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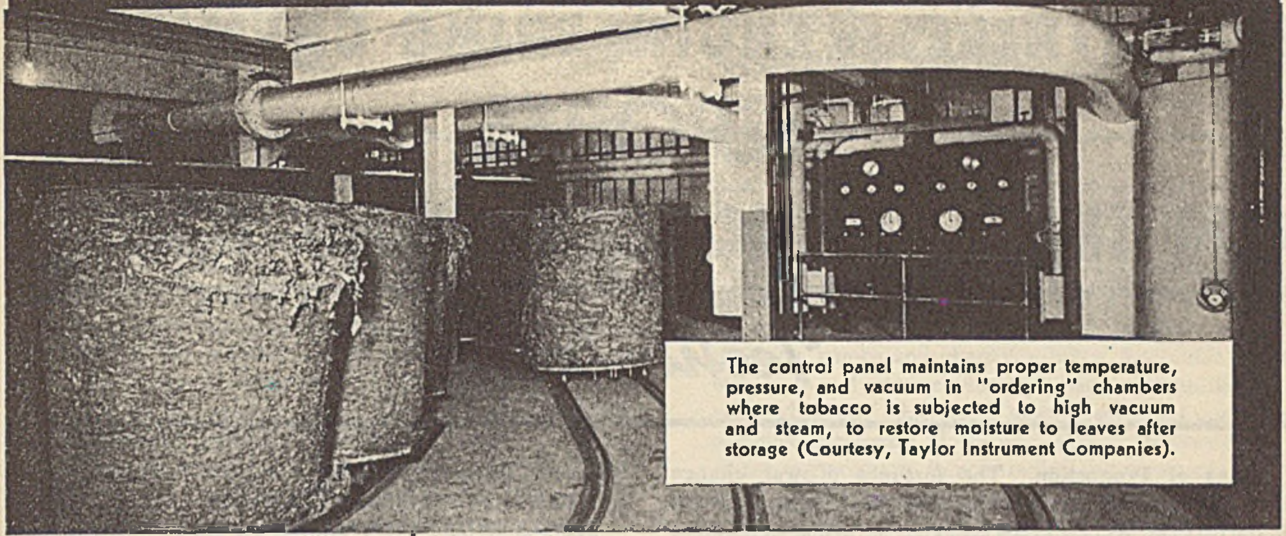

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INDUSTRIAL AND ENGINEERING CHEMISTRY
REPORTS
ON THE CHEMICAL WORLD TODAY

Technology

Tides of Production. The fortunes of war change demands for matériel. We have witnessed striking examples in the past two years, and the latest has particular significance for chemical industry. The original plan for output of explosives, based on the experiences of World War I when artillery played a major role, soon proved excessive when major dependence was placed on aerial warfare. Cutbacks were ordered, and several producing units and bag-loading plants were placed in stand-by condition or abandoned completely.

The Italian campaign following the landings at Salerno and Anzio indicated that artillery was still a prime essential; the Russians had proved this point at Stalingrad. Somewhat belatedly, the Army has ordered an immediate increase by several hundred per cent in the production of heavy artillery ammunition to meet unprecedented demands from the combat zones. Virtually all ammunition-loading plants of the Ordnance Department will be expanded, and a similar expansion has been ordered in chemical and explosives plants.

Indexes of United States ammunition production substantiate the history as depicted. Output in December, 1940, is assigned the arbitrary figure 3. One year later (Pearl Harbor), it stood at 11. Thereafter, output rose steadily until November, 1943, when an index number of 120 was reported. Declines then are noted (101 in January, 1944), but April is represented by 113.

One immediate repercussion has been an order curtailing the use of ammonium nitrate for fertilizer purposes beginning in the autumn, and complete cessation of such shipments about December 1. This is a reversal of policy, for ammonium nitrate has been moving freely into fertilizer channels for many months. To offset this tonnage loss, the fertilizer industry has been promised a minimum of a million tons of Chilean nitrate by May 15, 1945.

The effect of the critical shortage of trained technical personnel is a cause for deep concern, at least by those who understand the complex ramifications of chemical production. While ways and means are available for deferring those directly engaged in manufacture of explosives, no satisfactory provision is made to hold, in the production army, those technical men engaged in the manufacture of several basic chemicals vital to the production of explosives. This is a serious inconsistency pointed out again and again in INDUSTRIAL AND ENGINEERING CHEMISTRY.

There is probably little comfort for the Axis in American ammunition production figures. In the past 28 months we have produced almost 8 million tons of artillery ammunition and bombs, and more than 71 million artillery propelling charges. We wonder if Mr. Hitler is surprised at American ingenuity which permitted companies in the automobile, rubber, oil, coal, soap, breakfast food, typewriter, and paint fields to turn to making munitions. Small wonder that he thought he could win when prior to 1939 there were but a pitiful few explosive, shell, and bag-loading plants in America. Almost overnight fifty-eight modern plants were constructed at a cost of nearly 2.5 billion dollars.

In a technological sense the advances made are worth reporting. TNT pilot lines were making 26,000 pounds of TNT per line per day in the first stages. It was estimated that TNT lines could be made to produce 33,000 pounds. A new method was discovered which increased TNT production from 33,000 pounds up to as high as 96,000 and 100,000 pounds per line per day.

In April, 1941, 7.61 gallons of alcohol were required for each 100 pounds of smokeless powder produced. Today we are producing 100 pounds of smokeless powder with 1.9 gallons of alcohol. It is estimated that 50 million gallons of alcohol valued at 41 million dollars have already been released and we are saving in excess of 4 million gallons of alcohol per month. Today TNT is being made for approximately 7 cents a pound as contrasted with 26 to 55 cents in World War I. Actually TNT has been produced at such astronomical rates that plants have been shut down. Some of our explosive and shell-loading plants have operated at 140 to 160% of estimated capacity. War Department plants in the first four months of 1944 have produced 386,713,000 pounds and 39,390,000 gallons of chemicals required in the making of explosives. These figures do not include the tremendous tonnages purchased from private industry.

Enemy Intelligence Division. I. & E. C. Editors are constantly putting together little bits of information, pretending we are enemy intelligence officers. For example, Eugene Holman, vice president and director of Standard Oil Company (New Jersey),

(Continued on page 8)

An interpretative monthly digest for chemists, chemical engineers, and executives in the chemical producing and chemical consuming industries

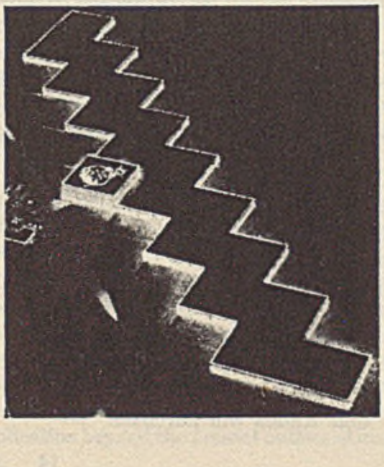
made a speech before the Chamber of Commerce of the State of New York in which he said, of TNT and toluene from petroleum: "A single plant in Texas has produced half of all this vital explosive ingredient produced in the United States from all sources so far in this war."

Immediately we assumed that Holman was speaking of the giant Humble Oil and Refining plant in Texas. We have no reason to assume this other than the freely circulated information about the vastness of the Humble project and the fact that Humble is Standard's affiliate in Texas.

Recalled, too, was the older well-known fact that the Humble plant is said to make yearly more than twice the amount of toluene produced in this country in any prewar year. Humble, if these figures are correct, must be producing at least 50,000,000 gallons. If our assumptions are logical, twice that figure, or 100,000,000 gallons, is our annual toluene capacity. Fourteen to seventeen pounds of TNT are obtained from every gallon of toluene. Our yearly capacity for production of TNT is between 700,000 and 800,000 tons. We assume that the production of toluene is more than this figure. Our purpose is to show that much may be done with pure speculation and generalization.

Factory of the Future. Newspapers, magazines, the mails, and even government publicity material are filled with postwar plans. Some are pinkish in hue, others are undisguised pleas for a return to a pre-1929 state of *laissez faire*. Government, money, foreign trade, reconversion, disposition of war plants—the entire gamut is run with monotonous regularity in any metropolitan newspaper.

A new angle, however, was introduced recently by the engineers of The H. K. Ferguson Company in a comprehensive study of "The Factory of the Future". The report points out two obvious but seldom realized facts: (1) Millions of Americans spend approximately one fourth of their lives in plants; (2) the philosophy of management-labor relations has undergone revolutionary changes. These and other factors call for a new approach to factory and plant design. The report is based on the premise that a happier workman is a more productive workman, and that money spent for plant "extras" is not money wasted, but money invested to bring dividends of greater output, eventual lower costs, and more harmonious labor relations.



Topics covered in the report include the coming importance of the air view of the factory, night architecture (see cut), benefits of the parkway approach to the plant, added conveniences for personnel, interior treatment of the

(*Continued on page 10*)

factory, boilerhouse improvements, basic layouts for typical manufacturing plants, and the effect of the large-scale introduction of female help.

Chemical management knows that considerable opposition developed in the past when chemical plants were proposed in or near residential areas. Possible problems of stream pollution, smoke and obnoxious odors, flammable materials, etc., have had adverse effects on many communities seeking new industries. One needs only to see what has been accomplished recently at chemical plants constructed as part of the war program, to note radical improvements over construction of a decade or more ago. We have made progress, but much can and will be done in the future. Developments will come gradually, for it is recognized that costs will be high. In the words of the report: "Time is the only remedy for high costs. Science teaches us relatively quickly how to produce more and better for less."

Safety Color Code for Industry. Industrial accidents, like the plague, should be avoided at all times and especially now when production and still more production mean fewer names in casualty lists and earlier victory on the war fronts. Du Pont, in presenting a Safety Color Code for Industry at the 15th Annual Convention of the Greater New York Safety Council, has provided to operating officials in chemical plants considerable material for thought and action.

I. & E. C. Editors have noted adoption of the principle here and there, while inspecting plants. But the idea is still in the embryo stage, and certainly industry has failed so far to agree on universal practice. If the use of color is to have order, sense, and meaning, if it is to assist workmen who are changing from one plant to another, it must obviously be used with purpose and direction. Safety Color Code for Industry, used in conjunction with "Three-Dimensional Seeing", offers definite possibilities for improving plant conditions and plant safety. The confusion of tongues which ended the building of the Tower of Babel was nothing compared with the confusion, twice-confounded, that has resulted from the misuse of color in speaking safety messages. Now is the time to seek uniform practice. Such a program enjoys the blessing of the National Safety Council.

Langmuir on the Fly. This may be an old story to some, but it was new to us and appealing for its closely reasoned, conclusive briefness. It is taken from an address by A. R. Stevenson, Jr., of General Electric Company, to the University of Wisconsin's student engineering group. It concerns Irving Langmuir and his reactions to a biologist's estimate from visual observation that the deer botfly travels 800 miles an hour. Langmuir raised several critical, fundamental questions: First, that the velocity of sound is but 740 miles an hour, and that nothing self-propelled by wings can fly faster than its buzz. Second, the power consumed can be calculated at one half horsepower; at high efficiency, the insect would consume one and one half times its own weight of food per second to deliver the required power. Then, attaching a piece of solder the size of the fly to a string and swinging it, Langmuir found that it became invisible a t 60 miles an hour.

(*Continued on page 12*)

I. & E. C. Reports on the Chemical World Today

Technology

One World. Technology is hastening the death of natural monopolies in rapid succession under wartime stimulus, and thus becomes a great leveler in its own right. At the end of the first World War, one of the plans for rehabilitation of the coffers of nations possessing a monopoly in rubber was a "soak the United States" policy which sent prices far beyond any reasonable figure. This proved annoying but relatively short-lived when Dutch production came of age and prices declined as a result. Nevertheless, the squeeze had proved expensive and had forced threats in the form of plantations owned by American rubber companies.

Witness the difference now. The United States is invited to participate in the international conference at London in August, which will see exploratory talks concerning the nature of postwar problems in both synthetic and natural rubber. Not only is a postwar squeeze impossible in the future but, as pointed out by a representative of the Dutch natural rubber interests a year ago, the potentiality of this country to produce its own rubber is causing utmost concern to both major rubber-producing empires. In the international rubber poker game, we appear to hold the aces. We probably will be magnanimous, but if necessary we can play our cards "close to the chest". If, to nations, no other reason exists for world cooperation, technology makes it a must.

One Step–Two Step. Four hundred thousand barrels of butylenes are being diverted from the rubber program into aviation gasoline channels to make a greater amount of urgently needed fuel. Many background facts are behind this action of the Rubber Director. One important factor is the production capabilities of the alcohol butadiene plants which, we now understand, were deliberately designed for overcapacity to care for unknown contingencies. Plans now call for alcohol plants to produce, for three months, some 70% of butadiene requirements.

This will be an expensive operation, for alcohol prices are still in the stratosphere, but once the unprecedented demands for aviation gasoline are over, the petroleum operations will return to full capacity. Our title to this item is a reference to a technical battle that was waged when the big push for rubber was on. Many of the country's petroleum technologists held out for the two-step process in which butane was dehydrogenated in the two steps necessary to form butadiene. The technologists felt that every spare barrel of butylenes that could be obtained would be needed, and argued for a plan that would enable butadiene plants to make their own butylenes from butane. To all intents and purposes, the proponents of the plan for using refinery butylenes won, and most of our large installations are now based on the one-step operation. Butane is a plentiful refinery gas despite its use in isomerization, and now that hindsight is the prophet, we can raise the question as to whether the two-step process was not the better choice. But the answer is in question, for at the time the discussions were underway, the need was for butadiene in a hurry, and though refinements are now possible in the light of experience, the decision made at the time was the best possible, everything considered.

(*Continued on page 14*)

I. & E. C. Reports on the Chemical World Today

Postwar Planning

Postwar Reserves. One of the most frequent criticisms of the present corporate tax structure is its failure to permit accumulation of adequate financial reserves to finance postwar industrial developments and thus provide jobs for returning veterans and for men and women now employed in war industries. The recent survey of the Federal Reserve Board supports the view that industry generally will lack sufficient reconversion funds. Indeed, R. M. Gaylord, president of National Association of Manufacturers, has labeled as dangerously misleading the recent statement of Securities and Exchange Commission that all industry has plenty of working capital to convert.

We do not presume to speak for other industries, but it is evident that the chemical industry will require substantial amounts of new capital if it is to utilize fully the fruits of research which has been carried on as part of the war program but which has important postwar significance. At the recent meeting of the Advisory Board of INDUSTRIAL AND ENGINEERING CHEMISTRY, one of the members estimated that the chemical industry would require a minimum of 500 million dollars and possibly close to a billion dollars of new capital. Obviously any such sums, minimum or maximum, must come from investors, for the chemical companies will have no such amounts in liquid assets available on V-day.

It is imperative, then, that the many uncertainties now facing private enterprise be eliminated as quickly as possible so that the private investor will be willing to gamble with "risk money" with at least a reasonable chance of success. There is no question that the public will not only have money to spend but money to invest. At the end of 1944 the people of the United States will have, as savings of only three prior years, more than 70 billion dollars of free funds.

The Baruch-Hancock Report has been in existence for several months without any tangible progress having been made in putting into effect the constructive program advocated. Even that report falls short of recognizing the problem of raising vast sums for new capital in industries, such as the chemical, where tremendous quantities of venture money will be necessary in the postwar period.

Foreign Markets, Postwar. Heavy, heavy, over the heads of the international delegates at Bretton Woods, N. H., hung the knowledge that suitable credit machinery must be set up before the end of the war if any good is to be realized from the expected postwar boom. The problems that will face the world will be enormous. China has already experienced a vicious inflation; Russia's internal and external finance must be reconciled to some degree. A defeated Germany will probably go through the same cycle of inflation that followed the last war. Italy and France will start anew. United States and Great Britain, symbols of sturdiness and 24-carat money, are in no position to predict what will happen to their own financial structures. The need for speed is not forecast in apparent crumblings of Nazi Germany alone, but in the forward-looking predictions and plans of American business itself.

Thus Eric Johnston, reporting on his conversations with Anastas Mikoyan, Soviet Foreign Trade Commissar, states that Russia will purchase

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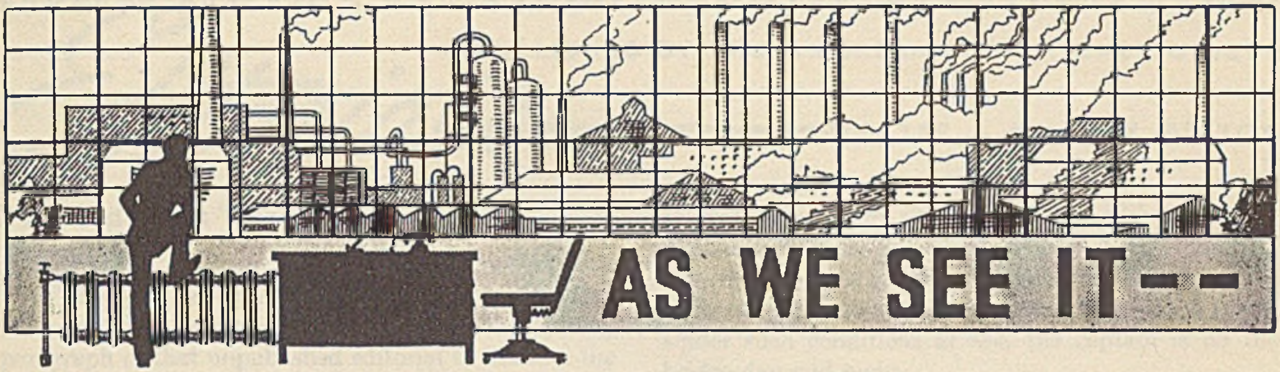

AS WE SEE IT--

This Month

METAL resinates, important products in many industries, are the subject of intensive research at the laboratories of Hercules Powder Company. From this source, under the authorship of Borglin, Mosher, and Elliott, comes a paper on fused metal resinates. Limits of metal content are noted, and means of overcoming blocking or crystallization, when too much metal is incorporated in the resin, are suggested. With resinates of polymerized rosin, however, no blocking is noted. Reasons are given.

Allen, of the American Viscose Company, makes his second bow to our readers on his favorite subject—instrumentation. His paper covers the application of process reaction curves, and actual experimental data are given along with flow sheets and recording charts. Procedures are described in detail, and the instrumentation department will find it of value.

Socony-Vacuum Oil Company, Inc., originators of the Thermofor catalytic cracking process about which an article is presented in this issue (see page 694), is represented by A. W. Francis who is responsible for an immense amount of work on solvent selectivity for hydrocarbons. This investigation has been carried out in the Socony-Vacuum research laboratories at Paulsboro, N. J. In measuring the affinity of solvents for hydrocarbons, Francis has used the critical solution temperatures as a measuring rod. With his method of selectivity, a determination may be made in a matter of minutes using only one ml. each of the hydrocarbon and solvent.

Leviton indicates in his paper that quantities of riboflavin are lost in the commercial preparation of lactose as it is now practiced. To remedy this loss he suggests that good yields of riboflavin can be obtained if the present practice is modified to a two-step operation. In the first step only a minute quantity of riboflavin would be absorbed; the greater part would be recovered in the second operation.

Emphasis on rubber continues with the publication of ten articles. Space prevents mention of each individually; suffice it to say that only by publishing information on this subject will the promise of independence in rubber supply come true for the United States. The advantages of our present position can easily be lost if the synthetic product, through lack of knowledge, is not capable of withstanding the onslaught, in peacetime, of natural rubber.

Redwood lumbering operations in the West create a huge waste of bark and bark dust. The Pacific Lumber Company financed a research program at The Institute of Paper Chemistry to help solve this problem. Lewis and others now report on the chemical composition of redwood bark. The bark dust, incidentally, is not sawdust in the usual sense, but is a powder formed when the bark dies and the cell constituents crumble. According to the authors, 50% of the bark as separated commercially is recovered as dust. The attack on the fundamentals will continue, and redwood bark will soon extend its application beyond the present outlets of insulation and textile uses.

X-ray, gimlet eye of molecular study, continues to aid in clearing up the mysteries of structure. This time, or rather once again (we have published two other studies on the subject) soap is having its internal fingerprints taken. The Procter & Gamble Company, through Ferguson and Nordsieck, uses the long spaces in the diffraction pattern to find out about crystallization behavior. They conclude that commercial soap crystallizes apparently as a solid solution and that there is no fractional crystallization in the 'commercial' product. Only one solid solution phase has been found in unbuilt soap systems of the familiar type.

When the plant superintendent allows solvents to escape into the sewer, he may bring down on his head the curses of the disposal plant chemists in addition to the invective of his own management for permitting the loss. Rudolfs gives the sanitation men ammunition on this problem; he is concerned with the effect of various solvents on biological sewage treatment and finds there are many types that slow down the steady rate of sludge digestion. Ethylene dichloride is extremely toxic, but apparently there are several solvents which, in small quantities, aid the process. Even so, it would probably be a pious idea to keep all solvents out of the sewer—to cut down swearing!

Next Month

In 1937, INDUSTRIAL AND ENGINEERING CHEMISTRY published an article from the Coal Research Laboratories, Carnegie Institute of Technology, on the reactivity of cokes. This proved to be so popular that the technique has been extended to all ranks of coal. Indices for sixty-eight coals will be given in September, the data being supplied by the same research laboratory. The precision of the method for coals is somewhat higher than it was for cokes; one remarkable conclusion is that, even for widely divergent fuels such as cokes, coals, and lignites, the volatile content determines the reactivity index.

A novel method of preparing hydrous oxide sols is on the way to our readers. The method involves ion exchangers and is quite original. Already in commercial fields it finds application in ceramics, textiles, detergents, and insecticides. In preparing silicic acid, the method calls for a solution of sodium silicate to be passed through a cation exchange material; the sodium is exchanged, and silicic acid is removed from the effluent substantially free from other ions. According to those who reviewed the paper before it was approved for publication, it will stimulate new interest in the use of zeolites for purification of various chemicals.

Alcohol production during wartime has provided impetus to the investigation of basic fermentation problems. Another of these studies seeking a more efficient fermentation operation will be printed in the September issue; it is based on the idea of using mold bran for saccharification. The findings indicate that wheat mashes fermented after such treatment yielded 2 to 14% more alcohol than similar mashes treated with malt.

F. S. Van Antwerpen

INDUSTRIAL AND ENGINEERING CHEMISTRY
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Editorials
WALTER J. MURPHY, EDITOR

The Tide Has Turned

JUST thirty days ago we wrote an editorial entitled "The Tide Is Turning" which was not published because of lack of space. We quote from the opening paragraph of that unpublished editorial to indicate the rapidity with which the military phases of the war are moving to a highly successful conclusion:

> American, Canadian, and British troops are in France, probably half a million, with the number increasing hourly. The fall of Cherbourg is imminent. Allied troops move up the Italian boot, literally booting the Germans off Italian soil. Nazis are in the dark as to whether we will strike at other points in Europe—Norway, the Balkans, southern France. Russia will start an all-out drive from the east. Turkey may cast her lot in active combat with the United Nations. As this is written, hints are heard of a major naval battle in the Pacific. We are moving closer and closer to the Philippines and down the road to Tokyo.

Cherbourg is ours, serving as a major port through which hundreds of thousands of Allied troops are pouring into France. No longer do we hold merely a bridgehead, but an area sizable enough to permit large-scale operations. The Russians are at the border of East Prussia. An attempt on Hitler's life has been made by German military officers, and radio reports hint at widespread disorders and even open revolt. Turkey is reported to have closed the Dardanelles and may overrun Bulgaria at any moment. The Tojo cabinet has fallen; Saipan is ours after a bloody battle, and we have established a beachhead on Guam. The Japanese Imperial Navy has a new head, but even he fails to respond to the taunts of Nimitz to come out and fight. By the time this issue reaches its readers, still more favorable news is likely. Events are now crowding one upon the other in rapid succession.

Will Germany collapse quickly—possibly before the end of this summer? No one can say authoritatively that she will. Is Japan closer to defeat than we have supposed her to be?

We may have hard fighting ahead and possibly reverses. If so, the subject of reconversion will be pushed into the background. Overoptimism is dangerous, but so is failure to keep close watch on developments. Executives face a difficult task in guiding the destinies of their respective concerns over the next twelve months; in many respects the job ahead will require even greater attention than that demanded during the past two years. At least in the latter period those in managerial positions were confronted with but one main objective—production and still more production.

We still must place the principal emphasis on production of war matériel, but it would be foolish not to recognize that many of the problems which have been discussed to date, largely in abstract terms, must be met suddenly, yet in a realistic and practical manner.

Shoals are ahead. How far away is anyone's guess. Under such conditions at sea, the captain is on the bridge day and night.

Reconversion

HUNDREDS of thousands of words have been written and spoken on this subject and, unfortunately, most of them indicate a plain battle royal between exponents of war production first and civilian production first. The question is simply one of degree consistent with the war effort. Certainly the Armed Forces should not be permitted to act as the sole arbiter, for plainly the military is not in a judicial sense a disinterested party. It is perhaps a trite but true statement that no military official has ever been court-martialed for buying too much. In short, it is the job of the military officials to win the war; their responsibility ceases once the enemy has been defeated. Therefore, opposition to reconversion from this group is understandable.

Donald Nelson's victory is a highly commendable one and he and James F. Byrnes, who is said to have made the final decision in favor of Nelson and against the military, are to be congratulated for making a start toward reconversion possible. Certainly the war effort will not be affected by the recently announced release by the War Production Board of aluminum and magnesium for civilian purposes.

Small wonder that the American public are confused by the conflicting statements originating from Washington, each group or agency emphasizing its particular viewpoint. It should be a relatively simple matter to arrive at intelligent decisions on the release of materials for civilian needs, without the fighting, bickering, and propagandizing that has prevailed for weeks in the Capital. Plainly it is this indecision that breaks down public morale, rather than the release of raw materials sorely needed on the civilian front now and for experimental work on postwar products.

It is hoped, and indeed expected, that Donald Nelson will appreciate the peculiarities of the chemical industry in any reconversion program placed in effect in the months to come. Nelson by training is a chemical engineer. He knows the fundamental differences between converting, let us say, the automobile industry and the chemical industry. The former is purely a fabrication industry. On the other hand, the chemical industry in developing new processes and new products requires under normal conditions several steps (test tube, pilot plant, semicommercial plant, large-scale plant) and years in which to engage in these successive steps. Certain facts about chemical progress should be reiterated for the uninitiated. It has been said that the difference between fundamental research and applied research is about twenty years; from test tube to full-scale operating requires from seven to ten years under normal conditions. True, we have learned to lessen this period under the necessities of war, but such gains have been expensive and often involve gambles not warranted in a peace economy. Already we, in the chemical industry, have suffered irretrievable time losses, and, in addition, will face the postwar period woefully short of adequate numbers of young technical personnel. It is well to remember, too, that the postwar era can be divided into two parts: one, the period immediately following the cessation of hostilities; the other, the years which will follow after the backlogs of demand created in the war years have largely been eliminated. Then it will be necessary to rely on new products and new industries. The chemical industry can and will play an important role if it is given a green light on postwar research now.

The chemical industry is not seeking favoritism, but does ask, in the interest of filling an important role in postwar employment, an intelligent understanding of its problems and a realistic approach by those who will dictate reconversion policies.

Fertilizer Legislation

AT THE recent convention of the National Fertilizer Association, held in Atlanta, a threat to free enterprise inherent in the Agricultural Adjustment Administration and Tennessee Valley Authority farm programs was strongly pointed out from the rostrum. At that time, the chief threat was a House bill introduced by Representative William Lemke (Minnesota) which would subject the industry to government inspection and control.

Since then, however, warnings sounded by association officials became a reality when Senator Lester Hill of Alabama dropped into the legislative hopper S.2035 entitled "National Fertilizer Policy and Program Act", calling on the TVA to formulate the policy and program. The Authority would be directed to make a study with a view to "increasing fertilizer available to farmers, improve its quality, and lower its cost". The government agency, naturally, would base its findings on its own operation, which "neither spins nor toils" as far as its commercial aspects are concerned. Yet, it would be installed as "czar" over a commercial industry which has been preaching to the farmer to fertilize and enrich his soil independent of help from the taxpayers.

The National Fertilizer Association, naturally, is girding for battle on the bill, if and when committee hearings are held. One item in the background of this legislation will hardly be brought out at the hearings. This is that Senator Hill's home State of Alabama stands to pick a juicy plum from the adoption of the Act.

The Tennessee Valley Authority already has purchased a site near Mobile, Ala., for a superphosphate plant. Only the fact that the War Production Board refused to grant the necessary priorities kept the TVA from rushing it to completion. Naturally, such a project would bring revenue into the State of Alabama and give employment to a goodly number of correct-thinking constituents. The plant, it might be pointed out, is but one phase of an integral part of the program which the Senator envisions. Again the question is arising—what are the proper "spheres" of activity of government and private industry. No one questions the major contribution of federal and state research organizations to the education of the farmer in the proper utilization of fertilizers. The fertilizer industry frankly acknowledges its indebtedness to these groups, but it disputes the necessity or desirability of government embarking into commercial production of fertilizer on a large scale. The proviso that at the end of a five-year period, TVA is authorized to lease the Mobile plant to a bona fide farmer's cooperative organization is naturally viewed with extreme suspicion. The entire problem resolves itself into the simple question of whether free enterprise so far as the fertilizer industry is concerned is to survive or be destroyed.

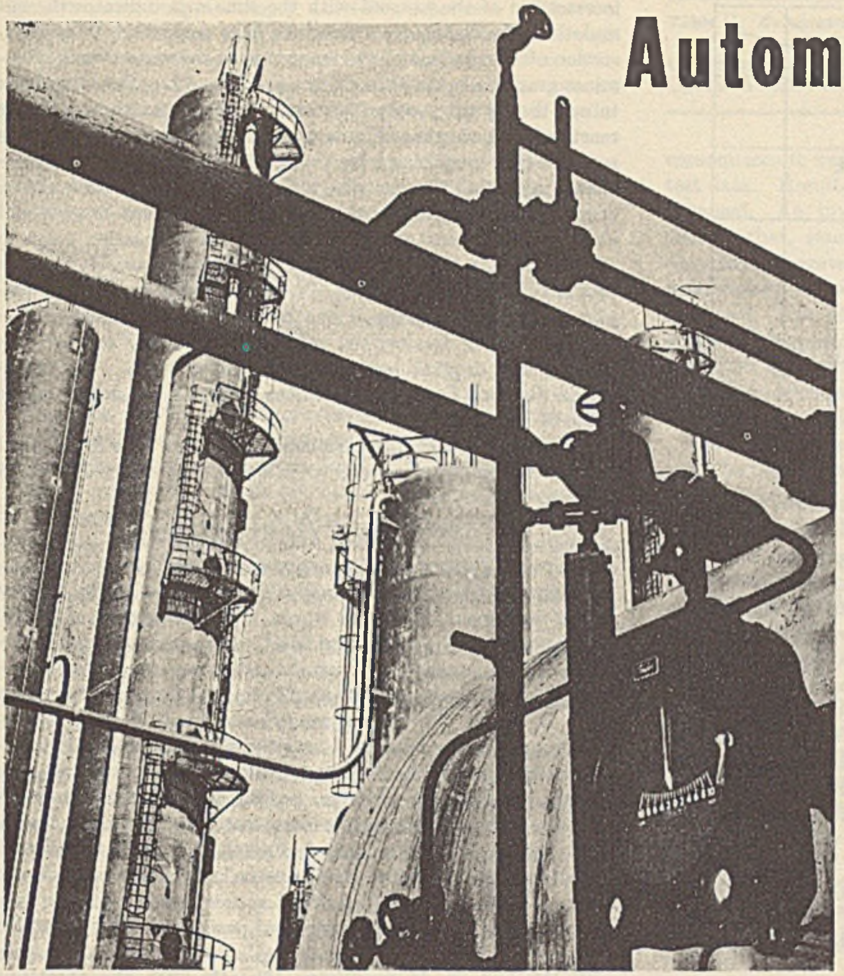
The 108th Meeting

READERS of *Chemical and Engineering News* will note an entirely different type of premeeting publicity in current issues. With the active cooperation of divisional officers, emphasis has been given to descriptions of the various symposia scheduled, with, of course, details of papers to be delivered. This premeeting publicity is designed to afford members an opportunity to decide whether the meeting warrants taking time away from busy war jobs. This new approach is in accord with the times, for the 108th meeting of the AMERICAN CHEMICAL SOCIETY in New York, with the North Jersey Section acting as host, will be held when undoubtedly unprecedented demands will exist for travel space.

The gathering is primarily a war meeting, its principal aim to further the successful prosecution of the war. It does have a secondary and likewise an important purpose—to lay the groundwork for new products and processes that will provide jobs for our returning heroes.

When the blessed days of peace return, the SOCIETY can resume such desirable, instructive, and pleasant practices as featuring plant trips and visits to historical places.

Automatic-Control Instrument Adjustment



A comparison is presented between the two methods of arriving at control instrument settings originally proposed by Ziegler and Nichols (*2*). Actual experimental data on obtaining instrument settings are given, and the relative merits of the two methods are compared. The reaction curve method and its use in evaluating processes for the application of automatic control is described in detail to supplement the description of the ultimate sensitivity method given in the author's previous paper (*1*).∼∼The liquid-level controller at the left is a Fulscope internal-float type used in a butadiene plant to supply an adjacent copolymer plant (Courtesy, Taylor Instrument Companies).

APPLICATION OF PROCESS REACTION CURVES

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A PREVIOUS paper (*1*) presented experimental data substantiating a method of establishing process control instrument settings proposed by Ziegler and Nichols (*2*). This method was based on establishing a proportional-response "sensitivity" setting for the control instrument, which produced an even-cyclic chart record indicative of "ultimate sensitivity". The optimum settings for sensitivity, automatic reset, and preact were then calculated by formulas provided by the authors and from characteristics of the ultimate-sensitivity control record. The confirming experimental work showed the value of this procedure as representing a relatively simple concrete method of attack on a problem which hitherto had relied for solution on individual judgment and trial-and-error adjustment.

Although the chief purpose of the Ziegler-Nichols paper was to present the method of arriving at control instrument settings from the characteristics of the ultimate-sensitivity control record, a second method was proposed, based upon the "process reaction curve". To describe this curve, let us assume a process to which we are to apply an air-operated temperature controller and its accessory diaphragm air-operated steam control valve. The installation of the instrument has been completed and the process is being controlled manually by adjustment of the remote hand-control air-pressure reducing valve in the instrument case preliminary to placing the instrument in operation. The air pressure on the diaphragm of the steam control valve has been properly adjusted so that the temperature record on the control instrument chart is at the desired control-point temperature, and the process is otherwise in dynamic equilibrium. Under these conditions there is a definite air pressure on the diaphragm of the steam control valve, as shown by the air-output pressure gage of the instrument. Now, let us suddenly change that pressure by some definite amount to produce a correspondingly sudden change in the quantity of steam flowing to the process, and then note the effect of this change on the temperature record shown by the instrument. The temperature response curve produced will normally be S-shaped; its characteristics are a function of the various lags and capacities of the entire process system, including the instrument itself. The process reaction curve is a plot of such a chart record on rectangular coordinate paper; the vertical axis represents inches of pen movement from its original position before the change in steam flow was produced, and the horizontal axis represents time in minutes following the change. A curve which might be obtained from our theoretical process is shown in Figure 1.

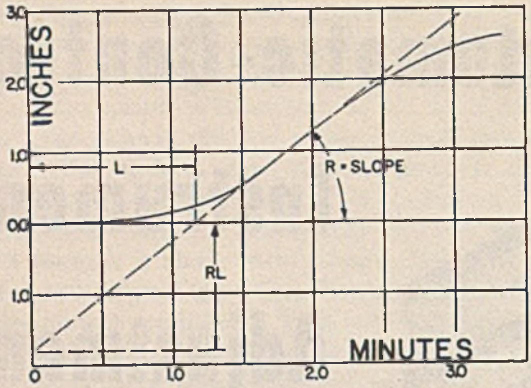


Figure 1. Process Reaction Curve for Theoretical Process

The graphical picture presented by this curve allows us to eliminate the intricacies of a mathematical analysis of processes involving a series of lags and capacities, and represents a summation of the process characteristics which must be considered in establishing proper instrument settings. Although it is characteristically S-shaped, an infinite number of variations are possible. They range from that shown by a liquid-level application where the curve comes to a maximum slope maintained until the tank runs over, to the curve showing a dead period lag in which there is no pen movement for a definite time; then it may either start to move at its maximum rate or slowly build up to it.

Ziegler and Nichols pointed out that two principal characteristics of the curve may be employed to establish optimum instrument settings. These are the maximum rate of pen movement at any instant, as shown by the point of maximum slope of the reaction curve, and the intersection with the horizontal time axis of a line drawn tangent to this point. The slope of the tangent represents the reaction rate of the process, R, and the intersection of the tangent with the time axis indicates the cumulative effect, L, of all the time lags involved. The intersection of a projection of the tangent with the vertical axis determines graphically the value of the product, RL. Referring back to our theoretical process, however, we find that the particular reaction curve shown in Figure 1 was plotted from a temperature response curve resulting from a control-valve diaphragm pressure change of definite magnitude, ΔF. If the diaphragm pressure change had been greater, the slope of the reaction curve would also have increased and thus shown a direct relation between ΔF and R. It therefore becomes necessary to convert reaction rate R to a unit reaction rate, R_1, which results from a unit diaphragm pressure change of one pound per square inch. This may be done by dividing the value of R by the ΔF employed in running the original temperature response curve. The intersected distance L generally remains constant, regardless of the value of ΔF employed.

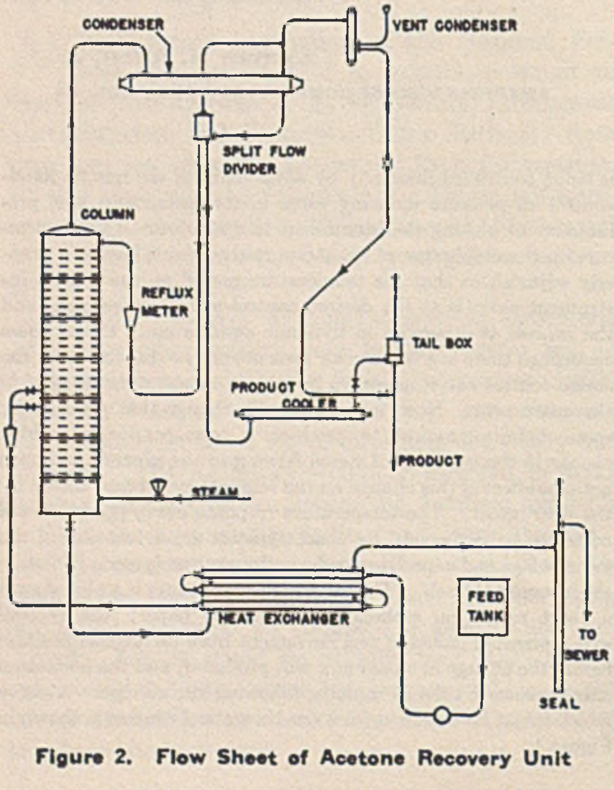


Figure 2. Flow Sheet of Acetone Recovery Unit

According to Ziegler and Nichols, we are now able to calculate the optimum instrument settings in accordance with the formulas listed in Table I.

DEFINITION OF TERMS AND UNITS

CONTROL EFFECTS. "Proportional response" gives an instrument air output or valve movement proportional to the amount of pen movement. In other words, a pen movement of 2° will give twice the valve movement of 1°. The ratio of valve movement to pen movement is called "instrument sensitivity" (percentage of full chart pen movement required for full valve movement is called "throttling range"). An on-off controller is merely one with a fixed high sensitivity. The proportional response instrument has only one definite air-output pressure or valve position for any given pen position; as a result it is unable to compensate for changes in process load which require a change in the rate of flow of the controlled medium and still to maintain the original control point. Changes in load with a proportional response instrument result in a final sustained pen deviation from the control point. This deviation of pen and pointer with load changes is called "offset", the degree of offset varying inversely with the instrument sensitivity (directly with the throttling range) and directly with the size of the load change.

