumulated. A sample of this had an initial boiling point of 116° F., a dry point of 125.7° F., and an A. P. I. gravity of 65.8. This material was charged to the second still for final fractionation. The still was brought to temperature and refluxed until equilibrium was established. During this final fractionation the still

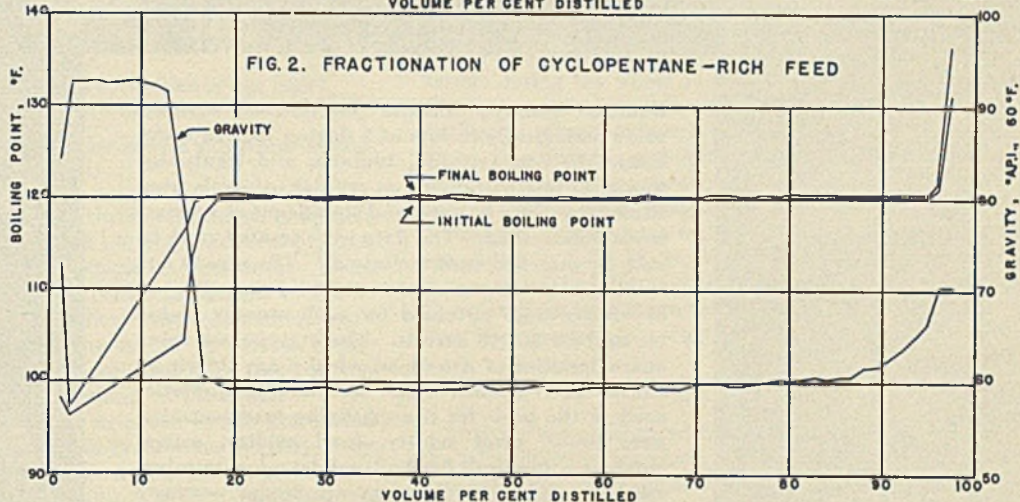
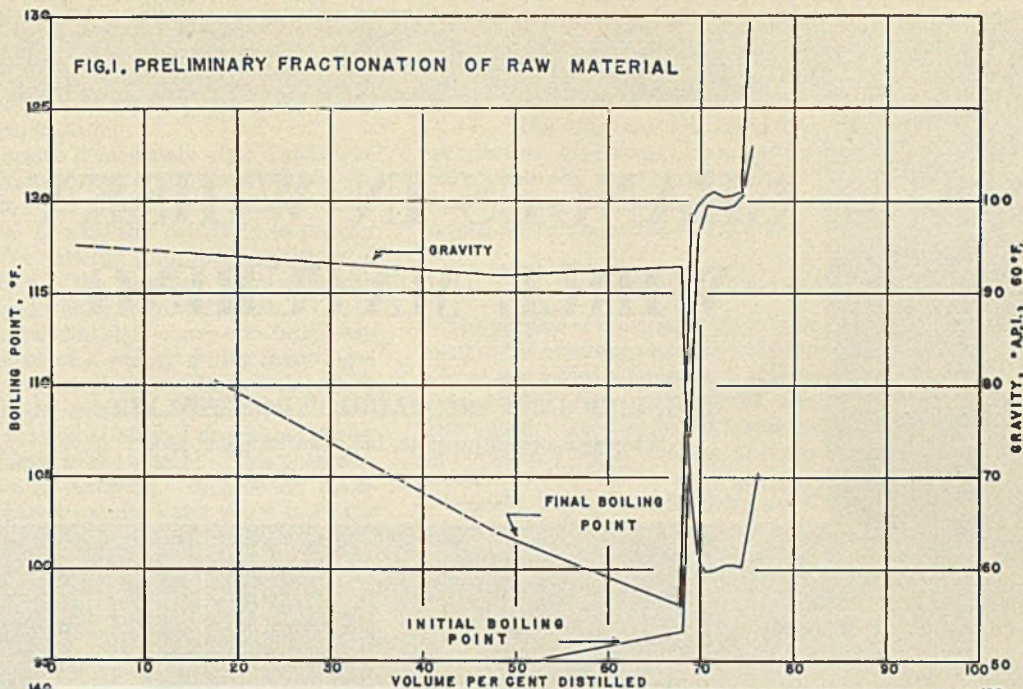
was operated at 40 pounds per square inch gage, with a vapor temperature of 201° and a kettle temperature of 204° F. Vapor removal from the head of the column was then started and continued at the rate of about 1.8 pounds per hour at a reflux ratio of 115 to 1. Condensate was collected in one-gallon cuts, and for each cut the boiling range and A. P. I. gravity were determined. Results are plotted in Figure 2.

RESULTS

Figure 2 shows that a long plateau occurred between 19 and 69 per cent distilled with only slight fluctuations in gravity and boiling point. Twice during the distillation the column flooded and was shut down until equilibrium was again established. After 69 per cent distilled, the gravity curve showed a definite though slight rise which continued until the end of the distillation. Figure 2 shows that, although good fractionation was obtained, the gravity never reached the value for pure cyclopentane, 57.1° A. P. I. (d_4^{20} 0.7460). This is attributed to the presence of a paraffin hydrocarbon which is thought to be neohexane.

Forty-four one-gallon cuts were selected from near the middle of the plateau and composited for further work. The characteristics of this composite are given in the following table, together with values for the "best sample" from the fractionation and those obtained from the literature for pure cyclopentane.

	This Work		Literature (#)
	Composite	Best sample	
Boiling point (760 mm. Hg), ° C.	49.1	49.1	49.3
Specific gravity, d_4^{20}	0.7363	0.7394	0.7460
Refractive index, n_D^{20}	1.4032	1.4050	1.4068



Assuming the contaminant to be neohexane only, the composite is estimated to contain 91 per cent cyclopentane and the best sample to contain about 95 per cent cyclopentane. Part of this composite sample was used to obtain antiknock characteristics.

The cyclopentane content of the original stock is estimated to be 5.7 liquid volume per cent, equivalent to 2.4 liquid volume per cent of a 12-pound Reid vapor pressure natural gasoline from a Burbank source.

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CHANGES IN WHISKY WHILE MATURING

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Bourbon and rye whiskies (108 barrels) were set aside periodically in lots of 5 during 1937 in warehouses in Pennsylvania, Indiana, and Kentucky. Samples were withdrawn at regular intervals from these barrels for 4 years, and significant characteristics determined. The data were treated statistically by punched card technique. The means and standard deviations of eleven major constituents of whisky were obtained for each storage period (or age) for all 108 barrels. The average maturing characteristics of American whisky are shown by charts and graphs. The eleven characteristics used as the basis for the maturing interpretation were proof, total acidity, fixed acidity, esters, aldehydes, furfural, fusel oil, solids, color, tannins, and pH. Because of the large sample size, accurate dispersion limits could be calculated. Limits of variation of "normal" whiskies are presented for different age levels of maturing from 0 to 4 years. The reliability of the results is indicated by showing that the data are approximately normally distributed and that averages from the 1938 set of barrels are not significantly different from those of the 1937 set. A table is presented as a set of empirical standards for American whisky, and the possibility of the use of the data as a basis for specifications for whisky is indicated. Further breakdown of the data in studies to follow is indicated in order to obtain standards for type, region of storage, cooperage, etc. Certain characteristics of maturing exhibit properties of regular curves, and preliminary mathematical treatment is presented.

THE quality of a beverage such as whisky is judged by the consumer on its properties affecting taste and odor. The development of the quality of whisky is dependent upon three fundamental production operations: fermentation, distillation, and maturing. This investigation is concerned solely with the last phase, maturing.

The maturing stage begins immediately after distillation, as the new colorless whisky is drawn into charred oak barrels. The barrels are placed in bonded warehouses (constructed of wood, brick, or concrete) and usually permitted to rest for four or more years under variably controlled conditions of temperature and humidity. The maturing stage ends with the withdrawal of the aged whisky from the barrels.

Three fundamental environmental factors are intimately related to the development of a whisky during maturing—temperature, humidity, and ventilation. The barrel, serving primarily as a container, also acts as a semipermeable membrane and permits the passage of alcohol and water vapors from the interior of the barrel to the outside. This phenomenon is an integral phase of maturing. In properly maintained warehouses, the barrel permits water vapor to escape at a faster rate than alcohol vapor; consequently, there is a gradual accumulation of alcohol at the expense of water inside the barrel. Thus the proof of the contents normally rises with age.

During this period, the maturing whisky undergoes definite and intended changes in aromatic and taste characteristics. These changes are caused by three major types of reactions occurring continually in the barrel:

1. Extraction of complex wood substances by the liquid.
2. Oxidation of the original organic substances and of the extracted wood material.
3. Reaction between the various organic substances present in the liquid to form new products.

The development of quality, therefore, consists of specific chemical and physical changes in the properties of the liquid, some of which are relatively simple to determine. These properties, or characteristics, are commonly used as a guide to and measure of quality. Experience and observation have shown that abnormalities arising in one or several of the physico-chemical characteristics will generally result in abnormalities of the taste characteristics of the liquid.

Due, in large measure, to the extended Prohibition period and to the empiricism of the pre-Prohibition industry, very little accurate information was available concerning the nature of maturing development. The two published investigations in this field originated in the laboratories of the Alcohol Tax Unit of the Treasury Department (3, 9). The techniques of sampling, analysis, and data presentation are almost identical in each case, although 28 years separate the two investigations.

The earlier work was based on thirty-one different barrels, all chosen from 3-month production in 1898. Most of these whiskies were distilled in types of stills now obsolete and stored in warehouses entirely different from those of today. The later work was based on twenty-two different barrels chosen from a 6-month production period of December, 1929, to May, 1930. Of the twenty-two barrels, three contained whiskies derived from such low-yield production as to indicate abnormal fermentation or distillation and thus result in atypical products.

These investigators worked under the handicap of being forced to rely on basic material and data furnished by producers not under their control, and on conditions not subject to their direct supervision. In both investigations, the average values for each characteristic were determined, and the minimum and maximum values (constituting the range) were used to indicate scatter. The exclusive use of the "range"

as a measure of dispersion must be treated with caution since it is subject to considerable individual variation. Indeed, Crampton and Tolman as well as Valaer and Frazier were forced either to indicate "next highest or lowest" values or to delete extreme values which were considered abnormal (4, 10). The subjective deletion of data, even when based on considerable experience, is a dangerous procedure. The limits of whisky characteristics set forth by both investigations (4, 10) are based on small sample sizes and one of the most inefficient measures of dispersion—the range.

HISTORY OF SAMPLES

The purpose of the present study is to examine the development of the maturing characteristics from data obtained from a large and varied sample which is characteristic of American type whisky. The dispersion of these data can then be determined, using the efficient function of standard deviation, and reliable limits of variation of normal whisky can be presented.

Straight whisky is defined by the Treasury Department (8) as "an alcoholic distillate from a fermented mash of grain distilled at not exceeding 160 proof . . . and aged for not less than 24 months in charred new oak containers." Bourbon whisky is usually produced from a mash containing 60-88 per cent corn; rye whisky generally comes from a mash containing 51 per cent rye. These two types make up the greater portion of American whisky.

The present work is based on 108 barrels of rye and bourbon whisky produced and set aside biweekly in lots of four to six barrels during the whole year of 1937. Table I shows the distribution of these barrels with respect to mash type, distillation characteristics, treatment, cooperage type, warehouse type, origin, and storage region. The 108 barrels afford an excellent cross section of the various methods of production used in manufacturing whisky.

One-pint samples were withdrawn from each barrel at the age of 0, 1, 3, 6, 12, 18, 24, 30, 36, 42, and 48 months, under the supervision of the plant chemist at each of the distilleries. These samples were forwarded to the research laboratory at New York immediately after withdrawal.

ANALYSES

Analyses were performed on all 1188 samples to determine the following characteristics: proof, total acidity, fixed acidity, esters, aldehydes, furfural, fusel oil, solids, color, tannins, and pH. The first eight characteristics were determined as outlined by the A. O. A. C. (2). All samples were brought to 25° C. before analysis.

PROOF. A National Bureau of Standards calibrated hydrometer, graduated in 0.2° C., was used for indicating proof. Temperature corrections were made with a Bureau of Standards calibrated thermometer.

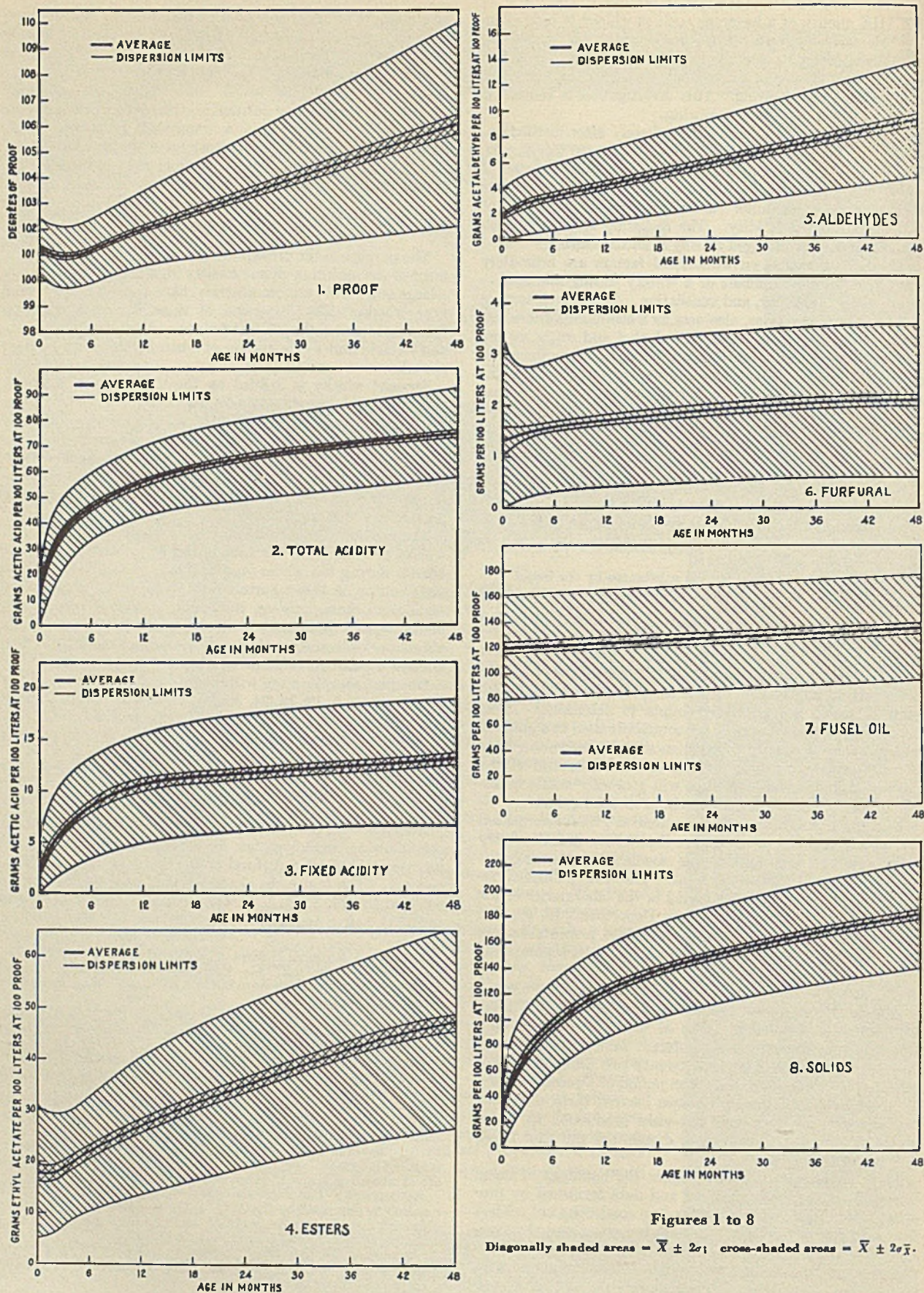
TOTAL ACIDITY. The method described by the A. O. A. C. was used without modification. The results are expressed as grams of acetic acid per 100 liters at 100 proof.

FIXED ACIDITY. The A. O. A. C. method was used without modification. The results are expressed as grams of acetic acid per 100 liters at 100 proof.

ESTERS. The distillate from a quantitative distillation through all-glass apparatus was saponified by permitting the sample to stand 24 hours at room temperature with excess sodium hydroxide. No blank was run. The excess sodium hydroxide was back-titrated with standard sulfuric acid. The results are expressed as grams of ethyl acetate per 100 liters at 100 proof.

ALDEHYDES. The titrimetric method, based on an iodometric reaction as described by the A. O. A. C., was used on the distillate obtained during ester determination. The results are expressed as grams of acetaldehyde per 100 liters at 100 proof.

FURFURAL. The A. O. A. C. method was used without modification. The results are expressed as grams of furfural per 100 liters at 100 proof.