"Automatic reset", as a control effect, has as its only purpose the elimination of offset. Its presence does create instability of control, but a slightly decreased instrument sensitivity eliminates this effect on stability. In operation, automatic reset detects pen deviation from the control point, and its action is to cause a slow, continuous rate of valve movement in the direction necessary to eliminate this deviation. The rate of valve movement is proportional to the degree of deviation of the pen from the set point, and in most industrial instruments this reset rate is adjustable, either in steps through the addition of lengths of capillary tubing to the instrument air circuit, or continuously through the adjustment of a precision needle valve.

UNITS OF MEASUREMENT. Proportional response "sensitivity" is measured by the air output pressure change produced by an instrument and resulting from a unit pen movement of one inch on the chart. The units, therefore, are pounds per square inch per inch.

Automatic reset produces a continuous rate of instrument air-output change proportional to the deviation between pen and set pointer. The deviation may be expressed in terms of propor-

Table I. Summary of Controller Adjustments (3)

		Reaction Curve		Ultimate Sensitivity
Proportional				
Sensitivity	=	$1/R_1L$	=	$0.5Su$
Proportional plus reset				
Sensitivity	=	$0.9/R_1L$	=	$0.45Su$
Reset rate	=	$0.3/L$	=	$1.2/Pu$

tional response output change; units for "reset rate", therefore, are pounds per square inch per minute per pound initial change.

"Ultimate sensitivity" is that sensitivity adjustment in a proportional response instrument applied to a particular process which gives an oscillating record of a fixed amplitude. A greater sensitivity will cause oscillations of increasing amplitude; sensitivity below ultimate will result in oscillations of decreasing amplitude which gradually approach straight-line control. A summary of control effect units of measurement (*2*) follows:

Response	Action	Measure	Unit
Proportional	$\frac{\text{Valve movement}}{\text{Pen movement}}$	Sensitivity	Lb./sq. in./in.
Automatic reset	$\frac{\text{Valve velocity}}{\text{Pen movement}}$	Reset rate	Per min.

PROBLEM

The work described in the previous paper (*1*) has proved the value of the ultimate sensitivity method of determining control instrument settings. The work reported in this paper was initiated in an effort to obtain similar confirming data for the reaction curve method and to compare the accuracies of these two procedures. It was felt that such data would be of considerable assistance to the instrument engineer, since it would place in his hands a second valuable tool to assist in the establishment of instrument settings.

The equipment was that used in the original investigation—a commercial-size acetone recovery unit. The column was 66 inches in diameter and contained thirty plates on a spacing of 12 inches. Figure 2 is a flow sheet of this unit.

The control system (Figure 3) consisted of: (*a*) reflux control through a fixed-ratio weir-type split flow divider which divided the total overhead into product and reflux streams to maintain a fixed reflux ratio; and (*b*) control of the heat input to the column by a Foxboro Model 30 Stabilog temperature controller. The temperature bulb of the instrument was located in the vapor space above the seventh plate from the bottom of the column, and the temperature at this point was controlled through the instrument action in positioning an air-operated diaphragm-type throttling valve in the steam line to the sparger pipe. As a result of the original application of the ultimate sensitivity method of determining instrument settings, the Foxboro instrument had a proportional response setting of 51% throttling range (sensitivity of 5.4 lb./sq. in./in.) and a reset rate of 0.19 lb./min./lb.

Several attempts were made to obtain correlation between the instrument settings obtained in the author's original investigation of the ultimate sensitivity method and those determined from the reaction curve, but results were extremely poor. As a consequence it was finally decided to run a check of the original test data. Results entirely different from the original data were obtained. An investigation of department records, however, showed that, shortly preceding this second investigation, the diaphragm-operated steam-control valve had been repacked with well lubricated packing, and the process load had been somewhat increased. The effect of these changes was a considerable decrease in the process lag. Evidence that valve friction had affected the original results was obtained from the data of that investigation which showed a wandering temperature record traceable to valve friction of approximately 0.35 lb./sq. in.

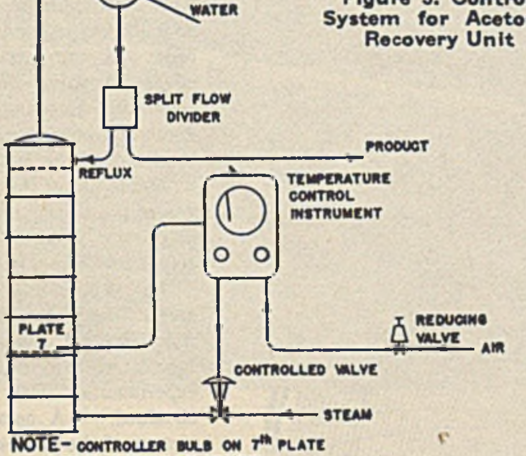


Figure 3. Control System for Acetone Recovery Unit

Table II. Calculation of Optimum Instrument Settings by Ultimate Sensitivity Methods

Optimum sensitivity = $0.45Su$ = 0.45×14 = 6.3 lb./sq. in./in.
Optimum reset rate = $1.2/Pu$ = $1.2/2.1$ = 0.57 per min.

Since it was apparent that the new ultimate sensitivity data could be justified on the basis of decreased valve friction and increased process load, a rerun of the complete ultimate sensitivity method, together with the reaction curve, was made the same day.

ULTIMATE SENSITIVITY METHOD

No attempt will be made to describe this method which was discussed in detail previously (*1*). Figure 4 shows the result of the determination of ultimate sensitivity, obtained at a sensitivity of approximately 14 lb./sq. in./in. (throttling range of 20%). The ultimate period of the oscillations at this point is approximately 2.1 minutes per cycle. With these values established, the optimum instrument settings are calculated as shown in Table II by the formulas for the ultimate sensitivity method as presented in Table I.

Figure 5 shows the controlled temperature record resulting from the optimum settings calculated in Table II. A reset rate of 0.435 per min. was used instead of the calculated rate of 0.57 per min., since this was the nearest approach to the rate calculated which could be obtained without trial-and-error cutting of capillary tubing.

REACTION CURVE METHOD

In running the reaction curve temperature records shown in Figure 6, the original 1 r.p.m. Telechron-clock sealed-motor unit in the instrument was replaced by a 60 r.p.m. motor to increase the speed of the chart. The sudden change ΔF in the steam-control-valve diaphragm pressure required to produce these curves was created by reducing the supply air pressure to the control instrument so that the difference between it and the air output pressure of the instrument when controlling the process was equal to the desired ΔF. The automatic-manual air switch in the instrument case was then turned to the manual position, and the chart motor was started at the same instant. The temperature response curves were then summarized as shown in Table III by measuring the deviation in inches of the recorded temperature from the original control point at each time division on the chart.

The reaction curves in Figure 7 were obtained by plotting the data of Table III. Each curve has an initial dip in the opposite direction to that taken, as the effect of the increased steam flow is felt at the temperature bulb location. The most probable explanation of this phenomenon lies in the effect of the sudden surge in steam flow on the existing material balance within the column. The vapor flow across any cross section of the column will increase almost instantaneously in a direct ratio to the increase in steam flow produced. This means that, immediately following the increase in steam flow, the volume of vapor passing through the liquid on any given plate is considerably greater than that flowing before the change was made. The effect of the increased volume of vapor is to decrease the volume of liquid on the plate by forcing it over the overflow weir and down the down-

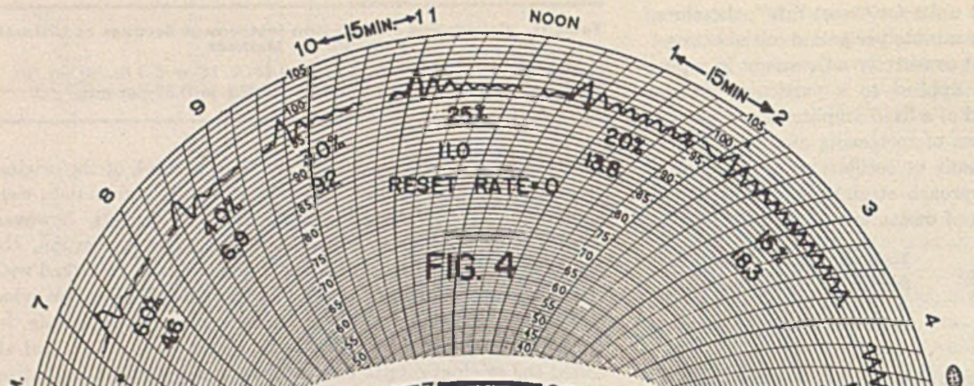


FIG. 4

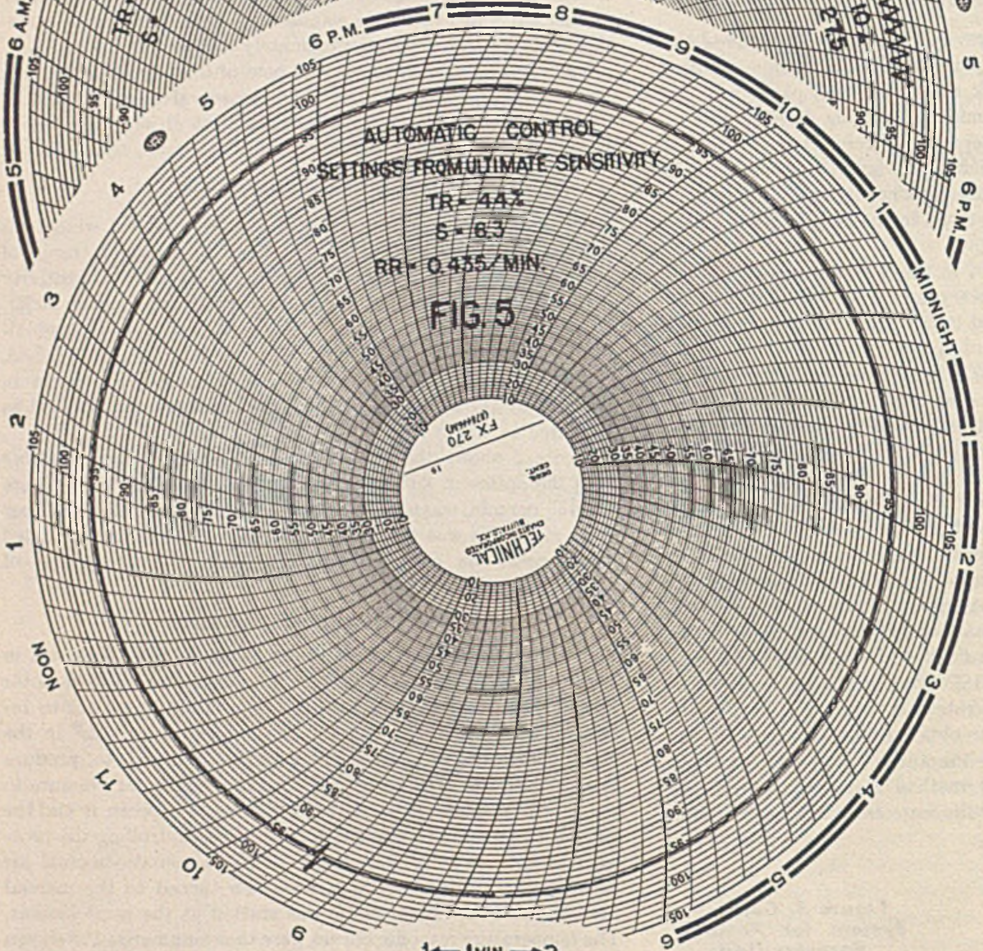


FIG. 5

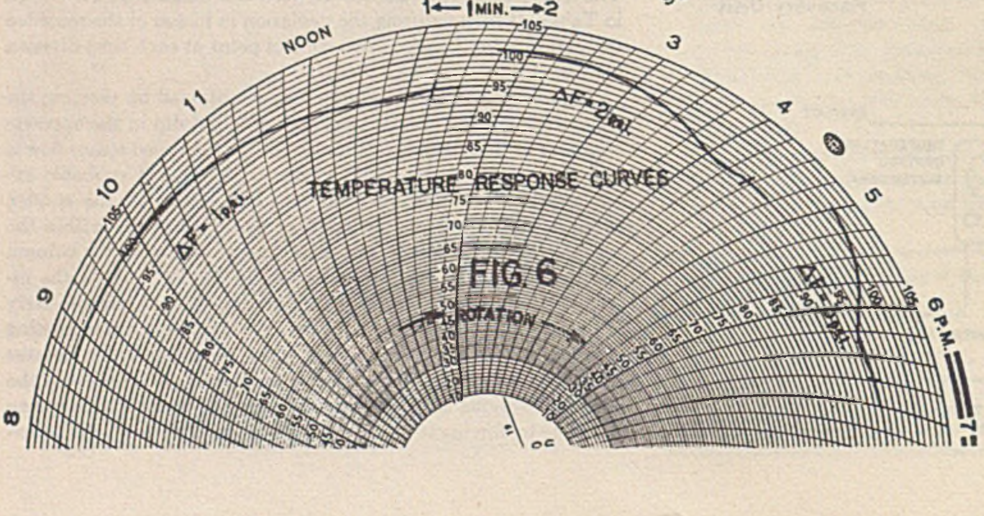


FIG. 6

pipe to the plate below. Thus, the initial effect of a sudden increase in steam flow to a fractionating column is a small downward shift in the concentration gradient through the column. In other words, a liquid of given concentration on any definite plate before the sudden surge in steam is made will suddenly be enriched in low boiler through the increase in downflow resulting from the steam flow change. This sudden increase in the rate of downflow and consequent slight downward shift of the concentration gradient through the column is the probable explanation for the initial lowering of the temperature on a given plate.

A second characteristic of the curves of Figure 7 is that the value of *L* for the reaction curve resulting from a diaphragm pressure change of 1 pound is greater than for the 2- or 3-pound curves. A possible explanation for this discrepancy lies in the effect of valve friction. It is obvious that the error introduced by valve friction is a large part of a small diaphragm pressure change and is progressively less important as the diaphragm pressure change increases. The author believes that the initial chart record from which the reaction curve may be plotted should always be based on as large a diaphragm pressure change as possible in order to minimize the effects of valve friction. Generally speaking, the diaphragm pressure change should never be less than 2 pounds unless there is a valve positioner on the diaphragm valve to overcome the effects of friction.

One reaction curve will give a true picture of the conditions existing in the system at the time the experimental data was obtained. A complete picture of the process can be obtained only through the determination of a complete family of reaction curves run at a number of different ΔF values with the process operating under several loads.

The following data were taken from the three reaction curves plotted in Figure 7:

ΔF, lb./sq.in.	1	2	3
R, in./min.	0.22	0.45	0.68
R_1, in./min./p.s.i.	0.22	0.225	0.227
L, min.	0.59	0.51	0.52
R_1L, in.	0.13	0.115	0.118

The optimum instrument settings were then calculated from these values and the formulas for the reaction curve method presented in Table I. The calculations are given in Table IV.

Figure 8 shows the control temperature record resulting from the optimum setting calculated in Table IV. Here again it will be noted that a reset rate of 0.435 per min. was used in place of the calculated reset rate of 0.59.

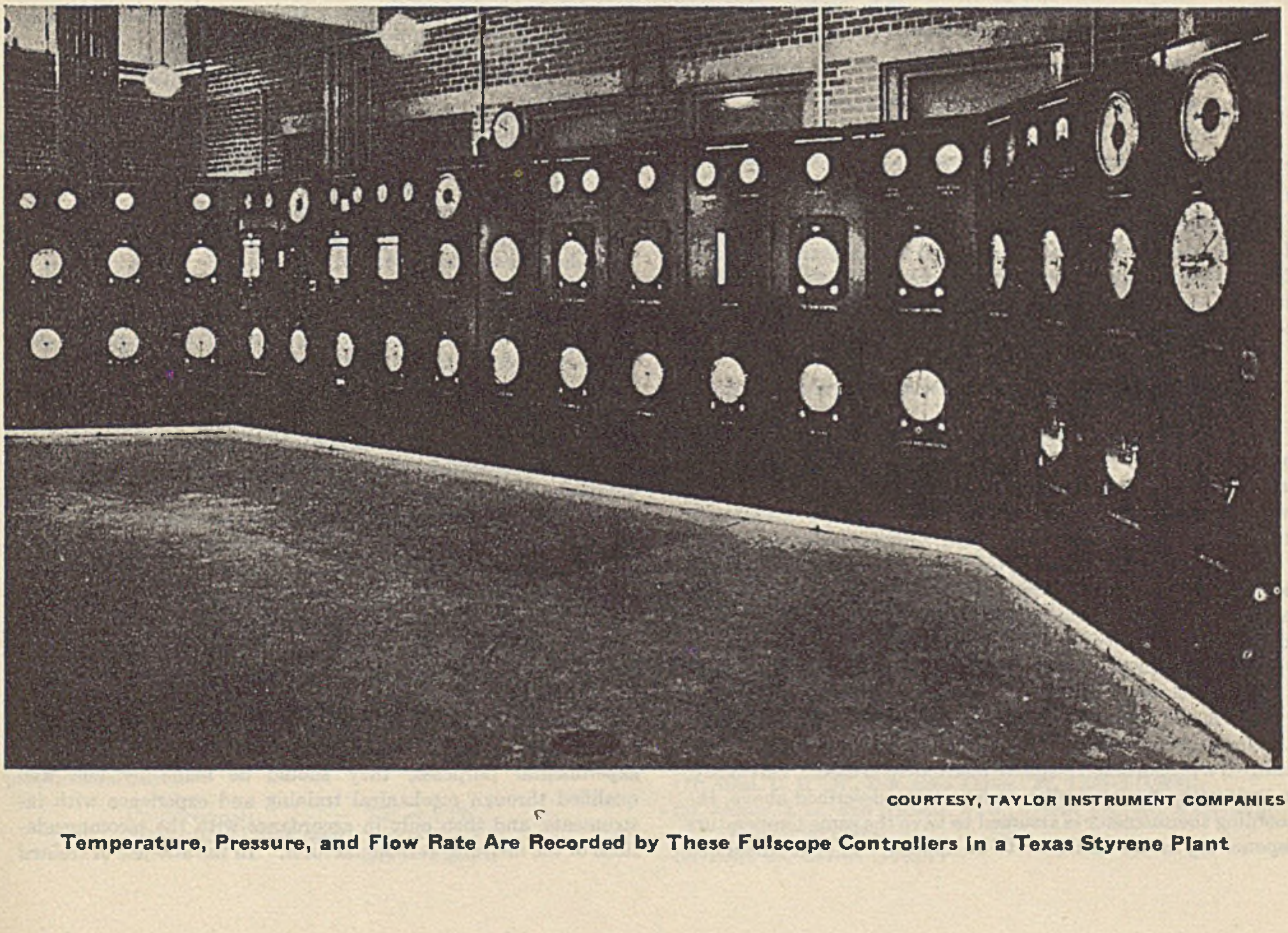
CONCLUSIONS

The calculated optimum instrument settings for both the ultimate sensitivity and reaction curve methods (Tables II and IV) show approximately equal reset rates, but the comparison between the values for sensitivity is not so favorable. The explanation for the discrepancy probably lies in the difficulty of accurately determining the correct value of ultimate sensitivity. Figure 4 shows that a cyclic chart record of apparent constant amplitude is obtained at any sensitivity setting between 11 and 18.3 lb./sq. in./in. (25 and 15% throttling range), but the actual value for ultimate sensitivity can only be estimated. The reaction curve method, on the other hand, gives an accurate determination of R, L, and R_1L; therefore the calculated values for the optimum instrument settings will be somewhat more accurate. The greater accuracy of the reaction curve method may be confirmed by comparing the controlled temperature records resulting from settings by the ultimate sensitivity method (Figure 5) and by the reaction curve method (Figure 8). These chart records were obtained with identical reset rates which, although somewhat slower than the calculated rates, do not vary sufficiently from them to introduce a serious error in the results obtained. Actually, however, the settings calculated from both methods will generally give equally satisfactory control.

ALTERNATE METHODS

The procedure described for obtaining a temperature response curve is based on the assumption that the particular instrument being used contains an automatic-manual air switch and a manual-control air-pressure reducing valve. Although this is generally the case in up-to-date instruments, many are in use which do not have these refinements. If the instrument is of one of the older types having an external-supply air-pressure reducing valve, a satisfactory temperature response curve may be obtained by first eliminating the reset response and then adjusting the instrument sensitivity so that a pen deviation from the set pointer of one major chart division will give the desired output pressure change, ΔF. Then when the process has been stabilized at the desired control temperature, the pointer is moved one major chart division from the pen and is kept that far ahead of the pen after it begins to move. It is necessary only to run the curve slightly beyond the point of maximum slope. If it is desired to determine lag only, any reasonable ΔF may be used since the value of lag is generally unaffected by ΔF.

In the case of the experimental method used to obtain the temperature response curve shown in Figure 6, the chart speed



COURTESY, TAYLOR INSTRUMENT COMPANIES

Temperature, Pressure, and Flow Rate Are Recorded by These Fulscope Controllers in a Texas Styrene Plant

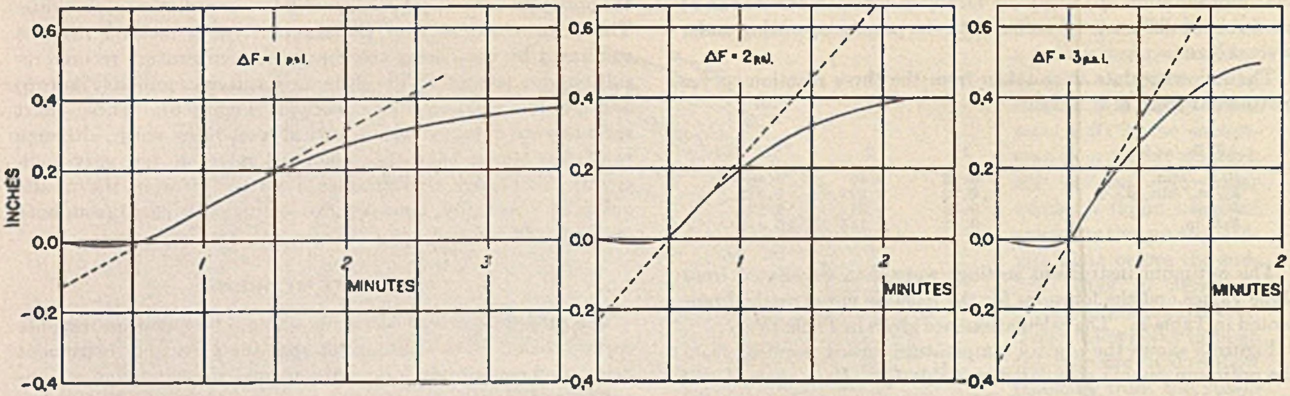


Figure 7. Reaction Curves Based on Data of Table III

Table III. Summary of Temperature Response Curves

Time, Min.	Time, Sec.	Pen Movement, Inches: ΔF = 1 lb./sq. in., 1st	ΔF = 1 lb./sq. in., 2nd	ΔF = 1 lb./sq. in., 3rd	ΔF = 1 lb./sq. in., Av.	ΔF = 2 lb./sq. in., 1st	ΔF = 2 lb./sq. in., 2nd	ΔF = 2 lb./sq. in., Av.	ΔF = 3 lb./sq. in., 1st
0	15	−0.01	−0.025	−0.005	−0.013	−0.005	−0.02	−0.0125	−0.02
0	30	0	−0.02	0	−0.0066	+0.005	+0.01	+0.0075	0
0	45	+0.045	+0.025	+0.045	+0.0383	+0.11	+0.11	+0.11	+0.142
1	00	+0.1	+0.08	+0.09	+0.09	+0.20	+0.195	+0.1975	+0.27
1	15	+0.16	+0.13	+0.15	+0.147	+0.265	+0.265	+0.265	+0.37
1	30	+0.205	+0.19	+0.19	+0.195	+0.32	+0.32	+0.32	+0.45
1	45	+0.24	+0.22	+0.23	+0.23	+0.36	+0.355	+0.3575	+0.49
2	00	+0.29	+0.25	+0.26	+0.266	+0.38	+0.38	+0.38	
2	15	+0.32	+0.28	+0.29	+0.296	+0.40	+0.40	+0.40	
2	30	+0.34	+0.30	+0.31	+0.316				
2	45	+0.36	+0.32	+0.33	+0.336				
3	00	+0.37	+0.34	+0.35	+0.353				
3	15	+0.38	+0.36	+0.36	+0.366				
3	30	+0.385	+0.37	+0.37	+0.375				

Table IV. Calculation of Optimum Instrument Settings by Reaction Curve Method

Optimum sensitivity $= 0.9/R_1L = 0.9/0.115$

$= 7.8$ lb./sq. in./in.

Optimum reset rate $= 0.3/L = 0.3/0.51$

$= 0.59$ per min.

was increased in order that the units of time could be easily read. However, such a change will usually be impractical. The same effect, however, may be obtained by using a stop watch and manually moving the chart ahead a small amount every ten or fifteen seconds, depending on the speed of pen movement obtained.

AUTOMATIC CONTROL THROUGH REACTION CURVES

The reaction curve may also be used to evaluate a manually controlled process for the application of a control instrument. For this purpose it is first necessary to determine the hand-control valve openings necessary for the process when operating at both minimum and maximum loads. Then, when the process is operating at maximum load, the hand valve is suddenly closed to the minimum load position and the temperature response curve obtained on a recording thermometer or by periodic readings from an indicating instrument. The procedure is then repeated with the process at minimum load, and the hand valve is suddenly changed to the maximum load position. RL and L are determined for both curves, and the highest values are taken. RL represents the offset which will result from a maximum load change if a proportional response instrument is used. Obviously, on tests without a controller such as those described above, the recording thermometer is assumed to have the same temperature response lag as the controller to be applied. It is also assumed that the hand valve is opened and closed at a rate approximately that at which a controller would move the diaphragm valve; therefore the effect of valve lag will be included in the process response curve.

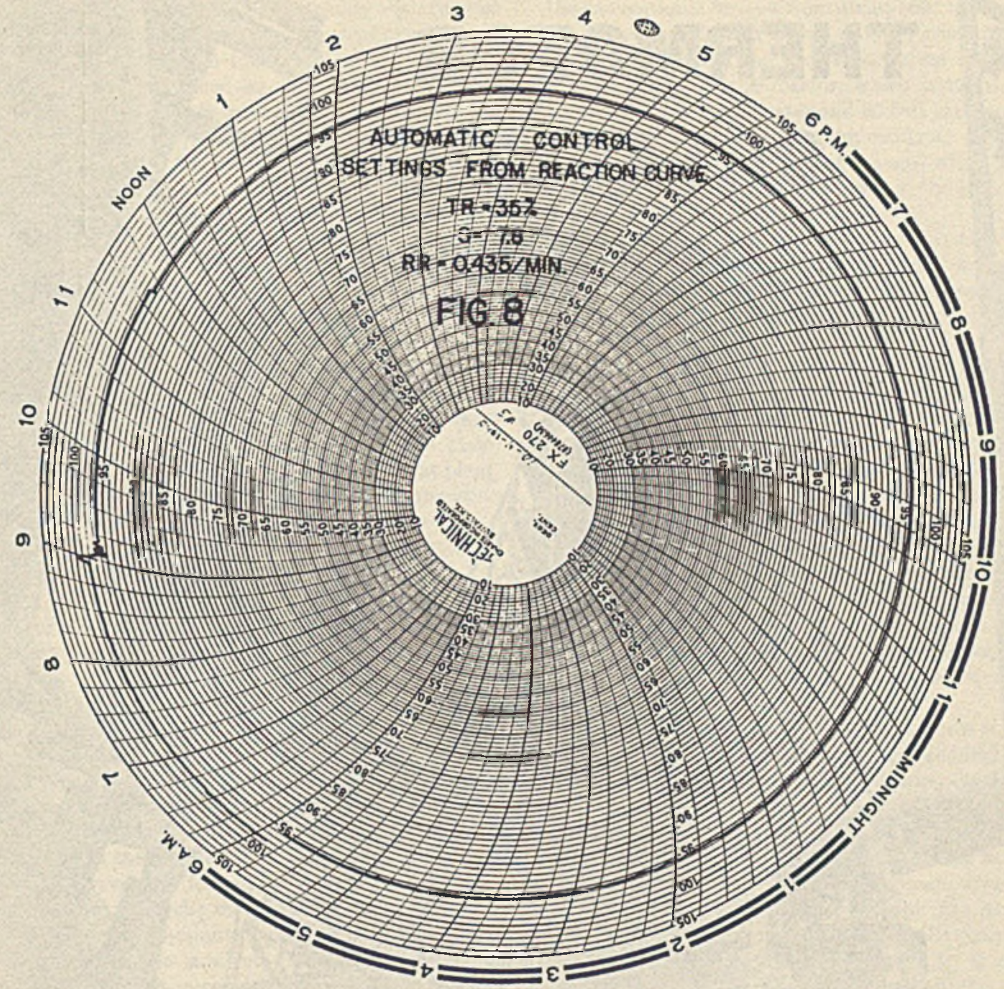
SUMMARY

This investigation confirms the reaction curve as a valuable tool for the instrument engineer. It provides a method of process analysis which can be of great value in industrial plants. Some of the possible uses for this method follow:

1. The reaction curve offers a second and somewhat more accurate method of determining controller settings.
2. The method may also be used in the evaluation of manually controlled processes for the application of automatic control instruments.
3. The reaction curve may be used to catalog processes as to their difficulty of control. Analysis of the reaction curve shows that, as R and L increase, the difficulty of control also increases. Ziegler and Nichols suggested the use of RL^2 as an index of controllability (*3*).
4. The reaction curve offers a method of analyzing a process for possible rearrangements in equipment which will lead to improved process control (*3*).

Since publication of the author's original paper (*1*), comments have been received which deserve mention here. In the first place, it is admittedly evident from the data in Table II of the initial work (*1*) that the original arrangement of the reset mechanism of the instrument tested was not functioning in accordance with manufacturer's design. Although this is a minor point, data received from the manufacturer of the instrument indicate that the reset mechanism of their instrument, as designed, will produce a maximum to minimum reset ratio in the order of magnitude of 16 to 1. The reset rate is adjustable in a geometric progression of five distinct steps.

The itemized procedure in the original paper (*1*) presented certain information which, in unskilled hands, could conceivably result in serious damage to a control instrument. It should be pointed out that alterations to the air circuit of standard industrial controllers are not necessary when they are functioning in accordance with manufacturer's design. If, however, such alterations are desired either to eliminate instrument defects or for experimental purposes, they should be made by one well qualified through mechanical training and experience with instruments, and then only in accordance with the recommendations of the instrument manufacturer. In the absence of trained



AUTOMATIC CONTROL SETTINGS FROM REACTION CURVE
TR = 35%
S = 7.6
RR = 0.435/MIN.
FIG. 8

personnel, it is suggested that the instrument manufacturer be requested to make the desired alterations.

To dispel the possible assumption that instrument adjustment procedures other than that confirmed by the writer's first article (*1*) are worthless, it should be stated that adjustment procedures appearing in the standard instruction forms of instrument manufacturers, for the last few years, generally give satisfactory instrument settings. The manufacturer of the instrument used in the original work has provided typical chart records showing periodic cyclical recovery as an indication of too narrow a proportioning band setting, as well as the wandering record as an indication of too wide a proportioning band. The basic difference, however, between those methods and that of Ziegler and Nichols is found in the exact determination of the ultimate sensitivity and the period of oscillation used by them. Although admittedly based on approximation, the Ziegler-Nichols method appears to be more concise and accurate, and does not depend for accuracy upon the judgment of the person performing the test work. The basic mechanical and mathematical relations of the Ziegler-Nichols method allow two operators to obtain identical settings for an instrument applied to a particular application.

It has been suggested that the author present alternate formulas employing throttling range, rather than sensitivity, for those who prefer that unit of measurement for the magnitude of proportional band:

$$\begin{aligned} &\text{Proportional:} && TR = 2TR_u \\ &\text{Proportional plus reset:} && TR = 2.2\ TR_u \\ & && RR = 1.2/Pu \end{aligned}$$

The author again wishes to point out that his work has been based upon the terminology presented by Ziegler and Nichols, but the relations presented by the latter may be readily converted to the terms of a generally accepted terminology when and if it is adopted.

NOMENCLATURE

L = lag
Pu = period at ultimate sensitivity
R = reaction rate
R_1 = unit reaction rate
S = sensitivity
Su = ultimate sensitivity
RR = reset rate
TR = throttling range
ΔF = air output pressure change
p.s.i. = pounds per square inch
TR_u = ultimate throttling range

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(2) Ziegler, J. G., and Nichols, N. B., *Trans. Am. Soc. Mech. Engrs.*, 64, 759–68 (1942).
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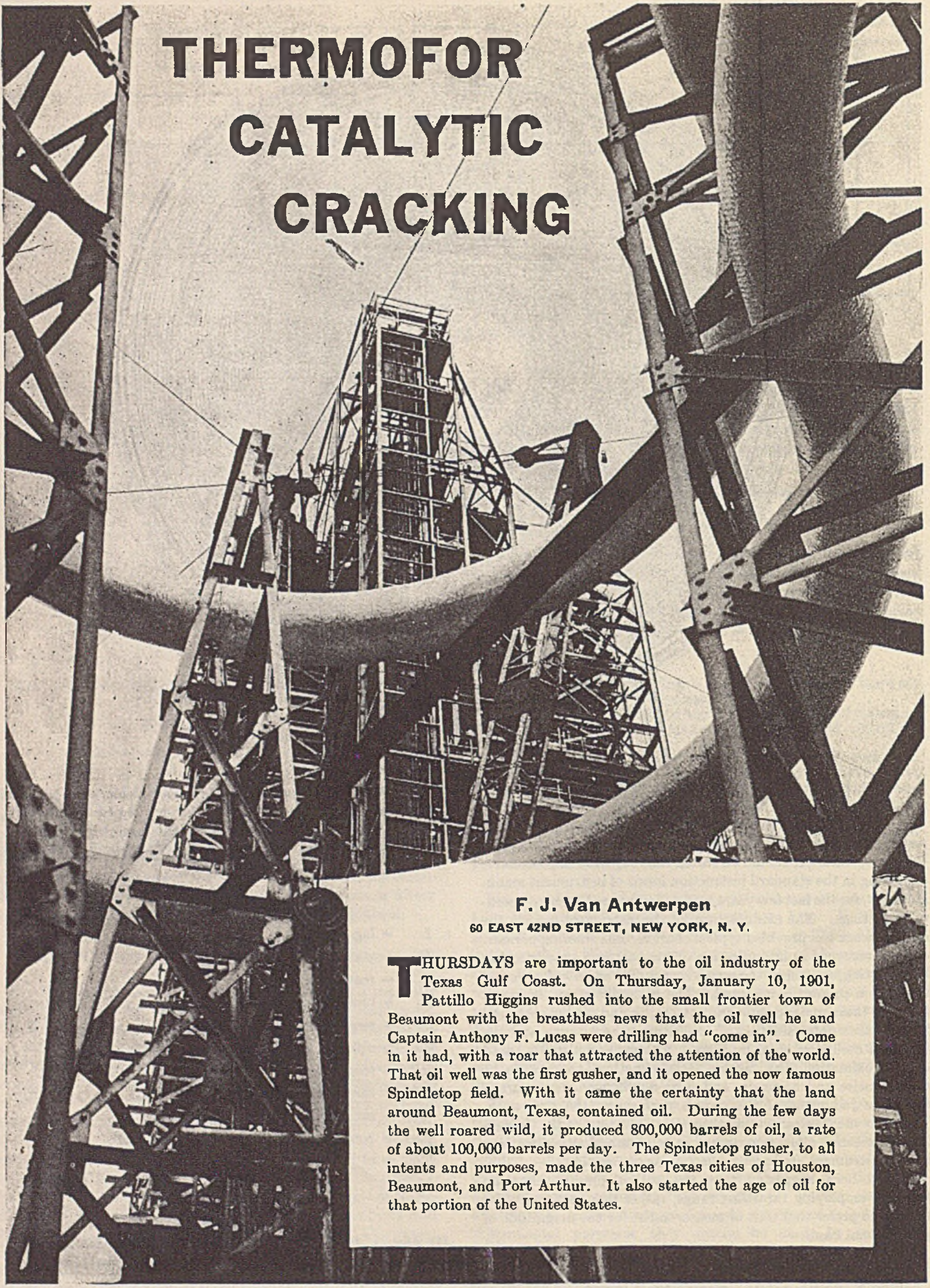
THERMOFOR CATALYTIC CRACKING



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THURSDAYS are important to the oil industry of the Texas Gulf Coast. On Thursday, January 10, 1901, Pattillo Higgins rushed into the small frontier town of Beaumont with the breathless news that the oil well he and Captain Anthony F. Lucas were drilling had "come in". Come in it had, with a roar that attracted the attention of the world. That oil well was the first gusher, and it opened the now famous Spindletop field. With it came the certainty that the land around Beaumont, Texas, contained oil. During the few days the well roared wild, it produced 800,000 barrels of oil, a rate of about 100,000 barrels per day. The Spindletop gusher, to all intents and purposes, made the three Texas cities of Houston, Beaumont, and Port Arthur. It also started the age of oil for that portion of the United States.

One of the organizations that developed steadily with the rise of oil was Magnolia Petroleum Company. Its chief plant, one of the largest petroleum refineries in the world, is in Beaumont. One Thursday last year it opened another chapter in Texas oil history which may prove to be as important as the discovery of oil in the Spindletop field—the world's first commercial Thermofor catalytic cracking unit. On Thursday, October 7, Frank Fahnestock, chief operator for Socony-Vacuum Oil Company, present owners of the Magnolia plant, pushed the button which automatically closed a huge by-pass valve and sent for the first time the hot vapors of a Mirando crude through the catalytic reactors of a commercial size Thermofor unit.

Technically the process is somewhat similar to all gasoline-petroleum catalytic operations. The chemistry with minor variations in the results can be interpreted in the light of experiences with other catalytic units. The equipment is impressive. At Beaumont the Thermofor installation towers some 200 or more feet over the surrounding flat Texas plain. The equipment, however including the gasoline treatment plant, covers only 1.6 acres. Utilities required for the entire operation top the consumption of the whole town of Beaumont.

THERMOFOR HISTORY

The history of the Thermofor process is tied up with the Houdry technique, the forerunner of most of the present successful catalytic methods. This connection was made possible by Socony-Vacuum Oil Company, one of the first companies to install the fixed-bed Houdry reactors and developers of the moving catalyst bed or Thermofor process. Catalytic processes in the petroleum field are divided into three types: (1) The fixed bed is the Houdry process in which the hot oil vapors pass over the catalyst. This is often called the "static" method, considering the mechanics from the viewpoint of the catalyst. The process is continuous, however, for the oil vapors alternate between several beds of catalyst, in cyclic repetition. The typical cycle for the Houdry units is a 10-minute period in which the oil is in intimate contact with the catalyst, followed by two other periods in which the catalyst is purged with steam, and finally the coke is burned from the bed by typical air burning. (2) The fluid technique (*1*, *4*) employs individual reactors and regenerators, the catalyst being carried along with the oil vapor and regeneration gases from which it is later separated. (3) The Thermofor process is continuous and employs the principle of a moving catalyst. However, the catalyst flows by gravity through the reaction zone, after having been carried by elevators to the top of the reactor and regeneration kiln.

In 1939 Socony-Vacuum engineers developed the Thermofor kiln for burning the carbon out of the clay used in filtering lubricating oil. Previously the clay was cleaned by burning off the carbon in rotary kilns or multiple-hearth burners. This was expensive and wasteful, since the clay was rapidly degraded and had to be replaced at a high rate. The Thermofor kiln did the job much more efficiently. It got its name from the word "thermophore", a device for controlling heat. The kiln was adapted to the TCC process after six commercial clay-burning plants in petroleum refineries had proved their value. In these installations considerable data were obtained on clay flow distribution, heat generation, attrition, diffusion rates in carbon burning, and other engineering values. In 1941 Socony-Vacuum designed and put into operation at their Paulsboro, N. J., refinery a continuous Thermofor catalytic cracking plant with a capacity of 400–500 barrels per day. Over a period of time it was proved that the combination of reactor and kiln could operate continuously, and the pilot-plant on-stream time was better than 95%.

The flow of the materials in the TCC units are shown in Figures 1 and 2. The feed is any vaporizable distillate with an initial boiling point of over 400° F. The first step is heating in the conventional furnace from about 500° to about 850° F. The hot vapors are flashed from a reduced crude in a tar stripper at 15 pounds pressure and then superheated to about 900–950° F. The oil passes to the reactor, which contains a reaction zone about $11^1/_2$ feet in diameter and 30 feet high, enters the bottom, and rises against the descending catalyst. During this passage the gas oil undergoes chemical changes which convert it to aircraft fuel. After catalytic processing, the hydrocarbons pass to a conventional fractionator.

The heart of the system is the reactor. Clay catalyst (as distinguished from synthetic or bead types) enters the top of the reactor through a feed leg, sometimes referred to as the clay leg, which is about 70 feet long and is, in turn, fed by the clay storage hopper surmounting it; the hopper receives catalyst from the top of the regenerated catalyst elevator. This partly explains the height of the TCC units, for the equipment is piled on top as contrasted to the usual refinery practice of spreading over a large area. The reactor operates at a low pressure of 10 to 15 pounds per square inch, and temperatures in the reaction zone remain about 850–950° F. The ratio of catalyst to oil can vary from 1 to 8, depending on design and product desired.

After passing through several distribution pipes at the top of the reactor, the catalyst passes over a series of baffles which bring the oil vapors and clay into intimate contact. At the bottom of the reaction chamber the clay is steam-purged to remove volatiles; then it passes through a depressuring pot to the bottom of the elevator which will bring it to the top of the Thermofor kiln where it is regenerated.

One of the interesting engineering features is that nothing was taken for granted. The unit was not coddled either in design, construction, or operating stages. During the construction of this first commercial unit, a discussion arose as to whether the pressure of the sealing gas could be raised high enough to retard the flow of catalyst through the clay leg. One of the first tests when the unit was put on stream was a deliberate attempt to blow the catalyst entirely out of the leg. Within the limits of safe pressure, it could not be done; and whereas the equipment is designed for low-pressure operation, the possibility of catalyst stoppage owing to such a cause was found to be unlikely. An illuminating fact about the men who worked to bring the idea to a producing stage is the freedom with which they shared knowledge. While Socony-Vacuum was getting the TCC on stream, operators from other petroleum companies who were building Thermofor units came into the plant for training in how to run it.

The number of instruments necessary to control the new plant is remarkably small. Only twelve instruments were needed for a single 10,000 barrel unit, a total for the twin units of twenty-four. The wartime scarcity of instruments during construction had little to do with this feature, for the men in charge state that there is only one instrument they will add to the board when it becomes available. The unit is in no way undercontrolled, as indicated by an emergency which was dealt with in a minimum of time. In changing over the bleed gas on the clay leg from steam to flue gas, the circuit breakers controlling the blowers which supply flue gas opened. The reason was that the circuit breakers were thermostatic and had been set too low for the Texas sun; when the additional load was added to the blower motors, the temperature limits were quickly approached. This failure meant that the petroleum vapors were about to escape through the clay leg, and it was necessary to re-establish the pressure seal with steam. By means of instruments remotely controlling this part of the operation, the differential was again established in a matter of seconds.

CLAY REGENERATION

After passing through the depressuring pot, the clay flows into the bottom of the first clay elevator. The elevator is the bucket type and carries the clay to the top of the structure to the

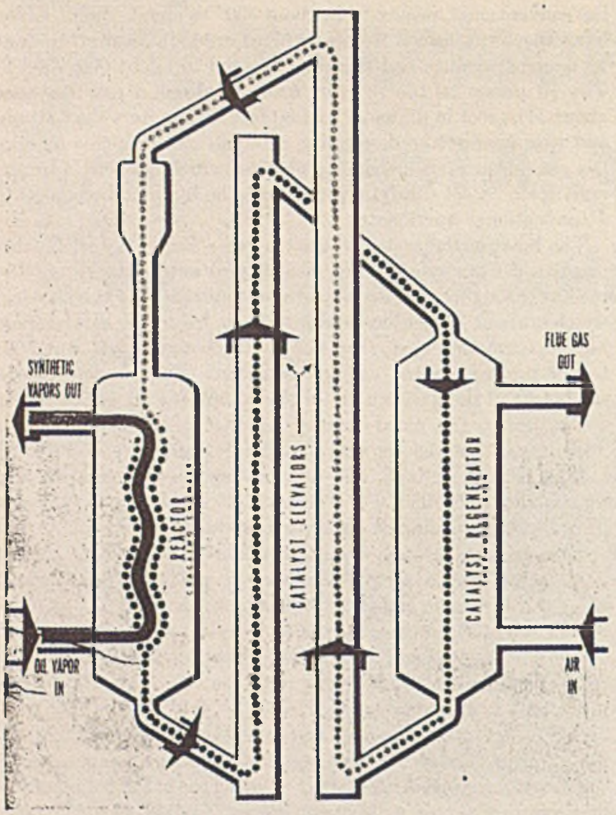


Figure 1. Simplified Flow Diagram of TCC Process

Fouling and cleansing of catalyst are indicated by the change in shading of the pellet.

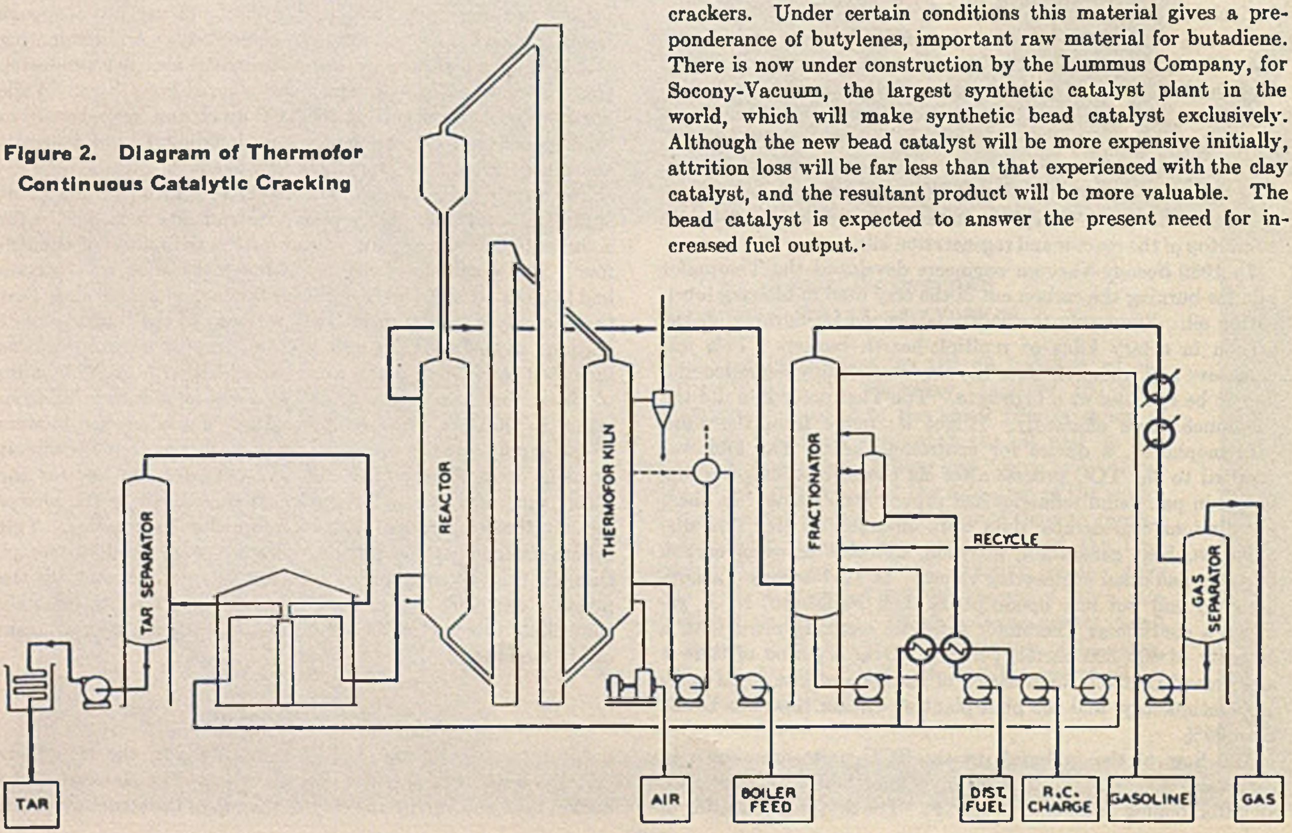
Thermofor kiln. From an engineering standpoint the construction of the elevator is important, for as the clay is picked up from the reaction vessel, its temperature is 850° to 900° F. Operation of bucket elevators at this temperature brought out some real problems, but several developments were made which enable the operation to run smoothly. The elevator is a chain-drive bucket type. To overcome uneven operation, the bottom sprocket is mounted on a walking beam, and the intermittent strain due to the chain's passing over the sprocket wheel is taken up by the motion of the walking beam.

The buckets show no uneven movement in travel. A patented improvement in the bucket conveyor has a twofold advantage: Welded construction is used throughout, and the bucket is suspended on two links instead of one as in conventional designs. The carrying system is driven from the top. In the most recently installed units, one link has been removed from both chains, and the system operates without uneven motion of any kind. Because of the high temperatures encountered in the elevators, the links are made of mild alloys resistant to heat stressing.

In the petroleum world there was considerable speculation about the ability of the elevator to stand continuous operation. Failure of vital bearings and other parts of the moving system was predicted. One trouble was supposed to be high temperatures, another the wear due to attrition of the clay catalyst which is about 6 mesh. Actual data show that the unit at Magnolia has been operating about 92.6% of the time since it started, and when the plant was off stream for routine inspection, no wear could be seen by the engineers. Attrition loss of the catalyst was another predicted weakness. Figures show that consumption of catalyst is less than one fourth pound per barrel of oil charged. In actual cost this is less than a cent per barrel of charge with the catalyst selling at 60 dollars per ton. Original design figures were based upon a loss of 1 pound per barrel, with the expectation that it might be half that.

All TCC plants now utilize the natural clay catalyst similar, except in form, to that originally used in the Houdry process crackers. Under certain conditions this material gives a preponderance of butylenes, important raw material for butadiene. There is now under construction by the Lummus Company, for Socony-Vacuum, the largest synthetic catalyst plant in the world, which will make synthetic bead catalyst exclusively. Although the new bead catalyst will be more expensive initially, attrition loss will be far less than that experienced with the clay catalyst, and the resultant product will be more valuable. The bead catalyst is expected to answer the present need for increased fuel output.

Figure 2. Diagram of Thermofor Continuous Catalytic Cracking



THERMOFOR KILN

The kiln for burning the carbon from the catalyst receives the clay from the elevators. Air, at about 10 inches of water, is directed into the clay, burns the carbon to the products of combustion, and forms flue gas, some of which is used for the differential seal at the top of the reactor. Residual carbon is 0.2–0.5% by weight of catalyst.

Uncontrolled, the temperatures of burning the petroleum coke would become too high; steam-generating cooling coils are provided to give the operator complete mastery over this operation. From these coils the kiln will generate 450 pounds of steam in immense quantities, some 30,000–45,000 pounds per hour for each 10,000-barrel unit. Recycling oil streams will generate 15,000 pounds of 150-pound steam, and 22,000 pounds of 450-pound steam will be developed from the tar stripper bottoms.

Part of the internal construction of the kiln is 4–6 silica–chrome steel although the kiln body is plain carbon steel.

At the bottom of the Thermofor kiln, elevators pick up the regenerated catalyst and lift it to the top of the structure to the feed hopper. From this hopper the clay enters the clay leg feeding the catalytic reactor. In effect the catalyst has passed through a figure 8, traveling from the top of the clay storage to the bottom of the catalyst chamber, back again to the top, and descending through the regeneration kiln to be picked up again and returned to the clay hopper.

Table I. Properties of Fuels from Single Pass and Recycling

	Single Pass	Recycle
Temperature, ° F.	850	860
Gage pressure, lb./sq. in.	10	10
Yields on fresh feed, % by volume		
Motor gasoline, C_4-free	39	56
Catalytic gas oil	48	26
n-Butane	3	2
Isobutane	4	5
n-Butylenes	5	6
Isobutylene	1	2
Total liquid products	100	97
Fuel gas, C_3, and lighter, % by wt.	5	9

Table II. Properties of 7-Pound Reid Vapor Pressure Aviation Gasolines Obtained by Two-Pass TCC with Clay Catalyst

Acid heat, ° F.	10–25
Accelerated-gum test (5 hr.), mg./100 ml.	3–5
Aromatics, % by vol.	20–30
Octane No. (AFD-1C)[a]	
Without tetraethyllead	77–80
+3 ml. TEL per gal.	92–95
+4 ml. TEL per gal.	94–97
100-octane alkylate blend[b] +4 ml. TEL per gal., % by vol. alkylate	22–45

[a] Aviation Fuels Division, CFR Committee.

[b] This gasoline has necessary combustion characteristics to comply with latest aviation gasoline specifications.

Table III. Properties of Typical Aviation Gasolines from TCC Processing of Gas Oils over Clay Catalyst

Source of Gasoline	Naphthenic Gas Oil		Paraffinic Gas Oil		High-Sulfur Gas Oil
Process	Cracking	Treating	Cracking	Treating	Treating
Properties of 7-lb. aviation gasoline					
Gravity, ° A.P.I.	63.1	56.5	67.7	60.9	60.1
Reid vapor pressure, lb.	7.1	7.2	7.0	7.0	6.9
Doctor test	Negative	Negative	Negative	Negative	Negative
Mercaptan sulfur test	Negative	Negative	Negative	Negative	Negative
Acid heat, ° F.	67	12	92	14	35
Bromine No.	37.2	4.6	46.1	6.6	17.9
Sulfur, % by weight	0.026	0.022	0.025	0.021	0.061
Accelerated 5-hr. gum (inhibited and leaded), mg./100 ml.	...	2	...	4	5
Octane No. (AFD-1C)[a]					
Without tetraethyllead	75.8	81.9	74.4	79.4	79.0
Plus 3 ml. TEL per gal.	87.3	95.9	75.1	94.3	91.7
Plus 4 ml. TEL per gal.	89.5	97.7	87.5	96.3	94.0
A.S.T.M. distillation, ° F.					
Initial B.P.	108	106	106	105	107
5% over	131	131	130	129	128
10%	139	140	138	140	136
20%	150	154	150	153	148
30%	164	169	165	165	160
40%	181	188	180	182	180
50%	200	207	198	200	202
60%	216	228	213	223	227
70%	230	246	224	243	250
80%	245	263	239	259	268
90%	264	278	260	277	284
End point	304	302	302	305	320
Recovery, % by volume	98.5	98.0	98.0	98.0	98.5
Loss, % by volume	0.5	1.0	1.2	1.0	0.7

[a] AFD-1C = 1C method, Aviation Fuels Division, CFR Committee.

GASOLINE PROCESSING

Magnolia is one of the largest refineries in the country, and its capacity of 100,000 barrels per day is just the daily amount of crude that the original Lucas gusher spouted in its first days. The installation of the new TCC unit accomplishes the first step in a two-pass treatment of the original charge stock, for it is necessary to process the cracked product further in a Houdry unit to make premium airplane fuel. Instead of constructing new processing plants, Socony-Vacuum engineers made necessary alterations in existing equipment, and the new cracker has been successfully integrated as a going operation in a going plant.

It is feasible to reprocess the hydrocarbon from the one-pass TCC operation through the same or another TCC unit to obtain high-octane fuel, and this type of operation will be followed in practically all other installations; but by utilizing Houdry equipment already available in the Magnolia plant, time and money were saved. The TCC product is fractionated conventionally. Products are a fuel oil meeting No. 2 specifications, a heavy residue which is recycled, and an overhead stream which

Table IV. Properties of Typical Motor Gasolines from TCC Cracking of Gas Oils over Clay Catalyst

	Naphthenic Gas Oil[a]	Paraffinic Gas Oil[b]	High-Sulfur Gas Oil[c]
Properties of 10-lb. motor gasoline			
Gravity, ° A.P.I.	52.7	60.6	55.2
Reid vapor pressure, lb.	9.5	9.6	10.2
Doctor test	Negative	Negative	Positive
Mercaptan sulfur test	Negative	Negative	Negative
Copper-dish gum, mg./100 ml.	10	16	20[d]
Glass-dish gum, mg./100 ml.	2	1	5[d]
Oxygen bomb test, hr.:min.	8:30	12:30	...
Sulfur, % by weight	0.025	0.028	0.106
Octane No.			
CFR motor method (without tetraethyllead)	82.0	76.9	78.6
CFR research method			
Without TEL	92.0	84.1	85.0
With 1 ml. TEL per gal.	96.5	91.9	88.5
With 2 ml. TEL per gal.	98.5	93.7	90.1
With 3 ml. TEL per gal.	99.2	95.1	91.0
A.S.T.M. distillation, ° F.			
Initial B.P.	88	90	93
5% over	110	110	118
10%	125	121	140
20%	156	145	168
30%	198	175	199
40%	237	209	237
50%	267	243	265
60%	294	276	297
70%	322	307	325
80%	346	337	350
90%	369	376	372
End point	410	404	404
Recovery, % by volume	97.5	97.5	97.5
Loss, % by volume	1.3	1.5	1.6

[a] Aniline point, 145° F.

[b] Aniline point, 176° F.

[c] This charge stock had a sulfur content of 1.9% by weight: aniline point, 154° F.

[d] Gum values after inhibiting with 1 part α-naphthol per 5000 parts gasoline.

contains the motor and aviation gasoline. The composition of fuels for single-pass and recycling operations on mid-continent gas oil charge stock when employing clay catalyst are as shown in Table I (*3*). A two-pass operation will yield butylenes equivalent to 8% of the gas oil. Butylene content may be increased by higher temperature operation. Table II gives properties (*3*) of two-pass TCC aviation gasoline prepared from gas oil charge stocks processed over clay catalysts.

Simpson recently revealed (*2*) that improvements were being made in TCC units. One of the most important is solid-bed type TCC reactors which can be operated at space velocities down to one fourth of the present at the same oil rate. Recent catalyst developments have made it possible to design reactors and kilns of high throughput capacity. Another important improvement is the bead catalyst mentioned previously. According to Simpson:

> Bead catalyst is the most important of these developments, and makes possible significant gains in the manufacture of aviation base stocks. With respect to the present aviation-fuel program the substitution of bead for clay catalyst will permit a large increase in plant output or a substantial rise in quality level.
>
> Although bead catalyst produces aviation-base stocks of exceptional quality in conventional multipass operation, its performance in one-pass operations is equally striking. For example, by one-step processing of properly selected charge stocks over bead catalyst, it is possible to produce good quality aviation-base stocks for direct blending in high grade aviation gasolines. This provides considerable flexibility in processing, and may be translated into substantial economic advantages either for wartime or postwar operations.

New developments also make it possible to process a wide variety of petroleum stocks to suitable gasoline using clay catalyst (Tables III and IV).

COSTS AND MATERIALS

For security reasons the total equipment used in the construction of a TCC unit cannot be described. But some indication of the scope of the project can be obtained from the following figures. The tonnage of steel used in the building was over 2000. More than 340,000 pounds of valves and fittings were purchased, well over 300,000 pounds of tubing for heat exchangers had to be used, and approximately $56,000 was paid for pumps. Some 89,000 feet of piping went into this first TCC plant. Although the number of instruments was small, they cost $47,000, and electric motors ran about $14,000. Insulating materials purchased would cover 20,000 square feet, and 186,000 square feet of lumber were used. About 50,000 pounds of nails, bolts, and metal lathe went into the building.

The cost of TCC processing, according to the operators, amounts to about 7 cents per barrel of gas oil charge, and this includes operation, supervision, fuel, steam, power, water, laboratory, and maintenance.

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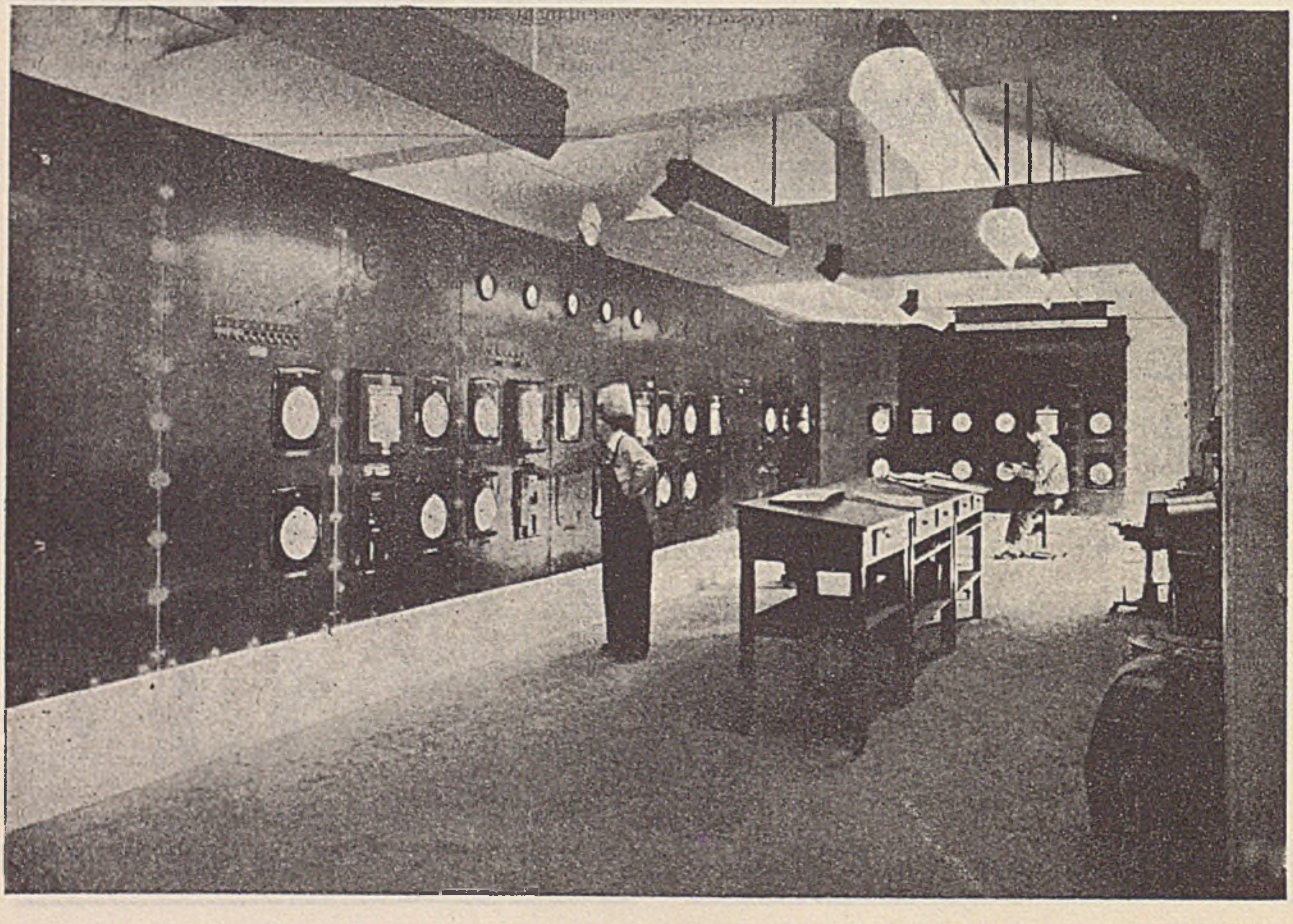
Control Panel of a Thermofor Catalytic Cracking Plant



EFFECT OF MILLING ON PROPERTIES OF *Hevea and Buna Rubbers*

The superior cut-growth resistance of Hevea tread stocks over similar GR-S tread compounds is ascribed in part to the relaxation and lengthening of the natural product when subjected to severe dynamic flexure, as contrasted with the failure of GR-S to relax and lengthen. GR-S is further handicapped by its original shortness. Means other than the use of softeners have been sought to overcome these shortcomings. The behavior of Hevea and some of the synthetic polymers has been studied under prolonged and repeated milling. A method of processing GR-S which lengthens it with resultant improvement in resistance to cut growth and heat embrittlement is described.

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MOST studies of the hysteresis and heat build-up properties of rubber polymers have been carried out at relatively low strains, corresponding to not more than 100%. The data have shown that GR-S has more hysteresis than Hevea. Using repeated extensions to fixed loads, Rohde (*2*) in 1939 showed that for tensile stresses above 500 pounds per square inch (corresponding to about 150% stretch on the first extension) Buna S showed less hysteresis than natural rubber. By generating the hysteresis loops to fixed extension rather than to fixed loads (Figure 1) it was recently shown (*1*) that not only was there a reversal in relative hysteresis rating (Figure 2) but at the higher elongations both the extension and retraction curves of GR-S lie above those of the natural rubber. Thus at the higher elongations GR-S not only has less hysteresis but after preworking is stiffer than natural rubber.

This fact appeared to be significant in the problem of cut-growth failures of GR-S tires. In a rolling tire the rubber is strained while making contact with the road, is held for a short time in this strained position, and is then released as it leaves the road. This occurs during about one sixth of the revolution. During the remaining five sixths of the revolution the rubber is allowed to recover. At the apex of a growing cut this strain reaches breaking elongation. As the apex of a growing cut nears an element of tread rubber in its path, that element is subjected to a series of stress-strain cycles or hysteresis loops of progressively greater severity.

A natural rubber and a GR-S tread compound were therefore subjected to a succession of extensions and retractions, and the effect on modulus, breaking elongation, and tensile strength was determined. Using a tensile testing machine operating at standard speed (jaw separation of about 20 inches per minute), dumbbell test pieces were stretched ten times to 100% *E*, then ten times to 200%, up to ten times ($N \times 100\%\ E$). (The limiting value for *N* was determined empirically in each case.) They were then immediately broken and the stress-strain curves generated in the conventional manner. The results are shown in Figure 3 where the values of $N \times 100\%$ are shown in the circles on the curves of the preworked samples. It is seen that natural rubber progressively increases in breaking elongation (from 700 to 900%). Its tensile strength, although declining, always remains higher than that of GR-S. On the other hand, GR-S gives no evidence of such relaxation or lengthening.

This relaxation failure in the case of GR-S has an important bearing on the forces which operate to extend a cut. The "preworked" modulus values correspond closely to equilibrium stresses. The following comparative figures are taken from Figure 3:

Max. Cyclic Preworking	Modulus, Lb./Sq. In.					
	300%		500%		600%	
	Hevea	GR-S	Hevea	GR-S	Hevea	GR-S
300%	450	500	1750	1600	2500	2025
500%	75	100	750	900	1600	1950

When the samples were preworked to low elongations (up to 300%), the more plastic properties of GR-S showed up in the form of prevailingly lower modulus values. But when the preworking was carried to high strains, such as those encountered in the path of an advancing or growing cut, Hevea relaxed and developed the lower retractive stresses. Despite its lower tensile strength, GR-S retained higher equilibrium modulus values.

The relaxation or lengthening of cured Hevea tread stocks through repeated working at high extensions may be regarded as analogous to oxidative scission or breakdown. This phenomenon is difficult if not impossible of attainment in the case of vulcanized GR-S, where the prevailing tendency is a shortening or hardening due to gel or cross-linked structure development. It was therefore decided to approach the problem from a different angle. A study of milling conditions was decided on in the hope that suitable conditions of mastication, with carefully controlled temperatures, might result in a softening or lengthening of the GR-S tread stock due to one or more of the following factors:

1. Breakdown of the cross-linked or gel structure itself.
2. Deflocculation of the carbon black, resulting in lowered modulus, increased breaking elongation, together with increased tensile strength.
3. More perfect disposition or lodgment of the carbon particles as a continuous-phase enveloping and bonding the discrete polymer units, resulting in improved reinforcement coupled with higher subpermanent set.

The effect of milling technique and procedure was the first factor investigated. At conventional temperatures (130° F. water circulating continuously), the initial series of comparative studies between Hevea and some synthetics are summarized.

REMILLING AT NORMAL TEMPERATURES

The quality of a rubber compound depends not only on the kind and particle size of the reinforcing pigment selected but also on the degree of dispersion of the pigment. The importance of proper milling and of correct order of mixing has been emphasized for many years.

Carbon blacks in general, and the finer or channel carbons in particular, require careful attention in the mill room in order to secure maximum reinforcement. Optimum dispersion is not easily obtained and is difficult to evaluate. The degree of dispersion is frequently judged by the gloss and texture of cut or torn surfaces, directly or with the microscope. These methods are far from satisfactory since for carbon black, "true dispersion of carbon black (in rubber) begins where the microscope leaves off."

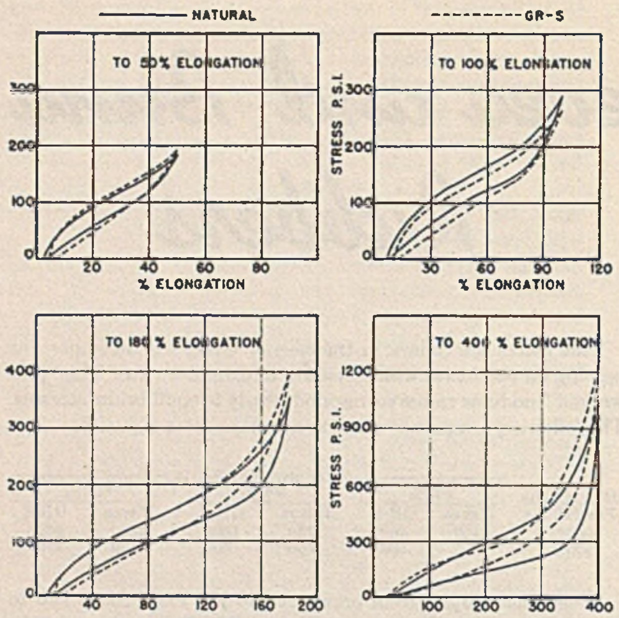

Figure 1. Hysteresis, Loops for Natural Rubber and GR-S Treads (Tenth Loop)

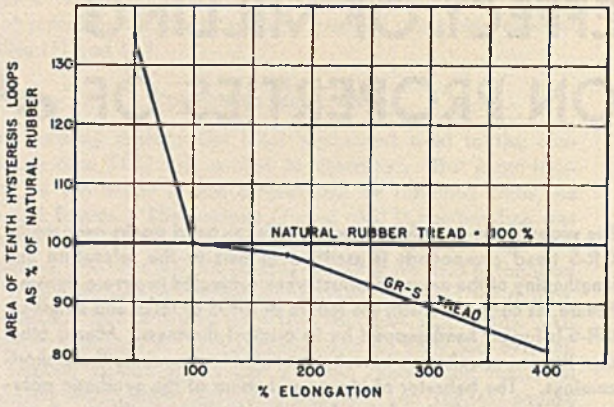

Figure 2. Effect of Elongation on Hysteresis of GR-S and Natural Rubber

Tensile Strength and Electrical Resistivity. As a control over the proper amount of milling or processing of natural rubber tire treads, it has been found in these laboratories that the electrical resistivity of either the raw or cured stock is a quick and useful test. As illustrated in Figure 4, the tensile strength of a tread stock passes through a maximum and the electrical resistivity through a minimum as time of milling is increased. Three stages may be recognized:

Region A. In the early or mixing stage, free or unreinforced rubber disappears and tensile increases. Large aggregates of carbon simultaneously disappear, conducting flocculates or chains of carbon multiply, and electrical resistivity (log R) eventually reaches a minimum.

Region B. The second stage of milling can be described as the bonding stage where the carbon is further distributed or lodged within the rubber phase. There is some disaggregation of the rubber which increases its surface and so increases log R slightly. On balance, reinforcement of the rubber, through more complete lodgment of the carbon, dominates over breakdown of the rubber itself and tensile continues to rise.

Region C. In the overmilling stage, disaggregation of the rubber takes over, tensile falls off, and, through the development of considerable new rubber surface, electrical resistivity rises sharply.

Direct-current resistivity thus affords a clue to optimum processing of a natural rubber tread compound. It has repeatedly been found useful as a control for the factory processing of such compounds.

Effect of Repeated Remilling. Figure 5 compares natural rubber with Perbunan (imported), Buna S (GR-S), amd Butyl B when similarly processed on a 6 × 12 inch laboratory mill. In this case the first milling of the compounds produced a normal laboratory mix, the time varying for the various polymers and being particularly prolonged for Perbunan. This initial mixing was followed by alternate 24-hour rest periods and 5-minute remillings, with 130° F. water circulating through the rolls; i.e., no special effort was made to keep down roll or stock temperatures.

Natural Rubber. Up to one remilling tensile strength is, in general, maintained without sensible loss in modulus or hardness and with little or no rise in elongation. It seems best milled when log R has reached a minimum.

Perbunan. Best tensiles are reached only after two to four remillings. This has also noticeably increased elongation. Modulus and hardness have sensibly declined. At the end of the first remilling, log R is already rising rapidly and so provides no clue to optimum dispersion. Milling time is dictated by practical considerations. If high tensile and elongation are desired regardless of cost, extensive milling and remilling are indicated. Where modulus is to be maintained at its maximum even at the sacrifice of some tensile, shorter milling time is indicated.

Buna S. The picture is similar to natural rubber only in respect to tensile strength; i.e., tensile reaches its maximum at about one remilling. Modulus and elongation show similar and distinctive trends in that they also have maxima at about one remilling. This falling off in elongation as Buna S is overmilled is of prime importance because of the shortness and tenderness of Buna S stocks under dynamic conditions. As with Perbunan,

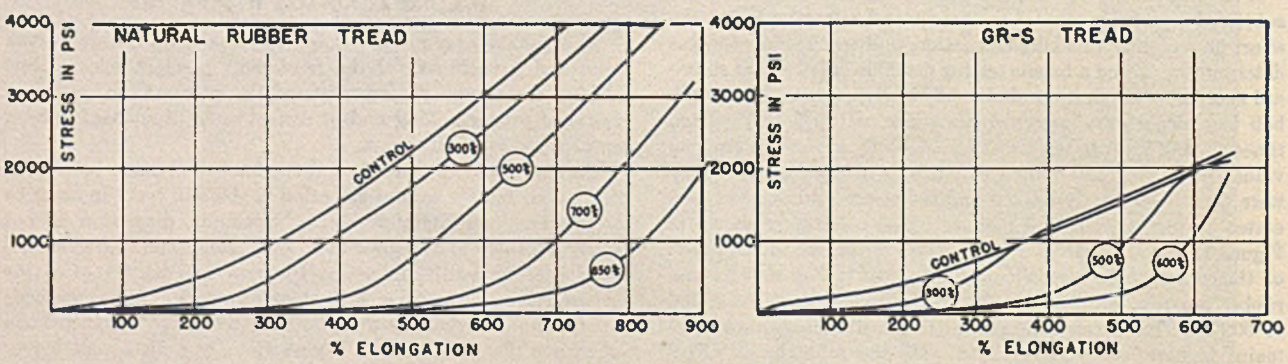

Figure 3. Effect of Progressive Flexing on Stress-Strain Properties of Natural Rubber and GR-S Treads

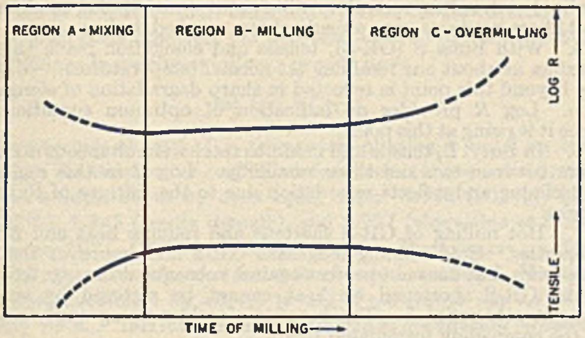

Figure 4. Progress of Log *R* and Tensile with Time of Milling (Schematic)

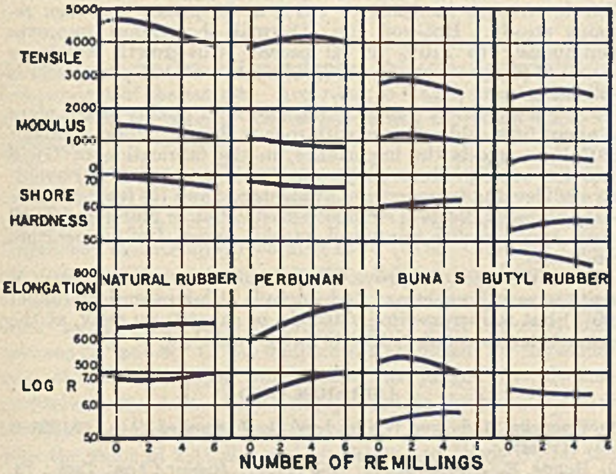

Figure 5. Effect of Remilling on Tread Stocks

log *R* rises continuously and so affords no clue to optimum physical properties as processing proceeds. The possibility of log *R* minima for Buna S and Perbunan is, however, not entirely precluded since in this work undermillings were not carried to the extremes necessary to establish this point.

Butyl. The picture appears to be more similar to that of Buna S than to either of the other two polymers. Tensile and modulus reach a simultaneous maximum as in Buna S. This indicates that in Butyl, as in Buna S, maximum tensile can be, and probably should be, developed since it involves no penalty in modulus. However, with Butyl this maximum occurred between two and three remillings, compared with one for Buna S. The shortening of Butyl elongation with remilling is less than that shown for Buna S, and what loss occurs may be ignored against its background of excess. Log *R*, on the other hand, shows a slow but steady downward trend which may correspond to the left, or declining, arm of "natural rubber–carbon black" trends. This is rendered plausible by the softness of Butyl stocks, which would be expected to lengthen this declining left arm of the resistivity *vs.* milling trend.

COMPARISON OF HOT AND COLD MILLINGS

Of particular interest in the preceding comparative study was the distinctive and serious decrease in elongation of GR-S on repeated milling. Because of the large surface area of reinforcing carbon blacks, a need appeared for severe milling to assure adequate dispersion or carbon surface development in the GR-S, particularly since it is handicapped with low gum strength.

The temperature build-up resulting from ordinary high-viscosity milling techniques is undesirable for GR-S because of its shortening tendency. Gordon plastication or other hot milling of raw GR-S effects an apparent improvement in the dispersion of the carbon black introduced after hot plastication, but this improvement is at the expense of increased modulus, decreased elongation, and impaired cut-growth resistance. A study of various combinations of temperature and milling conditions was indicated.

Raw GR-S was hot-plasticized by 30-minute milling in a laboratory Banbury, with the rotors and case heated to 270° F. Other lots of the same polymer were cold-refined by passing through a tight 6 × 12 inch mill with rolls at 80° F.; the sheeted rubber was then festooned to facilitate cooling until the entire batch passed through the rolls. This was repeated twenty times. The results are summarized in Table I.