Figures 1 to 8

Diagonally shaded areas = $\bar{X} \pm 2\sigma$; cross-shaded areas = $\bar{X} \pm 2\sigma_{\bar{x}}$.

FUSEL OIL. The Allen-Marquadt method as described by the A. O. A. C. was used. The carbon tetrachloride extractions and subsequent washings were done mechanically, and all distillations and reflux reactions performed in all-glass apparatus. The results are expressed as grams of amyl alcohol per 100 liters at 100 proof.

SOLIDS. The solids were determined by evaporation and weighing the residue in a tared aluminum dish, as described by the A. O. A. C. The results are expressed as grams per 100 liters at 100 proof.

COLOR. The color of the sample was determined on a null-type photoelectric colorimeter, designed by the Schenley Laboratories. A 100 W tungsten filament lamp was used as a source of light which passed through a matched pair of Corning daylight color glass filters before striking the photoelectric cells. The sample was reduced to 100 proof, brought to 25° C., and placed in a cell which presented one inch of path for the passage of light. The instrument was calibrated to read directly in per cent transmission (T) based on water as 100 per cent. The results are expressed in terms of color density ($d = \log 1/T$).

TANNINS. This determination is based on the Folin-Denis reagent which reacts specifically with compounds containing an oxyphenyl bond. This method was refined to conditions of optimum sensitivity (γ) and used for tannin determination in whisky. The results are expressed as grams of tannic acid per 100 liters at 100 proof.

pH. The pH was determined on samples reduced to 100 proof at 25° C. with a glass-electrode electrometer (Coleman model 3C). The application and limitations of this determination were described in a previous publication (6).

The units for expressing all values in this study are grams per 100 liters calculated back to an alcoholic concentration of 100 proof (except color, pH, and proof itself). For color and pH, the standard 100 proof was obtained physically by reduction of the sample prior to determination.

The earlier investigators used the same system of units. In addition, however, they presented the data in a system of units based on a calculation back to original volume. This method of expressing the results was suggested by the fact that an actual loss in volume occurs during maturing by evaporation from the barrel.

The technique of expressing results in this latter fashion is merely of academic interest since it involves a wholly imaginary liquid. Nowhere during or following maturing does there exist a physical process which parallels this calculation.

in exceptional cases, as low as 80. A standard proof is necessary to correct for aqueous dilution following maturing, and the proof of 100 has been established as customary.

STATISTICAL TREATMENT OF DATA

The data were recorded on master cards and transferred to specially designed punched cards. The latter were sorted and tabulated mechanically. Two primary statistical functions were used to represent the mass of assembled data: The mean value as a measure of central tendency (\bar{X}) and the standard deviation as a measure of dispersion (σ). These two values were calculated for each characteristic at each age period for all 108 barrels; the summary is shown in Table II.

The rate of development of the mean value of each characteristic is charted in Figures 1 to 11, as well as the intervals of probable variation of single-barrel and 100-barrel lots.

The wide shaded region is obtained by laying off on either side of the mean for each age an interval of 2σ (Table II). This region defines the analytical normalcy of American whisky. Any barrel chosen at random will exhibit characteristics that lie within this region with a probability of 95 per cent.

The narrow cross-hatched region is obtained by laying off on either side of the mean for each age an interval of $2\sigma_{\bar{X}}$ (11). This region defines variation in analytical characteristics to be expected when 100-barrel lots are chosen at random. The 100-barrel lot is equivalent to a commercial batch unit and, therefore, serves as a basis for setting up specifications for the finished product.

The various types of whiskies studied are here reported without further breakdown into types and according to various definite techniques in production. The development of maturing characteristics as related to definite factors will be reported in later papers.

PROOF

The bonding proof (at zero age) is fixed by the distiller and is customarily set at 102 proof. The large variation of proof

TABLE I. HISTORY OF SAMPLES

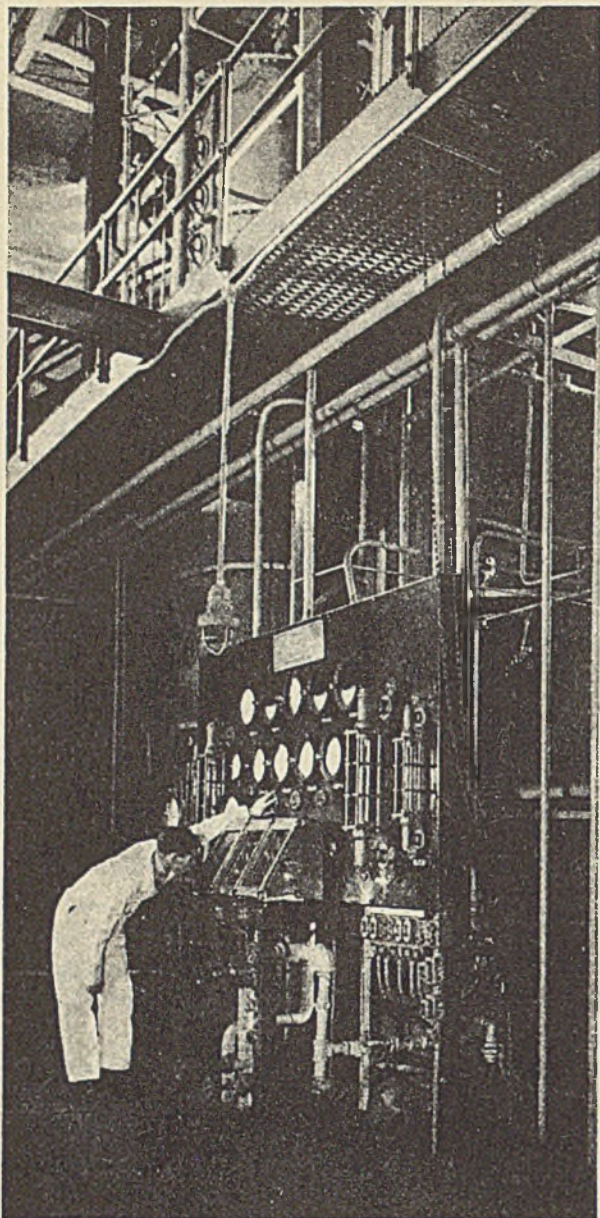
	Grain Formula		Distn. Proof		Treatment		Warehouse		Storage Region	
	Type	No. %	Proof	No. %	Type	No. %	Type	No. %	Location	No. %
Bourbon										
60% corn + 40% small grain		21 19	110-119	11 10	Untreated	52 48	Rack	40 37	Louisville, Ky.	19 18
			120-129	19 18	Oak chip	54 50	Concrete	68 63	Schenley, Pa.	28 26
80% corn + 20% small grain		2 2	130-139	60 55	Activated carbon	2 2			Lexington, Ky.	18 17
88% corn + 12% small grain		67 62	140-149	6 6	Total	108 100	Total	108 100	Lawrenceburg, Ind.	17 16
Rye									Frankfort, Ky.	26 23
61% rye + 49% other grains		18 17	150-159	12 11					Total	108 100
Total		108 100	Total	108 100						

Furthermore this method of expressing results may be misleading. In the investigation of Valer and Frazier, for example, the results calculated back to original volume in the case of aldehydes indicate a loss of aldehydes during maturing. The matured whisky, however, actually showed an increase in concentration of aldehyde, and it is this whisky which is the final product and the actual object of interest. It is immaterial whether the increase has occurred through loss in volume of solvent or by actual production of aldehyde through chemical reaction. The expression of the results in terms of 100 proof, however, is justified since the final product may be found in the barrel at a proof of 120 or higher, or may be adjusted for the purpose of bottling, sale, and consumption to a lower proof, usually ranging from 100 to 86 and,

values at zero age (Figure 1) is due chiefly to the fact that most samples were taken before, and a small portion was taken immediately after entry into barrels. The latter samples were invariably lower in alcoholic content by about 0.5 proof.

The most striking characteristic in proof development is the initial drop prior to the regular increase. This drop is caused by the residual moisture in the wood of the barrel.

The minimum average proof occurs at about 3 months of age. By the end of 6 months the whisky has regained its initial proof and then begins its linear increase. Neither of the previous investigators reported this phenomenon of initial drop, since the relatively large time period between successive samples in their studies did not permit observation



Courtesy, Old Quaker Company

Control Panel Board for Continuous Beer Still Unit

of the initial lowering in proof. After stabilization of proof increase has occurred at 6-9 months, the rise in proof as indicated by the average line is uniform and equivalent to about 1.3° proof per year.

The scatter of the values about the average proof increases with age. This fact implies that those barrels which initially gain proof more or less rapidly continue to do so during the later maturing. This further indicates that the external conditions surrounding the barrels are probably the deciding factors in proof development.

The average increase in proof of whisky during 4 years of maturing is 4.7 proof.

TOTAL ACIDITY

The total acid development (Figure 2) is characterized by an extremely rapid increase during the early stages of maturing. Indeed, during the first 4 months the average acid content is

quadrupled. Between 6 and 15 months of age, the rate of increase of average acid content begins to fall off more rapidly and finally assumes a typical asymptotic approach to a maximum value which appears to be not greater than 80 grams per 100 liters at 100 proof.

This maximum average acid value is also of theoretical interest, since it is obviously related to the maximum amount of acid material extracted from the barrel by an alcoholic solution of 51 to 55 per cent alcohol by volume.

The characteristics of the curve emphasize the relatively greater importance of the first 6 to 12 months of maturing, since it is during this short period that the acid content increases to about two thirds its final value.

It is important to note that the region of scatter increases only during the first 6 to 9 months and then remains substantially constant. This type of scatter variation is characteristic of an "exhaustion" reaction; namely, there is only a limited amount of material to be extracted and, as this limit is reached, the region of scatter must necessarily remain constant.

Because of the nature of acid development, it can readily be seen that this characteristic is not a reliable indicator of age beyond the 2-year period. After 2 years the increase in acid content with time is negligible; it is considerably less than the amount of normal variation to be expected in the average value itself.

The total concentration of acid developed in the whisky is related to the quality of the whisky by influencing to a large extent the taste characteristics of the liquid. The average increase in total acid content of whisky during 4 years of maturing is 68 grams (calculated as acetic acid) per 100 liters at 100 proof.

FIXED ACIDITY

Normally, the fixed acid content of a new whisky is zero. Figure 3 indicates a fixed acid content at zero age of about 2 grams per 100 liters at 100 proof. This is a result of treating a portion of the whisky with oak chips prior to barreling. A part of the production was subjected to such treatment during the first few months of 1937.

The general features of this curve, indicating the development of the fixed acids during maturing, are similar to those for total acids. The rapid initial rise in acid content is considerably reduced in the case of fixed acids, and the limiting value is approached at the end of 12 months. The maximum average value appears to be not greater than 15 grams per 100 liters at 100 proof.

The difference between the average total and average fixed acids at 4 years (60.0 grams per 100 liters at 100 proof) is the volatile acid content. It appears difficult to believe that the major proportion of acid material extracted from the wood is volatile in nature. It is also improbable that this volatile acidity is obtained by simple oxidation of alcohols and aldehydes in the whisky since there would then be no limiting value to the total acid increase with time. The fact that the total acid content increases asymptotically points to a relation with a limited supply of extracted material.

It may be suggested at this point (experimentally unverified) that the volatile acids increase with age is indirectly dependent on extraction from the barrel. It appears likely that some of the extracted material is readily oxidized and that the original material is thus converted to acid material, volatile in nature. This possible mechanism of volatile acid formation is important from a quality consideration, since these volatile acids contribute to the aroma of the final product.

The average increase in fixed acid content of whisky during 4 years of maturing is 12.1 grams (calculated as acetic acid) per 100 liters at 100 proof.

ESTERS

The curve of average ester development during the maturing period has several interesting features (Figure 4). For the first time an initial drop in ester content is observed following the entry into the barrel. This lowering of ester content is not an apparent average drop but occurred in each of the barrels during the first three months. The two earlier studies by Crampton and Tolman, and Valaer and Frazier did not report this phenomenon because of the relatively large time period between sampling.

ALDEHYDES

The curve for average aldehyde development during maturing (Figure 5) indicates that after a slight irregular increase, the aldehyde concentration increases at a linear rate of about 1.7 grams per 100 liters at 100 proof per year.

This development of aldehydes is evidently obtained from the oxidation of the alcohols present in the liquid and by loss in volume of liquid by evaporation. Losses of aldehydes are also continually occurring as a result of evaporation from the barrel and conversion to acids by oxidation. The factors

TABLE II. CHARACTERISTICS OF WHISKY^a

Age, Mo.	Proof		Total Acidity		Fixed Acidity		Esters		Aldehydes		Furfural		Fusel Oil		Solids		Color		Tannins		pH	
	\bar{X}	σ	\bar{X}	σ	\bar{X}	σ	\bar{X}	σ	\bar{X}	σ	\bar{X}	σ	\bar{X}	σ	\bar{X}	σ	\bar{X}	σ	\bar{X}	σ	\bar{X}	σ
0	101.4	0.53	6.8	4.0	2.0	1.4	18.2	6.3	1.7	1.1	1.2	1.1	118	21	11.4	8.5	0.048	0.050	1	2	4.76	0.18
1	101.0	0.60	21.6	7.2	3.9	2.1	17.2	6.0	2.2	1.0	1.3	0.8	120	20	50.2	16.8	0.178	0.052	14	7	4.60	0.16
3	100.9	0.54	38.2	7.1	6.5	2.9	18.9	5.3	3.1	1.2	1.5	0.6	123	22	74.4	18.8	0.234	0.056	25	8	4.45	0.09
6	101.2	0.63	45.6	6.2	8.4	2.2	22.1	5.3	3.3	1.4	1.6	0.7	122	24	96.2	17.5	0.273	0.058	31	10	4.37	0.19
12	102.1	0.67	56.9	7.0	10.8	3.3	26.8	6.9	4.0	1.4	1.7	0.7	124	21	123.1	18.0	0.305	0.050	37	8	4.29	0.07
18	102.6	0.88	60.4	7.9	11.1	3.5	31.4	7.4	4.9	1.5	1.8	0.9	127	19	139.1	16.9	0.335	0.049	40	6	4.27	0.09
24	103.4	1.17	66.1	7.3	11.5	3.2	35.3	8.0	6.0	1.8	1.9	0.7	126	18	151.6	18.3	0.361	0.045	43	7	4.26	0.10
30	103.9	1.43	68.6	8.6	11.8	2.8	38.7	9.1	7.1	2.1	2.0	0.7	128	20	162.6	18.3	0.380	0.046	46	9	4.24	0.10
36	104.5	1.55	70.6	8.2	12.2	2.7	41.6	8.8	7.8	1.9	2.0	0.8	136	21	167.5	21.2	0.395	0.046	50	7	4.23	0.10
42	105.4	1.61	71.7	8.8	12.6	3.0	45.4	8.2	8.0	2.4	2.1	0.6	135	19	175.2	19.7	0.407	0.045	56	8	4.21	0.10
48	106.1	1.97	75.1	8.6	14.1	2.8	46.2	10.1	9.2	2.3	2.1	0.7	138	22	185.3	21.3	0.419	0.045	59	7	4.19	0.10

^a All figures are expressed as grams per 100 liters at 100 proof, except proof (expressed as degrees proof), color (expressed as density), and pH.

$$\bar{X} = \frac{\sum X}{n} = \text{average value} \quad \sigma = \sqrt{\frac{\sum (X - \bar{X})^2}{n}} = \text{standard deviation}$$

The nature of the curve indicates that a condition exists initially which tends to lower the ester content; later this initial condition is overcome by one which favors the increase of ester content. During the first few months the acid content is low and there is little ester formation. The presence of a large surface of charred wood in the interior of the barrel, however, probably results in an adsorption of esters and thus lowers the ester concentration in the liquid. The rapid rise in acid content, however, soon drives the ester formation reaction forward, and the increase in ester concentration makes itself evident. Further work is planned on this phase of ester formation.

The rate of increase of average ester content after 6 months in the barrel is positive and regular, and shows signs of slackening only after the 4-year period. It is probable that the increase in ester content is asymptotic, since ester formation is dependent upon the acid concentration which, in itself, is represented by an asymptotic curve. It is evident that the region of slow ester development has not been reached at the 4-year period and that the ester content can therefore be used as an indicator of age in a more reliable manner than the acid content.

The region of scatter for individual barrels ($\bar{X} \pm 2\sigma$) increases slowly with age and at 4 years is relatively large. This extended range of scatter is probably the result of two factors: (a) the scatter from the acid content values, the magnitude of which creates the driving force for ester formation, and (b) the effect of temperature variation on the equilibrium constant of ester formation. Factor *b* probably predominates. The fluctuations of temperature throughout the year and in different parts of different warehouses are well known. At the present time this important variable is not under the positive control of the distiller.