Conclusions to be drawn from Table I are: (1) Hot plasticizing of GR-S shortens the rubber and detracts from heat and flex resistance. (2) Cold refining of GR-S lengthens the rubber and improves heat and flex resistance. (3) Cold refining does not protect GR-S from subsequent hot processing. (4) GR-S shortened by hot plasticizing is not restored by subsequent cold refining. (5) The benefits of cold refining apply also to the completely formulated tread compound.

These results invited an intensive investigation of the cold-refining approach. A preliminary series involving 20, 30, and 40 passes through the cold mill had not developed an optimum; the improvement in flex resistance and hot-iron life continued. Obviously GR-S, unlike natural rubber, was being fundamentally changed for the better in chemical or colloidal structure by the strenuous cold mastication. Disaggregation was being confined to the injurious gel and not extended to the long primary chains since tensile strength as well as breaking elongation had improved. Either for better vulcanization, better reinforcement, or both, the structural deformities of the copolymer had apparently been lessened.

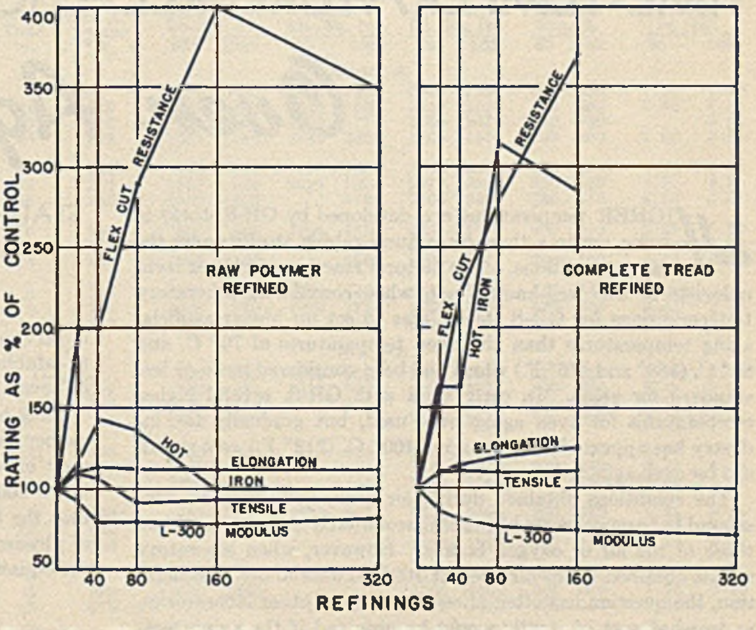

Figure 6. Effect of Cold Refining of Raw GR-S and of GR-S Tread Compound on Cut Growth and Thermal Shortening

Table I. Effect of Hot and Cold Processing on GR-S

Treatment	Physical Properties as % of Normal Lab. Milled Control				
	Modulus at 300%	Tensile at Break	Elongation at Break	Flex Cut Resistance	Hot-Iron Life
Raw GR-S hot-plasticized, 30 min., 270° F.	161	82	69	12	7
Raw GR-S cold-refined 20 passes, 80° F. mill	96	105	107	247	350
Raw GR-S cold-refined, then hot-plasticized	134	82	73	23	5
Raw GR-S hot-plasticized, then cold-refined	127	78	75	47	4
Complete tread compound cold-refined	85	106	111	310	111

EXTREME COLD REFINING

The raw polymer and the complete tread compound were refined on cold laboratory rolls for a succession of passes up to 320. The results are shown in Figure 6. The curves illustrate the progressive lengthening effect of repeated cold refining, whether of GR-S or of the complete tread compound. Best all-round quality developed at the equivalent of about 50 passes of refining on the laboratory mill. Mill roll temperature was kept at 80° F., corresponding to a stock temperature of about 120° F.

SUMMARY AND CONCLUSIONS

1. The superior cut-growth resistance of Hevea tread stock is partly ascribed to its pronounced relaxation or lengthening when subjected to repeated severe cyclic extensions. Under such conditions the breaking elongation increases from 700 to 900%. GR-S under similar treatment fails to develop any lengthening.

2. As a consequence of this failure to lengthen under repeated severe strains, such as those antecedent to cut-growth failure, GR-S exhibits higher modulus (i.e., at 500 or 600% elongation) or higher retractive forces than does Hevea. This also promotes cut growth.

3. In Hevea, progressive milling (at normal temperature) of tread stocks tends to develop a tensile maximum. At this point of optimum milling d.c. resistivity reaches a minimum. Overmilling, characterized by a decrease in tensile, shows a sharp rise in log *R*.

4. With Perbunan, highest tensiles and elongations are realized only after several remillings, at which point modulus and Shore hardness have already shown marked decline.

5. With Buna S (GR-S), tensile and elongation reach their maxima at about one remilling (at normal temperatures). Milling beyond this point is reflected in sharp degradation of elongation. Log *R* provides no indication of optimum conditions, since it is rising at this point.

6. In Butyl B, tensile and modulus reach a simultaneous maximum between two and three remillings. Log *R* in this region is declining and reflects retardation due to the softness of Butyl stocks.

7. Hot milling of GR-S shortens and reduces heat and flex properties. Cold refining lengthens GR-S and improves these properties, but does not protect against subsequent damage from heat. GR-S shortened by heat cannot be restored by subsequent cold refining. The benefits of cold refining apply also to the completely formulated tread.

8. Extreme development of the cold-refining technique produces the following results (based on treatment of complete tread mixing): Modulus declines continuously to less than 50% of control. Elongation increases continuously to 125% of control. Tensile strength increases to 110% at 20 passes and then remains steady. Hot-iron life (thermal shortening) improves continuously to 310% at 80 passes. Cut-growth resistance improves progressively to 370% of control at 160 passes and is still rising.

9. The fact that such striking all-round quality takes place at about fifty cold refinings with rolls at 80° F. (stock at about 120° F.) suggests the importance, in the fabrication of GR-S tires and other products subject to dynamic usage, of (*a*) avoidance of elevated temperatures at all stages, and (*b*) further study of the remedial effects of strenuous mastication or refining of GR-S tread type, carbon-reinforced stocks under low-temperature conditions.

10. Attempts to improve GR-S should be oriented in two opposite senses: to decrease its hysteresis at low extensions (under 100%) but to increase its hysteresis, or capacity to relax, at the higher extensions antecedent to cut growth.

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TIME-TEMPERATURE RELATIONS IN *Oven Aging of GR-S*

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HIGHER temperatures are developed by GR-S stocks in some services than by natural rubber stocks under the same conditions. The natural reaction of rubber technologists to this well-known fact, when considering laboratory test conditions for GR-S stocks, was to set up higher artificial aging temperatures than the oven temperatures of 70° C. and 80° C. (158° and 176° F.) which had been considered more or less standard for years. In early work with GR-S, several higher temperatures for oven aging were used, but gradually the industry has appeared to agree upon 100° C. (212° F.) as a standard for oven aging tests.

The conditions obtained during air oven aging may be considered to be more nearly like those encountered in tire service than those of the air or oxygen bombs. However, when laboratory results obtained in the air oven at 100° C. were under consideration, the question has often arisen, in this and other laboratories, as to what sort of results would be obtained if the aging temperature was more nearly that to be encountered by the stock in service. The object of the work described in this paper was to establish temperature coefficients for the effects of oven aging on several commonly measured properties of GR-S stocks.

Time-temperature relations for aging and oxidation of natural rubber have been determined by several investigators, although they have generally been based on experimental temperatures below 100° C. Nagai (*5*), working at 55° to 100° C., showed that the time required to reach a definite point of deterioration of physical properties at any temperature could be expressed by the equation,

$$t = ae^{bT}$$

where t is the time, T is the temperature, a and b are constants

Results of laboratory stress-strain and dynamic cut-growth tests show that, in all cases observed, the time-temperature relations for a definite change in properties follow a general form:

$$\log t = kT + C$$

where t = time of aging, T = temperature of aging, k and C are constants. The temperature coefficients for changes in stress-strain properties brought about by oven aging were: 1.972 (200%), 2.00 (300%), 1.945 (tensile strength), and 1.957 (elongation at break) for every 10° C. (18° F.) rise in temperature. These figures are close to 2.0, the value observed for most chemical reactions. The temperature coefficient for change in rate of cut growth was 1.715 for every 10° C. This lower value is attributed to the effect of hysteresis and/or relaxation during the test. After aging, the properties of overcured samples were superior to those of optimum cured samples.

★

depending on the type of sample, and the aging temperature is independent of the sample. According to Nagai, overcure causes properties to deteriorate sooner but is not the direct cause of poor aging.

The temperature coefficient of a reaction is generally expressed as the factor by which the rate at any temperature must be multiplied to give the rate at a 10° C. (18° F.) higher temperature. Ingmanson and Kemp (*2*) working at 70° to 85° C., found a temperature coefficient of approximately 2.0 for the deterioration of physical properties of natural rubber stocks during oxygen bomb aging. The same investigators (*3*) later reported that between 60° and 80° C. the temperature coefficient for the oxidation of natural rubber vulcanizates, as judged by physical properties, was 2.38. This corresponded to doubling the rate for each 8° C. rise in temperature. This coefficient agrees well with the value of 2.41 reported by Bierer and Davis (*1*) for the range 60° to 75° C. Williams and Neal (*9*) reported that between 0° and 100° C. the temperature coefficient of oxidation (oxygen absorption) of natural rubber stocks was 2 for a 7° to 10° C. rise in temperature. Nagai's data (*5*), upon analysis by the present authors, gave a value of 2.62 for the temperature coefficients of stocks ranging in sulfur content from 2 to 10%, based on the rubber.

Juve and Garvey (*4*) showed that the rate of change of stress-strain properties of GR-S stocks was approximately doubled for each 10° C. rise in aging temperatures. These investigators also pointed out that the effect of aging on the overcure of GR-S stocks was less than on the normal or optimum cure. In this respect the effect on GR-S stocks was different from that on natural rubber stocks which generally show poorer aging properties in the overcure. Other scattered references to the time-temperature relations in aging of GR-S stocks have been observed. However, no organized effort to establish aging temperature coefficients other than the above has been published.

STOCKS AND TEST CONDITIONS

In order to determine the effect of aging time and temperature on normal- and high-sulfur GR-S stocks having the same rates of cure, two tread type stocks containing 45 parts of EPC black were used. Stock A contained 1.7 parts of sulfur and 1.2 parts

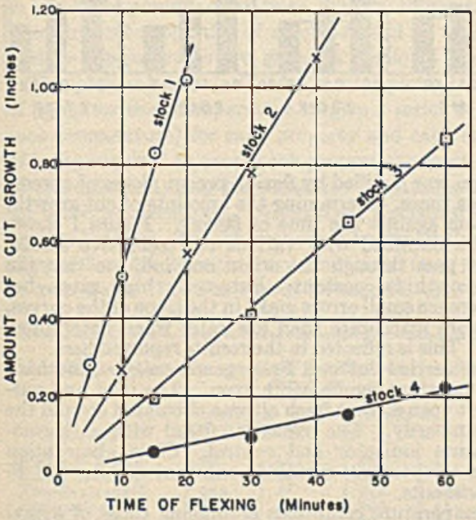


Figure 1. Cut Growth vs. Flexing Time

Table I. Formulas and Original Properties of Stocks Used in Aging Tests

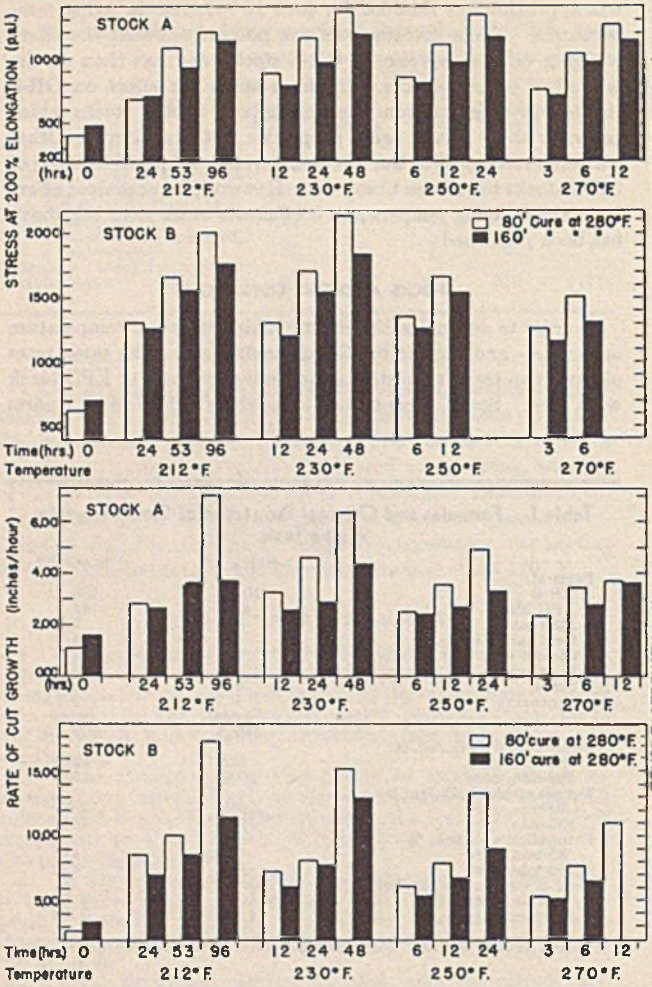
	Stock A[a]	Stock B[a]
Parts of:		
GR-S	100	100
EPC black	45	45
Pine tar	2.6	2.6
Coal tar softener	4.0	4.0
Stearic acid	2.5	2.5
Zinc oxide	2.4	2.4
Sulfur	1.7	2.5
Santocure	1.2	0.75
	159.4	159.75
Stress at 300%, lb./sq. in.		
80-min. cure	825	1250
160-min. cure	1000	1525
Tensile strength, lb./sq. in.		
80-min. cure	2950	2800
160-min. cure	2850	2650
Elongation at break, %		
80-min. cure	590	480
160-min. cure	520	420
Rate of cut growth, in./hr.		
80-min. cure	1.10	2.70
160-min. cure	1.60	3.35

[a] Cured at 280° F. (138° C.); optimum cure, 80 minutes.

Table II. Physical Properties of Stocks A and B after Aging at Different Temperatures

Aging Time, hr.	Aging Temp., ° F.	Stress at 200%, Lb./Sq. In. 80[a]	160[a]	Stress at 300%, Lb./Sq. In. 80	160	Tensile, Lb./Sq. In. 80	160	Ultimate Elongation, % 80	160	Rate of Cut Growth, In./Hr. 80	160
					Stock A						
Original		400	475	825	1000	2950	2850	590	520	1.10	1.60
24	212	775	800	1525	1500	2450	2550	400	380	2.82	2.63
53	212	1075	925	1900	1775	1900	2375	300	380	...	3.62
96	212	1200	1125	2100	2025	2100	2550	300	360	7.02	3.69
12	230	875	775	1675	1500	2575	2575	400	420	3.24	2.55
24	230	1150	950	2025	1800	2275	2300	330	350	4.61	2.85
48	230	1350	1175	...	2125	2100	2400	280	340	6.35	4.34
6	250	850	800	1700	1550	2650	2575	400	410	2.51	2.38
12	250	1100	950	2075	1825	2550	2375	350	360	3.58	2.68
24	250	1325	1150	...	2075	2100	2075	280	300	4.93	3.27
3	270	750	700	1525	1475	2550	2725	410	440	2.36	....
6	270	1025	950	2000	1725	2225	2400	320	360	3.44	2.75
12	270	1250	1125	...	2000	2000	2200	280	320	3.69	3.61
					Stock B						
Original		625	700	1250	1525	2800	2650	480	420	2.70	3.35
24	212	1300	1250	2325	2225	2325	2225	300	300	8.59	7.01
53	212	1650	1550	...	...	2150	2200	240	260	10.12	8.60
96	212	2000	1750	...	...	2150	2050	220	220	17.40	11.49
12	230	1300	1200	...	2250	1850	2450	240	320	7.30	7.19
24	230	1700	1525	...	...	2150	1950	240	240	8.22	7.82
48	230	2125	1825	...	...	2125	1900	200	200	15.28	12.97
6	250	1350	1250	2250	2275	2250	2400	300	320	6.21	5.24
12	250	1650	1525	...	...	1950	2025	230	250	7.90	6.72
24	250	...	...	...	...	1850	1625	180	180	13.45	9.19
3	270	1250	1150	2100	2075	2175	2200	300	320	5.40	5.3.
6	270	1500	1300	...	...	1500	1850	200	260	7.75	6.52
12	270	...	...	...	...	1400	1450	160	180	11.05	...7

[a] Minutes of cure at 280° F.



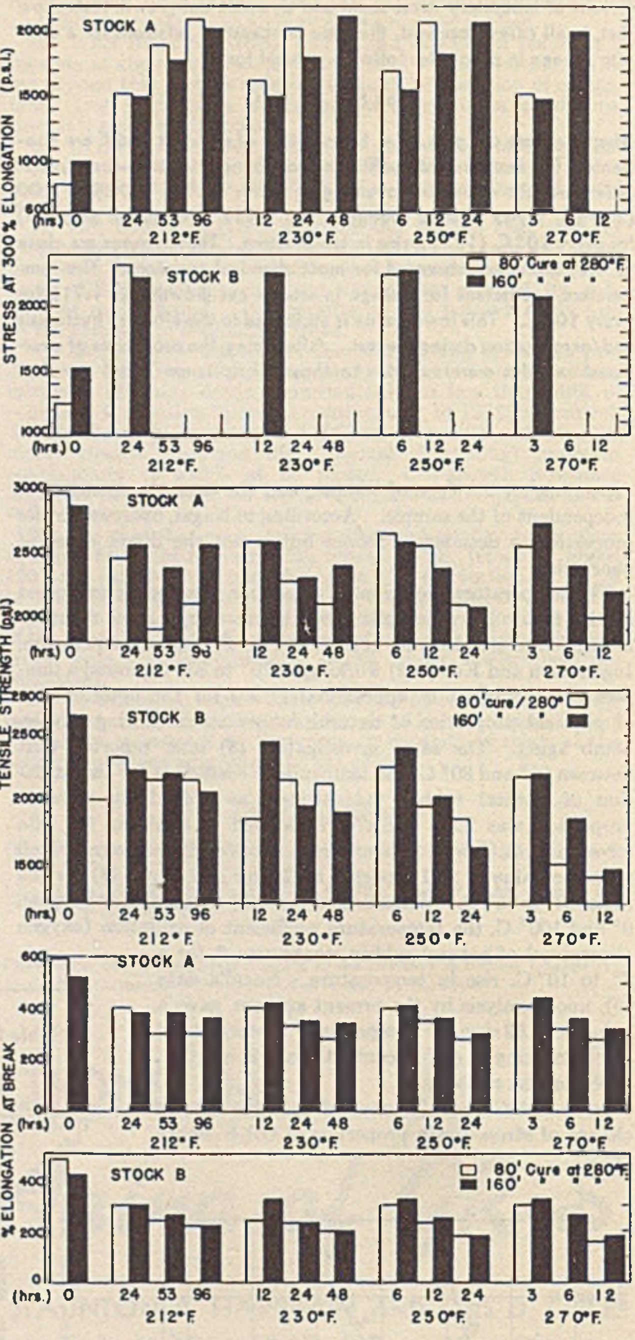


Figure 2. Effect of Oven Aging Conditions on Physical Properties of Stocks A and B, Cured at Various Times and Temperatures

of Santocure; stock B contained 2.5 parts of sulfur and 0.75 part of Santocure. All loadings were based on 100 parts of GR-S. The other ingredients (softeners, activators, etc.) were the same for the two stocks. The formulas and original physical properties are shown in Table I. Although their rates of cure were approximately the same, high-sulfur stock B was somewhat stiffer as judged by modulus (stress at 300% elongation) and elongation. Two cures, the optimum and 100% overcure (80 and 160 minutes at 280° F., respectively) were studied. The overcure was included in order to compare its effect on the various properties as contrasted with high temperature aging.

The properties studied were stress at 200 and 300% elongation, tensile strength, elongation at break, and rate of cut growth. The stress-strain properties were determined in the conventional manner, using dumbbell-shaped test pieces and a Scott recording rubber-tensile testing machine. The rate of cut growth was determined by the twelve-station groove cracking machine described by Prettyman (7). Four pieces were used for each cut-growth test. They were precut approximately 0.20 inch in the center of the groove and measured to the nearest 0.01 inch before testing. The *A* setting was used, which allowed the test pieces to flex through a cycle of 43% compression and 21.5% tension. After testing, the length of the cut was again measured and the amount of growth was determined. To put all results on a comparable basis, the pieces were not allowed to break, but were measured and the time was recorded when the cut had grown to approximately four fifths of their length. The rates were calculated and expressed in inches per hour.

The calculation was justified by flexing precut pieces of several stocks for various times, determining the amounts of cut growth, and plotting them against the time of flexing. Figure 1 shows the straight lines obtained with various representative stocks. All these curves pass through the origin and indicate that the rate of crack growth is constant. Extremely high rates, because of the difference small errors make in the slope of the curves, are obviously more inaccurate than low rates when determined in this manner. This is reflected in the results reported here.

The aging was carried out in a Freas precision-type, mechanical-convection, constant-temperature oven. The inlet and outlet ports were left open so that fresh air was circulated around the test pieces continuously. The oven was fitted with a thermocouple temperature indicator and control. Close observation showed that the temperature remained constant within ±1° F. during the experiments.

A range of temperature conditions embracing those of actual service was chosen in order to establish aging temperature coefficients in that range: 0, 24, 53, and 96 hours at 212° F. (100° C.)

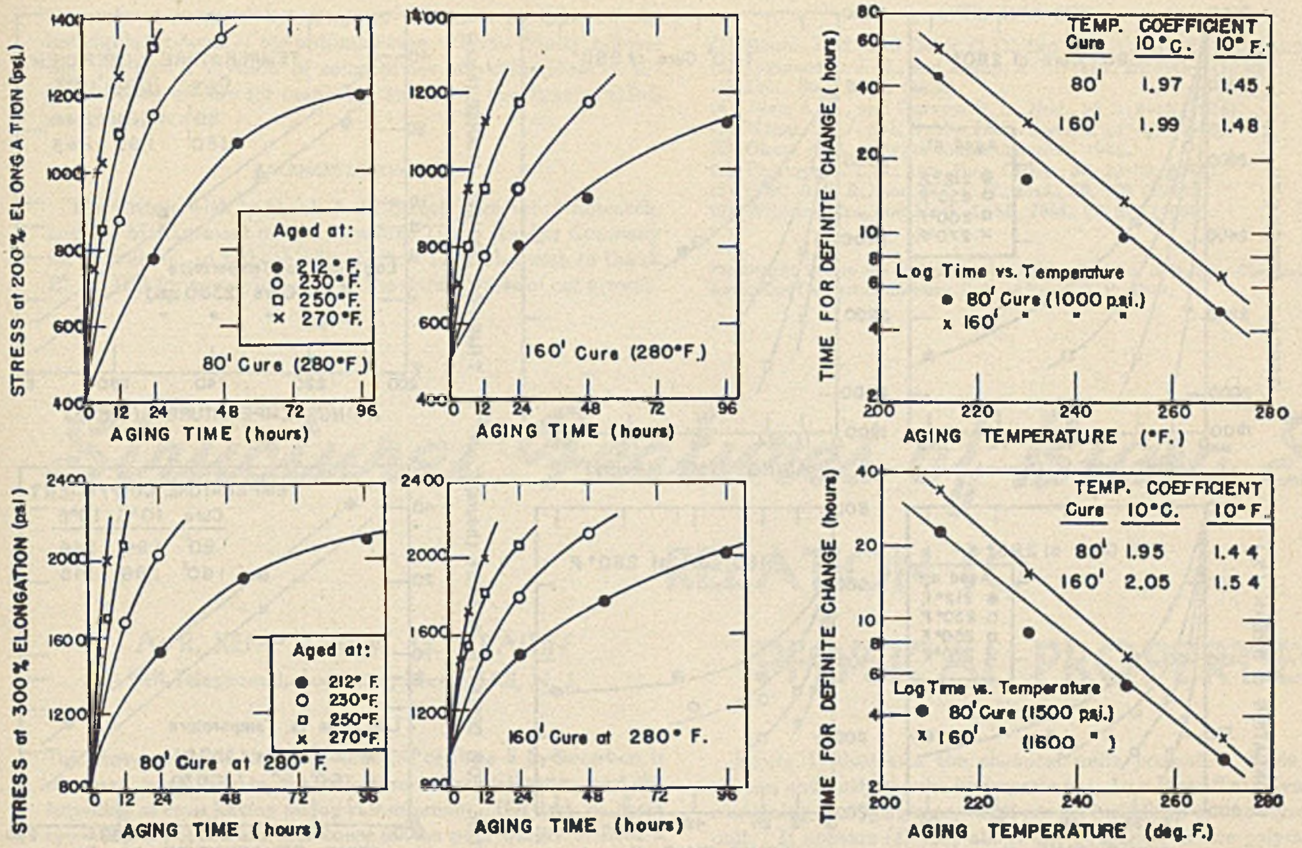


Figure 3. Curves Obtained from Data of Table II on Stress at 200 and 300% Elongation, for Stock A

(through an error, the 48-hour period was allowed to extend to 53 hours); 0, 12, 24, and 48 hours at 230° F. (110° C.); 0, 6, 12, and 24 hours at 250° F. (121° C.); and 0, 3, 6, and 12 hours at 270° F. (132° C.).

PLOTTING THE DATA OBTAINED

The test pieces were arranged in the oven so that the air could circulate around them freely. Test pieces designated for aging at one temperature were placed in the oven, and a sufficient number for the tests required were removed at the end of each aging period. All physical testing was done at one time in order to eliminate possible variations due to different operators, etc. The physical properties of stocks A and B after aging at the various temperatures are given in Table II and Figure 2.

The physical data in Table II were plotted against the time of aging for each temperature to give a series of curves (one for each temperature) for each property and each cure. The times of aging required to cause each property to reach a definite value at the different aging temperatures were taken from the curves for those temperatures. When these temperatures were plotted against log time, straight lines could be drawn through the points. Figures 3 and 4 show the curves obtained from the data on stock A from Table II. The curves for stock B take the same general form as those for A; the curves for stress at 300% elongation for stock B could not be drawn because of lack of data in Table II.

Table III. Aging Temperature Coefficients for Physical Properties of GR-S Stocks

Property	Stock A		Stock B		Average	
	10° C.	10° F.	10° C.	10° F.	10° C.	10° F.
Stress at 200%	1.98	1.465	1.965	1.44	1.972	1.452
Stress at 300%	2.00	1.49	...	...	2.00	1.49
Tensile strength	1.945	1.42	1.945	1.445	1.945	1.432
Elongation	1.95	1.445	1.965	1.45	1.957	1.447
Cut growth	1.73	1.36	1.70	1.34	1.715	1.35

The average aging temperature coefficients for the properties of both stocks were determined from the log time *vs.* temperature curves. The values of these average coefficients are summarized in Table III. For convenience the values are given for 10° F. also.

DISCUSSION OF RESULTS

These results show that the general aging time-temperature relations reported for natural rubber for lower temperatures appear to hold for GR-S in the temperature range 212° to 270° F. (100° to 132° C.). The values of the aging temperature coefficients agree with those previously reported for GR-S, but are somewhat lower than those reported for natural rubber.

All chemical reactions approximately double their rate for each 10° C. (18° F.) rise in temperature. In other words, their temperature coefficient is approximately 2.0. Thus, the coefficients in Table III for the change in stress, tensile strength, and elongation with change in aging temperature appear to be those of a chemical reaction or of several simultaneous reactions taking place during aging.

The nature of the changes in the stress-strain properties point to at least two different types of reaction. The stiffening and reduction in elongation may be attributed to the formation of cross linkages between molecules, or the setting up of a three-dimensional network structure. This may be induced by oxidation, although it can be shown to take place in the absence of atmospheric oxygen (*8*). The absence of atmospheric oxygen, however, does not preclude the presence of peroxides in the stock which could induce cross-linking polymerization reactions.

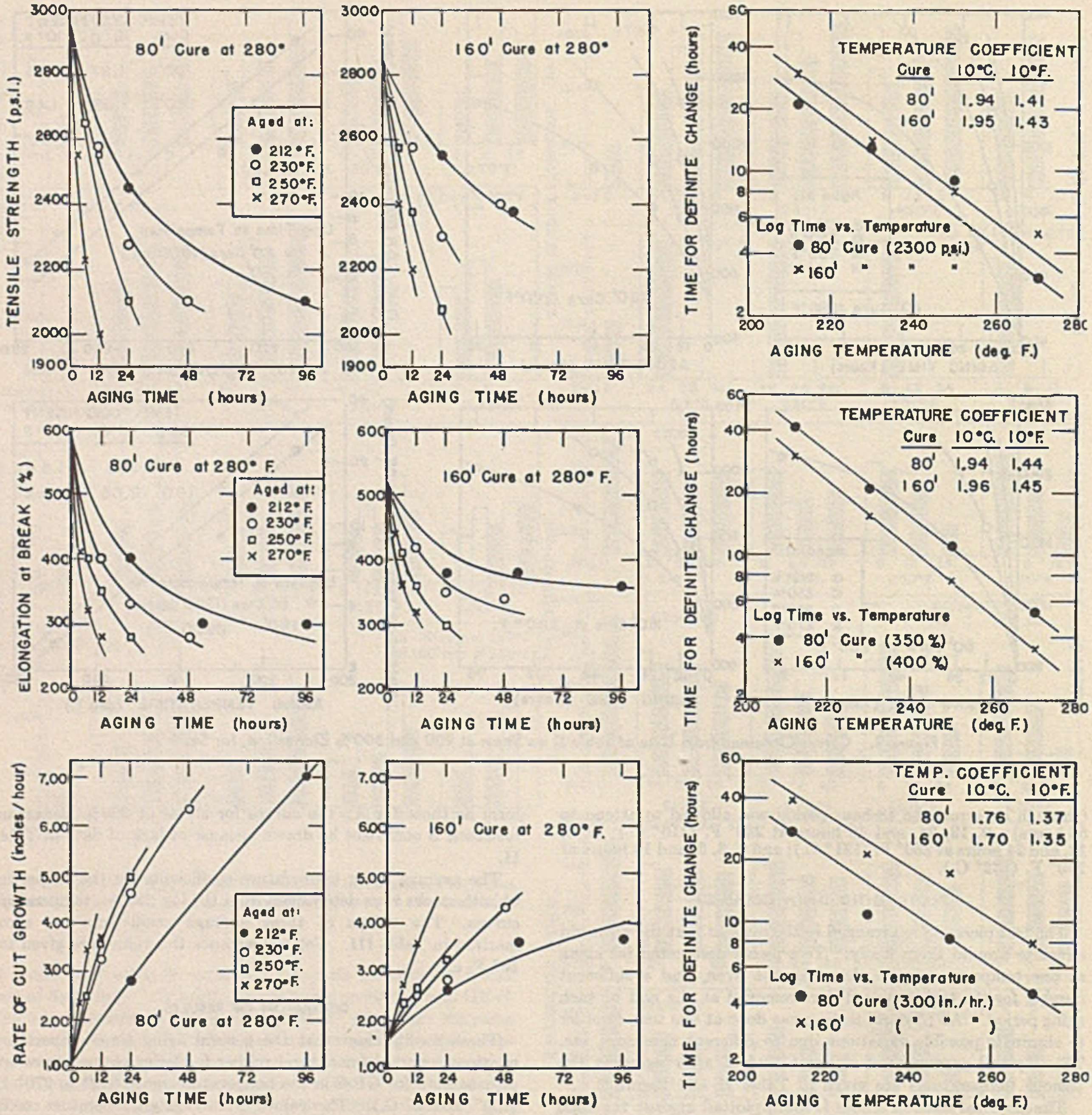


Figure 4. Curves Obtained from Data of Table II on Tensile Strength, Elongation at Break, and Cut Growth, for Stock A

The reduction in tensile strength is probably caused by oxidative breakdown of the long-chain hydrocarbon molecule.

The definitely lower temperature coefficients obtained in tests on rate of cut growth may be indicative of a fatigue effect caused by the nature of the test. Since the samples received the same aging treatment, the same reactions, if they took place in the tensile strips, must obviously have occurred in the samples used for rate of cut growth tests. The hysteresis effect induced by the rapid flexing at low elongations, therefore, appears to be a possible explanation for the lower temperature coefficients observed.

These results may be interpreted to mean that the only difference in aging at higher temperatures compared to the temperatures ordinarily used will be in the rates, and not in the character, of the changes observed. Thus, rapid aging tests can be made by using higher temperatures; for example, 1 day at 248° F. would be equivalent to 4-day aging at 212° F.

The data in Table II and Figure 2 are interesting in another respect. In most cases the actual value of properties of stocks A and B in the overcure, after aging, are not inferior to those of the optimum cure but are superior. That is, the stress at 200 and 300% elongation is lower, the tensile strength is higher, the elongation at break is higher, and the rate of crack growth is lower for equal aging treatment. The properties of the overcure are inferior to those of the optimum cure only in the case of unaged samples. This phenomenon has been observed in numerous other cases not reported here and by other investigators (*4*, *6*, *8*). This fact must be construed to mean that the mechanism of oven, or heat, aging is not simply that of continued cure. A possible explanation is that more stable reaction products are formed by the longer curing time. These products have somewhat poorer properties originally, but are less susceptible to changes during oven aging. However, the temperature coefficients of these changes caused by aging are the same as those of the less stable products of the optimum cure. These results indicate that perhaps a revision of some of our prevailing ideas on the correct state of cure for maximum service of this type of GR-S stocks is in order.

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Structural Features of Buna S

RELATION TO PHYSICAL PROPERTIES

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The nonsymmetry in the chain structure of Buna S hydrocarbon is discussed in relation to the prevention of crystallization and the impeding of cross linking during vulcanization. This lack of chain symmetry is put forward to account for the poor quality of Buna S vulcanizates in comparison with corresponding vulcanizates prepared from natural rubber. Fractionation data on a regular benzene-soluble crude Buna S indicates the presence of an objectionable broad range of polymer sizes. It is shown that the lowest-molecular-weight polymer fractions in Buna S are not chemically bound in the vulcanizate but remain soluble in chloroform. By removing most of this low polymer from Buna S, the chloroform extract of its vulcanizate decreases accordingly. Vulcanizates were prepared from high- and low-molecular-weight fractions of Buna S. The high fractions were tough, dry, and difficult to handle on the mill; the lower-molecular-weight fractions was soft and sticky. The tensile strength of vulcanizates from the high fraction was somewhat greater than that of the whole polymer, but the modulus was considerably increased. For the low-molecular-weight polymer both tensile and modulus values were much lower. Vulcanizates prepared by mixing natural rubber and gutta-percha hydrocarbons show lower strength that neither of the hydrocarbons separately tested in the same formula.

THE low tensile strength of Buna S gum stocks is generally believed to be due to failure to obtain effective cross linkage as the result of vulcanization with sulfur and accelerators. Combined with this is the complete absence of crystallization of Buna S upon stretching which, in the case of natural rubber, reinforces and strengthens the vulcanized gel structure.

The absence of crystallization in Buna S can be explained on the basis of nonsymmetry along the polymer chains. Strictly speaking, Buna S is not a true polymer since ozonolysis shows that the styrene units are not evenly spaced in the chain but are grouped together in some locations (*1*). Ozonolysis also has proved the presence of vinyl groups attached to the chain, resulting from the polymerization of butadiene in the 1,2 instead of the 1,4 position (*1*). These vinyl groups must be unevenly spaced along the chain, and mixed *trans* and *cis* isomers must be present.

Figure 1 illustrates the chemical units present in Buna S, rubber, and gutta-percha hydrocarbons. In a Buna S copolymer containing 24.5% styrene, there are six butadiene to one styrene unit. It appears (*1*) that about one butadiene in five polymerizes in the 1,2 position in the chain. It should be emphasized that, in Buna S, ozonolysis (*1*) has shown that no regular order exists in the location of *A*, *B*, and *C* units in the polymer. An entire lack of symmetry in the positioning of these units in the chain would be expected in view of the nature of the polymerization reaction.

Consequently, we can readily see how impossible it is for Buna S to crystallize. Since double bonds in the butadiene chain units and in the vinyl groups are unevenly spaced along the chain, they cannot be uniformly or frequently matched up with those in neighboring chains. This fact may result in an ineffectual cross linking of Buna S chains with active sulfur atoms during vulcanization. In contrast, the more or less perfect chain symmetry of sol rubber hydrocarbon should result in a higher frequency of alignment of the double bonds and, therefore, a more effective vulcanization reaction to produce more frequent and more evenly spaced cross links in the vulcanizates.

Where vinyl and benzene side groups are located in the Buna S chain, the separation of adjacent chains will be considerably greater than in natural rubber chains with shorter methyl side groups. This wider chain separation of Buna S chains may also reduce effective cross linking with sulfur during vulcanization and thereby cause weak areas in the vulcanizate structure.

Good physical characteristics of Buna S vulcanizates can be obtained only by pigment reinforcement. The factors determining the extent and nature of this reinforcement are amount of loading, size and size distribution of pigment, shape of pigment particles, and dispersion quality or uniformity of separation of pigment particles in the vulcanizate. Because Buna S does not wet pigments so readily as rubber, it is more difficult to obtain a uniform Buna S stock in conventional rubber mixing equipment.

The physical properties of Buna S compounds deteriorate faster with a rise of temperature than do those of natural rubber compounds. This behavior can be explained on the basis that the physical properties of Buna S stocks depend to a greater extent on association forces and less on chemical cross linking than do those of similar natural rubber vulcanizates. These association forces between the polymer chains and between the pigment particles and Buna S chains are greatly reduced at elevated temperatures; a weaker gel structure results in Buna S than in the more highly and effectively cross-linked rubber gel.

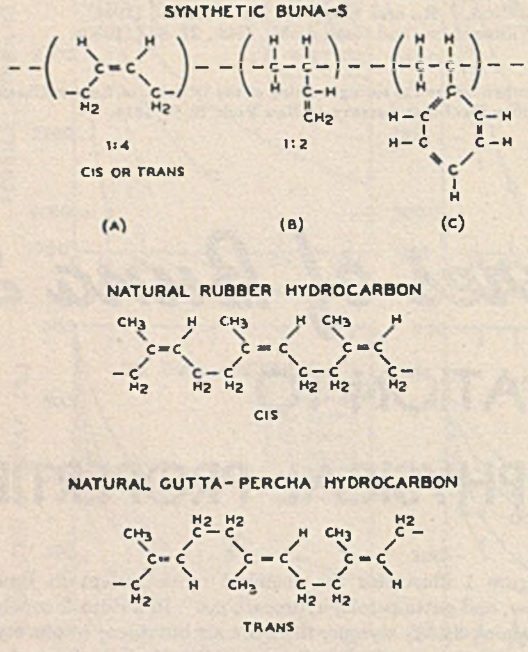

Figure 1. Chemical Units in Buna S, Rubber, and Gutta-Percha Hydrocarbons

Gelation resulting from branch chaining and cross linking may be present in Buna S in widely varying degrees, depending upon the polymerizing conditions and subsequent treatment of the polymer. In cases where the polymer is completely soluble in benzene, it will become increasingly insoluble in benzene or chloroform if antioxidant is absent and the polymer is exposed to air. For example, a pure white Buna S polymer changed from 100% benzene solubility to 39% solubility upon exposure to air at room temperature for 4 days, whereas no gain in weight could be detected on an ordinary analytical balance.

The rate of oxidation of purified Buna S polymer is indicated by the weight gain curves for two different preparations in finely cut form in Figure 2. After 64-day exposure to air in the laboratory, the material became yellowish and was hard and brittle on the outside surfaces. Gelation will also take place in solution in the absence of antioxidants. Pure rubber hydrocarbon will absorb oxygen somewhat more rapidly than Buna S hydrocarbon when exposed to air, but unlike the Buna S hydrocarbon, it remains soluble in chloroform(*2*). Possibly the vinyl side groups in GR-S may be the seat of oxygen cross linking which results in gelation. It is well known that a complete gelation of linear polymers can result from a limited number of cross links.

Improvements in Buna S from a structural point of view are made extremely difficult if not impossible by the fundamental nature of the polymerization reaction which leads to the features of chain asymmetry just described. Aside from a small amount of gel, not only does the rubber hydrocarbon in crude rubber possess chain symmetry, but it is all in the *cis* configuration.

Another weakness of Buna S is poor processing characteristics. It is very nervy, and its compounded stocks show a large shrinkage when slabbed off a mill following mixing and cooling. A shrinkage of 40% in length is not uncommon. A lack of tack or cohesive bonding to itself is also a well known defect of Buna S. The nerve or poor processing is due to the presence of a high-molecular-weight fraction associated with a considerable portion of soft, liquid, low polymers. In other words, Buna S has too broad a distribution of polymer sizes. These large molecules are highly elastic and, if deformed, spring back when the distortion force is removed.

The presence of the liquid low polymers together with the excessive amount of stearic acid and other nonhydrocarbon constituents is also objectionable; they contribute to poor wetting of pigments and poor vulcanization which, in turn, lead, to deficient physical properties.

When crude rubber is broken down by mastication the large molecules are placed under strain and, in the presence of ozone and oxygen, are split into shorter segments. A well masticated crude rubber is made up of polymer units with a narrow range in chain length (*6*) since the longer chains are apparently preferentially split.

A considerable improvement in the processing characteristics of Buna S would result if a narrower range of polymer sizes could be effected. This new range should contain a lower-molecular-weight high fraction and should eliminate the lowest-molecular-weight fractions which vary from oils to a taffy-like substance. In any case, gelation of the polymer should be prevented. As long as the present higher-polymer fractions remain, the removal of the lower fractions results in a dry, nervy polymer which is practically unmanageable on the mill.

This paper presents data on the fractionation of a benzene-soluble type of Buna S polymer. Data are given on the effect of fractionation of Buna S on the nature of vulcanizates made from different fractions. The effect of polymer size on the chloroform extract obtained after acetone extraction of the vulcanizates is also reported. This chloroform extract is a soft pasty solid having a composition like the vulcanized hydrocarbon. It has a very low molecular weight and tends to crystallize in long fern-like needles. Its presence appears to result from the smaller polymer

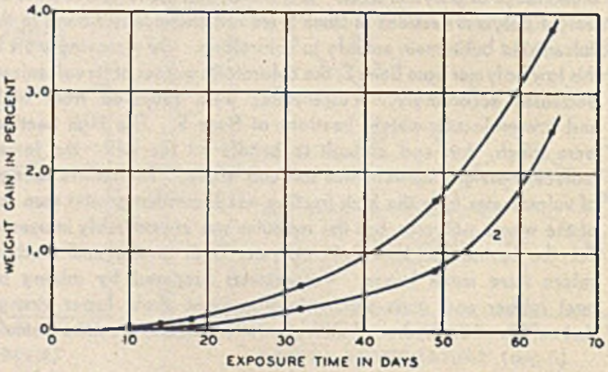

Figure 2. Rate of Oxidation of Buna S Hydrocarbon

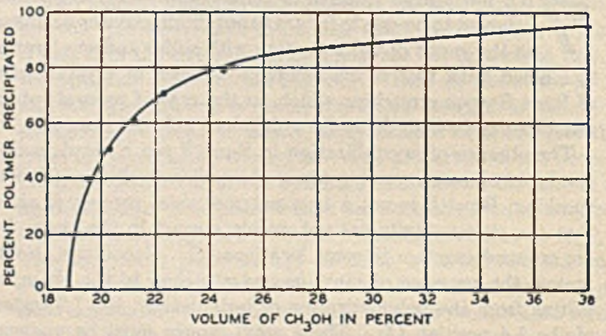

Figure 3. Relation of Alcohol Content to Precipitation of Buna S from Benzene Solution

molecules which react with sulfur intramolecularly but not intermolecularly, and therefore remain soluble in chloroform. A small amount of chloroform-extractable crystalline substance is present in vulcanized crepe rubber.

Table I. Fractionation of Buna S

Hydrocarbon Fraction	CH_3OH Added, % by Vol.	Yield, % On Buna S	Yield, % On total hydrocarbon	Description
1	19.5	37.0	40.0	Moderately tough and elastic, not tacky
2	20.3	10.0	10.9	Somewhat elastic, not tacky
3	21.2	9.3	10.1	Soft, plastic, stringy, not tacky
4	22.3	8.7	9.5	Soft, taffy-like, somewhat tacky
5	24.5	8.0	8.6	Soft, taffy-like, very plastic and tacky
6	28.5	8.0	8.6	Highly viscous, sticky liquid
7	38.0	6.3	6.8	Viscous, sticky liquid
8[a]	....	5.0	5.5	Viscous oil
1A[b]	19.3	23.0	24.9	Tough and elastic like smoked sheets

[a] Supernatant liquid from fraction 7 was evaporated to dryness, and residue repeatedly washed with hot methanol followed by one cold acetone wash to remove nonhydrocarbon substances; residue was fraction 8.

[b] Fraction 1 was redissolved in benzene, containing antioxidant, to form a 0.5% solution. A 50-50 methanol-benzene solution was added gradually with vigorous mechanical stirring to precipitate partially the higher-molecular-weight portion.

Table II. Chemical Analysis of Buna S Fractions

Fraction No.	Carbon, %	Hydrogen, %	C/H Ratio	Ash, %	Iodine No.	Styrene, % from C/H	Styrene, % from I No.[a]
1	88.90	10.37	8.57	0.88	356.1	21.3	23.4
2	88.97	10.32	8.61	0.19	359.3	22.5	22.7
3	88.97	10.27	8.66	0.27	359.1	24.1	22.8
4	89.26	10.26	8.70	0.18	359.8	25.4	22.6
5	89.27	10.29	8.64	0.29	359.6	23.5	22.7
6	88.57	10.33	8.58	0.89	355.5	21.6	23.5
7	88.06	10.30	8.56	0.98	352.1	21.0	24.3
8	87.74	10.25	8.55	0.35	348.1	20.7	25.2
Whole hydrocarbon[b]	88.27	10.25	8.63	0.80	356.7	23.2	23.3

[a] Styrene content $= \dfrac{(465 - \text{iodine No.}) \times 100}{465}$.

[b] Acetone-extracted GR-S.

Table III. Polymer Length of Buna S Fractions in Comparison with Natural Rubber[a]

Polymer Fraction	C	Φ	η_r	(η)	$\dfrac{\text{Log } \eta_r}{\Phi}$	N*	N_1
1	0.218	0.00234	2.32	3.84	156.2	3577	2693
2	0.300	0.00322	1.98	2.28	92.1	2109	1589
3	0.432	0.00465	2.08	1.69	68.4	1566	1180
4	0.400	0.00430	1.66	1.26	51.2	1172	883
5	0.609	0.00655	1.69	0.86	34.8	797	600
6	0.446	0.00469	1.27	0.54	22.1	506	381
7	0.642	0.00690	1.21	0.30	12.0	275	207
8	2.610	0.02801	1.66	0.19	8.0	183	138
1-A	0.101	0.00109	1.85	6.09	245.1	5613	4228
Whole	0.185	0.00197	1.60	2.54	103.6	2372	1787
Buna S							
Hydrocarbon							
Unmilled	0.304	0.00327	1.97	2.23	90.0	....	1542
5 min. on cool roll	0.348	0.00374	1.97	1.95	78.7	....	1358
10 min. on cool roll	0.349	0.00375	1.96	1.93	77.7	....	1340
30 min. on cool roll	0.342	0.00368	1.88	1.84	74.5	....	1285
60 min. on cool roll	0.350	0.00376	1.82	1.70	69.2	....	1194
Crepe							
Whole sol	0.049	0.000527	1.41	6.99	283.1	6285	....
Milled 15 min., 96° C.[b]	0.221	0.00238	1.70	2.40	96.9	2152	....
Milled 15 min., 35° C.[b]	0.476	0.00512	1.81	1.24	50.3	1117	....
Milled 200 min., 35° C.[b]	0.313	0.00337	1.32	0.83	35.8	795	....

[a] Nomenclature:

C = grams per 100 cc. of solution

N = average number of carbon atoms in chains

Φ = cc. of solute per cc. of solution

$N = \dfrac{\log \eta_r W}{\Phi K_{ca}}$; $N_1 = \dfrac{\log \eta_r W_1}{\Phi K_{ca}}$

W = 0.734 based on 23.4% styrene in Buna S used

W = 0.71 in case of natural rubber

W_1 = 0.552, assuming 30% 1,2 addition of butadiene in Buna S

K_{ca} = 0.032

* See Kemp and Peters (5).

[b] Mill roll temperature.

Table IV. Viscosity of Benzene Solutions of Extracts 1, 2, and 3

Extract No.	Concd. CH_3OH in C_6H_6, %	Extraction Time, Weeks	% Extracted	$\dfrac{\text{Log } \eta_r}{c}$
1	20.2	1	8.0	...
2	19.2	2	16.0	0.342
3	20.0	1	16.5	0.372

FRACTIONATION BY PRECIPITATION

A benzene-soluble type of Buna S was dissolved in benzene to form a 2% solution. A 50-50 mixture of methanol-benzene by volume was added slowly with vigorous stirring until cloudiness appeared. All solutions were kept at 20° C. The solution was warmed to 40° C. to redissolve the precipitated polymer, cooled to 20° C., and allowed to stand overnight; during this time the fraction precipitated and settled. The fraction was separated by decantation and coagulation with pure alcohol.

Data on the fractionation, analysis, and relative chain lengths of these fractions are given in Tables I, II, and III. The first fraction is large in comparison with the others because only a small spread in the quantity of alcohol used for precipitation was required to throw a large part of the high-molecular fraction out of solution.

Figure 3 shows the effect of alcohol on the precipitation of Buna S hydrocarbon from benzene solution. Each point on the curve represents a fraction of precipitated hydrocarbon which was removed by decantation of the supernatant liquid followed by the addition of more pure alcohol to harden the coagulum so it could be removed. The fractions were dried under vacuum at 50° C. in a stream of lamp nitrogen and weighed.

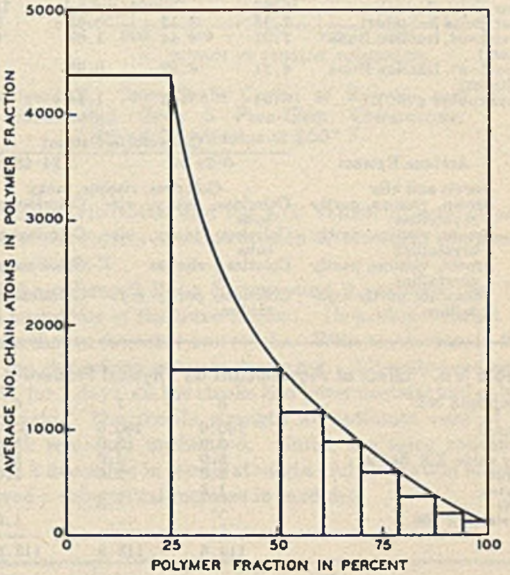

Figure 4. Molecular Weight Distribution of Buna S

In Figure 4 average chain length is plotted against percentage of each fraction. It must be realized that each fraction still contains polymer units of varying sizes, as one fractionation is only partially effective in separating the different sized specimens present. In no case can one expect to approach perfection in any number of repeated fractionations.

If Buna S with narrow polymer distribution could be prepared with average chain lengths in the range of fractions 2 or 3 (Table III), a much needed improvement in processing would result. Better control of the polymerization reaction is needed to accomplish this. The physical properties of pigment-loaded stocks probably would not be greatly improved by such a change for reasons already stated although hysteresis and heat build-up might be improved.

Table V. Tensile Strength Data on Optimum Cures

Compound No.	1	2	3	4	5
Regular Buna S	100.00	100.00	...	...	...
High-mol.-wt. Buna S	...	...	100.00	100.00	...
Smoked sheet	...	...	...	...	100.00
Statex black	...	50.00	...	50.00	...
Zinc oxide XX72	10.00	10.00	10.00	10.00	10.00
Stearic acid	2.00	2.00	5.00	5.00	5.00
Sulfur	0.50	2.00	0.50	2.00	0.30
Accelerator 808	0.75	0.75	0.75	0.75	0.75
TMTMS	0.10	0.10	0.10	0.10	0.10

Compound No.	Cure, Min. (° F.)	Rate of Extension, In./Min.	Lb./Sq. In. Modulus at 300%	Lb./Sq. In. Tensile strength	Elongation at Break, %	Hardness, Shore A
1	45 (280)	22	50	875	1125	25
2	60 (280)	22	1350	3150	575	57
3	45 (280)	22	250	670	520	37
		22	180	750	610	
		22	260	920	650	
		12	290	750	610	
		12	210	820	650	
4	60 (280)	22	2400	3380	350	65
		22	2370	3070	320	
		22	2360	3380	370	
		12	2470	3350	370	
		12	2340	3040	350	
5	40 (280)	22	50	...	...	26
		22	50	1400	900	
		22	50	1300	900	
		12	50	1720	950	
		12	50	1460	970	

Table VI. Data on Acetone and Chloroform Extractions of Compounds 1 to 5

Compound No.	Acetone Ext., %	Chloroform Ext., % 0–24 hr.	Chloroform Ext., % 24–48 hr.	Total, %
1 (regular Buna S gum)	10.33	Continuously		15.4
2 (regular Buna S–Statex)	7.35	3.13	0.81	3.94
3 (high-mol.-wt. fraction Buna S gum)	7.01	4.44	1.67	6.11
4 (high-mol.-wt. fraction Buna S-Statex)	4.21	0.82	0.83	1.65
5 (natural rubber gum)	6.04	5.54	1.14	6.68

Compound No.	Acetone Extract	Chloroform Extract 0–24 hr.	Chloroform Extract 24–48 hr.
1	Brown and oily	Colorless, viscous, tacky	
2	Brown, viscous, partly crystalline	Colorless, tacky, viscous	Colorless, glassy
3	Brown, viscous, partly crystalline	Colorless, tacky, viscous	Colorless, glassy
4	Brown, viscous, partly crystalline	Colorless, viscous	Colorless, glassy
5	Yellowish, partly crystalline	Colorless, partly crystalline	Colorless, glassy

Table VII. Effect of Accelerators on Physical Properties

Compound No.	6	7	8
Buna-S	100.0	100.0	100.0
Bardol	5.0	5.0	5.0
Zinc oxide XX Red 4	5.0	5.0	5.0
Sulfur	2.0	2.0	2.0
Captax	1.5	...	...
DPG	...	1.5	...
Accelerator 808	...	...	1.5
	113.5	113.5	113.5

Cure, Min. at 292° F.	Original Tests Lb./sq. in. Modulus at 300%	Original Tests Lb./sq. in. Tensile strength	Original Tests Elongation at break, %	Air-Aged 7 Days at 100° C. Lb./sq. in. Modulus at 300%	Air-Aged 7 Days at 100° C. Lb./sq. in. Tensile strength	Air-Aged 7 Days at 100° C. Elongation at break, %
Compound 6 (Captax)						
20	25	220	920	...	...	...
30	50	180	650	...	...	...
40	70	150	510	...	...	...
50	70	180	510	...	...	...
60	70	180	420	...	...	...
120	120	157	377	...	...	...
Compound 7 (DPG)						
20	None	None	250	40	130	620
30	None	None	2200	60	210	610
40	None	230	1500	100	250	550
50	17	290	1330	100	290	530
60	23	160	907	140	180	360
120	50	220	640	220	220	295
Compound 8 (808)						
20	95	575	715	230	340	370
30	90	590	650	210	340	360
40	115	520	620	225	285	360
50	120	450	575	200	380	420
60	110	510	610	220	400	420
120	150	420	500	220	290	350

The expression of polymer size by chain atom lengths (Table III) is desirable; it places polymers of questionable chain linearity on a more comparable basis with those whose chains are more certain to be linear. Since average polymer length determines viscosity, the argument for using this term in comparing polymers is apparent.

EFFECT OF REMOVING LOW POLYMERS

Two hundred grams of Buna S were sheeted out to a thickness of about 0.002 inch on a laboratory mill, cut into 1-inch strips, and dropped separately into a 5-liter round-bottom flask containing 4 liters of a 20.2% by volume mixture of methanol in benzene. The flask and its contents were placed in the dark and kept at room temperature (18–23° C.). On standing, the Buna S slowly changed into a liquid, swollen gel which collected on the bottom of the flask. After one week the extract was decanted, and 4 liters of fresh solvent were added. This time the concentration of methanol in benzene was reduced to 19.2% in order to hasten the extraction process. From time to time during the next two weeks the mixture was thoroughly agitated, and at the end of this time the extract was replaced with fresh solvent. The concentration of methanol in benzene was then 20% by volume. During the following week the mixture was agitated as before. Finally, the extract was decanted, 1.5% Neozone D was added to the gelatinous mass, and it was coagulated with pure methanol. The coagulum was pressed and placed in a vacuum oven at 40° C. until free of solvent. Its weight was 116 grams or 58% of the original material.

Aliquots from the various extracts were dried in a weighed crystallizing dish, weighed, and then dissolved in 100 ml. of pure benzene. The viscosity of the benzene solutions was determined in an Ostwald viscometer at 25° C. The results are given in Table IV.

The extracted Buna S was very tough, had little plasticity, and sheeted out on the laboratory mill rolls with difficulty. It resembled closely the higher-molecular-weight fractions of Buna S rubber which had been separated by fractional precipitation. It was soluble to the extent of 99% in benzene, and the log η_r/C value for this solution was 1.13. The average log η_r/C value for the highest-molecular-weight fractions of Buna S, which represent 60% by weight of the polymer, was found to be 1.34. The lower log η_r/C value of the former probably resulted from breakdown during the sheeting-out operation. It is also probable that more of the low-molecular-weight copolymer molecules remained in the extracted material than in the case where precipitation procedure was employed.

Table V gives the composition of compounds prepared with extracted Buna S, two similar compounds made with the original Buna S, and one made with natural rubber. The two regular Buna S compounds (1 and 2) were mixed according to the War Production Board mixing schedule. The two high-molecular-weight Buna S compounds (3 and 4) and natural rubber compound 5 were mixed on the regular 12-inch laboratory mill with special guides to reduce the working length of the mill rolls to 5 inches.

The mixed compounds were permitted to stand overnight, refined twice through tight mill rolls, and vulcanized in a 0.075-inch-thick mold. There was just enough compound to make one 6 × 6 inch sheet cure. After vulcanization the cured sheets were placed in the aeration rack in a constant temperature-humidity room for 24 hours. They were then removed, and five tensile test specimens were cut from each sheet with a razor-sharp $^1/_4$-inch dumbbell die. The results of tensile strength tests on optimum cures are shown in Table V. The rate of extension of the specimens was changed from 22 to 12 inches per minute. The results show that this had no effect on tensile strength values.

ACETONE AND CHLOROFORM EXTRACTION

One-gram samples of the optimum cured compounds (1 to 5) were diced and extracted with acetone in the regular extraction

Table VIII. Data on Acetone and Chloroform Extraction of Compounds 6, 7, and 8

Compound No.	Cure, Min. at 292° F.	Acetone Ext., %		Chloroform Ext., %	
		Unaged	Aged	Unaged	Aged
6 (Captax)	20	14.89	...	13.90	...
	50	12.77	...	6.04	...
	120	11.98	...	4.34	...
7 (DPG)	20	14.03	9.03	25.81	10.65
	50	13.80	7.50	19.47	4.55
	120	11.41	6.43	7.29	1.85
8 (808)	20	11.03	7.35	7.91	2.39
	50	10.78	7.00	5.94	2.54
	120	10.37	6.66	4.84	2.41

Table IX. Chemical Analysis of Chloroform Extract of DPG Stock 7, Cured 50 Minutes at 292° F.

Hr. of Extn.	C, %	H, %	S, %	Ash, %	Iodine No.	C/H Ratio	Styrene from I/No.	Ext., %
18	87.57	10.31	1.26	0.10	350.3	8.49	22.2	11.8
18–48	87.45	9.87	1.31	0.27	344.7	8.84	23.3	4.14

Table X. Viscosity of Benzene Solutions of Extracts 6, 7, and 8

Extract	Cure, Min.	Concn., G./100 Ml.		$\frac{\text{Log } \eta_r}{c}$
6 (Captax)	20	1.254	1.51	0.143
7 (DPG)	50	2.012	2.19	0.169
8 (808)	20	0.769	1.15	0.079

apparatus for 20 hours. They were then chloroform-extracted for a total time of 48 hours, the chloroform being replaced at the end of 24 hours. Results and physical properties are given in Table VI. During the chloroform extractions compounds 2 and 4 (Statex black) swelled very little, and compounds 1 and 3 (pure gum) swelled considerably and to about the same extent. Compound 5 (natural rubber) swelled to about the same extent as did the Buna S gum compounds.

The acetone and chloroform extracts of both pure gum and Statex black high-molecular-weight Buna S compounds were reduced considerably. It is of interest to note the lower chloroform extract of those stocks containing Statex black. It appears possible that carbon black tends to bond the smaller Buna S molecules. The physical properties of the extracts are also described. Kemp and Peters (*4*) showed that crepe rubber contains a small percentage of low-molecular polymer which, combined with the low sulfur content in compound 5, probably accounts for its substantial chloroform extract.

EFFECT OF DIFFERENT ACCELERATORS

The three compounds in Table VII were prepared to test the effect of acid and alkaline type accelerators on the vulcanization of Buna S. The mixing schedule was slightly modified in that Buna S was allowed to work only 1.5 minutes before the compounding ingredients were added, as compared with 10 minutes recommended by the WPB schedule. Table VII gives the physical properties of the cured sheets after conditioning at 75° F. and 45% relative humidity and of the same cures after aging for 7 days in the hot air oven at 100° C. (212° F.). The acetone and chloroform extraction data on these compounds are given in Tables VIII and IX.

Compound 7 swelled most when chloroform-extracted, compound 6 was intermediate, and compound 8 swelled least. The 7-day-aged samples swelled only about half as much as did the unaged samples. The acetone extract of each unaged compound was brown and viscous; the chloroform extracts were colorless viscous liquids which, on standing, crystallized into radial monoclinic crystals arranged into a fern-shaped pattern.

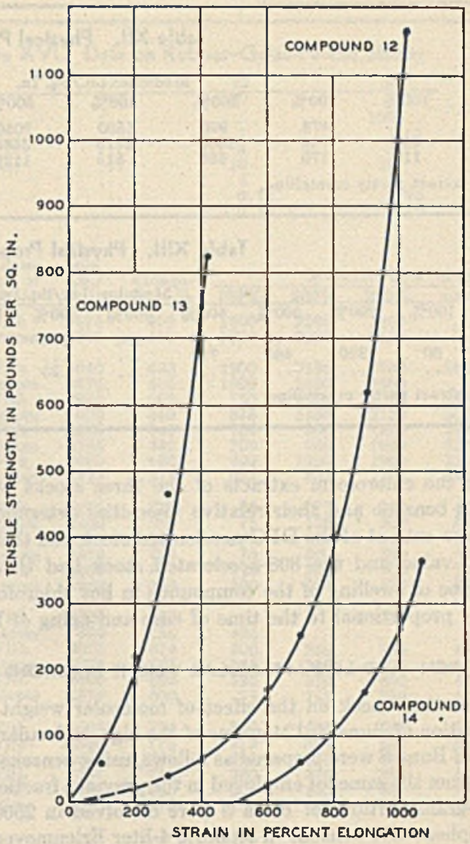

Figure 5. Stress-Strain Curves of Regular and Fractionated Buna S Pure-Gum Compounds, Cured 20 Minutes at 260° F.

The relative viscosities and log η_r/C values of benzene solutions of the chloroform extracts of each of the three compounds are given in Table X.

The 808-accelerated Buna S compound 8 possessed the best physical properties of the three studied. Its acetone extract was lower than that of the other two stocks. With an increase in time of cure, the chloroform extracts decreased. After air-oven aging at 100° C. for 7 days, all the stocks had lower acetone and chloroform extracts. The tensile strength at optimum cure of the DPG stock remained unchanged. Under the same conditions compound 8 decreased in tensile strength and elongation at break but showed a substantial increase in modulus.

Table XI. Formulas of Tread Compounds 9, 10, 11, and of Pure Gum Compounds 12, 13, 14

Compound No.	9	10	11
Buna S	100	100[a]	100[b]
Bardol	5	5	5
Zinc oxide XX-4	5	5	5
Kosmobile 77	50	50	50
Sulfur	2	2	2
Captax	1.5	1.5	1.5
Stearic acid	...	4.0	4.0
Cure		50 minutes at 292° F.	

Compound No.	12	13	14
Buna S	100	100[a]	100[b]
Zinc oxide XX72	10	10	10
Stearic acid	2	6	6
Sulfur	0.75	0.75	0.75
808	0.75	0.75	0.75
TMTMS	0.10	0.10	0.10
Cure		20 minutes at 260° F.	

[a] High mol. weight. [b] Low mol. weight.

Table XII. Physical Properties of Tread Compounds 9, 10, and 11

Compound No.	Modulus, Lb./Sq. In. 100%	200%	300%	400%	500%	600%	700%	Tensile Strength, Lb./Sq.In.	Elongation, %	Shore A Hardness	Acetone Ext., %	Chloroform Ext., %[a]
9	...	478	990	1500	2050	2515	...	2670	615	..	...	...
10	240	715	1500	2475	3585	...	...	3770	515	57	5.70	1.58
11	110	270	550	815	1125	1440	1730	1900	760	47	6.56	8.73

[a] Dry extract partly crystalline.

Table XIII. Physical Properties of Pure Gum Compounds 12, 13, and 14

Compound No.	Modulus, Lb./Sq. In. 100%	200%	300%	400%	500%	600%	700%	800%	900%	1000%	Tensile Strength, Lb./Sq.In.	Elongation, %	Shore A Hardness	Acetone Ext., %	Chloroform Ext., %[a]
12	..	...	40	65	100	170	250	400	620	1000	1170	1025	..	10.23	10.16
13	60	220	465	750	...	...	...	...	...	...	825	425	40	5.23	2.45
14	..	...	...	...	...	25	60	105	165	265	365	1075	17	8.14	16.89

[a] Dry extract partly crystalline.

When the chloroform extracts of the three stocks were dissolved in benzene and their relative viscosities determined, the chloroform extract of the DPG-accelerated stock had the highest log η_r/C value and the 808-accelerated stock had the lowest. The degree of swelling of the compounds in hot chloroform was inversely proportional to the time of cure and aging of Buna S.

HIGH- AND LOW-MOLECULAR WEIGHT FRACTIONS

As a further check on the effect of molecular weight on the vulcanization of Buna S, 124 grams of the high-molecular-weight portion of Buna S were prepared as follows, using benzene soluble Buna S from the same lot employed in the previous fractionation: Five 50-gram portions of Buna S were dissolved in 2500 cc. of c.p. thiophene-free benzene in separate 4-liter Erlenmeyer flasks. The solution was heated to 40° C., and 1525 cc. of a 50-50 benzene-methanol solution were slowly added with vigorous stirring. This resulted in a methanol concentration of 18.95% which was sufficient to precipitate the high-molecular-weight fraction of Buna S.

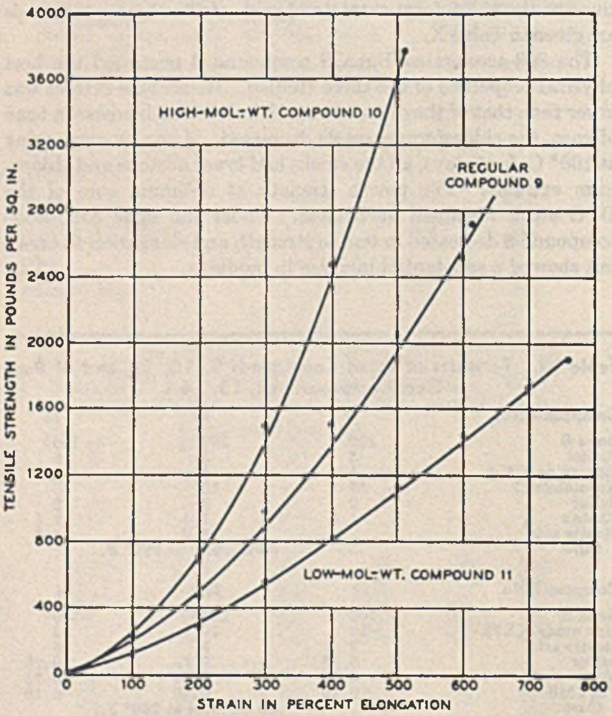

Figure 6. Stress-Strain Curves of Regular and Fractionated Buna S Tread Compounds, Cured 50 Minutes at 292° F.

Table XIV. Data on Pure Gum Crepe Rubber Stocks

Compound No.	15	16	17	18
A. Crepe (62,000 mol. wt.)	100	...	...	...
B. Crepe (32,000 mol. wt.)	...	100	...	...
C. Crepe (20,000 mol. wt.)	...	...	100	...
D. 50*A* + 50*B*	...	...	...	100
Zinc oxide XX72	10	10	10	10
Stearic acid	2	2	2	2
Sulfur	3	3	3	3
808	0.75	0.75	0.75	0.75
TMTMS	0.10	0.10	0.10	0.10
Neozone A	1	1	1	1
Curing temp., ° F.	287	287	287	287
10-minute cure				
Tensile, lb./sq. in.	5185	4775	3935	4070
Elongation, %	775	790	830	735
Modulus at 500%, lb./sq. in.	915	760	515	810
20-minute cure				
Tensile, lb./sq. in.	4830	4770	3930	4290
Elongation, %	685	715	670	705
Modulus at 500%, lb./sq. in.	1465	1280	1250	1250
30-minute cure				
Tensile, lb./sq. in.	4175	4340	...	...
Elongation, %	650	660	...	...
Modulus at 500%, lb./sq. in.	1550	1680	...	...
40-minute cure				
Tensile, lb./sq. in.	4160	4050	...	...
Elongation, %	640	650	...	...
Modulus at 500%, lb./sq. in.	1540	1680	...	...
Hardness, Shore A (20 min.)	43	43	38	43
Acetone ext., %	5.85	6.28	6.28	5.87
Chloroform ext., %[a]	0.77	0.75	1.15	0.90

[a] Chloroform extracts were partly crystalline.

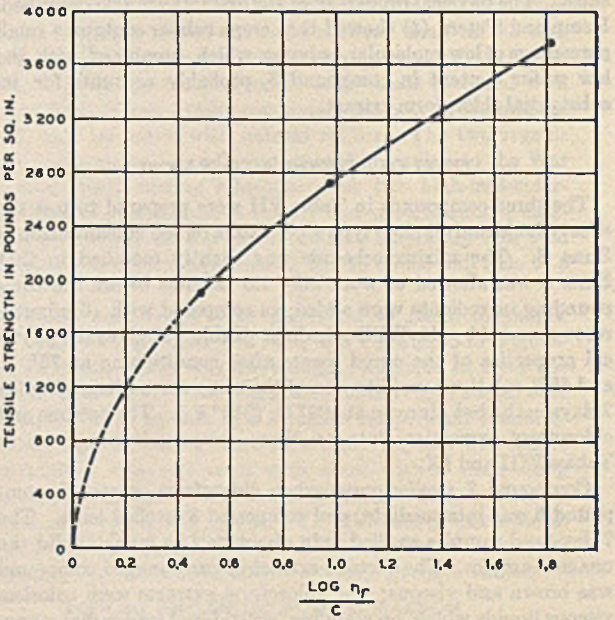

Figure 7. Tensile Strength of Tread Compounds vs. Molecular Weight Index of Starting Buna S

Table XV. Data on Crepe Rubber Tread Stocks

Compound No.	19	20
Crepe (62,000 mol. wt.)	100	...
Crepe (20,000 mol. wt.)	...	100
Neozone D	1	1
Captax	1.50	1.50
Kosmobile 77	50.00	50.00
Zinc oxide XX72	5.00	5.00
Stearic acid	3.00	3.00
Sulfur	3.00	3.00
Curing temp., ° F.	287	287
20-minute cure		
Tensile, lb./sq. in.	4280	2935
Elongation, %	655	500
Modulus at 300%, lb./sq. in.	1210	1350
40-minute cure		
Tensile, lb./sq. in.	4910	3645
Elongation, %	560	505
Modulus at 300%, lb./sq. in.	2000	1840
60-minute cure		
Tensile, lb./sq. in.	4730	3400
Elongation, %	555	455
Modulus at 300%, lb./sq. in.	2060	2030
80-minute cure		
Tensile, lb./sq. in.	4600	3340
Elongation, %	520	420
Modulus at 300%, lb./sq. in.	2180	2120
Hardness, Shore A (40-min.)	65	65
Acetone ext., %	4.7	4.8
Chloroform ext., %	0.84	1.22

The flasks were set aside to cool slowly to room temperature, which resulted in precipitation. The flasks were placed in water at 20° C. for several hours, and the supernatant liquid was then decanted from the precipitate. A 0.4-gram portion of Neozone D was added to the gelatinous precipitate in each flask, and the coagulum was solidified by adding more 50-50 benzene-alcohol and finally pure alcohol. The high-polymer fraction was dried under an 8-cm. vacuum in a stream of lamp nitrogen. The yield was 45.6% of the original Buna S. To the decantate was added pure methanol to a 40.13% alcohol concentration. After the temperature was brought to 20° C. as before, the supernatant liquid was decanted from the coagulum. The coagulum was dried as before, and the yield was 40.1% of a soft, tacky, plastic product. The log η_r/C value of the high fraction was 1.86, of the low fraction 0.50, and of the whole Buna S 0.97.

Compounding was carried out under carefully standardized conditions on a small Thropp mill. The compositions of the tread stocks (9, 10, and 11) are given in Table XI; results of physical tests are listed in Table XII. Additional stearic acid was added to each fraction to replace that removed by fractionation. Exhaustive acetone and chloroform extraction was made to show the lack of cross linking of the low polymers during vulcanization, as indicated by the amount of polymer extractable with chloroform. In Table XI and XIII the pure gum vulcani-

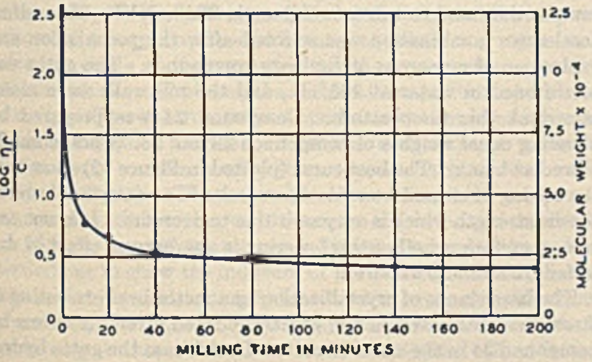

Figure 8. Effect of Milling Time at 95° F. on Viscosity Index and Molecular Weight of Pale Crepe

Table XVI. Data on Rubber–Gutta-Percha Stocks

Compound No.	21	22	23	24
Gutta BR-19	100	100	...	50
Crepe rubber	...	...	100	50
Neozone A	1	1	1	1
Sulfur	...	3	3	3
Zinc oxide (Kadox B.L.)	...	10	10	10
Stearic acid	...	2	2	2
808	...	0.75	0.75	0.75
TMTMS	...	0.10	0.10	0.10

Compound No.	Cure at 287° F., Min.	Direction of Grain	Tensile, Lb./Sq.In.	Elongation, %	Modulus, Lb./Sq. In.				
					100%	200%	300%	400%	500%
21	Uncured	With	4475	350	1800	2200	3100	...	...
		Across	4000	410	1800	2200	3100	...	...
22	Uncured	With	4040	425	1900	2125	2900	3800	...
		Across	3675	400	1500	1650	2600	...	...
	10	With	3985	505	750	1000	1975	2900	...
		Across	4600	540	875	1150	2150	3050	4000
	15	With	4355	540	700	950	1950	3050	3875
		Across	4335	540	700	950	1950	3000	3850
	20	With	3970	480	600	1000	1900	3100	...
		Across	4110	515	625	825	1775	3900	...
23	10	With	4875	730	75	175	300	475	1025
		Across	4600	800	75	125	200	325	625
	15	With	4725	720	75	200	300	550	1200
		Across	4910	725	75	200	300	500	1050
	20	With	4800	675	110	225	400	700	1550
		Across	4640	680	100	225	375	625	1400
24	Uncured	With	1200	50	...	...	...	...	...
		Across	520	140	425	...	...	...	...
	10	With	3075	675	200	250	350	600	1100
		Across	3075	685	125	200	275	475	975
	15	With	2400	605	125	210	300	475	1100
		Across	2310	600	75	150	250	475	1050
24	4[a]	With	3600	770	350	400	450	750	1300
	6[a]	With	3640	770	275	350	430	640	1230
	8[a]	With	4060	785	265	320	415	630	1210
	10[a]	With	3395	710	230	270	335	560	1150
	12[a]	With	3155	680	200	250	320	560	1120
	14[a]	With	2980	670	170	200	265	430	830

[a] Cured at 274° F.

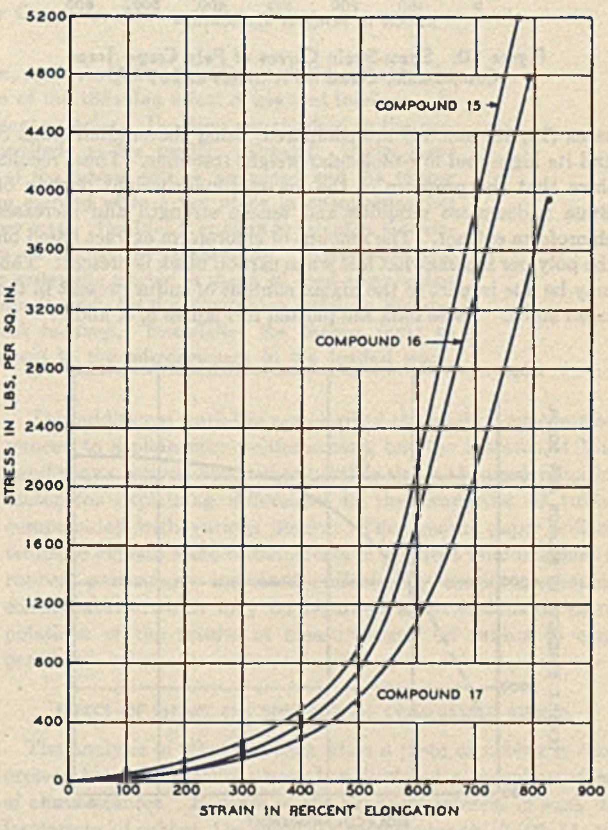

Figure 9. Stress-Strain Curves of Pale Crepe Pure-Gum Compounds Made with Rubber of Different Molecular Weights

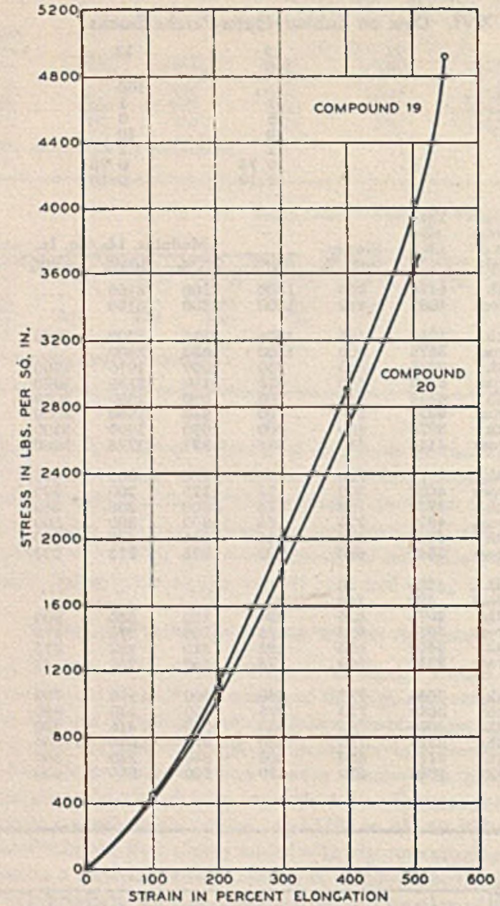

Figure 10. Stress-Strain Curves of Pale Crepe Tread Compounds, Cured 40 Minutes at 287° F.

zates (12, 13, and 14) are compared, using the original Buna S and its high- and low-molecular-weight fractions. These results show that the presence of the low-molecular-weight portion of Buna S decreases modulus and tensile strength and increases chloroform extract. The amount of chloroform extract based on the polymer is somewhat less when carbon black is present. This may be due in part to the higher content of sulfur present in the tread stock. These data are plotted in Figures 5, 6, and 7.