The average increase in ester content of whisky during 4 years of maturing is 28 grams (calculated as ethyl acetate) per 100 liters at 100 proof.

favoring increase in aldehyde concentration exceed those favoring decrease by the amount given above.

The average increase in aldehyde content of whisky during 4 years of maturing is 7.5 grams (calculated as acetaldehyde) per 100 liters at 100 proof.

FURFURAL

This characteristic is of minor significance, primarily because of its very small variation with time. By custom it has usually been included in a complete analysis of whisky. The present data, as did those of the earlier investigators, indicate that its determination does not add to the evaluation of the product and, therefore, might be omitted from whisky analysis.

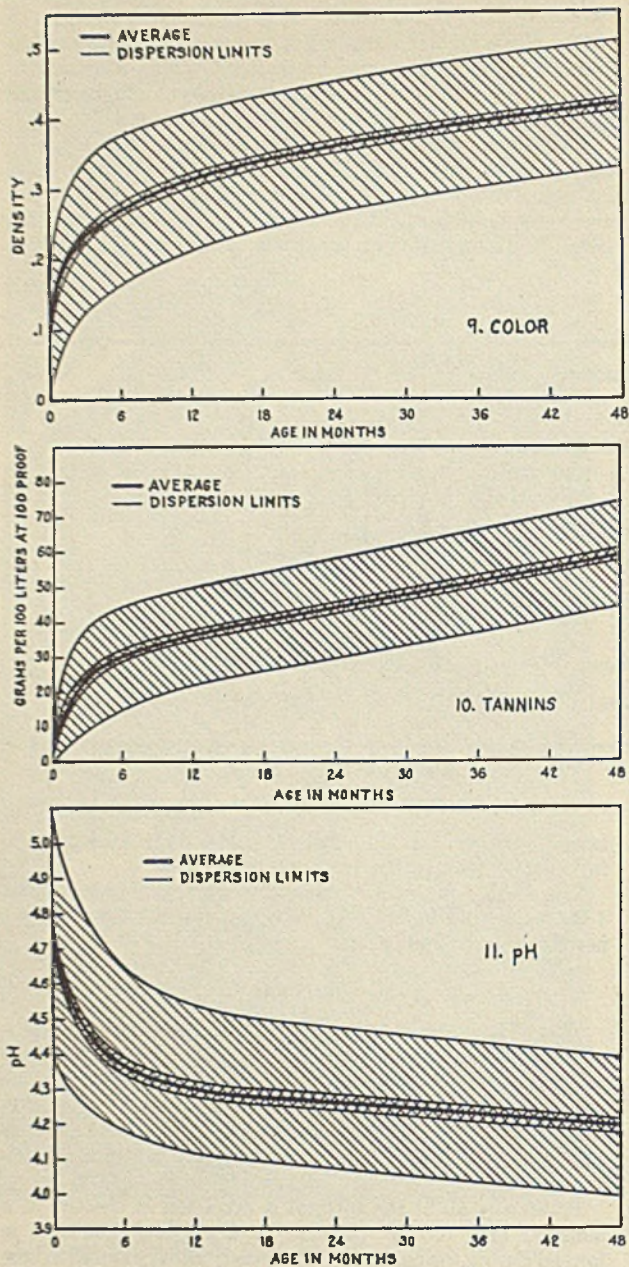
Practically all of the furfural is extracted at the end of 6 months, and further increase is negligible. Furfural is formed during the charring of the wood; whisky stored in new uncharred oak wood develops only traces of this substance.

During the first 6 months of maturing, there is an anomalous region of scatter. This occurrence is due to the fact that a small portion of the whisky received chip treatment prior to entry into the barrel. The large scatter at zero age reflects the variation in the chips, principally the degree of toasting. The rapid lowering of the scatter during the succeeding 3 months is due to the equalizing effect of the barrel, and as soon as the chip effect is overcome, the region of scatter remains constant.

The maximum average furfural content of whisky will not exceed 2.5 grams per 100 liters at 100 proof.

FUSEL OIL

The fusel oil content of a whisky is practically independent of maturing conditions. This characteristic is largely determined by the two factors of production preceding maturing, fermentation and distillation.



Figures 9, 10, and 11

Diagonally shaded areas = $\bar{X} \pm 2\sigma$; cross-shaded areas $\bar{X} \pm \sigma$.

The results (Figure 7) indicate that a slight increase in fusel oil concentration occurs during maturing. This increase is probably due to evaporation of solvent from the barrel, since the percentage increase in fusel oil concentration is approximately equal to the percentage loss in volume (12-15 per cent). The average increase in fusel oil concentration of whisky after 4 years of maturing is 20 grams (calculated as amyl alcohol) per 100 liters at 100 proof.

SOLIDS

The development of solids content during maturing is similar to that of the total acidity (Figure 8). The typical rapid initial increase of the average value and the increase in the region of scatter only during the first year are to be noted.

After 6 months of maturing the average solids content has increased to five times its original value. Thereafter the rate of increase drops off sharply and slowly approaches a limiting value.

The solids content, however, does not approach its asymptotic value as rapidly as does the total acidity. Even at the 4-year stage the increase in solids is appreciable. This characteristic of maturing cannot, therefore, be used as an indicator of the age of whisky. The maximum average value of the solids content cannot be reliably determined from the graph at this stage. It will probably not exceed 210 grams per 100 liters at 100 proof. The average increase in solids content of whisky during 4 years of maturing is 174 grams per 100 liters at 100 proof.

COLOR

The color of matured whisky is derived exclusively from the charred oak barrel and gradually shifts in hue (1) from colorless through yellow and amber to deep reddish brown.

The color development curve (Figure 9) is similar to those for total acidity and solids. The initial color of the zero age sample of 0.05 is again due to the chip treatment of a portion of the whisky prior to barreling. Within 2 months the color intensity has quadrupled. After 3 months the rate of color development begins to fall off and approaches a maximum average value which appears to be not greater than 0.45. The average increase in color intensity of whisky during 4-year maturing is 0.37.

TANNINS

The tannin content of a whisky is derived wholly from the barrel by extraction. The first portion of the tannin content-time curve (Figure 10) is similar to those of total acidity, solids, and color. A rapid increase in tannin concentration occurs during the first 6 months, followed by a decrease in rate. The curve, however, does not indicate an ever-decreasing rate to a maximum value, as might be expected from a study of the other extracted characteristics. Instead, after 12 months of maturing, the rate of increase of tannin concentration appears to become linear and increases indefinitely. Further data, beyond the 4-year period which are being gathered, will throw additional light on this phase of tannin development.

The observed indefinite increase in tannin concentration is probably apparent. The analytical determination for this characteristic is not specific, but includes the general group of organic compounds containing the oxy-phenyl bond. Although this grouping predominates in the tannin class, it is possible, as a result of the complexity of wood structure, that additional substances are extracted from the barrel which contain this grouping. The latter substances may cause the steady increase indicated by Figure 10. Eventually, however, even these substances will be exhausted, and the curve should flatten out to a typical asymptotic approach to a maximum value.

The average increase in tannin content of whisky during 4 years of maturing is 58 grams (calculated as tannic acid) per 100 liters at 100 proof.

pH

Due to the definition of pH, involving the reciprocal of hydrogen-ion concentration, the graph of pH development (Figure 11) is the mirror image of those for total acidity, solids, and color. Otherwise the features of this curve are similar to those mentioned.

Here again there is a rapid decrease of pH during the first 6 months of maturing, followed by a less rapid decrease during the next 6 months. The typical slow approach makes its

appearance after 1 year of maturing. The minimum average pH value appears to be not less than 4.15. The average decrease of pH of whisky during 4 years of maturing is 0.57.

MATHEMATICAL REPRESENTATION

It has been shown that the development of maturing characteristics of whisky by the extraction of a limited quantity

this equation is related to the maximum value that can be attained. The maximum value (y_{∞}) is equal to $1/b + y_0$.

In the case of total acidity the visual maximum value as obtained from the graph is approximately 80, and that calculated from the equation is 80. In the case of solids the comparison is approximately 210 and 201. In the case of color the comparison is approximately 0.49 and 0.44.

TABLE III. MATHEMATICAL REPRESENTATION OF MATURING CHARACTERISTICS

TOTAL ACIDITY				SOLIDS				COLOR			
$y = \frac{t}{0.069t + 0.0124t} + 6.8$				$y = \frac{t}{0.0367t + 0.00524t} + 11.4$				$y = \frac{t}{11.54 + 2.55t} + 0.05$			
t	$y_{\text{obed.}}$	$y_{\text{calcd.}}$	Difference	t	$y_{\text{obed.}}$	$y_{\text{calcd.}}$	Difference	t	$y_{\text{obed.}}$	$y_{\text{calcd.}}$	Difference
0	6.8	6.8	0.0	0	11.4	11.4	0.0	0	0.048	0.048	0.000
1	21.6	18.8	2.8	1	50.2	35.2	15.0	1	0.178	0.119	0.059
3	38.2	34.0	4.2	3	74.4	68.5	5.9	3	0.234	0.204	0.030
6	45.6	46.4	-0.8	6	96.2	99.2	-3.0	6	0.273	0.271	0.002
12	56.9	58.2	-1.3	12	123.1	131.5	-8.4	12	0.305	0.332	-0.027
18	60.4	63.9	-3.5	18	139.1	148.3	-9.2	18	0.335	0.361	-0.026
24	65.1	67.2	-2.1	24	151.6	158.6	-7.0	24	0.361	0.377	-0.016
30	68.6	69.4	-0.8	30	162.6	165.6	-3.0	30	0.380	0.388	-0.008
36	70.6	71.0	-0.4	36	167.5	170.6	-3.1	36	0.395	0.396	-0.001
42	71.7	72.1	-0.4	42	175.2	174.3	0.9	42	0.407	0.402	0.005
48	75.1	73.0	2.1	48	185.3	177.3	8.0	48	0.419	0.406	0.013
∞	∞	80.0	∞	∞	∞	201.3	∞	∞	∞	0.440	∞

of wood material leads to an asymptotic approach to a maximum value. This type of growth, under certain conditions, can be expressed mathematically by an equation in the form of a hyperbola. Three of the characteristics, due to the regularity of their development, appeared to lend themselves to such treatment—total acidity, solids, and color.

The general family of hyperbolas,

$$y = \frac{t}{a + bt} + y_0$$

where t = age, months
 y = value of characteristic
 y_0 = value of characteristic at $t = 0$
 a, b = constants

was found to give a satisfactory representation of the observed data. By plotting $t/(y - y_0)$ against t , a straight line is obtained with b as the slope and a as the y -intercept. The equation of this line was obtained by the method of least squares.

TOTAL ACIDITY. For this characteristic the equation was found to be:

$$y = \frac{t}{0.069t + 0.0124t} + 6.8$$

Table III compares the observed values with those calculated from the equation; the agreement is good in this case.

SOLIDS. For this characteristic the equation was found to be

$$y = \frac{t}{0.0367t + 0.00524t} + 11.4$$

Table III compares the observed values with those calculated from the equation, and the agreement is fair. At the 1-month period, where the rate of increase is extremely great, the agreement is poor.

COLOR. For this characteristic the equation was found to be

$$y = \frac{t}{11.54 + 2.55t} + 0.05$$

The agreement between the observed values and those calculated from the equation (Table III) is fair.

These equations can be used with reliability for the interpolation between the periods of observation. Constant b in

RELIABILITY OF THE DATA

Two fundamental assumptions have been the basis of the foregoing discussion:

1. The 108 barrels are representative of normal whisky; i. e., these barrels constitute a large enough sample so as to be characteristic of the totality of whisky production.

If this is true, then the effect of additional samples will cause negligible changes in the averages (\bar{X}) and the standard deviations (σ). An additional 50 barrels randomly set aside in 1938 were carried through the same analyses and treatment. The averages (\bar{X}') and standard deviations (σ') were calculated for this set and tested for significant differences with the 1937 set. The differences between the two sets of data were found to be statistically insignificant for all characteristics. Assumption 1 can, therefore, be considered true.

2. The 108 barrels are normally distributed with respect to their analytical characteristics.

The chi-square test for goodness of fit (χ^2) was applied to several of the characteristics at several age levels. The test indicated that the observed distribution of the data did not differ significantly from a theoretically derived normal distribution. The data can, therefore, be considered as approximately normally distributed at least.

CONCLUSION

The results of observation of 108 barrels of whisky under normal maturing conditions have been chemically and statistically analyzed.

Each curve of average values shown in the figures, describing the rate of development of maturing characteristics, is surrounded by two regions of dispersion. The diagonally shaded region in each case determines an "area of variation" for normal individual barrels of whisky. Any normal barrel chosen at random will exhibit analytical characteristics that lie within these regions. Values falling outside these regions indicate abnormal maturing behavior. The limits of these regions have been determined from the inherent variation among whiskies caused by current methods of maturing.

Table IVA summarizes the analytical characteristics of normal whisky during 4 years of maturing, showing the average values (\bar{X}) and, the maximum and minimum normal

TABLE IV. ANALYTICAL CHARACTERISTICS OF WHISKY^a

Age, Years	Value ^b	Proof	Total Acidity	Fixed Acidity	Esters	Aldehydes	Furfural	Fusel Oil	Solids	Color	Tannins	pH
A. Individual Barrels												
0	<i>L_V</i>	102.5	14.8	4.8	30.9	3.9	3.1	160	28.3	0.148	6	5.12
	\bar{X}	101.4	6.8	2.0	18.2	1.7	1.2	118	11.4	0.048	1	4.76
	<i>L_L</i>	100.3	0.0	0.0	5.5	0.0	0.0	76	0.0	0.000	0	4.40
1	<i>L_V</i>	103.4	71.0	17.4	40.5	6.8	3.2	166	159.1	0.405	52	4.43
	\bar{X}	102.1	56.9	10.8	26.8	4.0	1.7	124	123.1	0.305	37	4.29
	<i>L_L</i>	100.8	42.8	4.2	13.1	1.2	0.2	82	87.1	0.205	22	4.15
2	<i>L_V</i>	105.7	80.6	17.5	51.4	9.6	3.3	162	188.2	0.451	57	4.46
	\bar{X}	103.4	66.1	11.5	35.3	6.0	1.9	126	151.6	0.361	43	4.26
	<i>L_L</i>	101.1	51.6	4.6	19.2	2.4	0.5	90	115.0	0.271	29	4.06
3	<i>L_V</i>	107.6	87.0	18.0	59.2	11.6	3.5	178	209.9	0.487	64	4.43
	\bar{X}	104.5	70.6	12.2	41.6	7.8	2.0	136	167.5	0.395	50	4.23
	<i>L_L</i>	101.4	54.2	6.5	24.0	4.0	0.5	94	125.1	0.303	34	4.03
4	<i>L_V</i>	110.0	92.4	19.0	66.3	13.8	3.6	182	227.9	0.509	73	4.39
	\bar{X}	106.1	75.1	14.1	46.2	9.2	2.1	138	185.3	0.419	59	4.19
	<i>L_L</i>	102.2	57.8	6.8	26.1	4.6	0.6	94	142.7	0.329	47	3.99
B. 100-Barrel Lots												
0	<i>L'_V</i>	101.5	7.8	2.7	19.7	2.0	1.3	122	13.5	0.061	2	4.80
	\bar{X}	101.4	6.8	2.0	18.2	1.7	1.2	118	11.4	0.048	1	4.76
	<i>L'_L</i>	101.3	5.8	1.3	16.7	1.4	1.1	114	9.3	0.035	0	4.72
1	<i>L'_V</i>	102.2	58.3	11.4	28.1	4.3	1.8	128	126.6	0.315	38	4.30
	\bar{X}	102.1	56.9	10.8	26.8	4.0	1.7	124	123.1	0.305	37	4.29
	<i>L'_L</i>	102.0	55.5	10.2	25.5	3.7	1.6	120	119.6	0.295	36	4.28
2	<i>L'_V</i>	103.6	67.5	12.1	36.8	6.3	2.0	130	155.1	0.370	44	4.28
	\bar{X}	103.4	66.1	11.5	35.3	6.0	1.9	126	151.6	0.361	43	4.26
	<i>L'_L</i>	103.2	64.7	10.9	33.8	5.7	1.8	122	148.1	0.352	42	4.24
3	<i>D'_V</i>	104.8	72.0	12.7	43.3	8.2	2.2	140	171.6	0.404	50	4.25
	\bar{X}	104.5	70.6	12.2	41.6	7.8	2.0	136	167.5	0.395	49	4.23
	<i>L'_L</i>	104.2	69.2	11.7	39.9	7.4	1.8	132	163.4	0.386	48	4.21
4	<i>L'_V</i>	106.5	76.8	14.6	48.2	9.7	2.2	142	189.5	0.428	61	4.21
	\bar{X}	106.1	75.1	14.1	46.2	9.2	2.1	138	185.3	0.419	60	4.19
	<i>L'_L</i>	105.7	73.4	13.6	44.2	8.7	2.0	134	181.1	0.410	59	4.17

^a All figures expressed as grams per 100 liters at 100 proof, except proof (expressed as degrees proof), color (expressed as density), and pH.

^b *L_V* = probable maximum = $\bar{X} + 2\sigma$; *L_L* = probable minimum = $\bar{X} - 2\sigma$; \bar{X} = average; *L'_V* = probable maximum = $\bar{X} + 2\sigma\bar{X}$; *L'_L* = probable minimum = $\bar{X} - 2\sigma\bar{X}$.

variation among individual barrels to be expected in each case (*L_V* and *L_L*).

The regions of dispersion discussed above are relatively large in many cases. This is a consequence of considering individual barrels, and of including within the region individuals which are normal and yet a considerable distance from the average value.

This effect is minimized to a great extent in industrial practice by the usual mixing of a large number of barrels to form a convenient operating unit. This unit frequently consists of 100 barrels. In this case the effect of a few individual barrels which exhibit characteristics away from the average value is practically eliminated. Therefore, the variation among these 100-barrel lots will be much smaller than among individual barrels.

The cross-hatched regions surrounding the average curves show quantitatively how much smaller the dispersion becomes for 100-barrel lots. Table IVB summarizes the analytical characteristics of normal whisky during 4 years of maturing, showing the same average values (\bar{X}) and the maximum and minimum variation among 100-barrel lots to be expected in each case (*L'_V* and *L'_L*).

Since these 100-barrel lots are the units of the finished product, Table V may be used as a basis for setting up specifications for the control of whisky quality.

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Recovery of Free Acid from PICKLING LIQUORS

Acetone has been found superior to solvents previously tried for promoting the crystallization of copperas from pickling liquor. While not satisfactory for the treatment of continuous-process liquor, batch liquor responds well from the standpoints of ferrous sulfate removal, acid concentration, quality of separated copperas, and acetone separation. A system for applying this process without appreciable acetone loss may be of practical value.

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taining the crystals was then vacuum-filtered, pressed, and washed with 10 ml. of acetone on the filter to displace acid filtrate. The filtrate was passed through a packed and heated rectifying column which delivered almost water-free acetone at the top and acetone-free acid at the bottom. The recovered acid was analyzed for free acid and copperas content.

A series of five 250-ml. samples were treated by this method, using 100, 200, 300, 400, and 500 ml. of acetone. The percentages of acid and ferrous sulfate in the recovered liquors are shown in Figure 1. These curves show that optimum results, in terms of copperas removal, were obtained when 400 ml. of acetone were employed, the concentration of ferrous sulfate dropping from 15.75 to slightly under 1 per cent. Acid concentration, due to loss of water with the crystallized salt, reached a maximum of 8.36 per cent when 250 ml. of acetone were used. The ferrous sulfate

NUMEROUS processes have been devised for the recovery of acid from spent pickling liquors. They were reviewed by Hodge (1) in his summary on acid wastes. Most of these processes consist of separating ferrous sulfate from the liquor by crystallization brought about by evaporation and cooling. Many types of operating techniques were developed to separate the maximum quantity of copperas. The best of these processes left considerable copperas in solution and hence did not prove attractive to industry.

A process patented by de Lattre (2) differed markedly from the others in that methanol was employed to produce crystallization. The alcohol was recovered by distillation and the recovered acid made up to strength and returned to the pickling vats. The crystalline copperas was dried and stored.

This process seemed to lend itself to improvement through the possible use of solvents now available at relatively low cost. Preliminary experiments were made in which the relative effectiveness of several alcohols and ketones for promoting crystallization of the copperas was determined. Of the several solvents employed, acetone proved most effective. When added in sufficient volume, the copperas could be rapidly separated to a high degree from spent liquor. The results obtained appeared to justify further study of this method of treatment.

BATCH LIQUOR

The first liquor studied was of the batch type and had the following percentage analysis: ferrous sulfate 15.75, sulfuric acid 4.88, water 79.37. The treatment consisted of adding 250 ml. of the liquor slowly to a measured volume of acetone which was constantly agitated at a high rate. The liquor con-

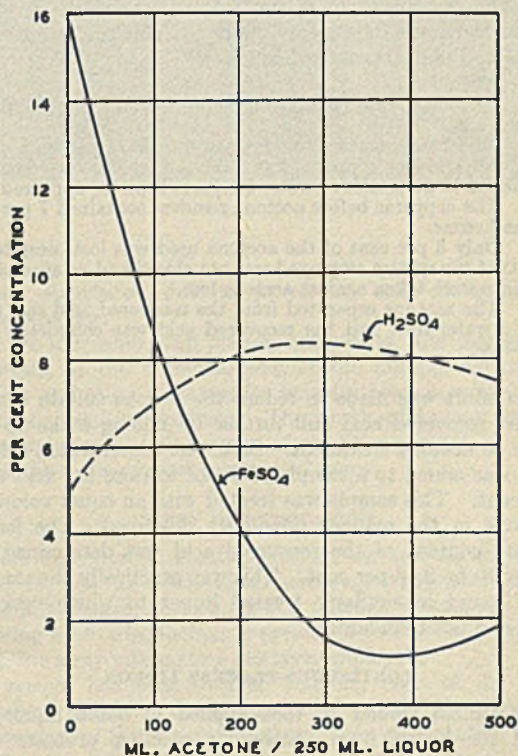


Figure 1. Acid and Copperas Concentrations Produced by Treatment of Batch Pickling Liquor with Acetone

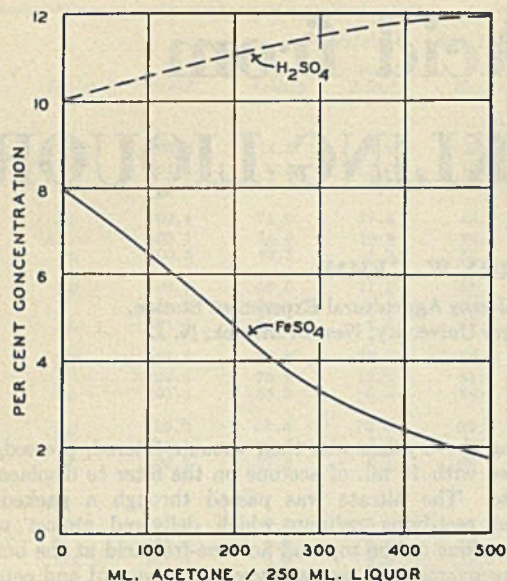


Figure 2. Acid and Copperas Concentrations Produced by Treatment of Continuous-Process Pickling Liquor with Acetone

content of this recovered liquor was 2.45 per cent. The above concentration of ferrous sulfate would be again reduced on the addition of make-up acid and water. Since no great difference existed between the acid concentration when 250 or 400 ml. of acetone were used, and the ferrous sulfate content of the recovered liquors was low in each case, the volumes of 250 ml. of liquor to 250 ml. of acetone or a 1 to 1 ratio was selected for further study of this process.

A run employing these proportions was made in which all the pertinent data were obtained. This run is presented in Table I and summarized as follows:

1. Ferrous sulfate content of the liquor was reduced almost 85 per cent.
2. Acid concentration was increased over 71 per cent.
3. An acid-free copperas was produced which, while containing about 10 molecules of water of crystallization, appeared dry.
4. The copperas before acetone removal contained 7 per cent of the ketone.
5. Only 3 per cent of the acetone used was lost, despite the fact that the system employed was not closed and no special precautions were taken against acetone loss.
6. The acetone separated from the recovered acid was practically water-free, and the recovered acid was completely acetone-free.

An effort was made to reduce the ferrous sulfate content of the recovered acid still further by adding make-up acid prior to acetone treatment. Sufficient concentrated sulfuric acid was added to a sample of liquor to raise the acid to 10 per cent. This sample was treated with an equal volume of acetone in the manner previously described. The ferrous sulfate content of the recovered acid was determined and found to be 2.46 per cent. This was practically the same as that found in similarly treated liquor to which make-up acid had not been added.

CONTINUOUS-PROCESS LIQUOR

Treatment similar to that applied to batch liquor was tried for liquor from continuous pickling process. This liquor had the following percentage analysis: ferrous sulfate 7.88, sulfuric acid 10.00, water 82.12 (by difference). A series of tests were made by treating 250-ml. samples of liquor

with 50, 100, 250, 325, and 400 ml. of acetone, respectively. Acid and ferrous sulfate concentrations were determined in the recovered liquors.

Results of this treatment are shown in Figure 2. Optimum treatment was obtained when 400 ml. of acetone were employed. This treatment reduced the ferrous sulfate content from 7.88 to 2.3 per cent and increased the acid concentration from 10 to 11.8 per cent.

DISCUSSION

Experimentation revealed that acetone was superior to the fatty alcohols, such as methanol, used in the de Lattre process for promoting crystallization of copperas from spent pickling liquors. Batch liquor was best treated with an equal volume of acetone, producing 85 per cent removal of ferrous sulfate and an increase in acid concentration of 71 per cent. From 1000 gallons of this waste treated, 680 gallons of acid would be recovered. When brought up to the original 15 per cent acid concentration and volume, with strong acid for re-use, the ferrous sulfate concentration could be reduced to as low as 1.6 per cent.

For such a process to operate economically, high acetone recovery would be necessary. In the laboratory experiments 97 per cent recovery was obtained in an open system. Large-scale closed-system operation of such a process should realize recoveries well in excess of 99 per cent. The copperas obtained from this process was free of acid and in a relatively dry state. In this form it could be dumped or marketed, if possible.

TABLE I. TREATMENT OF BATCH PICKLING LIQUOR WITH AN EQUAL VOLUME OF ACETONE

Acetone	Copperas	Recovered Acid
Recovered from liquor, 231 ml; sp. gr. 0.789	Acetone-wet copperas, 108 g.	Vol. recovered liquor, 170 ml.
Remaining in copperas, 20 ml.	Acetone-free copperas, 94 g.	Wt. recovered liquor, 186 g.
Recovered from copperas, 14 ml.	FeSO ₄ present, 42.16 g.	Wt. FeSO ₄ present, 4.56 g.
	Water present, 51.84 g.	Wt. H ₂ SO ₄ present, 8.36 g.
		Wt. H ₂ O present, 166 g.
	Water of crystallization in copperas, 10 g.	
Total used 250 ml.	pH of copperas, 3.5	% FeSO ₄ , 2.45
Total recovered 245 ml.	Free acid, trace	% H ₂ SO ₄ , 8.35
Total lost 5 ml.		
Recovery 97%		

Efforts to improve the separation of copperas by pre-addition of make-up acid were without success. It is possible, however, that the quantity of acetone required to give similar results to equal volume addition could be reduced if make-up acid was added prior to treatment.

Spent liquor from the continuous pickling process could be treated to produce considerable reduction in ferrous sulfate content. Volumes of acetone almost twice that of the liquor were required, and only a small concentration of acid resulted. This occurred because the ferrous sulfate concentration in this liquor was too low to remove much water as water of crystallization.

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SOLID SOAP PHASES

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Four separate crystalline phases of importance exist in sodium soaps. These phases give rise to different properties when present in solid commercial soaps. Various soap manufacturing processes involve phase transformations among these solid forms. The identification and estimation of approximate proportions of solid soap phases rests on x-ray diffraction patterns, by means of which the phase condition of the final product may be ascertained and the processing history followed.

FOR over a decade the soap industry has had available a consistent body of theory to explain and predict the behavior of soap systems in the soap boiling process where liquid and liquid crystalline phases are involved (2, 4, 5). More recently, basic information has also become available on the peculiar phase transformations of soap at elevated temperatures, giving rise to a series of waxy and liquid-crystalline phases (16); some of them may concern soap making operations under particular conditions. On the other hand, aside from a few isolated results and some largely unsubstantiated speculations, no explanation in terms of fundamental theory has existed with respect to the physical state of the final bar and other solid soap products of the industry.

During the past several years an extensive mass of evidence has been accumulated in this laboratory to explain the behavior of solid commercial soaps in terms of phase composition and phase change. The purpose of this paper is to summarize some of the evidence which relates to the proof for the existence of four separate crystalline sodium soap phases. There has been no recognition of the existence or the importance of these phases in soap products in the past, and two of the forms have not been presented hitherto as phases with

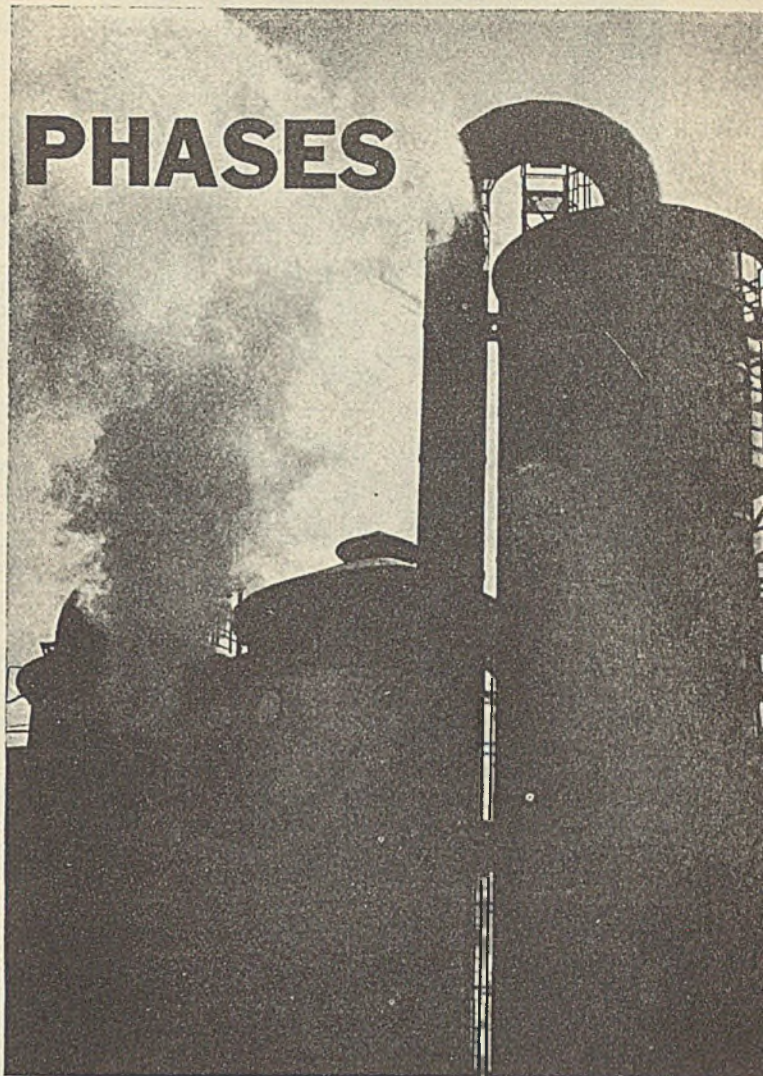
distinct structures, definite properties, and characteristic phase behavior.

Of the four solid soap phases, beta, delta, and omega are important in the understanding of the milling, extrusion, framing and other processes for finishing soap in solid form, and of the resulting products. The fourth solid phase, alpha, exists under so limited a range of conditions as not to come within the realm of most commercial soaps.

X-RAY IDENTIFICATION

Since the ultimate identification of the crystalline structures, as well as distinctions involving waxy and liquid crystalline phases, rests on x-ray diffraction patterns, the following brief introduction is presented to show the way in which the x-ray information has been employed.

A system has been evolved whereby each of the four crystalline phases of the sodium soaps can be identified by the presence of the one or two characteristic diffraction rings



The photograph shows spray-drying towers for making soap granules.

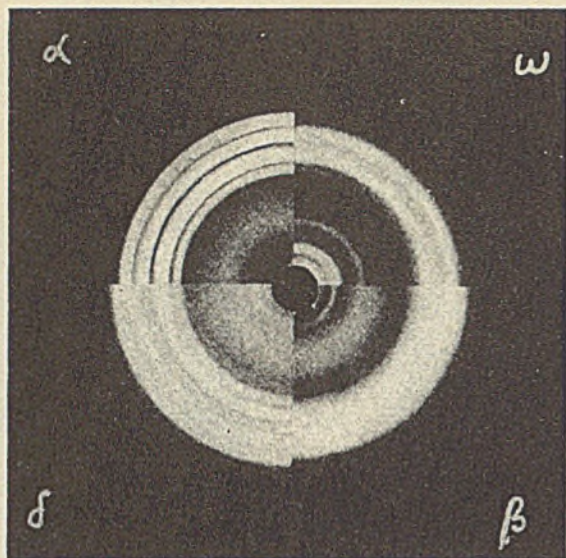


Figure 1. Quadrant Comparison of Short Spacing Rings of Four Crystalline Phases of Pure Sodium Stearate

listed in Table I. As will be illustrated later, these identifying spacings have been found independent of fatty stock composition and moisture content. The constancy of these spacings is exhibited not only in single-phase patterns but in patterns containing two or even three phases, as in numerous examples showing progressive conversion of one phase into another throughout a series of successive patterns. (An abbreviated series is shown in Figure 4). This is in contrast to the progressive variation in spacing exhibited in solid solution formation.