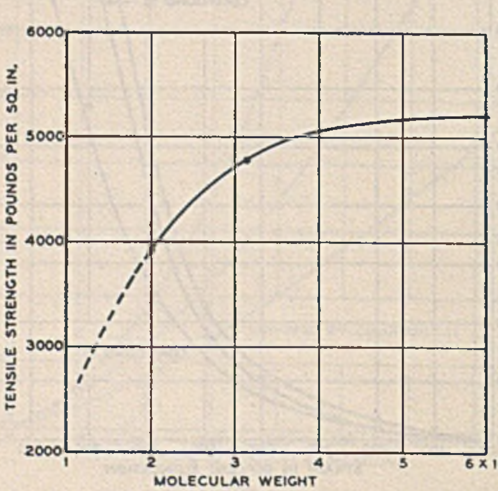

Figure 11. Tensile Strength of Pale Crepe Pure-Gum Compounds vs. Molecular Weight

EFFECT OF MILLING CREPE RUBBER

High-, medium-, and low-molecular-weight rubber were prepared by milling pale crepe 3 minutes at 212° F., 10 minutes at 95° F., and 200 minutes at 95° F., respectively. The average molecular weights determined by the viscosity procedure (3) were 62,000, 32,000, and 20,000, respectively. Compounds were also prepared by using a 50-50 mixture of high- and low-molecular-weight rubber. Effect of milling time on viscosity index and molecular weight of pale crepe is shown in Figure 8.

The data on pure gum stocks are given in Table XIV and on tread stocks in Table XV; they are plotted in Figures 9, 10, and 11. The effect of physical properties on reducing the molecular weight of crepe by excessive milling is not so pronounced as is shown by the high and low fractions of Buna S. The same is true for tread stocks 19 and 20. The low-chloroform extracts found in the natural rubber compounds along with their superior physical properties is evidence that natural rubber is more effectively cross-linked than Buna S during vulcanization.

Table XVII. Data on Balata Compounds

Compound No.	25	26
Balata hydrocarbon	94	96.5
Sulfur	5	2.5
Zinc butyl xanthate	1	1.0
Curing temp., ° F.	287	287
0.5-hour cure		
Tensile, lb./sq. in.	3920	3945
Elongation, %	480	445
Permanent set	245	250
1-hour cure		
Tensile, lb./sq. in.	3465	3615
Elongation, %	515	440
Permanent set	225	245
2-hour cure		
Tensile, lb./sq. in.	3125	3330
Elongation, %	570	470
Permanent set	155	230
3-hour cure		
Tensile, lb./sq. in.	2440	3385
Elongation, %	635	520
Permanent set	25	206
17-hour cure		
Tensile, lb./sq. in.	...	1685
Elongation, %	...	550
Permanent set	...	10

EFFECT OF MIXING RUBBER AND GUTTA-PERCHA

By mixing crepe rubber and leaf gutta-percha hydrocarbon BR-19 from the Tjipetir, Java, plantation it was thought that crystallization of each hydrocarbon would be inhibited. Rubber hydrocarbon having the *cis* configuration would not so readily form crystals in the presence of gutta-percha which has the *trans* configuration. The object was not to prevent crystallization of the gutta and rubber entirely but to reduce it considerably. The compositions and test data are given in Table XVI. The sulfur-accelerator combination was selected after the preparation and evaluation of numerous preliminary compounds. The gutta was presoftened in water at 195° F., and the mill rolls were maintained at this temperature. Compound 24 was prepared by blending equal weights of compounds 22 and 23. Compound 21 served as blank. The best cures (plotted in Figure 12) show that the mixing of *cis* and *trans* isomers results in a somewhat lowered tensile strength which is very sensitive to overcure. It is not certain, therefore, whether this lowering is a structural effect or due to failure to find best cure.

The importance of crystallization as a factor in contributing to strength is indicated in the greatly reduced strength shown by compound 24 in the uncured state. In this case the gutta hydrocarbon loses over 70% of its strength when mixed with an equal amount of lightly milled rubber. When vulcanized, this mixture

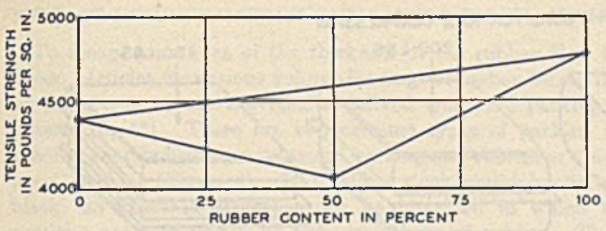

Figure 12. Effect of Mixing *cis* and *trans* Polyprene Isomers on Tensile Properties

increases in strength to about 90% of that of the original vulcanized whole gutta or whole rubber since the cross linking of the rubber has served to prevent its flow. The vulcanized gutta loses most of its strength when heated at 140–200° F. At the higher temperatures it becomes very short and tender, and is similar to vulcanized pure gum Buna S in strength and general appearance. Vulcanized pure gum rubber, on the other hand, retains a large part of its strength at these elevated temperatures. Since vulcanized rubber crystallizes on stretching, the importance of crystal reinforcement on the strength of polymers is indicated.

Gutta or balata hydrocarbons change permanently to a rubber-like vulcanizate when cured under certain conditions. XVII shows conversion of balata to an elastomer as a result of curing over a long period. The corresponding reduction in tensile strength is a further indication that the effect is the result of reducing the degree of crystallization.

The nature and extent of cross linking is also an important factor in contributing to tensile strength and elastic quality. Although only a few cross links are effective in eliminating plastic flow, tensile strength is probably not enhanced greatly by cross links unless they are sufficient in number and properly placed in the three-dimensional gel structure. In other words, the strength of a structure is determined by that of its weakest member.

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Stiffening Effect of Pigments in Rubber

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Results of measurements on gum stocks in compression, particularly those dealing with the effect of the shape of test piece on stiffness, furnish an explanation of the stiffening effect of pigment loadings. In a loaded stock, films of rubber exist between the pigment particles. The films are attached to the particles, and their thickness is of the same order of magnitude as the particle diameter. Under these circumstances it is to be expected that the stiffness of the rubber will be enhanced and the rubber will be working under conditions analogous to those existing when a test piece in compression has a high shape factor—i.e., high ratio of load area to free area. The idea is applied to calculate the relative effect of the volume loading of carbon blacks on stiffness in compression. Agreement with experimental curves is good. The theory explains the systematic change in shape of load-compression curves as pigment loading is increased. It accounts qualitatively for the divergence between the dynamic and static modulus for stocks with carbon black loadings. Essentially, the theory seeks to extend the compression results on large-scale test pieces to the microstructure in the loaded stock.

THE use of reinforcing pigments in rubber, especially in synthetic rubber, is important in securing desirable physical properties. The earlier literature on the subject has been reviewed by Shepard, Street, and Park (*15*). Several theories were advanced to explain the effectiveness of reinforcing pigments in rubber. Some of these emphasized the importance of particle size and shape, and others, the chemical composition and surface activity. The electron microscope has now furnished more reliable information on the particle size and shape of pigments, especially of carbon blacks, than was available in the earlier work (*2*, *18*, *19*). The carbon blacks used in rubber compounding are essentially spherical; the mean diameter varies from 28 to 274 mμ for different types. Systematic studies have been carried out to show the influence of particle size and surface area on various physical testing indices used to evaluate rubber compounds (*8*, *13*, *19*, *20*). The x-ray structure of rubber stocks containing carbon black has been investigated (*7*). Several articles dealing with the theory of pigment reinforcement have appeared (*14*, *18*) This additional work has not clarified the original concepts advanced to explain filler reinforcement, but the research of Wiegand shows beyond doubt that particle size is the predominating factor for explaining differences in the properties of rubber compounded with various blacks. The present paper will attempt to explain some of the effects of pigment reinforcement of rubber, particularly increased stiffness, by simple mechanical considerations which may be regarded as extensions or extrapolations of the results of measurements on rubber in compression.

EFFECT OF SHAPE ON STIFFNESS OF COMPRESSED RUBBER

The analysis of what happens when a piece of rubber is compressed between parallel plates has disclosed a complicated set of circumstances. Because of the practical interest in such deformations of rubber, the work has been thorough (*9*, *10*, *11*, *16*) and the principles are well understood. It has been found that, if the bearing surfaces are lubricated, the compression modulus

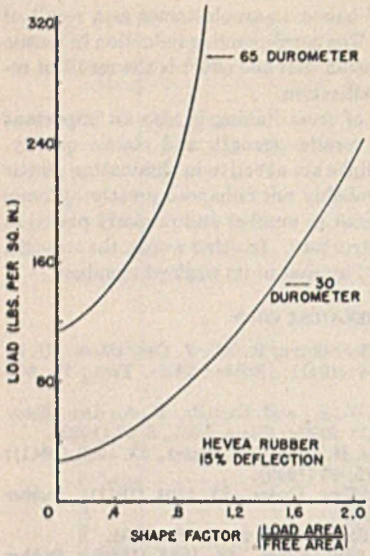

Figure 1. Shape Factor Curves (Data of Kimmich, *11*)

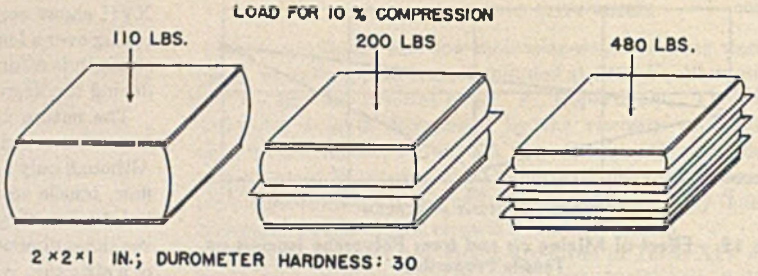

Figure 2. Effect of Restraining Surfaces on Stiffness

is independent of the shape of the test piece and is characteristic of the rubber compound. If the rubber is attached by vulcanization to the surfaces or is prevented by friction from slipping at the surfaces, the situation is different and the apparent modulus depends on the shape of the test piece, particularly on the ratio of load area to free area. When there is no slipping at the surfaces, the stress distribution is complicated. Not even the pressure on the loading plates is uniform but diminishes toward the edges.

As the load-bearing area is increased relative to the free area, the restraint at the surface becomes increasingly effective in raising the apparent modulus or stiffness of the rubber. It has been found empirically that the ratio, load area/free area, which is called "shape factor", can be employed, by the use of appropriate curves, to estimate the stiffness for a wide range of shapes and sizes of rubber pieces for compressive deformations. Figure 1 shows two such curves reproduced from data published by Kimmich (*11*). Test pieces of similar shape but varying in size undergo the same percentage deformation with the same applied compressive stress.

The principle of the increase in compression stiffness by the use of restraining surfaces is illustrated, in Figure 2, by the effect of passing parallel septa through a block of rubber. If the septa and end plates were lubricated, the stiffness would be unaffected by the number and position of the septa. When the rubber is adhered to the end plates and septa as shown, a large increase in stiffness occurs. Incidentally, it can readily be proved that the stiffness of such a system, for a given number of septa, is a maximum when the septa are uniformly spaced. In the picture which will be developed, the pigment particles will be considered to provide the restraining surfaces. If the simple model of Figure 2 can be used, it follows that a uniform pigment dispersion should give maximum stiffness.

Since the use of a shape factor rests entirely on empirical considerations, it is to be expected that there will be limitations on its range of applicability. Hirshfeld and Piron (*9*) observed that a square test piece, $^1/_8$ inch thick, was appreciably stiffer than a long, narrow piece with the same shape factor but twice the thickness. Kimmich confirmed this; his curves are reproduced in Figure 3. Thus there may be a limit to the range of the absolute thickness for which a shape factor, based on relative areas alone, can be consistently used. This does not necessarily mean that the idea of a useful shape factor no longer applies for thin pieces. It is more reasonable to suppose that curves which will be like those shown in Figure 1, but displaced to higher stresses, will apply in a range of smaller absolute thicknesses. At any rate, this will be assumed for the purposes of this theory of pigment reinforcement. More experimental data, especially for very thin pieces of similar shape, would be desirable.

THEORY OF PIGMENT REINFORCEMENT

An effort will be made to extend the relations discussed in the previous section to explain some of the effects of pigment reinforcement of rubber. In many respects the rubber in a loaded stock subjected to compression can be regarded as working under conditions analogous to those obtaining for a gum stock when the shape factor is relatively high. Rubber films exist between pigment particles to which they are firmly attached. For ordinary volume loadings, the thickness of these films is of the same order of magnitude as the particle diameter. X-ray patterns indicate that there is a complicated stress distribution in a loaded stock which also exists for a gum stock with high shape factor. The conditions when a film of rubber in a loaded stock is compressed between pigment particles do not correspond closely with the experimental conditions for which the shape factor relations were found. For spherical particles of carbon black, the loading surfaces are not flat and, strictly speaking, there is no free surface for the compressed films. Nevertheless, under compression the rubber in the thinner portions of the compressed films undoubtedly tends to move out into the adjacent regions where the rubber is thicker. The concept that the rubber in a loaded stock is working at a higher shape factor seems to account in a qualitative way for the general behavior of loaded stocks in compression, as will be shown in this article.

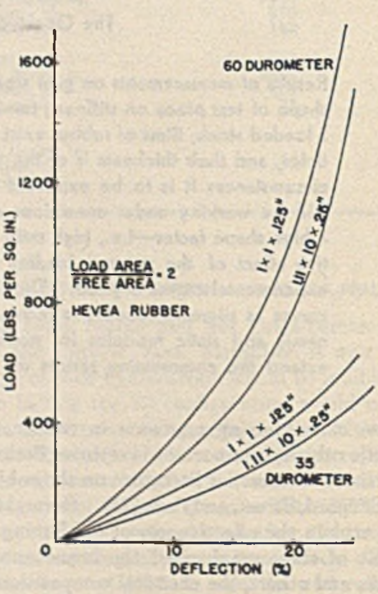

Figure 3. Effect of Thin Test Pieces (*11*)

EFFECT OF VOLUME LOADINGS AND PARTICLE SIZE ON STIFFNESS

To secure some idea of the thickness of the rubber films between particles for various volume loadings of carbon black, it is advantageous to use the results derived from the packing of spheres (*3*, *17*). There are two extreme types of packing for spheres, rhombohedral or "closest" packing and cubical or "most open" packing (Figure 4). In a rubber stock containing carbon black, an idealized structure can be imagined in which the particles are surrounded by spherical shells of rubber. These shells are thought of as packing according to one of the schemes in Figure 4. The interstices or pores are then to be regarded as filled with rubber (Figure 5). It should be emphasized that no physical distinction or boundaries are implied between the rubber surrounding the particles and the rubber in the pores. The picture is merely an aid to thinking and a help in applying the calculations from the packing of spheres. The following notation will be used:

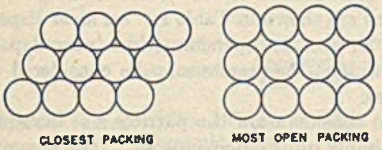

Figure 4. Two-Dimensional Illustration of Types of Packing

V = volume of pigment in 100 volumes of rubber
d = mean particle diameter
D = diameter of imaginary rubber shells around particles
p = porosity of packing of rubber shells = ratio of volume of imaginary pores/total volume

The number of pigment particles in a compound containing 100 volumes of rubber and V volumes of pigment will be $6V/\pi d^3$ (that is, V divided by the volume of a single particle). The total volume, $100 + V$, corrected for the imaginary porosity by multiplication by the factor $(1 - p)$ will equal the volume of the pigment rubber spheres. Since there are $(6V/\pi d^3)$ of these spheres, their total volume is $(6V/\pi d^3)$ multiplied by $(\pi D^3/6)$. Expressing these relations in the form of an equation,

$$(100 + V)(1 - p) = V D^3/d^3 \qquad (1)$$

For closest packing, $p = 0.26$ (from geometry); for most open packing, $p = 0.48$. Actually, p will probably have some intermediate value.

The average minimum thickness of the rubber films between particles will be $D - d$. From Equation 1,

$$D - d = \left[\sqrt[3]{\frac{100 + V}{V}(1 - p)} - 1\right]d \qquad (2)$$

This shows that the thickness of the rubber film between particles for any given volume loading is proportional to the particle diameter. If the type of packing does not change, the structure in the stock for large particles is simply a magnification of the structure for small particles. It follows from the principle of similarity (rubber test pieces of similar shape undergo the same percentage deformation under the same compressive stress) that the stiffness of the films should depend on the volume loading but not on the particle size.

The stress for 300% elongation, commonly called the 300% modulus, is, in fact, insensitive to particle size. As a result of his survey of carbon blacks varying in average diameter from 274 to 13 mμ Wiegand (*20*) concluded that "modulus (at 300%) presents little discernible response to increasing surface"—i.e., particle size. Shore hardness was more dependent on particle size. For GR-S (*1*) there is a secondary upward trend in both modulus and hardness with surface. There is a definite dependence of the compression modulus on the particle size for a given volume loading. This is shown by the curves in Figure 6. According to the theory here proposed, this is a second-order effect due to a dependence of the stiffness of the films, not only on shape factor but on the absolute thickness as illustrated for large test pieces by the curves of Figure 3. Since, as already shown, the thickness of the rubber between particles is proportional to the particle diameter, there is approximately a tenfold variation in film thickness for stocks containing the same volume loadings of Wyex and Thermatomic blacks (*5*). The data plotted in Figure 6 indicate a stiffness ratio for stocks with the two blacks of 1.56 at 10-volume loading and 2.14 at 30-volume loading. The variation in stiffness is small compared to the variation in particle size. The fact that the stiffness ratio for the two blacks increases with volume loading (that is, as the film thickness becomes smaller) tends to confirm the supposition that the effect is due to a dependence of stiffness not only on the shape factor but also on the absolute value of the film thickness.

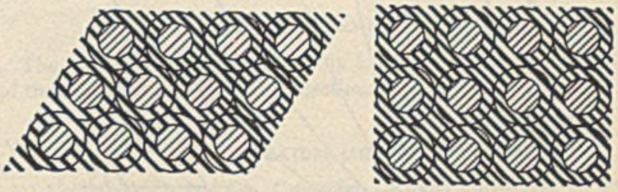

Figure 5. Representation of Pigment Dispersion in Rubber

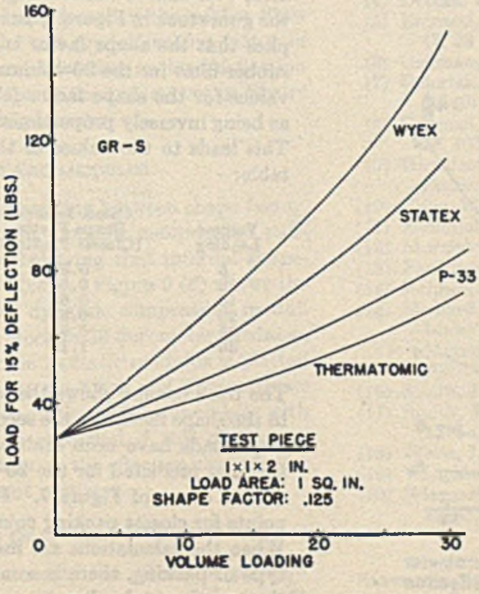

Figure 6. Load-Compression Curves

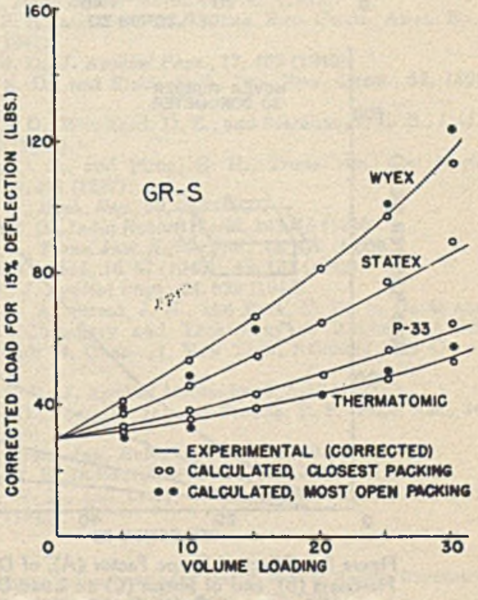

Figure 7. Comparison of Theory with Experiment

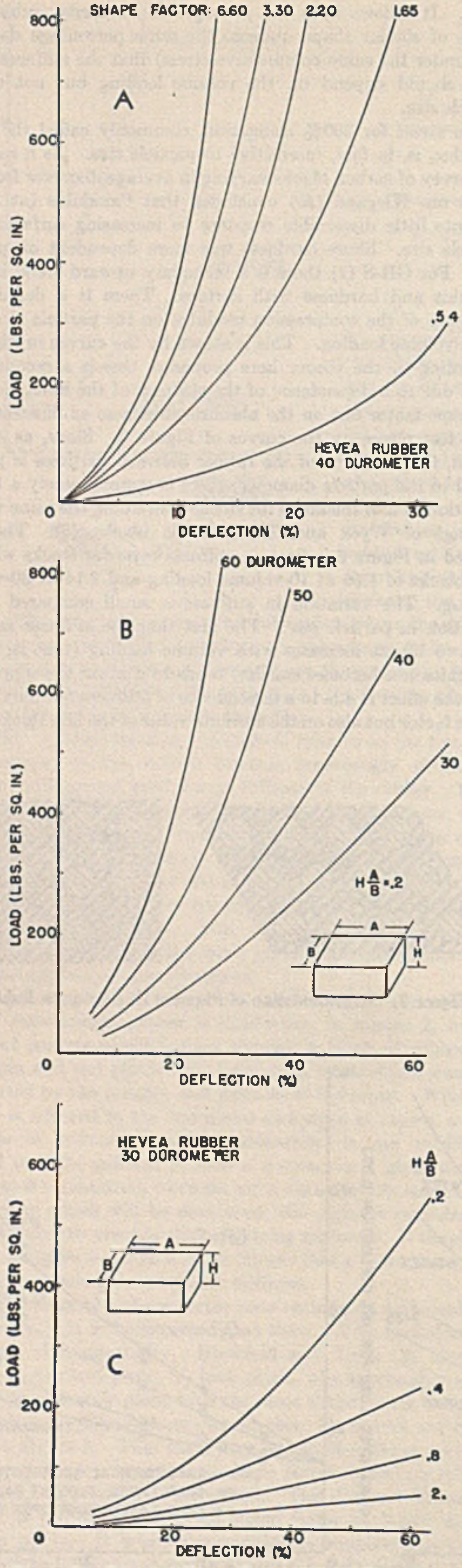

Figure 8. Effect of Shape Factor (*A*), of Durometer Hardness (*B*), and of Shape (*C*) on Load-Deflection Curves (*16*)

Table I. Thickness of Rubber Films between Particles

	Closest Packing		Most Open Packing	
V	$\frac{D}{d}$	Film thickness, $D - d$	$\frac{D}{d}$	Film thickness, $D - d$
5	2.50	1.50d	2.22	1.22d
10	2.01	1.01d	1.79	0.79d
15	1.78	0.78d	1.59	0.59d
20	1.65	0.64d	1.46	0.46d
25	1.55	0.55d	1.37	0.37d
30	1.48	0.48d	1.31	0.31d

Equation 2 can be used to compute the thickness of the rubber films between particles as a function of the volume loading. Results of such calculations are shown in Table I. An ideal dispersion is assumed. For an actual dispersion, which may depart from the ideal rather widely, the results may be considered to represent average values.

Actually, taking into consideration the particle size distribution, the packing is probably quite heterogeneous. The assumption of any systematic packing can be justified only by considering that it may give an average result. The results in Table I taken in conjunction with the shape factor curve for 30-durometer stock (gum stock) in Figure 1 can be used to predict the course of the curves for compression load *vs.* volume loading.

These curves (Figure 6) should first be corrected for the volume of black present. Some of the stiffness of a loaded stock is due merely to the fact that a certain volume of rubber has been replaced by pigment. Since practically all the strain takes place in the rubber, a given percentage strain of the compound implies a larger strain of the rubber in the compound. The correction factor, as pointed out by Morrison (*12*) is 100/(100 + V). If the compression loads for the same deflection are multiplied by this factor, they will all be on a comparable basis in regard to this volume effect. At the highest loading used (30 volumes) the correction amounts to 23%. This is the increase in stiffness to be expected because some of the rubber has been replaced by black. After being corrected in this way, the curves of Figure 6 are replotted in Figure 7.

To test the theory, it can be assumed that the effective shape factor for the rubber films between particles at different volume loadings of the same black is inversely proportional to the thickness of the film. A definite example will be cited to illustrate the procedure: The compression load at 15% deflection for the 20-volume Wyex loading (Figure 7) is increased in the ratio, 81/30 = 2.70, over that for no loading. From the shape factor curve for the gum stock in Figure 1, an increase in the load in this ratio implies that the shape factor is 0.83. If the shape factor for the rubber films for the 20-volume loading of Wyex is taken as 0.83, values for the shape factor for other loadings can be calculated as being inversely proportional to the film thicknesses in Table I. This leads to the values in the second column of the following table:

Volume Loading	Calcd. Internal Shape Factor (Closest Packing)	Load (15% Deflection), Lb./Sq. In.	
		From curve of Figure 1	Adjusted to actual load for $V = 20$
5	0.36	38	41
10	0.53	49	53
15	0.68	61	66
20	0.83	74	80
25	0.98	90	97
30	1.13	106	114

The third column shows the loads, from Figure 1, corresponding to the shape factors in the second column. In the fourth column these loads have been multiplied by a small correction so that the load predicted for the 20-volume loading will fit the experimental curve of Figure 7. Figure 7 shows that the calculated points for closest packing coincide with the experimental curves. When the calculations are made on the basis of the most open type of packing, there is some deviation of the calculated from the experimental values.

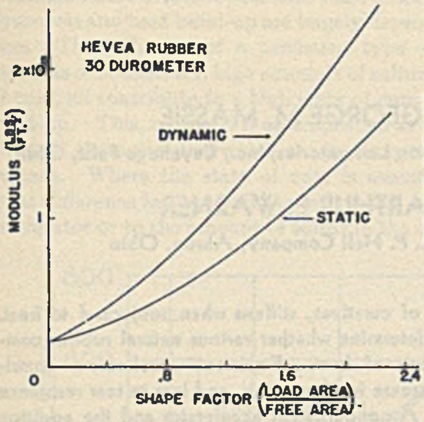

Figure 9. Effect of Shape Factor on Static and Dynamic Tests

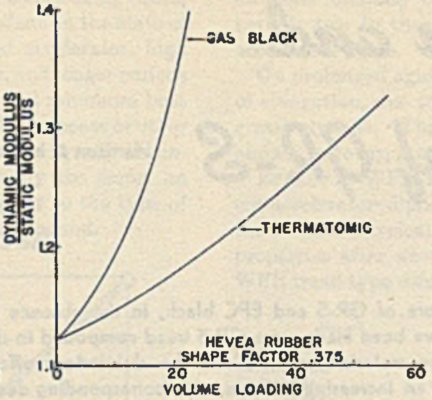

Figure 10. Effect of Pigment Loading on Static and Dynamic Tests

No great exactness can be claimed for the above procedure since the shape factor curve of Figure 1 cannot be expected to apply exactly for the thin films in a loaded stock. The agreement found does lend plausibility to the view that a similar type of curve explains the dependence of stiffness on volume loading.

SHAPE OF LOAD-COMPRESSION CURVES

Some of the general characteristics of the load-compression curves for loaded stocks can be interpreted as shape factor effects. The curves in Figure 8*A*, taken from a paper by Smith (*16*), illustrate the fact that, as the shape factor is progressively raised, the curvature near the origin increases. The curves in Figure 3 show the same sort of increased curvature for the 60-durometer stock as compared to the 35-durometer stock. In terms of the theory here proposed, this increased curvature is attributed to the fact that the rubber films between the pigment particles in the 60-durometer stock have a higher shape factor than in the 35-durometer stock because they are thinner.

The curves in Figure 8*B* (*16*) show the effect of durometer hardness, which is controlled by pigment loading, on the shape of the load-compression curves. The curves in Figure 8*C*, for comparison, show the effect of increasing the shape factor for a 30-durometer stock where the pigment loading is small or negligible. The similarity in the two families of curves in *B* and *C* is submitted as evidence that the shape factor of the rubber films between particles in loaded stocks is a predominating factor in accounting for the effects of pigment loading on load-deflection curves. The difference in the shape of the two curves in Figure 1 is also amenable to this type of explanation.

DYNAMIC AND STATIC MODULUS

An examination of the relations existing between shape factor, durometer hardness, and static and dynamic compression stiffness discloses further reasons for believing that internal shape-factor effects occur in pigmented stocks. Figure 9 (*6*) shows the divergence between the static and dynamic compression moduli at higher shape factors for a gum stock of 30 durometer hardness.

In Figure 10 the ratio of dynamic to static modulus is plotted as a function of volume loading for gas black and Thermatomic loadings. The ratio of dynamic to static modulus increases with pigment loading, which would be predicted if this divergence were a shape-factor effect dependent on the effective shape factor of the rubber films between pigment particles.

LIMITATIONS OF THEORY

The explanations offered for some of the effects of pigment loadings in rubber appear adequate for the range of phenomena considered and are so plausible that they should probably be taken into account in the explanation of all reinforcement phenomena. Many important aspects of pigment reinforcement, such as the effect on resilience, have not been touched on since no data were available on the resilience of thin films in compression. Experimental work on that point might well be successful in extending the theory. Undoubtedly there are many aspects of reinforcement which are not controlled by the relatively simple mechanical ideas advanced here to explain compression stiffness. Variations from results to be expected on the basis of a straightforward shape factor interpretation might occur for a number of reasons. Among these should be mentioned particle size distribution, particle shape, and especially pigment dispersion. Still the idea should persist that the effects are largely mechanical in a more complicated system. It should be pointed out that there is, in some cases, a variation in the stiffening effect of pigment loadings for different types of rubber. Thus pigment loadings are relatively ineffective in stiffening Butyl rubber (*4*). This may be related to the type of dispersion secured. At any rate, curves of the effect of shape factor on the stiffness of Butyl rubber gum stock would have to be studied before this fact could be advanced as an argument against the theory. One of the most important consequences of the theory should be to emphasize the importance of pigment dispersion.

ACKNOWLEDGMENT

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Vulcanization and Heat Aging of GR-S

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A mixture of GR-S and EPC black, in the absence of curatives, stiffens when subjected to heat. Tests have been made on a GR-S tread compound to determine whether various natural rubber compounding materials may reduce the deleterious effects of heat. Persistent accelerators contribute to an increasing stiffness with corresponding decrease in elongation, and loss in tear resistance with increasing time of cure and on air-oven aging. A nonpersistent accelerator and the addition of diphenyl ethylene diamine aid in reducing these effects. In a GR-S vulcanizate containing a nonpersistent accelerator, the amount of added sulfur has a marked effect on the rate of change in physical properties on air-oven aging; 5 parts of zinc oxide yield a more stable vulcanizate than lesser amounts; natural rubber antioxidants show varying degrees of effectiveness in maintaining elongation after air-oven aging.

IN COMPARISON to rubber, GR-S gives a vulcanized product which is more resistant to deterioration from oxidation than is the natural product (*8*, *9*). However, the changes resulting from the effect of heat on GR-S are rapid and are often evident during the course of vulcanization. Under normal service conditions, the vulcanizate may be subjected to heat of external origin or to that which arises from hysteresis effects. This is particularly true of GR-S inner tubes and tires, and is probably one of several factors contributing to premature failure.

The effect of heat aging on the physical properties of GR-S vulcanizates has been reported, and the magnitude of such changes has been compared to similar natural rubber compounds (*7*, *9*). In general, the effect of heat is a trend toward a shorter, more brittle stock, showing an increase in modulus and durometer hardness and a decrease in elongation, tear resistance, and tensile strength. The rate of deterioration for many of these physical properties is approximately doubled for an 18° F. (10° C.) rise in aging temperature. In contrast, natural rubber vulcanizates, upon continued heating, usually become softer and exhibit depolymerization.

During heat aging, the deterioration of natural rubber may be considered to be the combined effect of depolymerization, oxidation, and aftervulcanization. Other conditions being equal, the magnitude of the deterioration produced is dependent on the amount of sulfur present and its state in the vulcanizate, the type of accelerator, and the effectiveness of the added antioxidant. In many cases a combination of two types of antioxidants provides a protection which is greater than the additive effect of the components.

It is not unlikely that GR-S vulcanizates, when subjected to air-oven aging, undergo deterioration resulting from a combination of several effects. If such is the case, it might be expected that the amount and type of the curative would exert a considerable effect on heat aging. The addition of an antioxidant of a type different from that already present in the GR-S may show some value over a single-component antioxidant.

Up to the present time, much of the art of the compounding of GR-S has of necessity been confined to the adaptation of compounding materials normally used with natural rubber. The purpose of this investigation is to determine the effect of some of these materials on the stability of GR-S during heat of vulcanization, as well as the stability of the vulcanizate to heat aging as indicated by air-oven tests.

TESTING AND HEAT AGING

Data were obtained on three separate batches of GR-S, supplied by Rubber Reserve Company during June, August, and September, 1943. Comparison of physical properties was made only on stocks compounded from the same batch of GR-S, cured, and tested at the same time.

The following physical characteristics were determined at room temperature: stress strain (*1*), Shore durometer hardness type A (*4*), crescent tear resistance using die A (*3*). Air-oven tests were carried out at 250° F. and Geer oven tests (*2*) at 158° F. All tests were confined to a GR-S tread-type compound.

The nonpersistent accelerator used was lead (phenyl aminoethyl) dimethyl dithiocarbamate (*11*). It is referred to simply as lead dithiocarbamate type.

To illustrate the instability to heat of unvulcanized GR-S, a mixture was compounded and treated as follows: GR-S, 100 parts; EPC black, 50; softener, 5.

The stock was sheeted smooth and free from air bubbles on the back roll of a 12-inch laboratory mill and then heated in a vulcanizing press for 60 minutes at 287° F. (142° C.). Sufficient stiffening had taken place to permit the removal of the stock from the mold. Dumb bell strips were died out and aged in the air oven for 1, 3, 5, and 10 days at 250° F. (121° C.). The change in physical properties with time of aging is shown in Figure 1.

It is possible that the changes on heating are not entirely due to the instability of the polymer, but may be due in part to action of the carbon black on GR-S or to the presence of small amounts of sulfur or sulfur compounds in the polymer (*5*) and in the softener. Undoubtedly the carbon black contributes much to tensile strength and modulus. In any case, the striking point is that such a mixture, common to a large number of GR-S type compounds, undergoes a high degree of change even in the absence of added curatives. This instability possibly persists in the vulcanizate and causes much of the characteristic hardening of GR-S compounds on heating.

PERSISTENT AND NONPERSISTENT ACCELERATORS

Effect of Added Antioxidant. With regard to the general pattern of the change in physical properties with time of cure, accelerators are of two types (*6*, *9*). The persistent accelerators, of which mercaptobenzothiazole is typical, are characterized by a relatively slow development of physical properties and a comparatively greater change in properties with time of cure.

Derivatives of mercaptobenzothiazole, sulfamines, and mercaptothiazolines follow patterns similar to mercaptobenzothiazole (*9*). In contrast, the nonpersistent accelerators (dithiocarbamate types) show a more rapid development of physical properties and better maintenance of such properties on extended time of cure.

Accumulated evidence indicates that, other things being equal, hysteresis and heat build-up are largely dependent on the state of cure. Thus, the use of a persistent type of accelerator, high amounts of accelerator, high amounts of sulfur, and longer periods of cure, all contribute to a high state of cure and minimum heat build-up. This, however, is accomplished at the expense of other physical characteristics which are in many cases equally as important. Where the state of cure is essentially the same, no great difference in heat build-up exists due either to the type of accelerator or to the amount of sulfur in the compound.

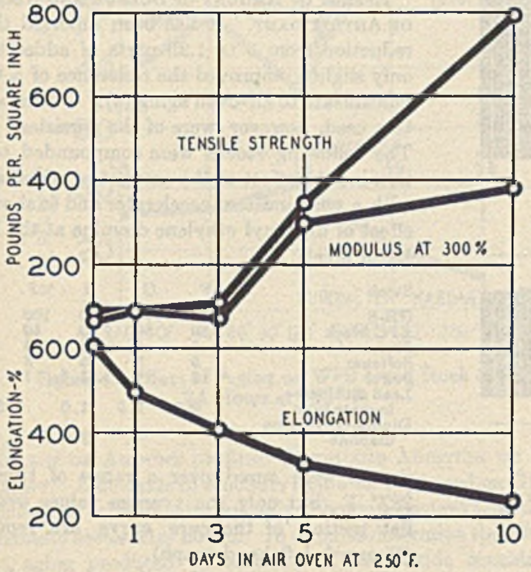

Figure 1. Change in Physical Properties after Air-Oven Aging

The effect of added diphenyl ethylene diamine, an antioxidant used in natural rubber, was investigated with a number of persistent and nonpersistent accelerators. Typical results obtained with one of each type of accelerator are reported. The base compound used was: GR-S, 100; EPC black, 50; zinc oxide, 5; softener, 5; sulfur, 1.6; accelerator and antioxidant as indicated. The stocks were cured over a range of time at 280° F. (138° C.). Original physical properties are shown in Table I.

At this sulfur level the persistent accelerator is less efficient and the resulting vulcanizate does not reach a state of cure as high as that attained in the compound containing the nonpersistent type. This is evident in lower moduli and excessively high ultimate elongations. In the compound containing the persistent type accelerator, diphenyl ethylene diamine appears to have a retarding effect on the increase in modulus and decrease in elongation with extended time of cure. This effect is more apparent with the nonpersistent type accelerator. The modulus remains constant at a lower level after a maximum value has developed. Ultimate elongation remains higher throughout a broader curing range.

The 60- and 30-minute cures for the compounds containing the persistent and nonpersistent type accelerators, respectively, were aged for 6, 12, 18, 24, 30, and 48 hours in the air oven at 250° F. The type of accelerator has a marked effect on the rate of change in elongation with time of aging (Figure 2). It is significant that, in maintaining relatively high percentages of the original elongation, the nonpersistent accelerator–diphenyl ethylene diamine combination is effective throughout aging periods two to three times longer than the persistent type of accelerator alone.

On prolonged aging at 250° F., differences in the maintenance of elongation, due to different types of accelerator, become progressively less. The protective effect of diphenyl ethylene diamine, however, is still evident after 48 hours.