Soap is like other materials of molecular formula containing long hydrocarbon chains in that the spacings revealed by the diffraction patterns of crystalline forms may be divided into two distinct groups, the long and the short spacings. The ring diameters listed in Table I are selected from those arising from the short spacings—i. e., the lattice spacings in the range 2–5 Å., involving for the most part the lateral separations between hydrocarbon chains.

While these short spacings have usually been ignored or their significance has been overlooked in studying soap, it has been found for a number of fatty derivatives that many short spacings (type $hk0$) for a given phase remain constant as the chain length is varied (9, 10). This is precisely true for the soaps, as will be shown later. In studying the processing behavior of a soap in terms of phase identification, it is to the short spacings that attention should be directed.

The long spacings—i. e., the lattice distances measured perpendicularly between $-\text{COONa}$ "sheets" (c or $c \sin \beta$), do reflect variation in chain length and hence in composition, since additional CH_2 groups will separate the $-\text{COONa}$ "sheets" still further.

The characteristic rings listed in Table I can be used for the estimation of approximate relative proportions of solid phases, by first making up synthetic mixtures of the pure phases and noting the presence and relative intensities of the characteristic rings. For example, a mixture of beta and omega, which gives approximately equal intensities of the characteristic rings, will actually contain about 75 per cent beta and 25 per cent omega phase.

The diagrams for the four separate phases are brought together for comparison in Figure 1, where the characteristic

TABLE I. CHARACTERISTIC DIFFRACTION RINGS OF CRYSTALLINE PHASES

	Ring Diameter ^a , Cm.	Lattice Spacing d/n , Å.
Alpha	7.5 and 4.5	2.45 and 3.65
Beta	6.35	2.75
Delta	6.05 and 4.65	2.85 and 3.55
Omega	5.85	2.95

^a For 5-cm. sample-to-film distance in a flat film camera.

short spacing rings are shown toward the outer part of the patterns. Table II compares the numerical values for the short spacings of alpha, beta, delta, and omega sodium palmitate. In Figure 2 the corresponding long spacing rings for the four phases are contrasted.

Long spacings are also of value in identifying soap phases, but their use requires even more cautious discrimination than that of short spacings. For the complicated mixtures represented by commercial soaps, there is no apparent way of using long spacings for identifying phases in the simple manner described in Table I. On the other hand, the long spacings are useful in such studies as possible fractionation during the cooling and crystallization of a molten mixed soap.

It will be evident that soap phases can be identified and their careers followed throughout a given processing history, without any space lattice calculations or any knowledge of the fundamental structures involved (3). To illustrate this principle, the ring diameters in the table of identifying values are given in centimeters as well as in Å., since by simple

TABLE II. COMPARISON OF SHORT SPACINGS OF ALPHA, BETA, OMEGA, AND DELTA PHASES OF SODIUM PALMITATE

Alpha		Beta		Omega		Delta	
d/n	In- tensity	d/n	In- tensity	d/n	In- tensity	d/n	In- tensity
..	..	1.78	VW
1.98	VW	1.98	VW
2.17	VW	2.15	VVW
2.32	VW	2.35	W	2.25	W
2.45 ^a	M	2.48	VW	2.30	VW
2.55	VW	2.52	VW	2.54	VW
..	..	2.62	VW	2.68	VW
..	..	2.80 ^{a,b}	M
2.85	VW	2.85 ^a	M
..	2.95 ^a	M
3.02	M	3.02	M
3.15	VW	3.13	M	3.13	VW
..	3.23	W
..	..	3.48	VW	3.40	VW
3.55	W	3.55 ^a	M
3.65 ^{a,c}	VS
3.85	W	3.85	S	3.85	S
..	3.92	M	3.92	VW
4.02	S	4.03	S
..	..	4.28	S	4.33	W
4.45	W
4.55	VS	4.55	VS
..	4.68	VS

^a These rings are those used for identification purposes. In addition, to aid in comparison of patterns, spacings having an intensity of medium (M) or more are underlined.

^b The difference between the value 2.80 Å. for anhydrous sodium palmitate (2.78 Å. for sodium stearate in Table IV agrees within the accuracy of determination) and our identifying value 2.75 Å. is real. The value 2.80 Å., however, has been found only for the anhydrous single soaps, 2.75 Å. serving to identify hydrous sodium palmitate and all commercial beta soaps encountered, as illustrated in Tables V and VI.

^c Agreement between us and Thiessen and Stauff for this important (210) spacing was not good until their tabulated value of $\sin^2 \theta$ was found to be in error. Substitution of the Miller indices in Thiessen's own equation

$$\frac{1}{d^2} = 0.01545h^2 + 0.0117k^2 + 0.000375l^2$$

leads to a value 3.69 Å., in agreement with our 3.65 Å. Their value of $\sin^2 \theta$ leads to a spacing of 3.54 Å.

measurement of lines on the diffraction pattern the phase identification can be made, provided the reduction or enlargement of a given print is known.

Before proceeding to a more detailed description of the various solid phases, a specific example will be given to illustrate the significance of certain phase changes on soap technology. A commercial milled soap of approximately 80 per cent tallow-20 per cent coconut oil was passed through the milling and plodding operations, and then consisted of practically 100 per cent beta phase; it was converted to omega phase by heating in a sealed container to about 190° F. and then allowing to cool quietly to room temperature. Another portion was converted to delta phase by reworking at a low temperature (50-60° F.). The three samples, of identical chemical composition but of different phase, were then compared in properties; results are shown in Table III. It is evident that each different treatment provided a product of different phase composition and at the same time led to widely varying performance and properties in the product.

The diffraction data were obtained using unfiltered copper K radiation from a standard General Electric diffraction unit. Hydrated soap samples were contained in thin, sealed Pyrex capillaries about 0.1 cm. inside diameter. The diffraction patterns were registered on flat film, 5 cm. from the sample or at 10 cm. for the long spacing patterns of Figure 2.

The single soaps studied were prepared by saponification of Eastman-grade fatty acids with carbonate-free sodium hydroxide, followed by oven drying at 150° C. to constant weight. Purity of the fatty acids used is indicated by the following typical acid values:

Acid	Eastman Catalog No.	Acid Value	
		Exptl.	Theoretical
Lauric	933	275	280.0
Myristic	1116	245.6	245.6
Palmitic	1213	215.5-218.4	218.8
Stearic	402	198.8-197.2	197.2

BETA PHASE

Beta phase has a direct and significant involvement in commercial soaps (i. e., soap-water systems) and is prominent in the phase behavior of pure single soaps also. For example, in low-moisture commercial soaps, simple cooling of neat soap may produce omega phase which, in many formulas, can be transformed into beta phase of more rapidly soluble form by agitation at temperature levels where beta is stable. In such systems the formation of beta is favored over omega by agitation in phase-composition areas and at temperatures where beta can exist.

The ability of beta crystals to exist in rapidly soluble, easy lathering form is an important and far-reaching characteristic utilized in the milling and plodding process and in the newer votating process of Mills (7). (The methods of

TABLE III. PROPERTIES OF THREE PHASES OF A TYPICAL COMMERCIAL SOAP

	Beta	Omega	Delta
Firmness, arbitrary units	8.0	7.2	3.0
% soap rubbed off bar in use in water ^a	2.4	0.5	1.7
Reaction to water when soaked	Swells and dis-integrates	No swelling or dis-integration	Cracks, with little swelling

^a This figure is a measure of the ease of lathering of the bar of soap; the pronounced difference between beta and omega is readily observed in ease of lather tests.

determining phase composition described in the present paper were applied by Mills to the interpretation of a process for making a new form of commercial soap, employing a rapid cooling device known as a votator.) It must be pointed out that those conditions under which beta is formed, which affect such factors as the size, orientation, coherence, etc., of the crystals, are important in influencing the properties of the final product.

In a soap composition which contains a large proportion of beta, the transformation of beta to omega may be followed easily by means of the x-ray when the soap is heated to a temperature (characteristic for the composition) at which beta is no longer able to exist. This soap, when cooled to room temperature, will be found to have lost its translucency (provided it was originally in the translucent condition), and to possess lathering properties of the lower degree consistent with omega phase. Its behavior in water is radically altered, as the comparative results in Table III show.

When heated further, the omega soap melts and the system finally becomes a homogeneous semiliquid neat soap which is liquid crystalline. In certain instances transformation to a waxy phase may occur, but the course of the melting, through single or multiphase fields, may be followed by ob-

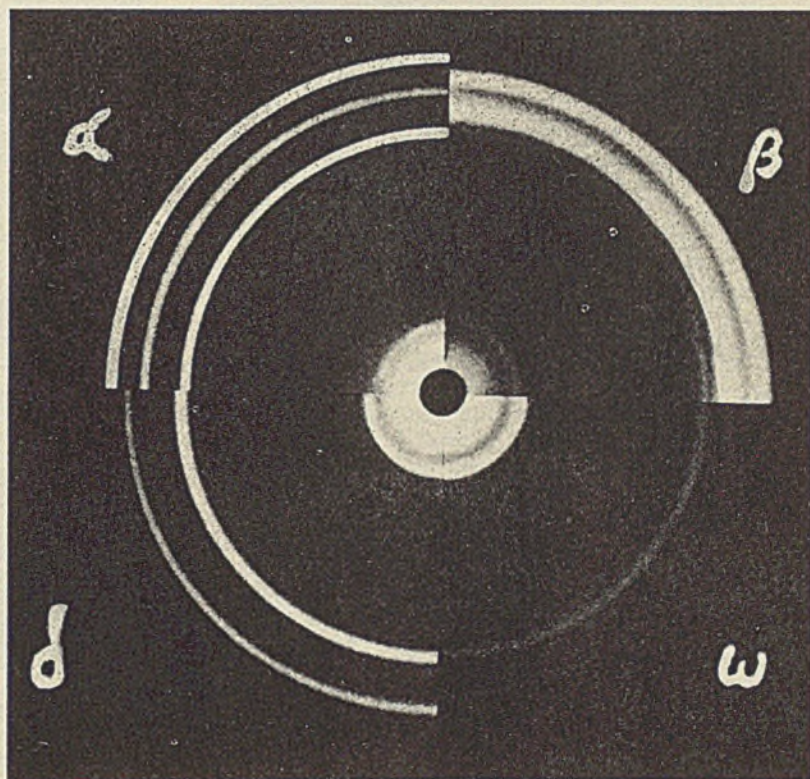


Figure 2. Quadrant Comparison of Long Spacing Rings of Four Crystalline Phases of Pure Sodium Stearate (Rings Closest to Center of Pattern)

taining diffraction patterns at the successive temperature levels. The point of complete melting to neat soap may be located more precisely by means of a dilatometer curve (6), but the specific identification of the phases present at any temperature is obtained from the x-ray pattern.

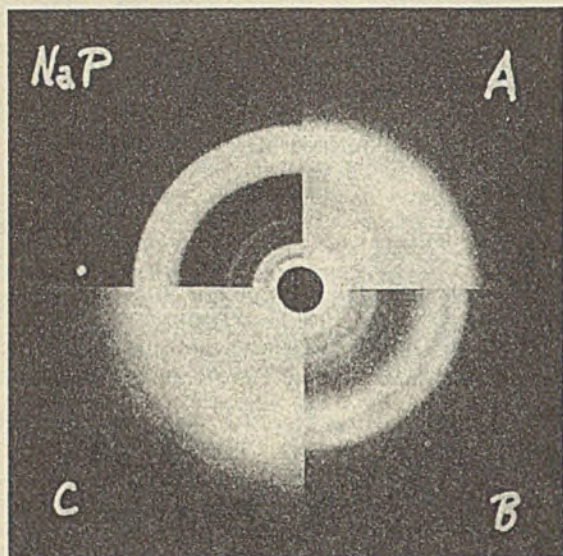


Figure 3. Quadrant Comparison of Identifying Beta Rings in Hydrous Sodium Palmitate and Commercial Soaps of Varying Composition and Moisture Content (Table V)

During any process in which omega is eliminated with the simultaneous production of beta, the gradual fading out of the characteristic omega ring, together with the gradual strengthening of the beta ring, not only gives a measure of the transformation but provides ample evidence of the reality of the phase change.

Since the identification of the solid phases hinges on the presence in an x-ray pattern of certain characteristic short spacing rings, Table II presents all the short spacings of the four known sodium soap structures. Of these four, only the alpha and beta structures have been reported in the literature¹ (12, 14, 15). Establishment of omega and delta as distinct soap structures will be considered later. The spacings that have been found reliable as criteria of the presence of a particular phase are marked *a* in Table II, and shown separately in Table I.

Since our identifying spacing for the beta phase is not found among the beta spacings of Thiessen and Stauff who announced this phase, it is necessary to justify our use of it. Actually we are in almost complete disagreement with Thiessen regarding the beta short spacings; we regard Thiessen's numerical data as inconsistent with his own published patterns. This was shown by (a) measuring the lines on his Figure 12 (14); (b) calculating a hypothetical "camera radius", assuming a value 4.28 Å. for the innermost strong short spacing (the only spacing on which we and Thiessen agree—4.28 compared to 4.21 Å.); and (c) reversing this calculation by using the computed camera radius to obtain

¹ Since this paper was originally submitted, McBain and de Bretteville [Science, 96, 470 (1942)] have announced a gamma modification of sodium stearate. Although they have so far quoted only a single long spacing value to characterize their gamma form, this value (44.6 Å.) and the history of their sample indicate that their gamma and our omega (44.4 Å.) modifications are identical.

the other spacings. Although Thiessen does not state the wave length of his radiation, step (b) of our calculation can be made by assuming any wave length, since wave length and hypothetical radius are interdependent and lead to the same set of derived spacings. This comparison is shown in Table IV (column 3 with columns 4–5), where it is also shown that our data for sodium palmitate and stearate (columns 1–2) are in close agreement with the values derived from his published patterns. Whatever the explanation, it is evident that there is an error in his paper. Since the matter will be considered in greater detail in a subsequent paper, we will merely state here that it is our own beta data which appear in the four-phase comparison of Table II and from which we have selected the identifying spacing.

The results in Table IV further demonstrate the constancy of short spacings in spite of the difference in chain length between sodium palmitate and stearate. Tables V and VI and Figure 3 show the constancy of the important beta spacings for soaps of widely varying composition. The three commercial soaps of Table V vary in tallow and coconut content, and soap C contains some potash soap. The moisture contents vary somewhat also, yet the phase identification in terms of beta content is specific and may be made fairly quantitative by proceeding according to the method stated earlier in this paper.

The short spacings used for the identification of the beta, omega, and delta structures are shown in Table VI to be independent of the moisture of the soap systems. In respect to the beta long spacings, we are in good agreement with Thiessen and Stauff for both sodium palmitate and stearate. The long spacings serve as a further means of identifying beta phase, although they are a much less useful tool than short spacings since long spacings vary with composition, which must therefore be known, and since they are represented by x-ray reflections close to the central undiffracted beam and are therefore less subject to precise determination than the short spacings. (In Figure 2 the long spacings are represented by the group of rings closest to the center of the pattern.)

TABLE IV. COMPARISON OF BETA DATA WITH THOSE OF THIESSEN

1 Beta Na Palmitate ^a		2 Beta Na Stearate ^a		3 Beta Na Stearate ^b		4 Beta Na Stearate ^c		5 Beta Na Palmitate ^d		
<i>d/n</i>	<i>I</i> *	<i>d/n</i>	<i>I</i> *	<i>d/n</i>	<i>I</i> **	<i>hkl</i>	<i>d/n</i>	<i>I</i> ***	<i>d/n</i>	<i>I</i> ***
..	1.31	M	040
1.78	VW	1.67	M	220	1.78	M
..	1.75	S	400
2.35	W	2.13	W	310
2.47	VW	2.46	(VW	206)	2.30	VW
..	023)
2.63	VW	2.64	(S	020)
2.80	M	2.78	M	2.78	M	2.76	M
3.13	M	3.13	M	3.15	M	3.19	M
..	3.37	(W	203)
..	205)
3.85	S	3.85	S	3.45	VS	200	3.90	S	3.88	S
4.28	S	4.3	S	4.21	VS	110	4.28	S	4.26	S

^a Authors' data.

^b Calculated from $\sin^2\theta$ values of Thiessen and Stauff (14).

^c Calculated from Figure 12 of Thiessen and Stauff (14).

^d Calculated from Figure 5 of Thiessen and Ehrlich (11) by taking as a standard the inner of the two strong reflections (4.28 Å.); it is this reflection for which Thiessen's numerical data (column 3) come closest to agreement with ours.

* Our intensity ratings on ring pattern. (Comparison of spot and ring patterns should not be expected to produce too close checks.)

** Thiessen's intensity ratings on a spot pattern.

*** Our intensity ratings on published pattern.

The long spacings of the four sodium soap structures are summarized in Table VII. For a given soap the beta spacings differ from both omega and delta spacings, and all three are distinctly less than the alpha long spacings.

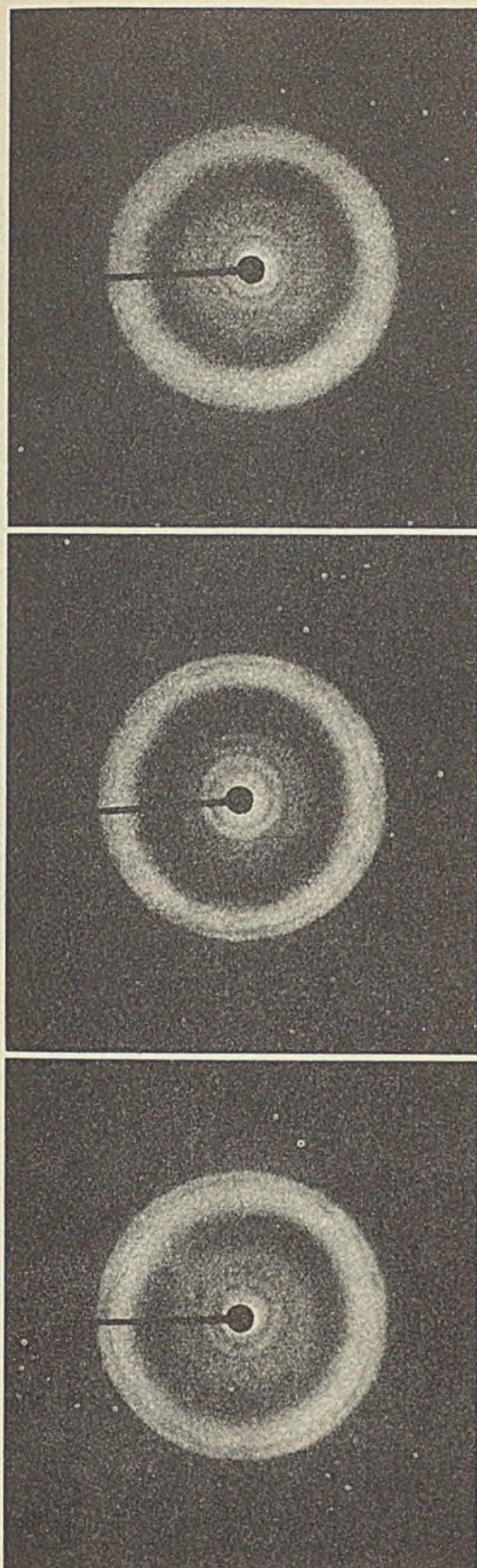


Figure 4. Change in Phase Composition in Soap Produced under Different Temperature Conditions (Table IX)

This decreased long spacing as we pass from the alpha to the beta, omega, and delta structures is due to inclination of the soap molecules to the basal planes containing the sodium atoms. The angle of tilt serves as a further distinction between the four structures, a distinction dependent on long spacings but more apparent because of the constancy of angle for a given phase. Table VIII shows that each phase exhibits a constant angle of tilt— 90° for alpha, 63° for beta, and 60° for omega and delta. Short spacings must be invoked to distinguish the latter two phases from each other, but the angle of tilt serves as a useful further item in the establishment of omega and delta as new phases.

PROPERTIES CONTRIBUTED TO SOAP BY BETA PHASE. The beta phase is able to exist in translucent form and lends a degree of transparency to soap when produced under conditions tending to orient and press together the crystals. A soap made up of beta crystals in such a condition is very firm, has an easier lathering ability, and takes up water when immersed to form a soft layer on the surface of the bar (Table III and Figure 5). If the beta phase is produced under conditions where the crystals are small and not joined coherently, the ease of lather is retained, but the bar tends to disintegrate in water and is in general far less firm.

OMEGA PHASE

Omega phase occurs in commercial framed and in most milled soaps, the proportion present depending on temperature, moisture, stock composition, and other processing conditions. It is the phase ordinarily obtained by rapidly chilling neat soap without agitation and always tends to form when low-moisture soaps of usual formulas are quietly cooled from a molten condition. In general, formation of omega is favored by higher temperatures, lower moistures, and lower molecular weights. In coconut oil soap it is the predominant phase and converts to beta with difficulty. In commercial sodium oleate soap it is perhaps the only stable form under most conditions. In the literature there is no recognition of any sodium soap structures other than alpha and beta (see footnote¹). In fact, much of the evidence we now consider as applying to the omega structure has been mistakenly attributed to beta.

It is thus necessary for us to establish omega as a separate structure. Examination of Figure 1 and the short spacing data of Table II shows the differences between omega and the other three phases in respect to short spacings and intensity, which establish omega as a separate structure. In addition the long spacings of omega sodium palmitate and stearate (Table VII), as well as the derived angle of tilt (Table VIII), present still further distinctions from the hitherto recognized alpha and beta structures. The designation "omega" was chosen in order to follow the Greek letter nomenclature of Thiessen and Stauff; the shift to the far end of the alphabet was motivated by a wish to avoid implying an analogy to gamma triglycerides and other long-chain structures. At the time omega was established, the fourth phase, since named "delta", was not recognized.

X-ray information supplementing actual quotation of spacings is furnished by following the solid transformation of the beta to the omega structure or vice versa. In the case of progressive conversion of omega to beta by successive millings or ploddings, or in the reverse case of gradual conversion of beta to omega by heating, the diffraction rings of the new phase appear faintly at first and then become stronger and stronger, while the rings of the phase being eliminated weaken gradually until completely absent. Figure 4 and Table IX show the accompanying property changes. In all cases, however, the ring diameters are fixed regardless of intensity, indicating that the omega structure is not just a

variation of the beta but is truly distinct. Such changes, followed in hundreds of examples, are illustrated in soap milling and similar practices.

As will be indicated in the section on Delta Phase, a similar gradation of relative proportions without change in spacing occurs in transformation to or from the delta structure.

TABLE V. COMPARISON OF FOUR STRONGEST BETA SPACINGS IN THREE TYPICAL COMMERCIAL SOAPS OF WIDELY DIFFERENT FORMULA WITH THOSE OF HYDROUS SODIUM PALMITATE (FIGURE 3)

Soap	Four Strongest Beta Short Spacings ^a			
	<i>d/n</i> , Å.			
Hydrous Na palmitate	2.75 ^b	3.18	3.90	4.32
Commercial soap A (20% H ₂ O)	2.75 ^b	3.18	3.95	4.40
Commercial soap B (14% H ₂ O)	2.75 ^b	3.20	4.00	4.43
Commercial soap C (19% H ₂ O)	2.75 ^b	3.20	4.00	4.40

^a It is recognized that the values for soaps A, B, and C run slightly higher than those of the hydrous sodium palmitate for the 3.18, 3.90, and 4.32 Å spacings, but it is important that all four soaps show strict agreement for the 2.75 Å spacing which we have chosen for the detection of beta phase. It is likewise recognized that there is a somewhat greater difference in identifying spacing between the typical commercial soaps and anhydrous sodium palmitate (Table II), but these all represent minor structure variations compared with the spacing and intensity differences used to distinguish between the four established phases, and do not in any way restrict the validity of the beta identification procedure.

^b The beta identification ring.

In addition to the diffraction data, other physical properties substantiate the individuality of the omega structure. In numerous commercial soaps dilatometer curves on material exhibiting the beta pattern in the original sample before the initial heating and the omega pattern on cooling from high temperature show that the beta soap has a higher density than the omega. The initial (beta) dilatometer curve lies entirely to the higher density side of the second (omega) curve until the two curves finally join close to the temperature at which x-ray patterns at elevated temperatures show transition from beta to omega structure. It can also be demonstrated for certain commercial soaps, in which both beta and omega phases can be obtained at a given moisture content, that the two phases differ in temperature of complete melting to neat soap by 2-3° C., as determined by dilatometer runs.

The striking difference of beta and omega with respect to their behavior in water is shown in Figure 5 where a bar of a commercial soap consisting largely of beta phase is compared with a bar of the same soap converted to omega. Although these bars are identical in fat formula and moisture composition, they possess radically different properties by reason of the phase change they have undergone.

In view of our x-ray and dilatometric detection of a waxy phase above omega phase in commercial soaps of sufficiently low moisture content, it is well to state here that both subwaxy and waxy phases show a pattern consisting of sharp, long spacing reflections, a strong, broad, blurred short spacing reflection at about 4-5 Å., and a similar but weaker reflection at about 3 Å. (the position of the identifying omega ring). This pattern has been established on anhydrous sodium palmitate in the regions to which the original terms "waxy" and "subwaxy" were applied. It indicates that the waxy phases resemble omega phase (the high-temperature crystal phase) more than they resemble alpha, beta, or delta. They are, however, distinguished from omega by the blurring of their two short spacing reflections and the absence of other short spacings than these, indicating uncertainty of molecular position. Liquid crystalline neat soap is best distinguished from the waxy phases by the absence of the 3 Å. short spacing reflection in the neat pattern.

DELTA PHASE

There is no recognition of the delta structure as such in the literature. There are, however, two bits of published evidence which can be applied to a consideration of delta. One of these is a reproduction of Brill's Figure 3 (1) which we consider to be delta. The pattern shows the important short spacings of delta phase, although the values quoted for the two strongest rings are not in very good agreement with our data. However, this is certainly a delta pattern, since the sample was obtained by drying a crystallized nigre (7 per cent soap) of commercial sodium stearate, and experience has shown that crystallized and dried nigras of both pure sodium stearate and high-tallow commercial soap contain delta phase. The long spacing quoted by Brill for this preparation is 43 Å. which would correspond to a delta soap with an average chain length of about 17 carbon atoms. Aside from the Brill pattern there is one other possible description that might refer to delta, the single long spacing value of Piper and Grindley for sodium stearate (8).

TABLE VI. CONSTANCY OF PHASE IDENTIFICATION SPACINGS WITH MOISTURE VARIATION

Phase	Soap	% H ₂ O	Spacings, Å.	
Beta	Na palmitate	3	2.74	
		8.5	2.74	
		15.1	2.74	
		30-40	2.78	
		58	2.74	
		85	2.76	
		95	2.76	
		80 tallow-20 coconut	6.3	2.76
		27	2.74	
		46 ^a	2.76	
Delta	Na palmitate	0	2.85, 3.52	
		30-40	2.85, 3.52	
		58	2.89, 3.58	
		85	2.87, 3.52	
		95	3.55	
		80 tallow-20 coconut	<15	2.87, 3.58
		24	2.87, 3.55	
		46	3.55	
		60	3.55	
		73	3.55	
80	2.85, 3.55			
90	2.85, 3.55			
Omega	Na laurate	0	2.96	
		22	2.96	
		80	2.94	
		80 tallow-20 coconut	0	2.93
		17	2.96	
		26.4	2.96	
		32.8 ^a	2.96	

^a At moistures much higher than this value, the phase concerned does not exist in soaps of this stock.

In neither case, of course, was there any realization that a separate phase was involved. As a matter of fact, Brill's discussion indicates that he considered his stearate to be equivalent in structure to the C₉ to C₁₄ soap of Thiessen and Szychalski (13), which we believe can be referred to omega phase.

That the delta pattern represents a single phase and not a mixture of phases is shown by the fact that the same pattern is obtained not only in sodium stearate, palmitate, and myristate, but also in the sodium soaps of many commercial stocks—e. g., straight tallow, 80 tallow-20 coconut, and 50 tallow-50 coconut. Among these soaps a variety of treatments is represented in our experience, including normal cooling, ice quenching, and deformation by orifice extrusion. The chance that this assortment of stocks and treatments would lead to exactly the same mixture of phases is very small, so that the delta pattern undoubtedly represents a single phase.

Distinction between the delta structure and the three other sodium soap structures is shown for short spacings in Table II, and for long spacings (and angle of tilt) in Tables VII and

TABLE VII. LONG SPACINGS OF ALPHA, BETA, OMEGA, AND DELTA SODIUM SOAPS

Soap	Long Spacings, Å.			Delta
	Alpha	Beta	Omega	
Na laurate	31.5	...
Na myristate	36.2	36.5
Na palmitate	46.6	42.1	39.6	40.6
Na stearate	51.4	45.8	44.4 ^a	45.0

^a See footnote 1.

VIII. Figure 1 shows the short spacing distinctions graphically by means of a quadrant comparison; Figure 2 shows the long spacing distinctions. The differences in spacings, though small in some cases, are sufficient to allow resolution of the identifying rings in powder patterns taken at 5 cm. sample-to-film distance on a flat film.

Advantage has been taken of this resolution to demonstrate directly the spontaneous conversion of alpha, beta, and omega phases to delta in sodium palmitate systems of high water content. Mechanical mixtures of each starting phase were made with 90, 80, 70, 60, and 50 per cent water. These systems were set aside at room temperature and sampled over a period of months. For each case (alpha, beta, and omega) over the period of sampling, the original rings were seen to fade gradually while the characteristic delta rings gained in intensity. All this was accomplished without any variation in the diameters of any one of the rings, an indication of the absence of solid solution influences (and incidentally the independence of the spacings of total water content).

TABLE VIII. ANGLES OF TILT^a OF ALPHA, BETA, OMEGA, AND DELTA SODIUM SOAPS

Soap	Angle of Tilt, Degrees			Delta
	Alpha	Beta	Omega	
Na laurate	59.7	...
Na myristate	60.5	61.4
Na palmitate	90 ^b	64.4	58.0	60.5
Na stearate	90 ^b	62.0	59.0	60.3
Average	90 ^b	63.2	59.3 ^c	60.7 ^c

^a Calculated from the long spacings of Table V using the relation:

$$\sin(\text{angle of tilt}) = \frac{\text{experimental long spacing}}{\text{spacing of alpha structure}}$$

^b See footnote 2.^c The average of the seven omega and delta values is 59.7°.

Just one fact should be added regarding the structure of delta—the apparent coincidence of the long spacing data for delta phase and omega. In Tables VII and VIII the long spacing values for delta and omega sodium myristate, palmitate, and stearate lie close to their average, although the delta values tend to be higher. It appears, therefore, that delta and omega phases have practically the same long spacing and angle of tilt, their differences being in cross-sectional arrangement.

TABLE IX. COMPARISON OF PROPERTIES OF A SOAP^a PREPARED WITH VARYING AMOUNTS OF BETA AND OMEGA PHASES

Sample	Processing Temp., ° F.	Approx. Phase Compn. in Bar, %			% Soap Rubbed Off Bar in Use	Firmness, Arbitrary Units	Soaking Tests at 80° F. ^b	
		β	ω	δ			Grams/sq. in. lost	% strength retained ^c
A	205	0	100	0	0.8	91	0.2	40
B	194	0	100	0	0.7	106	0.3	47
C	180	25	75	0	1.0	80	0.5	43
D	165	75	15	10	1.6	84	1.3	22
E	155	85	10	5	1.9	77	1.5	6
F	140	90	5	5	1.8	60	1.3	8

^a 80% tallow-20% coconut formula, 18 per cent moisture.^b Bars of soap cut to size and soaked 5 hours at 80° F. in distilled water.^c Figures as per cent strength retained after soaking and as loss of weight per unit surface. Measurements before and after.

The formation of delta phase is favored by higher molecular weights, lower soap content, and lower temperatures. It is thus obtained in sodium palmitate by quenching a nigre (from which beta crystallizes on ordinary cooling), but dominates

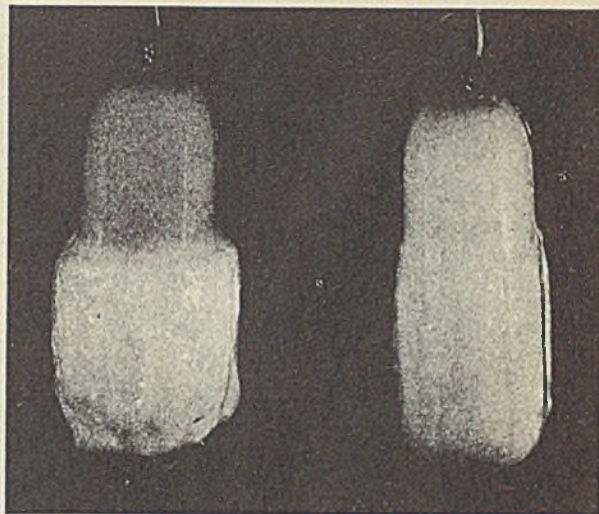


Figure 5. Commercial Soap in Beta Phase (left) and in Omega Phase (right) after Soaking in Water at 80° F. for 16 Hours

similar sodium stearate systems on ordinary cooling. In the palmitate, delta forms spontaneously at room temperature in mixtures of water with dry alpha, beta, and omega phases having real soap content up to at least 50 per cent. In addition, extrusion of high-moisture sodium palmitate systems at and somewhat above room temperature, and of high-moisture sodium myristate systems (at least at room temperature) converts beta to delta phase. In sodium laurate, however, neither quenching nor extrusion has enabled us to attain delta phase.