EFFECT IN WPB TREAD STOCK. The effect of the nonpersistent accelerator–diphenyl ethylene diamine combination above on the original physical properties and on the maintenance of these properties after air-oven aging was investigated in a practical WPB tread type compound (*10*):

Stock	A	B	C	D	E
GR-S	100	100	100	100	100
Stearic acid	1	1	1	1	1
Zinc oxide	3	3	3	3	3
MPC black	43	43	43	43	43
Bardol	4.5	4.5	4.5	4.5	4.5
Cumar MH 2½	2.0	2.0	2.0	2.0	2.0
Sulfur	1.6	1.75	2.5	1.6	1.8
Accelerator, 1.6+	0.1[a]	1.2[b]	1.2[c]	1.2[d]	1.0[d]
Diphenyl ethylene diamine	...	...	...	2.0	2.0

[a] Mercaptobenzothiazole–DPG mixture (persistent type).
[b] Sulfamine type (persistent).
[c] Aldehyde-amine thiazole derivative (persistent).
[d] Lead dithiocarbamate type accelerator (nonpersistent type).

The compounds were cured over a considerable range of time at 280° F. Values for all cures before and after air-oven aging for 24 hours at 250° F. are reported (Figure 3).

With regard to the change in properties with time of cure, stocks A, B, and C undergo what has been called "marching modulus", whereas D and E are remarkably flat curing. On aging, the nonpersistent accelerated stocks show better maintenance of tensile strength, and the increase in modulus is less than half of that shown by the persistent accelerators.

The average values over the cure range of 45 to 120 minutes for ultimate elongation, tear resistance, and durometer hardness for all stocks are nearly alike (Figure 4). On aging, stocks D and E are outstandingly superior in the maintenance of these properties. The degree of improvement in resistance to heat aging seems to be of the order of that reported for dinitrobenzene vulcanizates (*8*).

Juve and Garvey (*6*) showed that much of the continued stiffening of a persistent type accelerated stock with increasing time of cure is due to the availability of a considerable amount of free sulfur. The nonpersistent accelerators combine sulfur at a more rapid rate and to a comparatively greater extent; thus substantially no free sulfur is available after optimum cure is reached.

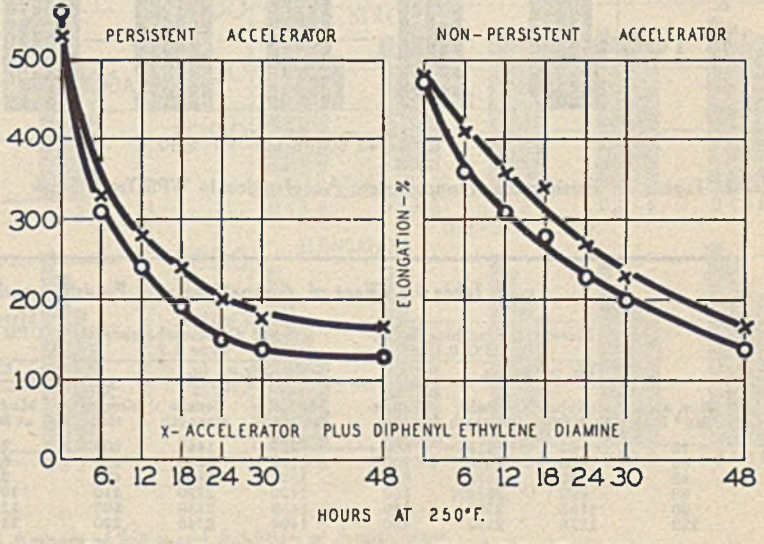

Figure 2. Change in Elongation with Time of Air-Oven Aging

It is believed that these differences in the amount of free sulfur in the vulcanizate contribute largely to the differences in the initial rate of deterioration on air-oven aging. Diphenyl ethylene diamine appears to have an activating effect on the antioxidant already present in the GR-S in that it shows an increased effect as an inhibitor of polymerization.

NONPERSISTENT ACCELERATION

Effect of Amount of Sulfur and Addition of Antioxidant. It has been reported that a reduction from 3 to 1.25 parts of added sulfur only slightly improved the resistance of a GR-S vulcanizate to air-oven aging (*8*). The accelerators used, however, were of the persistent type. The following stocks were compounded to determine the effect of the amount of added sulfur with a nonpersistent accelerator and to show the effect of diphenyl ethylene diamine at the lower sulfur levels:

Stock	F	G	H	J	K
GR-S	100	100	100	100	100
EPC black	50	50	50	50	50
Zinc oxide	5	5	5	5	5
Softener	5	5	5	5	5
Sulfur	2	1.5	1.5	1	1
Lead dithiocarbamate type	0.75	1.0	1.0	1.5	1.5
Diphenyl ethylene diamine	..	..	2.0	..	2.0

Stocks were cured over a range of times at 287° F., but only the average values over the flat section of the cure curve are reported (Figure 5, left-hand graph).

The results show that the original physical properties are not appreciably affected by a reduction in sulfur, provided the reduction is compensated by an increase in the amount of accelerator. The lower-sulfur stocks provide improved maintenance of tensile strength and elongation on aging. After 3 days in the air oven at 250° F. the elongation of the stock containing 2 parts sulfur is approximately half that of the stock containing 1 part sulfur. Diphenyl ethylene diamine shows additional improvement at both sulfur levels.

The above stocks were aged for 1, 3, and 6 weeks in the Geer oven at 158° F. (70° C.). The change in physical properties with time of aging follows the same general pattern as at 250° F. (Figure 5, right-hand graph). Aging at the lower temperature is markedly less severe. With regard to elongation, approximately 6 weeks at 158° F. are required to produce changes of the order of those obtained after 1 day at 250° F.

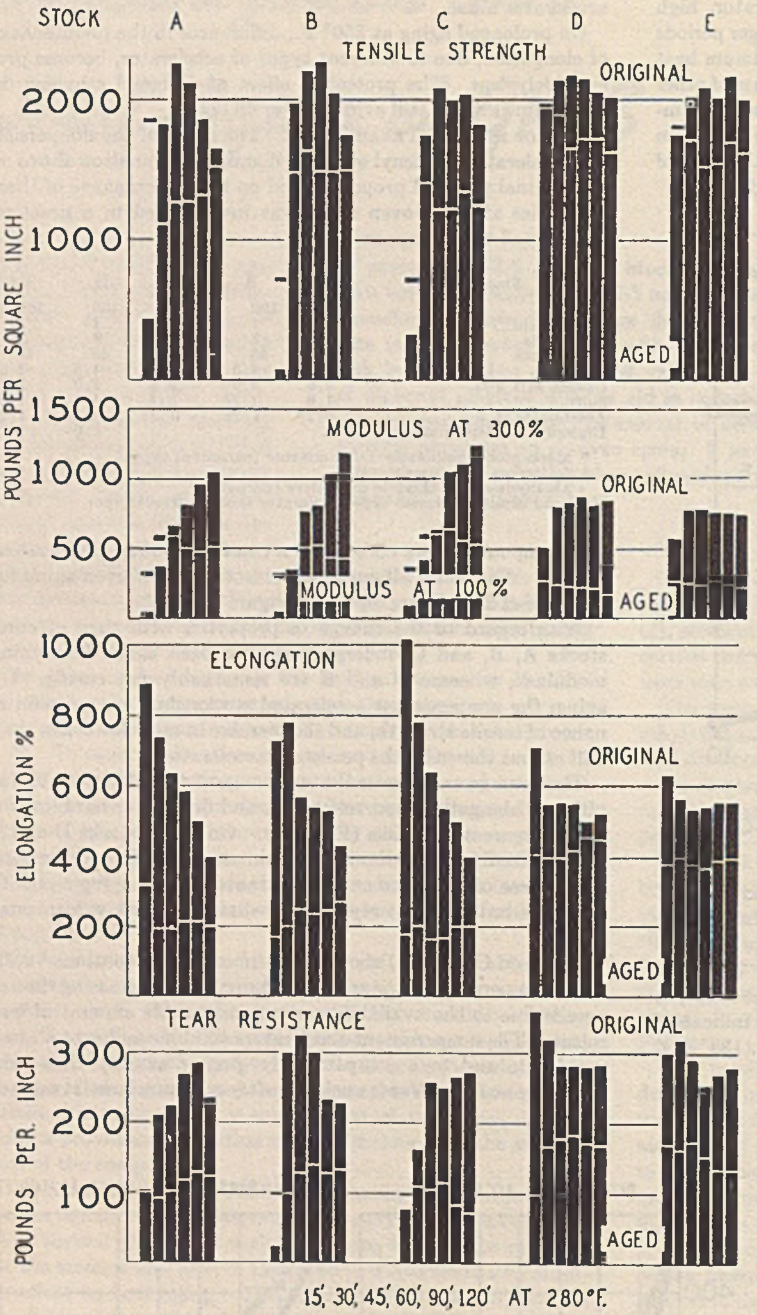

Figure 3. Persistent vs. Nonpersistent Acceleration in WPB Tread Stock

Table I. Effect of Antioxidant with Persistent and Nonpersistent Acceleration

Min. at 280° F.	Mercaptobenzothiazole 1.6 + DPG 0.1: Modulus at 300%, Lb. per sq. in.	Mercaptobenzothiazole 1.6 + DPG 0.1: Tensile strength, Lb. per sq. in.	Mercaptobenzothiazole 1.6 + DPG 0.1: % Elongation	Lead Dithiocarbamate Type 1.2: Modulus at 300%, Lb. per sq. in.	Lead Dithiocarbamate Type 1.2: Tensile strength, Lb. per sq. in.	Lead Dithiocarbamate Type 1.2: % elongation	Mercaptobenzothiazole 1.6 + DPG 0.1 + Diphenyl Ethylene Diamine 2: Modulus at 300%, Lb. per sq. in.	Mercaptobenzothiazole 1.6 + DPG 0.1 + Diphenyl Ethylene Diamine 2: Tensile strength, Lb. per sq. in.	Mercaptobenzothiazole 1.6 + DPG 0.1 + Diphenyl Ethylene Diamine 2: % elongation	Lead Dithiocarbamate Type 1.2 + Diphenyl Ethylene Diamine 2: Modulus at 300%, Lb. per sq. in.	Lead Dithiocarbamate Type 1.2 + Diphenyl Ethylene Diamine 2: Tensile strength, Lb. per sq. in.	Lead Dithiocarbamate Type 1.2 + Diphenyl Ethylene Diamine 2: % elongation
15	85	615	960	350	1445	700	245	1135	810	690	2265	600
30	460	2025	700	1110	2285	470	620	2245	650	1115	2280	480
45	750	2575	620	1320	2330	430	915	2510	570	1225	2410	470
60	970	2545	560	1420	2320	410	1010	2680	530	1225	2425	460
90	1185	2505	510	1430	2250	400	1115	2430	500	1245	2380	450
120	1275	2255	480	1490	2245	390	1190	2350	480	1220	2370	450

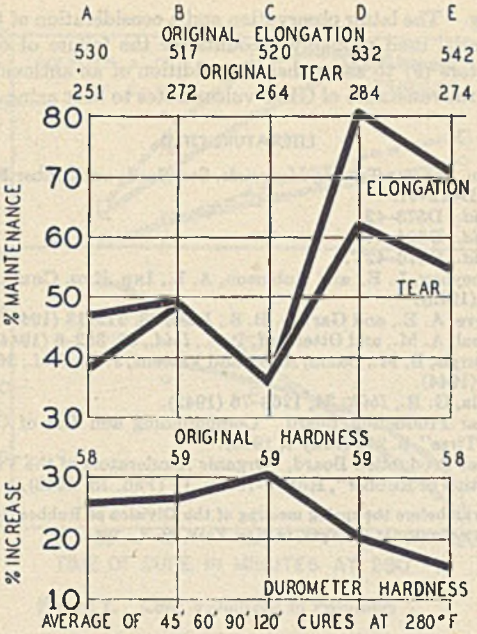

Figure 4. Effect of Aging on WPB Tread Stock after 24 Hours at 250° F.

Effect of Amount of Zinc Oxide and Addition of Antioxidant. Zinc oxide in amounts as low as 1% based on GR-S is sufficient to activate substantially the nonpersistent lead dithiocarbamate accelerator above. In order to determine the effect on heat aging produced by amounts of zinc oxide considerably higher than that required for activation and to show the effect of diphenyl ethylene diamine at each zinc oxide level, a series of stocks was compounded. The base compound used was: GR-S, 100; EPC black, 40; softener, 5.0; sulfur, 1.5; lead dithiocarbamate type accelerator, 1.25; zinc oxide and diphenyl ethylene diamine as indicated. These compounds were cured over a range of time at 280° F. and were tested both before and after aging 24 hours in the air oven at 250° F. The average physical properties are shown in Table II.

Table II. Effect of Antioxidant at Various Zinc Oxide Levels

(Average of 30-, 45-, 60-, and 90-minute cures at 280° F.)

Zinc Oxide, Parts	Diphenyl Ethylene Diamine, Parts	Age of Stock	Lb./Sq. In. Modulus at 200%	Lb./Sq. In. Tensile	Tear Resistance, Lb./In.	Elongation, %	Durometer Hardness
1.0	None	Original	299	2199	186	588	52.2
		Aged	655	1410	97	355	61.8
1.0	1.5	Original	254	2110	215	612	51.2
		Aged	542	1469	137	380	58.5
3.0	None	Original	451	2236	180	546	54.5
		Aged	774	1422	89	325	64.8
3.0	1.5	Original	418	2299	172	540	35.0
		Aged	570	1446	117	400	62.0
5.0	None	Original	540	2066	184	560	54.5
		Aged	649	1649	88	402	64.0
5.0	1.5	Original	401	1932	180	585	54.5
		Aged	506	1656	103	495	62.2

Table III. Effect of Various Antioxidants with Nonpersistent Acceleration

(Average of 30-, 45-, 60-, 90-, and 120-minute cures at 287° F.)

Added Antioxidant	Original Elongation, %	Elongation Retained after Air-Oven Aging at 250° F., % 24 hr.	48 hr.
None	385	71.7	62.6
Diphenyl ethylene diamine	454	84.1	71.1
sym-Di-β-naphthyl-*p*-phenylene diamine	417	78.9	69.3
Di-*o*-tolyl ethylene diamine	437	75.9	67.1
Ketone-amine reaction product	425	73.9	65.6
Ketone–diarylamine	430	69.3	61.2
Polymerized trimethyldihydroquinoline	420	75.0	67.8
Diphenyl propylene diamine	446	84.7	75.5

The higher amounts of zinc oxide result in a more stable vulcanizate with improved maintenance of tensile strength and ultimate elongation, and less change in modulus on aging. However, there appears to be no significant difference in the aged modulus values at all three zinc oxide levels. The amount of zinc oxide has no appreciable effect on tear resistance or on the maintenance of tear resistance.

The addition of diphenyl ethylene diamine at the lower zinc oxide level results in less change in modulus on aging. This effect is minimized as the amount of zinc oxide is increased to 5 parts; however, the aged modulus values are considerably lower At

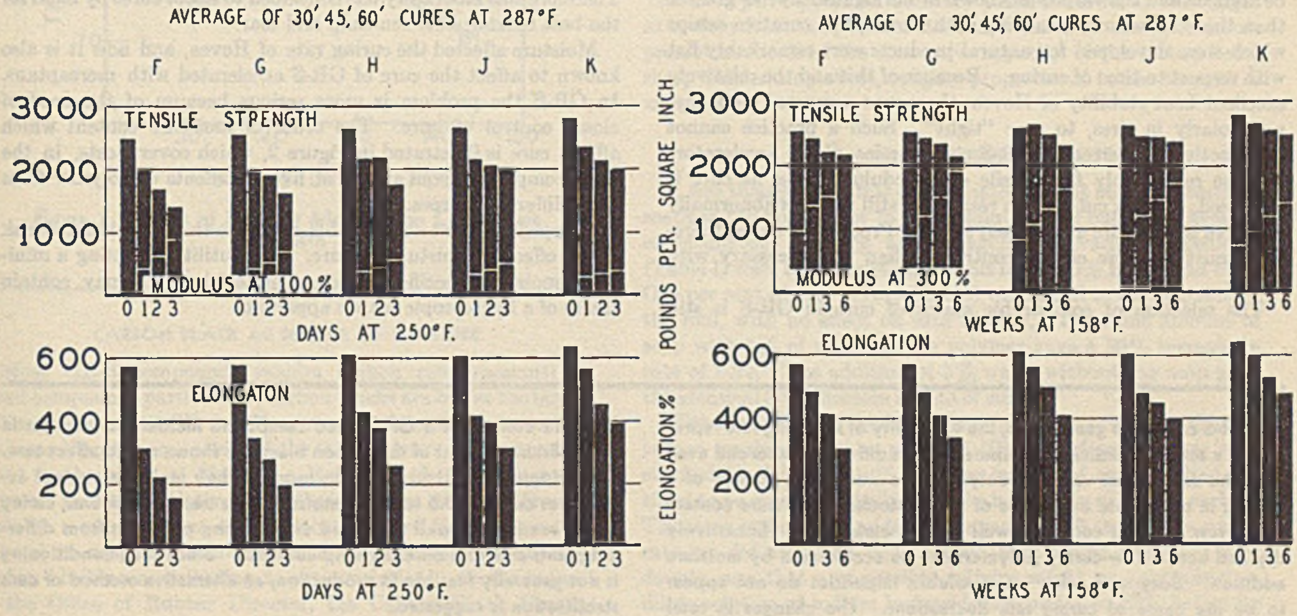

Figure 5. Effect of Amount of Sulfur and Addition of Antioxidant

each zinc oxide level there is improved maintenance of elongation and the degree of improvement is of a higher order at the higher zinc oxide level. Diphenyl ethylene diamine has no effect on the maintenance of tensile strength; the maintenance of tear resistance is, however, somewhat improved.

EFFECT OF VARIOUS ANTIOXIDANTS. To determine whether materials other than diphenyl ethylene diamine improved the resistance of GR-S vulcanizates to air-oven aging, a number of organic compounds having antioxidant properties in natural rubber were investigated. The base compound used was: GR-S, 100; EPC black, 50; zinc oxide, 5; sulfur, 1.5; and lead dithiocarbamate type accelerator, 1.2. Table III shows the percentage elongation retained after 24 and 48 hours of air-oven aging at 250° F. when 2 parts of these materials are added to the antioxidant already present in the GR-S.

The results show that these materials have varying degrees of effectiveness in maintaining elongation in this particular base compound. At higher sulfur levels and in compounds accelerated with persistent type accelerators, there is a tendency for the protective effect obtained with added antioxidant to be minimized or completely overshadowed by the comparatively more rapid rate of aging. The latter observation and a consideration of the type of material used probably accounts for the failure of other investigators (*8*) to show that the addition of an antioxidant improves the resistance of GR-S vulcanizates to heat aging.

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(10) War Production Board, "Compounding and Use of GR-S for Tires", p. 215 (May 1, 1943).
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PRESENTED before the spring meeting of the Division of Rubber Chemistry, AMERICAN CHEMICAL SOCIETY, in New York, N. Y., 1944.

EFFECT OF MOISTURE ON *Curing Rate of GR-S*

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ONE of the most serious variables in GR-S has been its curing rate. This is illustrated in Figure 1, where two shipments of standard GR-S are compared. The basic test compound was: GR-S, 100 parts; EPC black, 50; coal tar softener, 5; zinc oxide, 5; mercaptobenzothiazole, 1.5; sulfur, 2. It might be argued that the variations shown in curing rate are no greater than those sometimes occurring with Hevea, but curative setups which were developed for natural products were remarkably flat with respect to time of curing. Because of this and the relatively excellent heat stability of Hevea, there was a general tendency, particularly in tires, to cure "tight". Such a practice cannot be directly transferred to GR-S compounds. Some accelerators do give remarkably flat tensile and modulus curves as cure is increased, but flex cut-growth resistance still remains abnormally sensitive to overcure and to heat aging. Production cures, therefore, must be more closely controlled than was necessary with Hevea.

The selection of comparable states of cure in GR-S is still far from an exact science. Any system based on modulus is liable to confusion if normal variations exist in the gel content of the polymer as manufactured, as well as in the time and particularly the temperature of processing, to mention only two causes of modulus fluctuation not attributable to cure alone. Therefore this laboratory has continued to select cures by hand for the best balance between snap and tear.

Moisture affected the curing rate of Hevea, and now it is also known to affect the cure of GR-S accelerated with mercaptans. In GR-S the problem is more serious because of the need of closer control of cure. The order of moisture content which affects cure is illustrated in Figure 2, which covers tests, in the basic compound given above, of five shipments of polymer from three different sources.

It appears that at about 0.15% moisture there is a sharp break in the effect of moisture on cure. The futility of setting a minimum moisture specification on a material which may contain traces of a hygroscopic soap is apparent.

As GR-S came into general use, the variability of its curing rate represented a serious handicap. Shipments from different plants and even from the same plant varied widely. There was also evidence of a change in curing rate on storage of mixed stocks. Moisture content of the raw polymer correlates well with its curing rate. Excessively dry and hence slow-curing polymers can be accelerated by moisture addition. Soap and other water-soluble impurities do not appear to be the cause of curing rate fluctuations. The changes in total moisture content of a GR-S tread compound incident to changes in the moisture content of the carbon black are shown not to affect cure. Conditioning of mixed stocks to increase their moisture content accelerates cure; at 0.5 to 1.0% moisture on a tread compound, curing rate is reasonably well stabilized even among polymers from different plants and with differing soap contents. Since such conditioning is not generally feasible in production, an alternative method of cure stabilization is suggested.

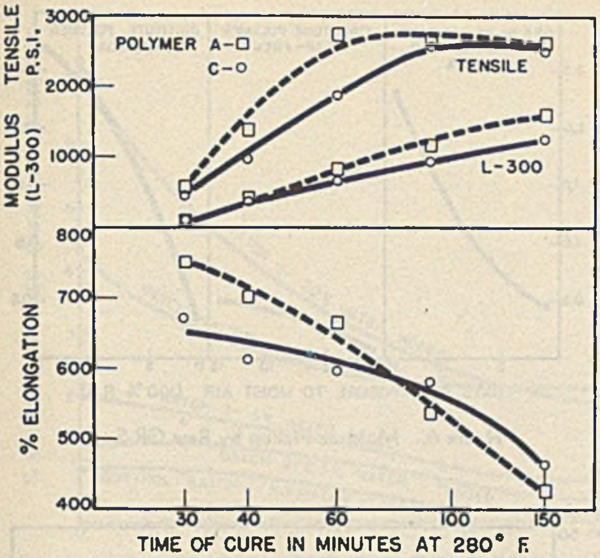

Figure 1. Cure Variations in Polymers

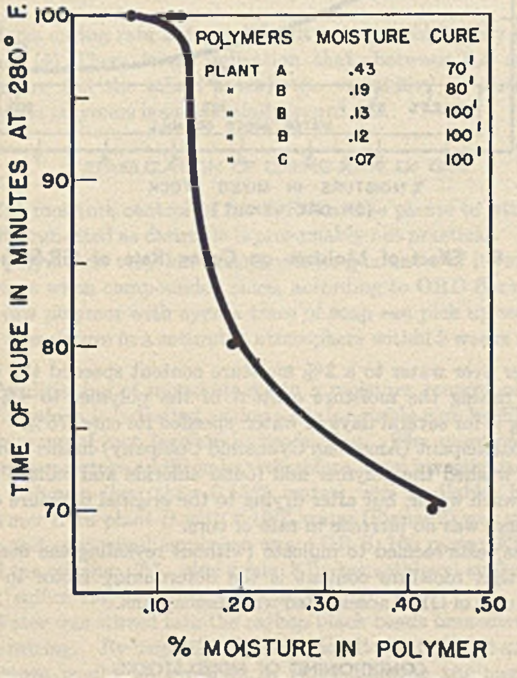

Figure 2. Effect of Polymer Moisture on Curing Rate of GR-S

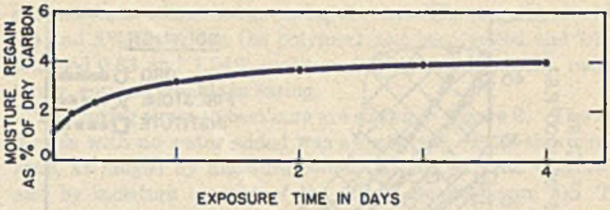

Figure 3. Moisture Regain in Rubber Channel Carbon over Water

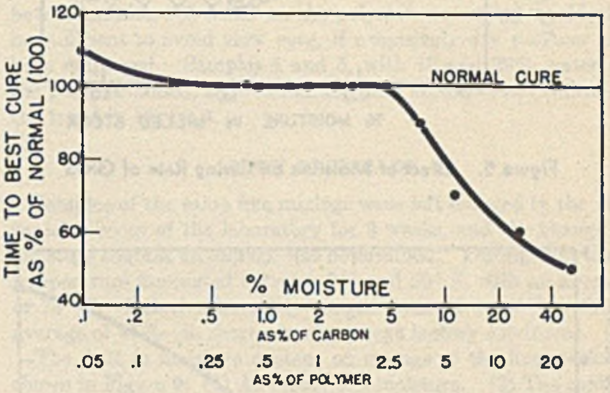

Figure 4. Effect of Moisture in Carbon Black on Cure of GR-S

CARBON BLACK AS SOURCE OF MOISTURE

Most GR-S compounds require carbon reinforcement; in tread compounds particularly, carbon blacks are by far the largest volume addition to GR-S. They may vary in moisture content by more than the equivalent of the 0.15% shown as the breaking point in the curve of Figure 2. Rubber-grade channel carbon exposed to 100% relative humidity at room temperature can pick up a maximum of 4% moisture (Figure 3). It was thus natural to suspect possible variations in moisture content of carbon black as contributing to cure variation. At the request of the Office of Rubber Director, the Carbon Black Nomenclature Committee investigated the effect of moisture in carbon black on the curing rate of GR-S. The results are summarized graphically in Figure 4. The normal moisture content of commercial rubber carbons, as delivered to the rubber manufacturer, varies between about 1 and 3%. The maximum content by absorption during shipping and storage is about 3%. The bone-dry sample of Figure 4 was artificially dried to 0.05% moisture and added to the mix directly from the drying oven. Samples were conditioned over water to various moisture contents up to 3.5%. For moisture contents in excess of this amount, it was necessary to add water to the carbon immediately before mixing. It is apparent that the normally occurring amounts of moisture on carbon black are held so tightly that they do not affect cure. The absorptive power of bone-dry black is shown to be so great as to dehydrate the polymer itself and retard its cure. Moisture present in excess of the absorptive capacity of the carbon has a sharp accelerating effect, roughly proportional to the amount of water added.

SOAP AND WATER-SOLUBLE SALTS

It was thought that this cure variation might be due to residual soaps in the polymer or to water-soluble salts remaining because of insufficient washing after coagulation; various expedients (Table I) were tried to determine this in the 50% EPC tread base. One per cent of soap (Ivory Flakes) was added to the polymer on the mill, with no effect on rate of cure. The same amount of soap with 5% of water on the polymer gave a 30% increase in rate of cure. The addition of 5% water without the soap gave the identical 30% increase in rate of cure.

With the idea that soluble sulfates might be present, a channel carbon produced with a pH of 7 (Hi-tear Micronex) was substituted for EPC; a 10% increase in rate of cure resulted, an effect to be expected wholly from the increase in pH of the carbon. The same carbon with added water gave a 50% increase in curing rate, as did standard EPC carbon with added water. To be doubly sure that any possible sulfates might be neutralized, a dilute solution of sodium hydroxide was added to EPC before its incorporation into the GR-S; there was a 60% increase in curing rate. This gave distinct evidence that water, rather than traces

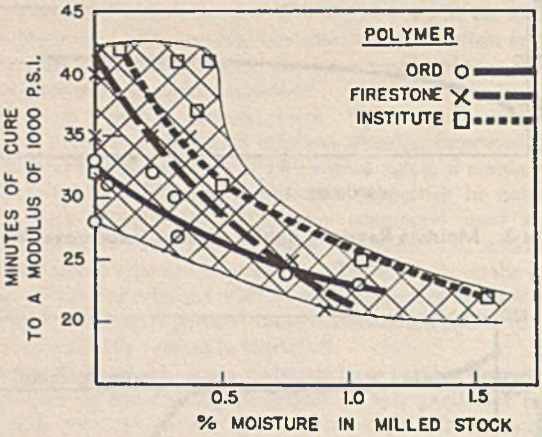

Figure 5. Effect of Moisture on Curing Rate of GR-S

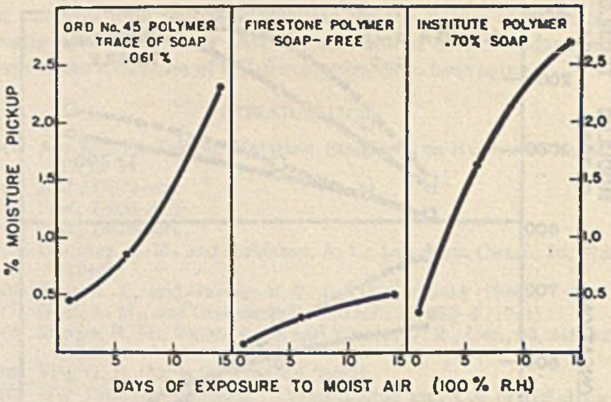

Figure 6. Moisture Pickup by Raw GR-S

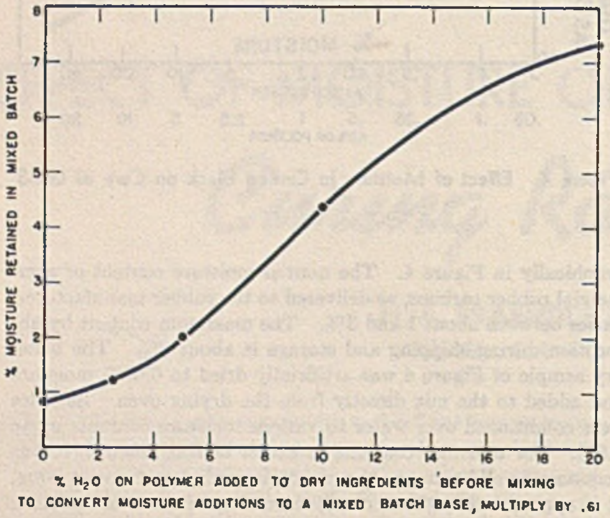

Figure 7. Moisture Retention of a GR-S Tread Stock, Mixed on a Laboratory Mill

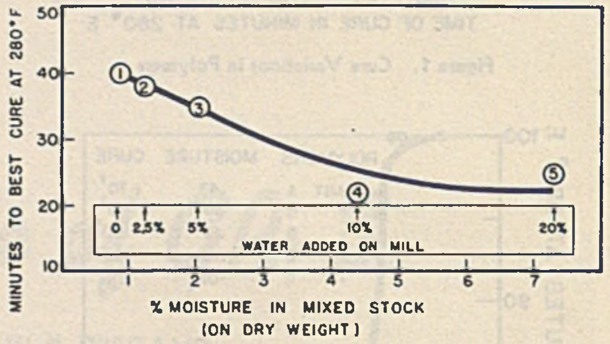

Figure 8. Effect of Moisture on Curing Rate of GR-S Tread

of sulfates or other electrolytes, was the determining factor in curing rate.

This laboratory was also invited to participate in the investigation of a sample of slow-curing polymer (ORD Survey No. 17) which had required recompounding to correct its slow cure. This polymer was found to be excessively dry (0.012 to 0.08% moisture). Addition of 5% water (on the polymer) with the carbon in the test compound speeded the cure 45%; conditioning the polymer over water to a 2% moisture content speeded the cure 60%; raising the moisture content of the polymer to 4% by soaking it for several days in water speeded its cure 75%. Another participant (American Cyanamid Company) in this investigation washed the polymer and found chloride and sulfate ions in the wash water, but after drying to the original moisture content there was no increase in rate of cure.

These tests seemed to indicate (without revealing the mechanism) that moisture content is the determining factor in the rate of cure of GR-S accelerated with mercaptans.

Table I. Effect of Soap and Water-Soluble Salts on Variation in Cure of GR-S (50% EPC Tread Base)

Variables	Cure Effect
1% soap (Ivory Flakes) added	No effect
1% soap + 5% water added	30% increase
5% water added	30% increase
Hi-tear Micronex (pH 7) substituted for EPC	10% increase
Hi-tear Micronex + 5% water added	50% increase
EPC + 5% water added	50% increase
EPC + 5% dilute NaOH soln.	60% increase
Slow-curing polymer (0.08% H_2O), ORD Survey 17	Control
5% water added	45% increase
Polymer preconditioned over H_2O to 2% moisture	60% increase
Polymer soaked in water to 4% moisture	75% increase
Polymer washed and redried	No effect

CONDITIONING OF MIXED STOCKS

In RRC–ORD Survey No. 18, the effect of moisture as varied through the conditioning of a mixed tread stock was investigated. The basic GR-S tread compound was formulated with three polymers (Figure 5) and conditioned as milled sheet, under 0, 60, and 100% relative humidity for periods up to 2 weeks. Three cures, 25, 50, and 90 minutes at 292° F., were given. A modulus of 1000 pounds per square inch at 300% elongation was selected as the criterion of comparable cure, and the times to this cure were plotted against moisture content of the milled sheet. This use of modulus was justifiable since all sheets of each base polymer were from a single blend of laboratory-mixed stocks with no reprocessing after conditioning. Examination of Figure 5 suggests the following: (1) The accelerating effect of moisture is confirmed. (2) The wide variability in curing rate of any single polymer and of all three polymers when moisture content lies below 0.5% (on the mixed stock) is apparent. (3) Moisture contents below 0.25% (of mixed stock) not only do not guarantee

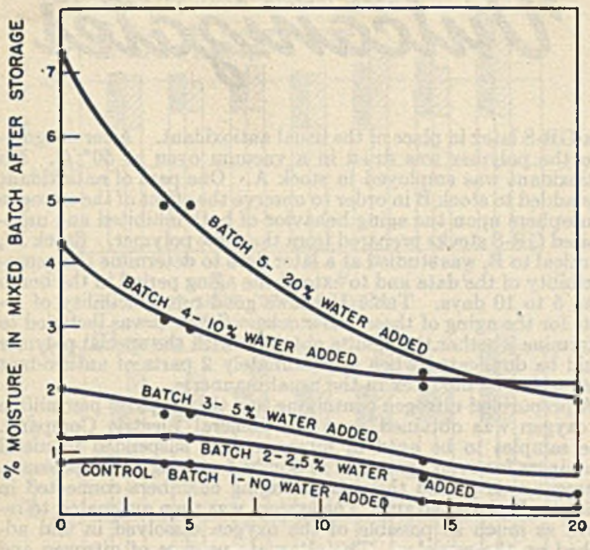

Figure 9. Effect of Storage on Moisture Content of GR-S Tread

uniform curing rate but are difficult to ensure in factory production. (4) There is an indication that, between 0.5 and 1% moisture (on the mixed stock), the variability in curing rate between polymers is substantially ironed out.

STABILIZATION OF CURING RATE OF GR-S

The moisture control of raw GR-S at the plants to within the limits indicated as desirable is presumably not practical. Drying the polymer to very low moisture is no guarantee of its moisture content when compounded since, according to ORD Survey No. 18, raw polymer with even a trace of soap can pick up well over 2% of moisture in a saturated atmosphere within 2 weeks (Figure 6).

Conditioning of mixed stocks to a moisture content of 0.5 to 1.0%, which is indicated as desirable for stable cure by Figure 5, is, in general, not feasible in production. The question of deliberate moisture addition has, therefore, been investigated. No dry polymer (less than 0.15% water) was available, but the polymer from plant B with 0.19% water (Figure 2) was selected. The test compound employed was: GR-S, 100 parts; EPC, 50; coal tar softener, 7.5; zinc oxide, 3.0; benzothiazyl sulfenamide, 1.2; sulfur, 1.8; water, 0, 2.5, 5, 10, and 20.

Water was stirred into the carbon black beads immediately before mixing. By using the higher ratios, it was felt that sufficient moisture would be retained to cause blowing troubles under factory curing conditions. Mill roll temperatures were kept at 120° F., and stock temperature ran 20° to 30° higher. This temperature is admittedly cool compared with factory mixings, but the ratio of surface exposed per pound of stock processed and time of exposure are also much higher and thus compensate in part for the lower temperature.

Stocks were mixed in 20 minutes, rested 16 hours, were remilled, and then sheeted out in 4 minutes. Moisture determinations were made after this resheeting. Stocks were cured within 16 hours of resheeting. Moisture was determined on mixed stock by oven drying of the laboratory-sheeted stock for 24 hours at 150° F. Allowance was made for the evaporation of coal tar softener, since the particular sample lost 9.25% of its weight when exposed under these drying conditions.

The moisture retention is illustrated in Figure 7. The samples to which 10 and 20% of water (on the polymer) had been added and which retained 4.4 and 7.3% of moisture (on the mixed stock) showed water stains in the curing molds. The samples to which 2.5 and 5% water (on the polymer) had been added and which retained 0.83 and 1.24% moisture (on the mixed stock), respectively, gave no trouble in curing.

The curing times to best cure are shown in Figure 8. The first sample with no water added was already out of the slow-curing zone, as judged by moisture content of the polymer (Figure 2) and by moisture content of the mixed stock (Figure 5). The extra water in the second and third samples produced only a 5-minute increase in rate of cure—i.e., within the range of cure variation shown for the three polymers of Figure 5—when conditioned to 1% moisture. The extra moisture retained by the batch to which 5% water on the polymer was added would also be sufficient to avoid slow cure, if excessively dry polymer had been employed. Samples 4 and 5, with 10 and 20% water on the polymer added, showed marked cure acceleration confirming the trend in Figure 4.

EFFECT OF STORAGE

Samples of the same five mixings were left exposed in the vulcanizing room of the laboratory for 3 weeks, and the change in moisture content on storage was determined. During that time, temperature fluctuated between 84° and 50° F. with an average of 73° F. Relative humidity ranged from 65 to 40% with an average of 47%—in short, about average factory conditions.

The drift in moisture content on storage of the five stocks is shown in Figure 9: (1) All stocks lost moisture. (2) The control stock in 3 weeks reached a low moisture level (0.19%) where slow and erratic curing rate might be expected according to Figure 5. (3) Up to 3-week storage, either of the next two stocks (2.5 and 5% water added) could be expected to vary but slightly in curing rate. (4) The stocks with the higher amounts of added water (10 and 20%) even after 2 weeks contained undesirably and unnecessarily large amounts of moisture.

CONCLUSIONS AND RECOMMENDATIONS

1. Moisture content of uncured GR-S compounds must be reckoned with because of its effect on curing rate and the serious consequence of overcure.
2. Excessively dry polymer (below about 0.15% water) will, in general, be slow curing (Figure 2).
3. Mixed stock with less than 0.5% water will, in general, be slow curing and erratic in curing rate (Figure 5).
4. The normal moisture range of carbon black does not affect the curing rate of GR-S (Figure 4).
5. The normal moisture content of carbon black is not available to the polymer for stabilizing its curing rate.
6. Mixed stock which is dry and slow curing may be conditioned to stable curing rate by storage under humid conditions. A moisture content of 0.5 to 1.0% is indicated. This moisture content seems also to iron out differences in curing rate between polymers.
7. Since conditioning of mixed stocks is not always feasible on the factory scale, the stabilization of cure by direct water addition during mixing should be given consideration.
8. Laboratory-scale tests on a GR-S tread compound indicate that an addition of about 2.5 to 5% water (on the polymer) during mixing will result in a mixed-stock moisture content giving minimal cure variation for normal-curing and slow-curing (very dry) polymers for periods of stock layover up to about 3 weeks.
9. Any additions of water as suggested above will, on the factory scale, require adjustment since moisture retention will be a function of the compounding ingredients, mixing cycle and temperature, storage time, and humidity conditions actually obtaining.