Analogous behavior is noted in the commercial soaps. Delta phase appears in the 80 tallow-20 coconut composition on cooling the more dilute systems, and under some conditions even up to about 75 per cent soap; it is also formed by orifice extrusion and milling, provided the temperature is sufficiently low. Delta is likewise encountered in 50 tallow-50 coconut soaps. On the other hand, coconut soaps, in the cooling and extrusion so far studied, show only small amounts of delta, if any. Its effect in reducing firmness of soap bars is quite marked, and its lathering power is superior to that of omega.

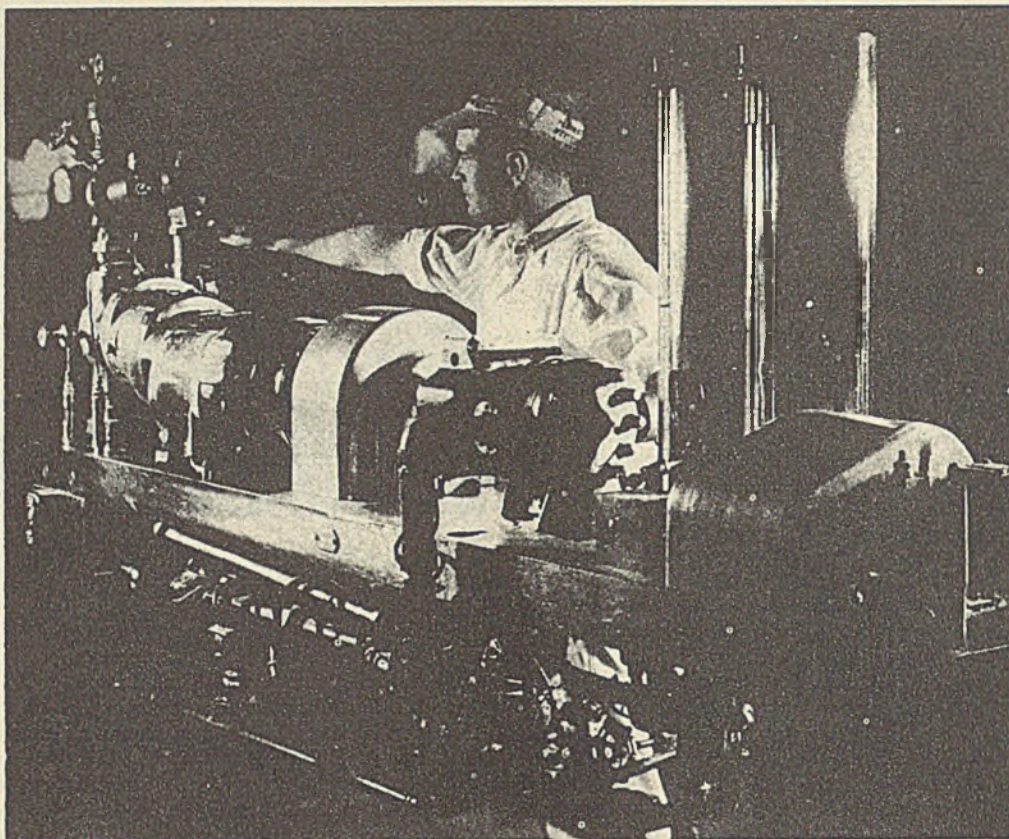
ALPHA PHASE

This phase, unlike beta, omega, and delta, has not yet been encountered in the usual commercial soap formulas. It has been observed in pure sodium palmitate and stearate (12, 14), and we have found it in mixtures of the two. Presumably it might occur in soaps derived from commercial stearic acid.

Our results, contrary to Thiessen's observation, indicate that alpha is in reality a hydrated phase, a small amount of water in the lattice being required for its existence. Thus when desiccated, single crystals of alpha palmitate and stearate can be observed

microscopically to convert spontaneously into polycrystalline aggregates retaining the general shape of the original alpha crystal, but actually existing as beta phase, as shown by x-ray analysis.

Since certain "acid soaps" show rings close to the identifying rings of alpha phase, considerable care must be exercised in studying systems in which there is a possibility of the existence of acid soaps.



The Soap Industry Is Making Increasing Use of Continuous Processes; Neat Soap Is Mixed with Perfume and the Other Constituents of the Balanced Soap Formula in These Continuous Crutchers

While the alpha phase is apparently not of practical interest in most commercial soaps, it is nevertheless of great importance as a starting point for the study of the structures of the beta, delta, and omega phases. Knowledge of these structures is, in turn, of value in understanding soap behavior.

Thiessen's structure (12, 14) studies show that the c spacings correspond to twice the molecular length, the molecules being arranged perpendicular to the planes of the sodium atoms in the alpha structure. In addition to its usefulness in connection with classifying the three commercially important inclined structures according to angle of tilt, the alpha c spacing (double molecule length) is of direct importance to calculations in cases where the x-ray determination of stock composition is the only available method².

² Since this paper was originally submitted, two papers by M. J. Buerger dealing with the alpha phase have appeared [*Proc. Natl. Acad. Sci.*, 28, 526-9, 529-35 (1942)]. The first verifies the hydrated nature of alpha. In the second, the newer moving film techniques have led to refinements in knowledge of the alpha unit cell. Buerger places alpha in the monoclinic system with an angle β of some 94° , and finds the unit cell to be substantially twice as long as Thiessen's. These refinements, while important in a study of the ultimate structure of the soaps, do not restrict the usefulness of our angle-of-tilt calculation and classification (Table VIII). Instead of Thiessen's value 51.8 \AA , which we have used for the alpha c spacing, we would have to use $51.8/0.9979 = 51.9 \text{ \AA}$, a negligible difference.

ACKNOWLEDGMENT

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Film Formation by Pure Liquids

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Water, benzene, nitrobenzene, ether, acetone, *n*-heptane, and methanol were tested for film-forming properties by three methods. It was found that when these liquids are highly purified, they do not form films. The purification of the organic liquids consisted largely in the drastic reduction of the amount of water in them. Additions of a few hundredths per cent of water to the purified liquids restored their film-forming properties.

ALTHOUGH it is generally believed that films consisting of thin layers of liquid with a gas or vapor phase on each side cannot be formed with pure liquids, the belief has apparently never been tested by experimenting with highly purified liquids. This serious lack in the data of film formation prompted the present investigation.

Films of the type considered in this paper are nearly always (perhaps always) formed in one of the following ways: (1) A solid frame is lifted from a liquid. (2) Bubbles touch each other under the surface of a liquid. (3) Bubbles rise through a liquid to the surface. Under conditions 1 and 2 flat films are formed; under 3, hemispherical ones result. These three ways have the common element that the films result from the approach to each other of two already existing surfaces. This is part of the balanced-layer theory of film formation; the details, with references to other investigators, were given by Foulk (3). It was criticized (7) and Foulk replied (4).

Method 2 is the two-bubble experiment described by Foulk and Miller (4, 5). It illustrates the effect of causing two liquid surfaces to approach each other. If two bubbles of gas or vapor touch each other under the surface of a liquid, they either merge to form one large bubble or flatten against each other and thereby form a film between them.

The merging of subsurface bubbles explains the fact that in the industrial operation of passing a gas through a porous septum into a liquid in order to produce a myriad of small bubbles, the size of the bubbles is not dependent on the size of the pores but on the chemical nature of the liquid—in other words, on its film-forming properties. The less the tendency to form films by the approach of bubble surfaces to each other, the larger will be the bubbles. This was first pointed out by Schnurman (10) and shows how the approach theory is useful in understanding this phenomenon.

FOAM FILMS

Many books were examined without success in finding a formal definition of the type of film described above excepting the one by Gibbs (6): "When a fluid exists in the form of a very thin film between other fluids, the great inequality of its extension in different directions will give rise to certain peculiar properties, even when its thickness is sufficient for its interior to have the properties of matter in the mass. . . . The most important case is where the film is liquid and the contiguous fluids are gaseous." Gibbs does not list the "certain peculiar properties" but the context shows that he meant

conditions of equilibrium. Also, his "most important case" is the kind of films considered in this paper. They are the kind of films in a foam, and hence the name "foam films" is proposed to distinguish them from the films consisting of thin layers of liquid spread on other liquids or on solids. A foam film is, therefore, a thin layer of liquid in metastable equilibrium, with a gas or vapor phase on each side. The equilibrium is considered as metastable because such a film cannot survive indefinitely under the disruptive influences of gravity and evaporation. In this connection Shorter's explanation (12) of how a film maintains itself by increasing its surface tension at weak spots is interesting.

MEASUREMENT OF FILM FORMATION

The three ways in which films are formed were used in measuring the film-forming properties of the liquids studied. One was a two-bubble apparatus (5) which consisted of two Pyrex capillary tubes enlarged to bell-shaped openings at the tips (*W*, Figure 1). Pure air was passed through these capillaries, with the bells under the surface of the liquid being examined. Bubbles were formed in the bell tips and touched each other on reaching a certain size. When they failed to coalesce, the layer of liquid between them was called a "film". This method has the advantage of being unaffected by surface contamination and by contact with any solid support. In other words, it responds only to the properties of the liquid in mass. It also has the practical value of measuring the initial stage in the production of foam, which is the formation of films between subsurface bubbles.

The second method was the lifting of a ring from the surface of the liquid and noting whether a film remained on it. It has the disadvantage that the formation of films is greatly increased by mere traces of impurities on the surface of the ring or liquid. Experiments with rings of platinum wire, chromel wire, and Pyrex indicated that the composition of the ring was not of primary importance, but that its dimensions had considerable effect. Another variable is the inclination of the plane of the ring to the surface of the liquid. Ring and surface should be parallel in order to obtain maximum film formation. Also, the per cent film formation increases with increasing speed of lifting the ring, up to a certain optimum speed beyond which it decreases due to physical shocks. A mechanical lifting device to give this optimum speed was used throughout the investigation. The ring was 13.0 mm. in diameter and was made of 0.5-mm. platinum wire. (These dimensions are those of the ring used with a du Noy surface tension apparatus). It was cleaned by ignition, and the surface of the liquid was cleaned by overflowing.

The third method of studying film formation consisted merely in shaking the liquid under examination in a closed tube or bottle and noting whether bubbles formed on the surface. It is purely qualitative.

APPARATUS. Figure 1 shows the apparatus for the two-bubble and the ring-lifting methods. It consisted essentially of a closed glass container into which the liquid under observation was distilled and through which was passed a stream of pure air (dried when nonaqueous liquids were tested). The air (taken from the compressed-air line) was bubbled through sulfuric acid, passed

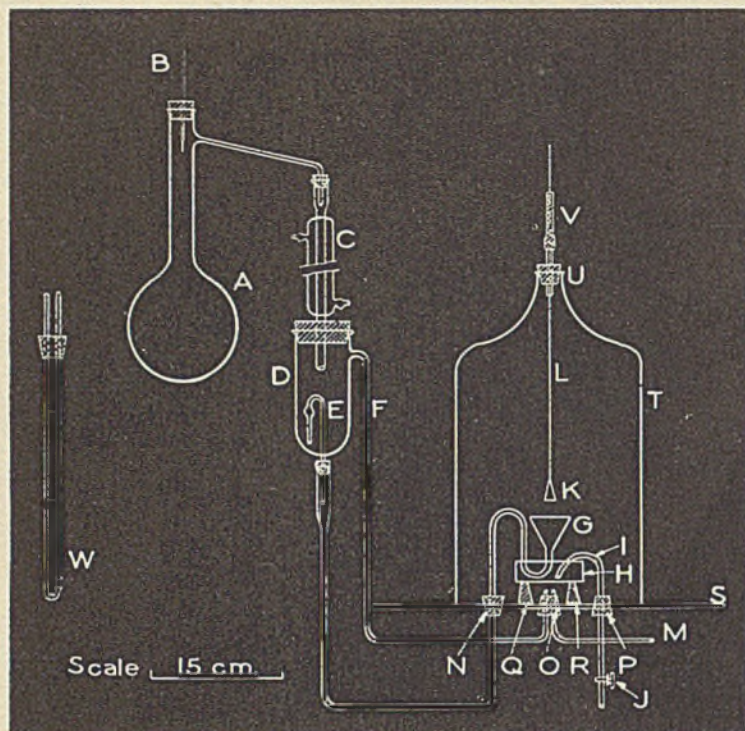


Figure 1. Apparatus for Measuring Film Formation

through a U-tube of ascarite, a second U-tube of glass wool, and a third one containing phosphorus pentoxide. The bell tips were on the ends of long capillary tubes, *W*, which passed through a rubber stopper. The outer ends of these tubes were attached to the source of purified air; in order to keep the pressure uniform, the air was first passed into a five-gallon bottle (not shown in the figure). Since the distance between bell tips affects the coalescence of the bubbles (4, 7), the tips were set 7 mm. apart; experiment showed that this distance gave maximum film formation.

Figure 1 shows platinum ring *K* with lifting device *V*. A glass rod, *L*, passes through a glass tube in stopper *U*. A piece of rubber tubing, *V*, stretched over the glass tube holds the glass rod tightly at the top. The central portion of tube *V* was split into four longitudinal strips which bent outward when the rod was pushed down to immerse ring *K* in the liquid in funnel *G*; when the rod was released, the rubber strips returned to their original position, which lifted the ring from the liquid. *T* is a 3-gallon bottle from which the bottom was cut and the edges were ground. *S* is a piece of plate glass, 40 × 26 cm. and 7 mm. thick. Holes bored through this glass base were fitted with rubber stoppers *N*, *O*, and *P*. Tube *M*, passing through stopper *O*, leads to the supply of pure air which escapes from the container through the tube at *U*.

The liquid under observation was placed in flask *A* with thermometer *B* and was distilled through condenser *C* into the automatic siphon chamber, *D*. When the liquid rose above the bend of tube *E*, it siphoned through the tube, entered the closed container at stopper *N* and caused a rapid overflow of the liquid in funnel *G*. Tube *F* maintained equal pressure in *T* and *D*. The liquid that overflowed from the funnel was collected in *H* and siphoned from the apparatus through *I*. Stopcock *J* was lubricated with graphite applied by rubbing the parts with a lead pencil. *Q* and *R* are supports for dish *H*. All rubber stoppers used in the apparatus were covered with tin foil.

PROCEDURE. Per cent film formation was determined by both the ring and the two-bubble methods. In the ring method the ring was dipped into the liquid, and the number of times a film formed in one hundred dips was noted. This was called "per cent film formation". Several counts of one hundred each were averaged. Once formed, the films usually persisted for several minutes. In the two-bubble method a

count was made of the number of pairs of bubbles which failed to coalesce (that is, which formed films between them) in each hundred pairs counted. The average of several counts was again taken as the per cent film formation. The apparatus was thoroughly cleaned and dried each time a different liquid was studied and also between the purification steps with each liquid. After the apparatus had been cleaned the general procedure was as follows:

1. The liquid was introduced into the system as received (without purification) and the per cent film formation determined.
2. The liquid was removed, placed in flask *A*, and distilled into the system. Observations were made as before.
3. The liquid was again removed and purified by the appropriate procedure. It was then redistilled from flask *A* and the film formation again determined. In most cases several means of purification were used and some of them were repeated a number of times until the results for the particular liquid were constant.
4. After the liquid had been purified until zero film formation was obtained, some impurity (usually water for the nonaqueous liquids) was added and the per cent film formation again determined.

PURIFICATION OF LIQUIDS

Liquids of the highest degree of purity commercially obtainable were used and were further purified as outlined below. The purification of the organic liquids consisted largely in the drastic reduction of the amount of water in them.

WATER was double-distilled as prepared by the Laboratory Supply Store of the university, and was further purified by distilling from potassium permanganate and potassium hydrogen sulfate.

BENZENE was purified by two distillations from sodium wire; only the middle fraction was collected (13). It was agitated with phosphorus pentoxide and allowed to stand for 18 hours in a stream of air dried with phosphorus pentoxide (2); then it was filtered and distilled from flask *A* over fresh sodium wire.

NITROBENZENE was filtered through anhydrous sodium sulfate, agitated with phosphorus pentoxide for several hours, and distilled; the middle portion was collected (2) and was then redistilled from fresh phosphorus pentoxide into the apparatus.

ETHER. Through the courtesy of M. S. Newman, purified diethyl ether was obtained. It had been dried for 2 days over sodium wire. The resulting product was kept in a large flask with Grignard reagent of ethyl magnesium bromide along with excess metallic magnesium. A large quantity of the ether had been distilled from the flask when it was received. The portion used in this investigation was distilled from that remaining in the flask. This was redistilled from sodium wire into the apparatus.

ACETONE was purified by making a saturated solution of sodium iodide in boiling acetone and distilling from the crystals obtained (9, 11). This procedure was repeated, and the resulting acetone was filtered through Drierite, refluxed for several hours over anhydrous potassium carbonate, and finally distilled; only the middle portion was collected. The refluxing and fractional distillation were repeated three times.

EXPERIMENTAL RESULTS

TABLE I. FILM-FORMING PROPERTIES OF SEVEN LIQUIDS

State of Purity	Av. % Film Formation	
	Ring method	Two-bubble method
Water		
1. As received	8	0
2. After distn.	4	0
3. Distd. from $KMnO_4$ and $KHSO_5$	0	0
3a. Stored in funnel 12 hr.	58	0
Benzene		
1. As received	100	90
2. After distn.	100	79
3. Dried over Na 4 hr., distd.	65	29
3a. Distd. (after adding fresh Na) in air dried with P_2O_5	13	0
3b. Fresh Na added, allowed to stand 48 hr. with current of air dried with P_2O_5 , passing over; distd. from Na	0	0
4. 0.02% by wt. water added	78	40
Nitrobenzene		
1. As received	0	0
2. After distn.	0	0
3. Filtered through Na_2SO_4 , agitated and stored over P_2O_5 , distd. from fresh P_2O_5	0	0
4. Effect of water		
0.02% by wt.	0	0
0.10% by wt.	31	11
Ether		
1. In purified condition as received	0	0
2. After distn.	0	0
3. Dried over Na, distd. from fresh Na	0	0
4. Effect of 0.02% by wt. water	65	48
Acetone		
1. As received	44	2
2. After distn.	39	0
3. Ptd. as $NaI \cdot 3CH_3 \cdot CO \cdot CH_3$, distd.	27	0
3a. Step 3 repeated, filtered through Drierite, refluxed over anhydrous K_2CO_3 , distd.	15	0
3b. Refluxed over anhydrous K_2CO_3 , fractionally distd.	5	0
3c. Step 3b repeated	4	0
3d. Step 3b repeated	0	0
4. Effect of water		
0.05% by wt.	2	0
0.20% by wt.	9	0
0.50% by wt.	38	47
n-Heptane		
1. As received	33	15
2. After distn.	30	15
3. Dried over Na 18 hr., distd. from fresh Na	27	13
3a. Dried over P_2O_5 48 hr., filtered through anhydrous Na_2SO_4 , distd.	26	10
3b. Dried over P_2O_5 18 hr., filtered through anhydrous Na_2SO_4 , distd. from Na	10	0
3c. Step 3b repeated	9	0
3d. Step 3b repeated	10	0
Methanol		
1. As received	65	42
2. After distn.	49	28
3. Refluxed with quicklime filtered through Drierite, distd.	37	16
3a. Metallic Mg added refluxed 36 hr., distd. middle fraction	8	1
3b. Fractional distn. (middle fraction)	2	0
3c. Fractional distn. (middle fraction)	0	0
4. Effect of 0.05% by wt. of 0.95% ethanol	11	0
4a. Effect of 0.05% by wt. of water	14	2

n-HEPTANE was obtained, through the courtesy of C. E. Boord, from the Hydrocarbon Research Organization of the American Petroleum Institute and was marked "high purity". It had been purified and fractionally distilled until freezing point, boiling point, index of refraction, and other properties were constant. The heptane as received was first dried by distilling from sodium wire and then from phosphorus pentoxide. It was then left over phosphorus pentoxide for 2 days and filtered through anhydrous sodium sulfate. Finally it was redistilled from sodium wire.

METHANOL was first refluxed with quicklime, filtered through Drierite, and distilled. It was treated with clean magnesium turnings, refluxed for 36 hours, and fractionally distilled (1). It was then fractionally distilled twice more, the constant-boiling middle fractions being collected.

Table I gives the averages of five to ten determinations of per cent film formation. As a rule, the individual results did not vary from one another by more than 4 or 5 per cent, and the averages usually agreed with any one determination within 3 per cent. These deviations were equally true for both methods. The numbers in the column headed "state of purity" (Table I) refer to the steps listed under procedure.

BUBBLES ON THE SURFACE. Bubbles formed on the surface of one of the purified, non-film-forming liquids when shaken in its bottle. This suggested that a surface-bubble technique might be a highly sensitive test for film-forming properties; accordingly it was tried with several of the liquids, after they were distilled into glass tubes which were then sealed off. These tubes were of Pyrex, 25 mm. in diameter and 15 cm. long. They were closed at one end, and to the other a 15-cm. length of 10-mm. tubing was sealed.

Two methods were employed in making this surface-bubble test: The tube was vigorously shaken while held in a horizontal position. Or the tube, inclined so that all the liquid was in the larger part, was quickly brought to the vertical position with the stem end down; bubbles of air or vapor would rise through the stem and break on the surface. No difference in the results by these methods was observed. A pair of tubes was employed for each liquid. One was sealed off with air in it. The other was evacuated, the liquid in it was boiled at a low temperature to expel the air, and it was then sealed off. Table II gives the results of the three liquids examined.

TABLE II. BUBBLE-ON-SURFACE TESTS OF PURIFIED LIQUIDS IN SEALED TUBES

Liquid	Evacuated Tube	Tube Containing Air
Water	No bubbles	A few evanescent bubbles
Ether	No bubbles	No bubbles
Nitrobenzene	Bubbles doubtful	Evanescent bubbles

The following tubes were also prepared: (1) Nitrobenzene (as received, in a tube containing air) gave evanescent but distinct bubbles; it will be recalled that no films were observed by the ring-lifting or the two-bubble method. (2) Benzene (as received, in a tube containing air) gave distinct bubbles.

DISCUSSION OF RESULTS

The results in Table I show conclusively that, as purification proceeded, the per cent film formation in the liquids grew less and finally became zero.

Consistently higher results were obtained by the ring method than by the two-bubble. The surface-bubble technique was also more responsive to film-forming properties than the two-bubble. This is probably due to the fact that in the ring and surface-bubble methods the upper surface of the films produced is a part of the original and therefore aged surface of the liquid—that is, a surface, which has reached a state of equilibrium and which also may be affected by surface contamination. In the two-bubble method, however, both surfaces of the film are relatively fresh and free from surface contamination. The effect of a contaminated surface is shown by step 3a in the measurements with water. A portion of highly purified water that gave zero film formation by both ring and two-bubble methods was allowed to stand 12 hours in the pure atmosphere under bell jar *T* (Figure 1). It gave 56 per cent film formation with the ring but still

showed zero formation with the fresh surfaces of the two bubbles. The importance of fresh surfaces is also shown in the precise surface tension measurements of Jones and Ray (8), who report that the reproducibility of their results was "greatly improved by protecting the water employed against surface contamination".

The following data on water solutions suggest that the large difference between the extent of film formation by the ring method and by the two-bubble method is independent of the nature of the dissolved matter. Additions to pure water of 0.003, 0.03, and 0.1 per cent saponin gave, respectively, 10, 96, and 100 per cent films by the ring method and 0.0, 0.0, and 12 per cent by the bubble method. Similarly, 0.0001, 0.001, 0.01, and 0.02 per cent gelatin gave 8, 27, 76, and 100 per cent films with the ring and 0.0, 0.0, 0.0, and 4 per cent with the bubbles. Concentrations of 0.001, 0.003, 0.005, 0.01, and 0.075 molar sodium chloride showed a regular increase in film formation until 100 per cent films were shown by the ring. Only the 0.075 *M* gave results (14 per cent) with the bubbles. Ammonium thiocyanate had much less effect than the sodium salt; 3.0 *M* was required to give 100 per cent films with the ring. This showed a bare 4 per cent with the bubbles.

Since most of the purification processes used with the organic liquids consisted in reducing the water content, the effect of adding water to the purified liquids was studied. Table I shows that as little as 0.02 per cent had a marked effect on the pure benzene and ether. More was required with the others, but even with these a distinct showing was made with 0.2 per cent water.

Only one of the liquids, nitrobenzene, gave no films before purification, even by the sensitive ring method; but in a sealed tube containing air, evanescent surface bubbles were

observed (Table II). As a routine procedure, however, this liquid as received was subjected to appropriate purification processes which, as expected, did not impart film-forming properties. It is also worth noting that more water than for the other organic liquids was required to cause film formation; as further evidence of its slight tendency toward film formation, the films on the ring (after addition of water) persisted for only 5 to 10 seconds.

n-Heptane was the only liquid examined in which repeated purification steps failed to give zero film formation by the ring method (Table I). No impurity was added because it was a borrowed specimen.

It is interesting that an addition of 0.05 per cent of 95 per cent ethanol to purified methanol had as much effect as the same amount of water.

ACKNOWLEDGMENT

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THE ALCHEMIST AND HIS WIFE

By Altus

In Dr. Tolle's *Mutus Liber*, published in La Rochelle, France, in 1677, appears this panoramic view of "alchemical experiments" without, however, any explanatory text. From another source we learn that Altus has depicted the alchemist, assisted by his wife, as later was the case with Lavoisier.

That the experiment here shown has been successful is proved by the conventionalized flower inside the retort and then in the flask held by the wife and eventually in the flask being delivered to the military officer, who no doubt paid amply for it. Actually the flower is meant to represent the blazing sun, the fifteenth century alchemical symbol for gold. Then in the last scene a new experiment is under way.

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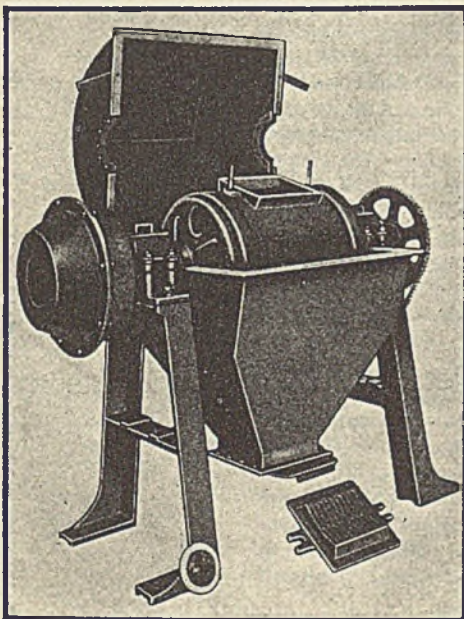
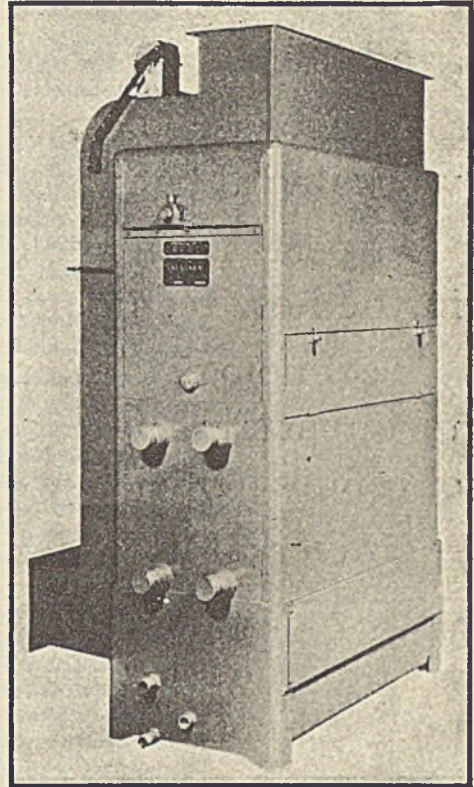
NEW PLANT EQUIPMENT

Aero Heat Exchanger →

A new development for adding heat to industrial liquids for the purpose of maintaining constant temperatures as desired, with automatic control, is announced by the Niagara Blower Company, New York, N. Y. An evaporative type of liquid cooling unit uses a water spray and fans to draw air over coils containing the liquid whose temperature is to be controlled. This is accomplished by either a steam coil or injector or an electric heating unit to heat the spray water. U. S. Patent 2,321,933 was recently granted on this equipment.

The result is control of liquid temperatures within prescribed limits, alternately cooling or heating as required. The heating device is put into operation by thermostatic control at the desired point and thus prevents the liquid from becoming too cold for the process in which it is used, from becoming viscous with retarded flow and loss of capacity, or from congealing or freezing. This also makes it possible for the heat exchanger to be successfully installed out of doors or to use outdoor air to increase its evaporative cooling capacity and avoid damage from handling air containing corrosive substances.

The exchanger with these features is used to control temperatures in chemical and electrical equipment by controlling jacket water temperatures; in quenching baths for heat treating metals; in cutting oils and lubricants in metal working, machining, and wire drawing; for controlling temperatures of chemical process liquids in many fields and of engine jacket water. It is also applied to air and gas compressors.



← Combination Grinding Mill

A mill has been developed which incorporates in one machine several functional variations which make it particularly useful for the multiple processing requirements of laboratories or for special plant operations. This mill was designed and built by Abbe Engineering Company, New York. It is similar to the usual ball or rod mill, and consists of a steel cylinder rotating in bearings. The main trunnions or shafts are hollow to permit the introduction and removal of the material to be ground or processed. The material is fed by a drum-type spiral feeder attached to one of the hollow trunnions. The hollow trunnion at the opposite end is provided with a grating to prevent the discharge of the grinding media. Provision is made for quickly closing both trunnion openings when the mill is to be used for batch grinding.

A manhole opening is located in the shell of the mill. It is provided with a solid cover, a slotted cover for dry discharge, and a wet discharge cover. The mill can be used for batch grinding (both wet and dry): as a pebble, ball, or rod mill, or as a chemical processing mill. It can be used also for continuous grinding: as a pebble, ball, or rod mill; for dry or wet materials; for gases or liquids; jacketed for heating or cooling; and to produce a granular product with little fines.

BOOK REVIEW

Organic Chemistry. An Advanced Treatise

HENRY GILMAN, EDITOR IN CHIEF. Second edition. Volumes I and II. xvii + 1983 pages. John Wiley & Sons, Inc., 440 Fourth Ave., New York, N. Y., 1943. Price \$7.50 each volume.

These volumes are a revision and expansion of Gilman's text published in 1938. Eight new chapters have been added to the original material and the older chapters have been brought up to date and extensively revised. Four chapters of the old edition have been omitted. Like the first edition, the revised is a collaborative work by specialists under the editorial direction of the distinguished group of American organic chemists: Henry Gilman, Roger Adams, Homer Adkins, Hans Thatcher Clarke, Carl S. Marvel, and Frank C. Whitmore.

Volume I (1077 pages) includes revised chapters carried over from the earlier edition on alicyclic compounds, aromatic character, stereoisomerism, organometallic compounds, free radicals, unsaturation and conjugation, molecular rearrangements, and comparison of chemical reactivity. The chapter on free radicals has been almost completely recast and notably has discarded the use of the term "trivalent carbon" (except in reference to the older literature), although this term still appears elsewhere in Volume I.

Five new chapters are added to Volume I. That on the reactions of aliphatic hydrocarbons is an excellent résumé and correlation of this field of reactions where generalizations frequently have to be qualified or stated in alternative terms. The chapter on synthetic polymers is well organized. The chapter on catalytic hydrogenation and hydrogenolysis well fulfills the purpose of the authors "to provide the fundamental background for an understanding of these reactions and for their employment in the laboratory". The chapter on organic sulfur compounds adequately covers a large field. The one on aliphatic fluorides shows good choice of material; it is not limited entirely to aliphatic compounds.

In Volume II (905 pages) are grouped nine chapters on natural products together with four other important chapters. The chapters revised and carried over from the old edition are those on natural amino acids, alkaloids, anthocyanins and the flavones, steroids, carbohydrates (three chapters), constitution and physical properties, electronic theory, and resonance. The chapter on the steroids has been appreciably expanded in the sections on sex hormones and closely related steroids. The chapter on constitution and physical properties has been made clearer and more effective. Three new chapters include a clearly written review of the chemistry of the porphyrins, the complementary chapter on chlorophyll, and a short discussion of the redistribution reaction.

There has been a noticeable improvement in arrangement and spacing in this new edition. The general index, given in full in each of the two volumes, has been expanded. The useful tables of contents have again been included. The number of literature references has been considerably increased. To those who own copies of the first work and to those few who might not be acquainted with this work, the new edition is highly recommended. The volumes are invaluable to the graduate student in organic chemistry and will serve as an excellent "refresher" course for the mature organic chemist.

R. L. JENKINS