Presented before the spring meeting of the Division of Rubber Chemistry, American Chemical Society, in New York, N. Y., 1944.

Aging of GR-S Vulcanizates

IN AIR, OXYGEN, AND NITROGEN

Comparison of the aging of GR-S type vulcanizates in a highly purified nitrogen atmosphere with the results obtained in both the oxygen bomb and air oven shows that oxygen plays an important part in the changes which take place. The tensile strength is virtually unchanged in nitrogen. The modulus increase obtained in the oxygen bomb at 80° C. is shown to be independent of oxygen in the aging atmosphere. At a temperature of 100° C., however, more than half of the hardening, as measured by the modulus increase after five days in air, may be attributed to the action of the oxygen.

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TEMPERATURE aging of rubber vulcanizates in the absence of oxygen has been studied by many workers. When oxygen is carefully excluded there is little change in physical properties, an indication that oxidation is the major factor in the aging of rubber vulcanizates. Jones (*1*) found no appreciable change in tensile strength and elongation after heating in a vacuum at 158° F. (70° C.) for 14 days. Kohman (*2*) heated rubber vulcanizates in both nitrogen and carbon dioxide at 80° C. and observed little decrease in tensile strength as compared to the marked decrease obtained in oxygen. At an oven temperature of 90° C. Reed (*3*) found little deterioration in either vacuum or pure nitrogen, but in commercial nitrogen the aging was essentially the same as in air.

Little work of a comparable nature has been reported with respect to GR-S. In a recent paper Sturgis, Baum, and Vincent (*4*) reported that they observed no significant difference in the results of aging GR-S vulcanizates in air and in purified nitrogen at either 70° or 100° C. from the standpoint of modulus, tensile, elongation, and hardness values. They concluded that the hardening of GR-S vulcanizates by heat may be primarily due to some other cause than oxidation.

The object of the study reported here was to determine whether the changes in physical properties which occur during aging in the air oven and in the oxygen bomb are caused by oxygen. If so, the substitution of a nitrogen atmosphere should show significant differences. The aging of GR-S type vulcanizates has therefore been studied in oxygen and nitrogen at 80° C. and 300 pounds per square inch, and in air and nitrogen at an oven temperature of 100° C.

A tread type stock was employed with the variations shown in Table I. The uninhibited GR-S employed in stocks A, B, and B′ was prepared with the addition of 2 parts of sulfur as stabilizer to a GR-S latex in place of the usual antioxidant. After coagulation the polymer was dried in a vacuum oven at 50° C. No antioxidant was employed in stock A. One part of antioxidant was added to stock B in order to observe the effect of the nitrogen atmosphere upon the aging behavior of both inhibited and uninhibited GR-S stocks prepared from the same polymer. Stock B′, identical to B, was studied at a later date to determine the reproducibility of the data and to extend the aging period in the bomb from 5 to 10 days. Table II shows good reproducibility of results for the aging of these two stocks. Stock C was included to determine whether the results obtained with the special polymer could be duplicated when approximately 2 parts of antioxidant were added to the latex in the usual manner.

A prepurified nitrogen containing less than 5 parts per million of oxygen was obtained from the General Electric Company. The samples to be aged in nitrogen were suspended in metal containers for oven aging and in bombs for aging under pressure. Nitrogen was passed through the aging chambers connected in series to displace the air. The system was then evacuated to remove as much as possible of the oxygen dissolved in and adsorbed on the samples. The alternate passage of nitrogen and evacuation was repeated several times, and finally a stream of nitrogen was passed through for several additional hours until analysis of the exit gas showed no detectable oxygen. An adaptation of the Winkler method (*5*) was used for the analysis. With careful manipulation and the use of blank titrations, the method is capable of detecting as little as 0.01% oxygen by volume.

After the air had been displaced as described above, the metal containers used for the oven aging were closed under a slight pressure of nitrogen (2 to 3 inches of water) sufficient to prevent any possible diffusion of air into the aging chamber. The closed containers were then placed in an oven at 100° C. along with an identical control set containing air under the same slight pressure. The nitrogen and oxygen bombs were filled to a pressure of 300 pounds per square inch and heated in a bath at 80° C.

BOMB AGING

The elongation, stress at 200 and 300% elongation, and tensile strength after aging in oxygen and nitrogen at 80° C. and 300 pounds per square inch are shown in Table II*A*. Each value represents the average of three test strips. The numbers in parentheses show percentage retention of the original value. The effect of nitrogen atmosphere upon aging results is shown more clearly by the graphs prepared from this data.

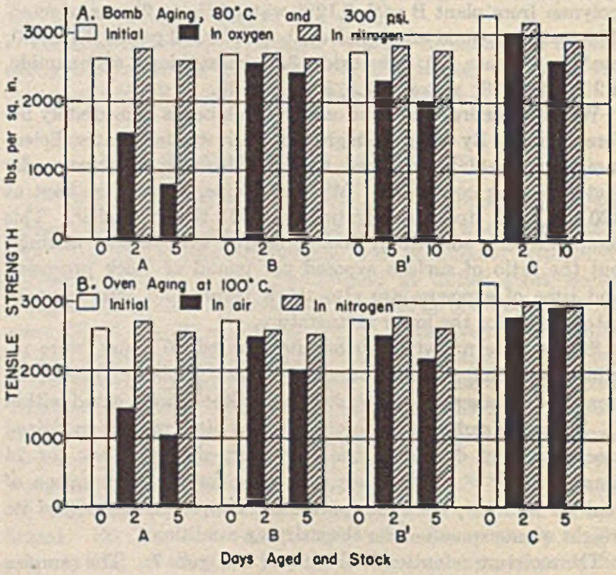

Figure 1. Effect of Aging upon Tensile Strength

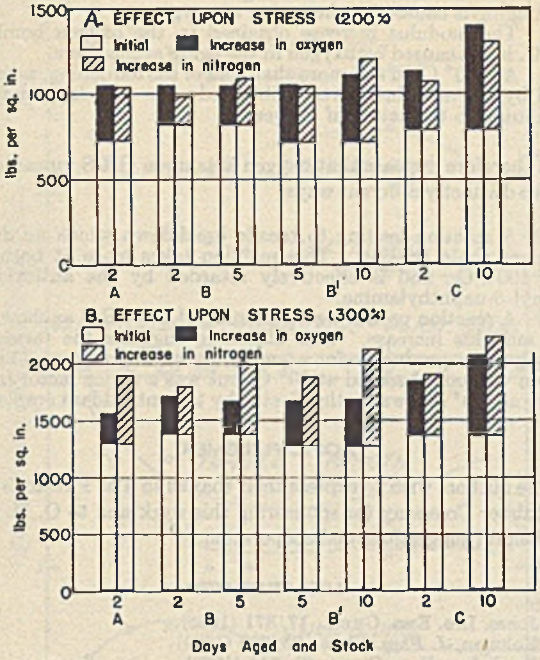

Figure 2. Effect of Bomb Aging in Oxygen and Nitrogen at 80° C. and 300 Pounds per Square Inch upon Stress

The tensile strength after aging is compared with the initial values in Figure 1*A*. In nitrogen the tensile strength was essentially unchanged except for stock C which showed a small decrease after 10 days. In oxygen, however, the uninhibited material broke down rapidly so that after 5 days only 30% of the original value was retained. Although inhibited stocks B, B', and C did not break down so extensively, the observed decrease in tensile strength is largely the result of oxidation. The fact that the tensile strength of the uninhibited material was unchanged in nitrogen is additional evidence that there was no significant amount of oxygen in the nitrogen employed.

The increase in stress at 200% elongation obtained at 80° C. was essentially the same in oxygen and nitrogen (Figure 2*A*). The stress at 300% elongation (Figure 2*B*) actually increased more in nitrogen than in oxygen. One possible explanation would be that chain scission, as evidenced by the decrease in tensile strength in oxygen, would logically have a softening effect. At any rate it is apparent that the modulus increase obtained in the oxygen bomb at 80° C. is not caused by oxygen in the aging atmosphere since an equal or greater increase was obtained in nitrogen. Most of the increase took place during the first 2 days of aging and remained relatively constant thereafter in oxygen, but increased slowly in nitrogen as shown for stocks B and B' in Figure 2*B*. The cause of the modulus increase at 80° C. has not yet been determined, aside from the fact that it is not due to oxygen in the aging atmosphere.

Table I. Composition of Stocks

Stock	A	B, B'	C
Uninhibited GR-S	100	100	...
Inhibited GR-S	...	...	100
Bardol	5	5	5
Fat acid	1.5	1.5	1.5
Channel black	50	50	50
Zinc oxide	5	5	5
Santocure	1.2	1.2	1.2
Sulfur	2[a]	2[a]	2
Phenyl-β-naphthylamine	...	1	2[a]

[a] Added to latex before coagulation.

The elongation values in Table II*A* show little difference between the decrease obtained in oxygen and nitrogen in the case of the inhibited stocks. The uninhibited material, however, shows considerably better retention of elongation in nitrogen. The greater decrease in ultimate elongation in oxygen, together with the extensive tensile breakdown, may be attributed to a reaction with oxygen which leads to chain scission.

OVEN AGING

The data for oven aging at 100° C. in air and in nitrogen is presented in Table II*B*. The tensile strength values from this table are compared in Figure 1*B*, which shows the same relation obtained in the oxygen bomb—namely, little change in the presence

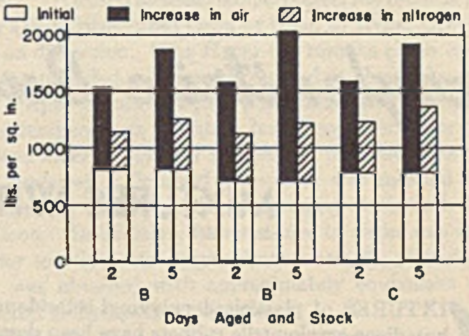

Figure 3. Effect of Oven Aging at 100° C. in Air and in Nitrogen upon Stress at 200% Elongation

Table II. Aging of GR-S Type Vulcanizates

	A. Bomb Aging, 80° C., 300 Lb./Sq. In.						B. Oven Aging at 100° C.					
	Aging conditions		Ultimate elongation,	Modulus, lb./sq. in.		Tensile strength,	Aging conditions		Ultimate elongation,	Modulus, lb./sq. in.		Tensile strength,
Stock	Gas	Days	%	200%	300%	lb./sq. in. (%)	Gas	Days	%	200%	300%	lb./sq. in. (%)
A (uninhibited), 45-min. cure at 298° F.	Initial		490	730	1300	2630	Initial		490	730	1300	2630
	O_2	2	295 (60)	1050	1560	1540 (58)	Air	2	170 (35)	..	..	1440 (55)
		5	80 (16)	...	...	800 (30)		5	120 (25)	..	..	1045 (40)
	N_2	2	380 (78)	1040	1900	2780 (106)	N_2	2	330 (67)	1250	2380	2720 (103)
		5	350 (72)	1160	2150	2620 (100)		5	315 (64)	1340	2395	2560 (97)
B (1% PBNA), 55-min. cure at 298° F.	Initial		510	820	1380	2720	Initial		510	820	1380	2720
	O_2	2	440 (86)	1050	1710	2570 (95)	Air	2	275 (54)	1590	..	2490 (92)
		5	450 (88)	1050	1670	2440 (90)		5	210 (41)	1875	..	1980 (73)
	N_2	2	420 (82)	965	1800	2730 (100)	N_2	2	355 (70)	1150	2060	2590 (95)
		5	375 (74)	1090	2000	2650 (98)		5	320 (63)	1260	2320	2540 (93)
B' (same as B)	Initial		555	720	1280	2760	Initial		555	720	1280	2760
	O_2	5	435 (78)	1045	1665	2325 (84)	Air	2	290 (52)	1585	..	2525 (92)
		10	380 (69)	1110	1685	2040 (74)		5	210 (38)	2030	..	2180 (79)
	N_2	5	415 (75)	1040	1885	2850 (103)	N_2	2	380 (68)	1130	2025	2785 (101)
		10	380 (69)	1200	2130	2800 (101)		5	340 (61)	1220	2200	2630 (95)
C (2% PBNA), 50-min. cure at 298° F.	Initial		615	790	1370	3290	Initial		615	790	1370	3290
	O_2	2	485 (79)	1125	1840	3030 (92)	Air	2	320 (52)	1590	2615	2805 (85)
		10	405 (66)	1400	2070	2625 (80)		5	290 (47)	1920	..	2920 (89)
	N_2	2	455 (74)	1065	1905	3180 (97)	N_2	2	395 (64)	1235	2185	3020 (92)
		10	375 (61)	1310	2240	2915 (89)		5	360 (58)	1360	2365	2935 (89)

of nitrogen but a definite decrease after aging in air. The difference between the results in air and nitrogen becomes less as the concentration of antioxidant increases, as shown by the extensive breakdown obtained with uninhibited stock A; B and B′ with 1 part and C with 2 parts of antioxidant show progressively less deterioration.

The stiffening or hardening of the vulcanizates, as measured by modulus increase, was drastic in air at 100° C. as shown by the black bars in Figure 3. After 5 days the stress at 200% elongation was more than doubled in every case. In nitrogen, however, the modulus increased only to about the same extent as in the bomb. If we attribute the increase observed in nitrogen to other factors, then the additional increase obtained in air represents the hardening due to the action of oxygen. On this basis more than half of the observed hardening of GR-S vulcanizates after 5 days of aging in air at 100° C. may be attributed to the action of oxygen.

The ultimate elongation was much better after aging in nitrogen than in air at 100° C. (Table II*B*). Since the elongation reflects changes in both tensile and modulus, these values confirm the observation that oxygen plays an important part in the aging of GR-S in the air oven at 100° C.

The results obtained by the aging of GR-S type vulcanizates in air and nitrogen at 100° C. are not in agreement with the work of Sturgis, Baum, and Vincent (*4*) who reported the same amount of hardening upon heating in air and nitrogen. Their stock was the same as stock C in Table I except for the softeners and accelerator employed. This may have contributed to the difference in the results.

CONCLUSIONS

The results of aging GR-S type vulcanizates in air, oxygen, and nitrogen show:

1. The decrease in tensile strength observed in both bomb and oven aging is caused by the action of oxygen.
2. The modulus increase obtained in the oxygen bomb at 80° C. is not caused by oxygen in the aging atmosphere.
3. At 100° C. in air, more than half of the hardening, as measured by the modulus increase obtained after five days, may be attributed to the action of oxygen.

It therefore appears that oxygen acts upon GR-S vulcanizates in two distinctly different ways:

1. A reaction leading to tensile breakdown which no doubt involves chain scission. This reaction takes place at both 80° and 100° C., and is effectively retarded by the antioxidant, phenyl-β-naphthylamine.
2. A reaction producing a stiffening of the GR-S as shown by the modulus increase. This stiffening suggests the formation of polymeric products—for example, by cross linkage. This reaction was not observed at 80° C. but was a major factor in the aging at 100° and was little affected by the antioxidant employed.

ACKNOWLEDGMENT

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Acrylonitrile-Butadiene Copolymers

MIXTURES WITH PLASTICIZED POLYVINYL CHLORIDE

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MIXTURES of plasticized polyvinyl chloride resins with butadiene-acrylonitrile rubbers have been described (*10, 13*) as having many interesting and useful properties. The object of this study was to determine which of the complementary properties of acrylonitrile-butadiene copolymers and plasticized polyvinyl chloride resins could be combined in mixtures of the two.

Data are presented on compounds prepared by blending master batches (Table I) so that Geon concentrations, ranging from 0 to 100%, were obtained. A mixture of 75% Hycar OR-15 with 25% Geon (Table II) was selected as the basis for a comprehensive compounding study.

MIXTURES OF HYCAR OR AND PLASTICIZED GEON

The compounds were prepared by blending master batches (Table I) in which the relative amounts of Geon to Hycar OR, in the polymer combinations, were varied from 0 to 100%. The master batches were blended by mixing the Hycar OR compound, without sulfur, into plasticized Geon on a mill at 220° F. After thorough blending, the batches were cooled to 120–150° F. and sulfur was added. All compounds were cured at 300° F. to their respective optima. Physical tests run on the compounds of this study follow:

STRESS-STRAIN. A.S.T.M. procedure (*3*).

HARDNESS. Shore durometer, type A (tested on molded pellets $^3/_8$ inch thick, $^1/_2$ inch in diameter).

REBOUND. Schopper method tested on pellets described above.

COMPRESSION SET. A.S.T.M. procedure, method B (*2*), tested on pellets described above.

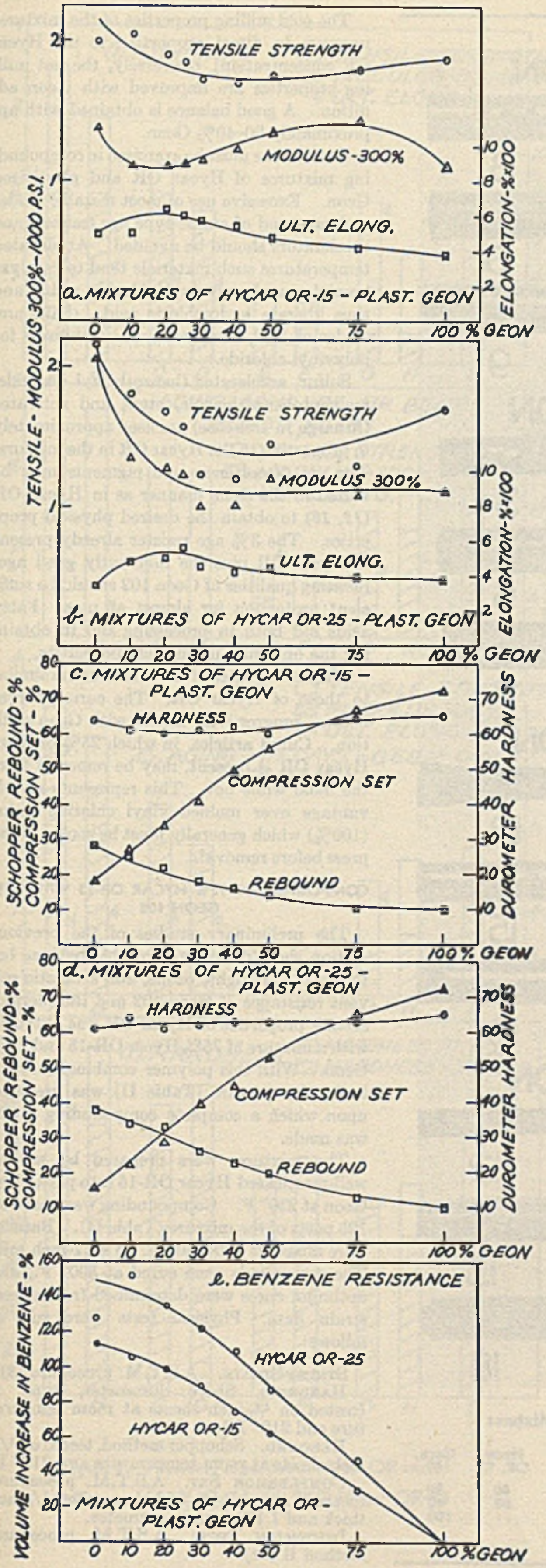
BENZENE RESISTANCE. A.S.T.M. procedure, method A (*6*), 48 hours at room temperature.

SUNLIGHT RESISTANCE. A.S.T.M. procedure, methods A and B (*7*); specimens shown in Figure 2 were exposed 12 months in Akron by method B.

OZONE RESISTANCE. Specimens 1 inch wide bent to 1-inch loop, exposed 60 hours at room temperature to 0.05% ozone.

DISCUSSION OF RESULTS. Changes in physical properties with varying percentages of Geon 102 are shown in Figures 1 and 2. The addition of Geon to Hycar OR effects several marked improvements; the most outstanding are the excellent sunlight and ozone resistance (Figure 2) obtained with 20–30% of the polyvinyl chloride. Resistance to swell in benzene (Figure 1, *e*) is also improved.

Tensile strength, 300% modulus, and rebound (Figure 1, *a–d*)



Mixtures of acrylonitrile-butadiene copolymers (Hycar OR) with plasticized polyvinyl chloride (Geon 102) have been prepared covering the range of concentrations of polyvinyl chloride from 0 to 100%. These combine, in varying degrees, the sunlight, ozone, and aromatic solvent resistance of the polyvinyl chloride with the oil-resistant and thermosetting properties of the Hycar OR. A favorable combination of properties was found with a mixture of 75% Hycar OR-15 and 25% Geon 102. Comparative compounding data are given on Hycar OR-15 and a blend of 75 parts Hycar OR-15, 25 parts Geon 102, and 25 parts tricresyl phosphate in typical compounds. These data show that, in addition to its superiority in sunlight and ozone, the mixture has improved resistance to tearing, flex cracking, and aging as compared with Hycar OR-15.

★

are lowered by Geon addition. Compression set (Figure 1, *c* and *d*) is increased in direct proportion to Geon concentration. Elongation reaches a maximum at 20% Geon (Figure 1, *a* and *b*) which may be attributed to the combined effect of increased plasticizer and lowered pigmentation.

The tensile curve for mixtures of Hycar OR-25 with Geon passes through a greater minimum than that for Hycar OR-15 mixtures with Geon. This is caused by the somewhat poorer compatibility of Geon with Hycar OR-25 than with OR-15.

The addition of Hycar OR to plasticized Geon imparts thermosetting properties with all of their attendant advantages and reduces the tendency of plasticizers to bloom from the vinyl chloride resin. Hycar OR may also be used as a nonextractable plasticizer for Geon.

MIXING AND COMPOUNDING. Mixtures of Hycar OR and plasticized Geon are most satisfactorily prepared on a hot mill (220-250° F.). If mixed at these temperatures, the order of addition—Hycar OR to plasticized Geon or Geon to Hycar OR—has little effect on dispersion. The Hycar OR may be either compounded or uncompounded. If uncompounded it should be well masticated. Approximately equal plasticities are required at these mixing temperatures to obtain best dispersion. For this reason the Geon must be suitably plasticized, the ester-type plasticizers being preferred. Tricresyl phosphate was selected because of low volatility and mutual compatibility with both Hycar OR and Geon. In addition, its resistance to ozone was found to be superior to other ester type softeners tested. The desired plasticity was obtained with approximately equivalent weights of plasticizer and polyvinyl chloride.

Table I. Hycar-Geon Master Batches

	Geon 102	OR-15	OR-25
Hycar OR-15	...	100	...
Hycar OR-25	...	...	100
Geon 102 (polyvinyl chloride)	100	...	...
Tricresyl phosphate	95	...	...
Lead silicate	2	...	...
Semireinforcing black	...	80	100
Litharge	...	5	5
P-25 Cumar	...	15	15
Dibutyl phthalate	...	15	15
Agerite powder	...	1.5	1.5
Benzothiazyl disulfide	...	1.5	1.5
Sulfur	...	1.5	1.5
	197	219.5	239.5

Table II. Basis of Compounding Study, in Parts by Weight

Hycar OR-15	75
Geon 102	25
Tricresyl phosphate	25
	125

← Figure 1. Effect of Increasing Percentages of Geon 102 on Physical Properties of Hycar OR

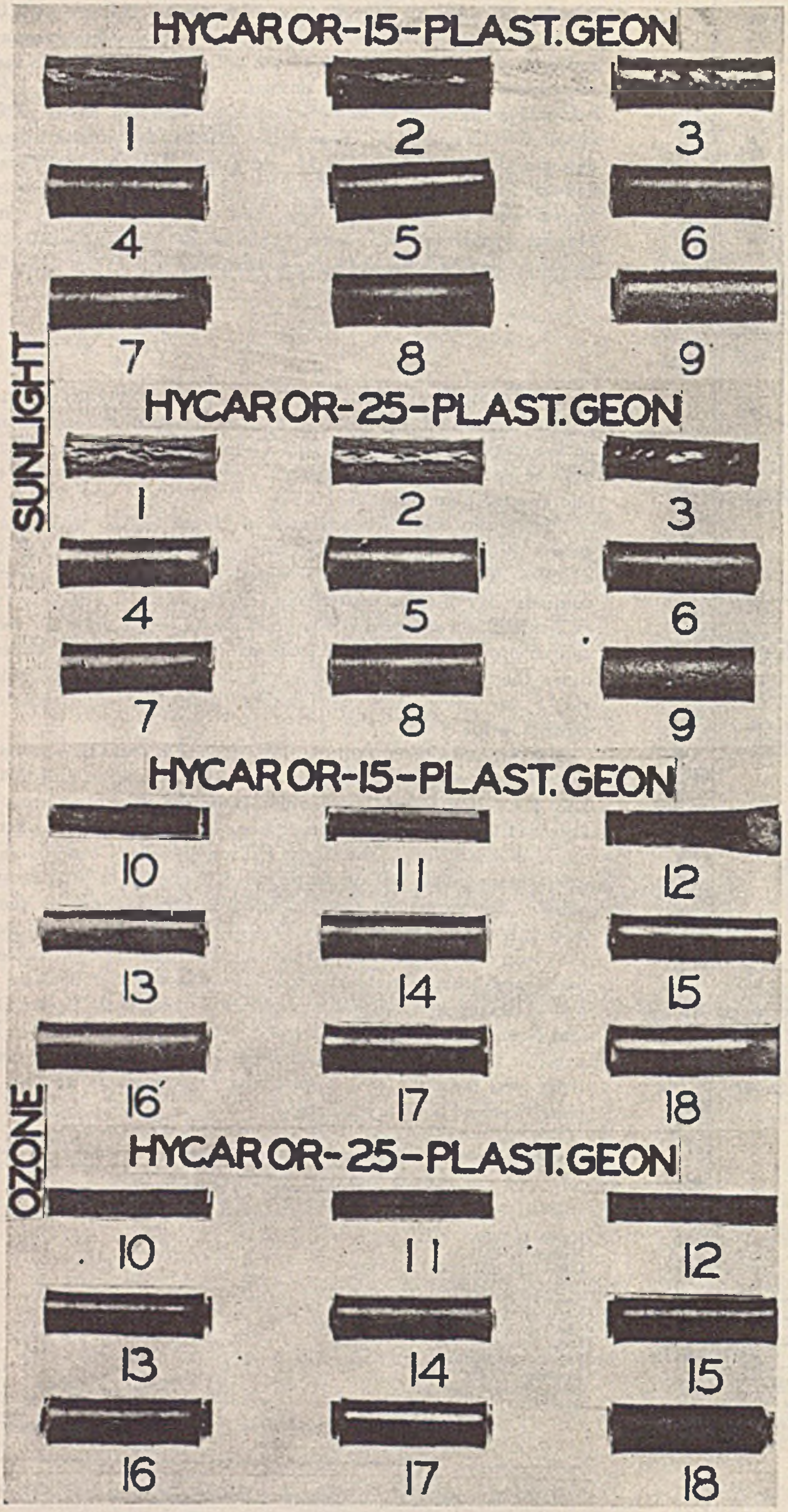


Figure 2. Sunlight and Ozone Resistance of Hycar-Geon Mixtures

Mixt. No.	Hycar OR, %	Geon, %	Mixt. No.	Hycar OR, %	Geon, %	Mixt. No.	Hycar OR, %	Geon, %
1, 10	100	..	2, 11	90	10	3, 12	80	20
4, 13	75	25	5, 14	70	30	6, 15	60	40
7, 16	50	50	8, 17	25	75	9, 18	..	100

The cold milling properties of the mixtures improve in direct proportion to the Hycar OR concentration; conversely, the hot milling properties are improved with Geon addition. A good balance is obtained with approximately 20–40% Geon.

Precautions must be exercised in compounding mixtures of Hycar OR and plasticized Geon. Excessive use of most metallic oxides and salts and of amine-type age resisters and accelerators should be avoided. At elevated temperatures such materials tend to catalyze breakdown of polyvinyl chloride resins and thus liberate hydrochloric acid. (Salts and oxides of lead, however, act as stabilizers for polyvinyl chloride.)

Sulfur, accelerator (benzothiazyl disulfide, mercaptobenzothiazole, etc.), and activator (litharge in this case) are used approximately in proportion to the Hycar OR in the mixture. The use of softeners and pigments may be varied in the same manner as in Hycar OR (*12*, *16*) to obtain the desired physical properties. The 3% age resister already present in Hycar OR plus the inherently good age-resisting qualities of Geon 102 should be sufficient protection for almost all uses. Fatty acids aid both in processing and in obtaining the optimum in physical properties.

The curing rates of the mixtures are similar to those of Hycar OR. The curing curves become progressively flatter with Geon addition. Cured articles, in which 25% or more Hycar OR is present, may be removed from the mold while hot. This represents an advantage over molded vinyl chloride resins (100%) which generally must be cooled in the press before removal.

COMPOUNDS OF 75% HYCAR OR-15 WITH 25% GEON 102

The preliminary studies of the previous section showed that a favorable balance between the sunlight, ozone, and aromatic solvent resistance of Geon 102 and the thermosetting properties of Hycar OR was obtained with a mixture of 75% Hycar OR-15 and 25% Geon. With this polymer combination as a basis, the mixture (Table II) was prepared upon which a complete compounding study was made.

The mixtures were prepared by milling well-masticated Hycar OR-15 into plasticized Geon at 220° F. Compounding was based on 125 parts of the mixture (Table II). Batches were mixed at 120–160° F. on a 12-inch mill. The compounds were cured at 300° F., and optimum cures were determined from stress-strain data. Physical tests were run as follows:

Stress-Strain. A.S.T.M. procedure (*3*).

Hardness. Shore durometer, type A (tested on $^1/_4$-inch sheets at room temperature and 212° F.).

Rebound. Schopper method, tested on $^1/_4$-inch sheets at room temperature and 212° F.

Compression Set. A.S.T.M. procedure, methods A and B (*2*), tested on pellets $^1/_2$ inch thick and 1.129 inch in diameter.

Immersion Tests. A.S.T.M. procedure, method B (*11*).

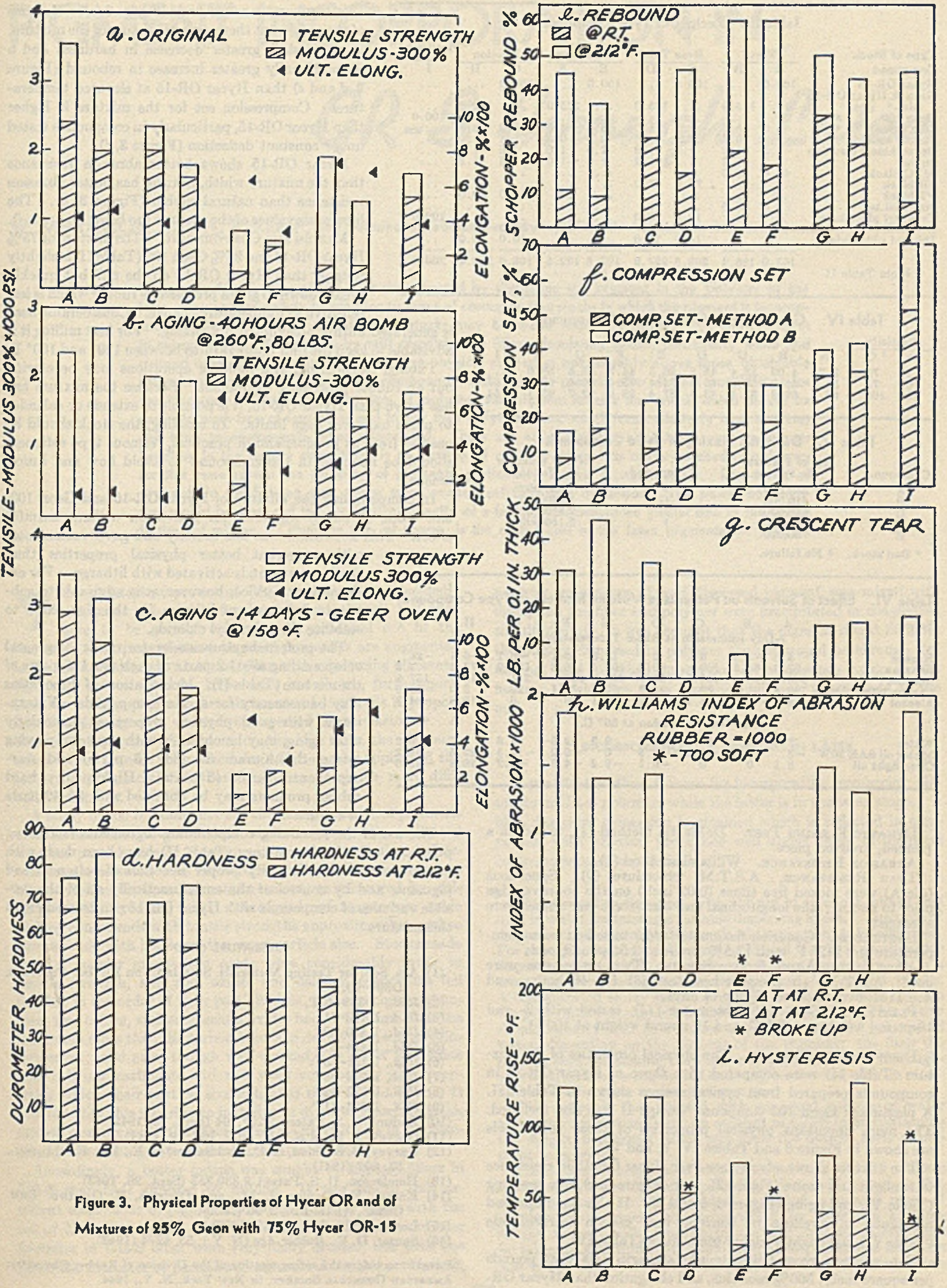


Figure 3. Physical Properties of Hycar OR and of Mixtures of 25% Geon with 75% Hycar OR-15

Table III. Recipes of Type Compounds

Type of Stock	Tread		Hose Tube		Pure Gum		Friction		Molded Plasticized Geon
Compound	A	B	C	D	E	F	G	H	I
Hycar OR-15	100.0	...	100.0	...	100.0	...	100.0	...	...
Geon & Hycar OR-15 mixt.[a]	...	125.0	...	125.0	...	125.0	...	125.0	...
Geon 102	...	...	...	...	...	...	...	...	100.0
Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	...
Stearic acid	0.5	0.5	0.5	0.5	0.5	0.5	...	...	...
Benzothiazyl disulfide	1.5	1.2	1.5	1.2	1.0	1.0	1.5	1.2	...
Sulfur	1.5	1.2	1.5	1.2	1.0	1.0	1.5	1.2	...
MPC black	50.0	50.0	...	...	...	...	...	...	...
SR black	...	...	75.0	75.0	...	...	...	...	...
FT black	...	...	...	...	...	...	50.0	50.0	...
Soft coal tar	3.5	3.5	...	...	...	...	...	...	...
Tricresyl phosphate	...	...	10.0	10.0	...	...	...	...	100.0
Bardol B	...	...	...	...	...	...	30.0	30.0	...
Dibutyl phthalate	...	...	10.0	10.0	...	...	10.0	10.0	...
	162.0	186.4	203.5	227.9	107.5	132.5	198.0	222.4	200.0

[a] From Table II.

Table IV. Goodrich Plasticity of Type Compounds

Plasticity Lb.	Plasticity ° C.	A	B	C	D	E	F	G	H	I
2	70	3.74	4.09	38.4	48.3	26.5	44.7	60.6	66.0	..
10	70	31.5	35.2	68.8	76.0	71.4	75.4	90.6	92.5	1.07
10	100	69.5	69.2	81.1	83.3	87.4	88.5	92.7	95.1	2.54

Table V. DeMattia Flexing of Type Compounds

Compound	No. of Flexures to Failure	Compound	No. of Flexures to Failure
A	230,000	F	550,000[a]
B	410,000	G	1,040,000
C	650,000	H	2,110,000[b]
D	700,000	I	2,150,000[b]
E	750,000		

[a] Bad stock. [b] No failure.

Table VI. Effect of Solvents on Percentage Volume Increase of Type Compounds

Solvent	A	B	C	D	E	F	G	H	I
7-Day Immersion at Room Temperature									
Hexane	4.5	−1.5	3	0	12.5	6.1	−6.1	−6.1	−26
Benzene	97.3	84.3	100	60.2	192.4	135.3	114.2	77.2	−7.7
Acetone	146.0	138.0	168.6	109.7	314	238	211	212	157.1
Carbon tetrachloride	36.8	21.3	33.1	15.8	52.1	33.1	26	3.0	−22.6
Alcohol	14.9	−7.5	6.1	−9.2	19.1	0	0	−10.8	−24.3
14-Day Immersion at 80° C.									
Water	7.6	4.5	10.8	10.8	9.2	12.5	7.6	7.6	9.2
Motor oil SAE 20W	−3	−7.6	−6.1	−12.5	0	−9.2	−12.5	−22.5	−48.2
Circo light oil	6.1	0	0	−6.1	−9.2	−4.5	−9.2	−20.8	−40.5

DYNAMIC FLEXING TEST. DeMattia method (*4*), tested on a pierced, grooved piece.

ABRASION RESISTANCE. Williams method (*1*).

TEAR RESISTANCE. A.S.T.M. procedure (*9*). Specimens (die A) were nicked five times (0.02 inch) on the concave edge prior to testing; the longitudinal and transverse tear values were averaged.

HYSTERESIS. Goodrich flexometer (*15*), tested at room temperature and 212° F. with 17.5% stroke and 55-pound load.

ACCELERATED AGING STRESS-STRAIN. Two procedures were used: A.S.T.M. air pressure heat test (*5*) for 40 hours, and A.S.T.M. oven method (*8*) for 14 days.

PLASTICITY. Goodrich plastometer (*14*), tested with 2- and 10-pound weights at 70° C. and 10-pound weight at 100° C.

DISCUSSION OF RESULTS. The physical properties of the mixture (Table II) were compared with those of Hycar OR-15 in compounds prepared from typical recipes shown in Table III. A plasticized Geon 102 compound (recipe I) was also included. The more important physical properties of these compounds are shown in Figure 3 and Tables IV, V, and VI.

The mixture shows advantages over Hycar OR-15 in resistance to sunlight and ozone (Figure 2), tear (Figure 3, *g*), flex cracking (Table V), and aging (Figure 3, *b* and *c*). It also has improved resistance to swelling in benzene and carbon tetrachloride (Table VI) and slightly higher plasticities (Table IV).

The mixture gives lower tensile strength (400–800 pounds per square inch), 300% modulus, and elongation than Hycar OR-15 in comparable compounds (Figure 3, *a*). Because of the somewhat thermoplastic nature of the mixture, it manifests a greater decrease in hardness and a proportionally greater increase in rebound (Figure 3, *d* and *e*) than Hycar OR-15 at elevated temperatures. Compression set for the mixture is higher than Hycar OR-15, particularly in compounds tested under constant deflection (Figure 3, *f*).

Hycar OR-15 shows better abrasion resistance than the mixture which, in turn, has better abrasion resistance than natural rubber (Figure 3, *h*). The hysteresis values of the mixture are high (Figure 3, *i*).

MIXING AND COMPOUNDING. The mixture of 75% Hycar OR-15 and 25% Geon 102 (Table II) is slightly tougher than Hycar OR-15 on the mill but quickly breaks down to give a processable rubber which is less sensitive to temperature change. Considerable heat is generated during breakdown and mixing. For best milling it is advisable to keep the mill temperatures between 120° and 160° F.

Tubing, calendering, and molding operations may be carried out on rubber processing equipment. Because the mixture has less nerve than Hycar OR-15, it is possible to extrude or calender to much narrower gage limits. In molding, the stock should be used as fresh as possible and, if practical, resinous type softeners should be included in the compound to avoid flow and fusion cracks.

In compounding the mixture of Hycar OR-15 and Geon 102, zinc oxide (5 parts) was used for activation without harmful effect. This activation was less scorchy and gave vulcanizates with somewhat better physical properties than similar compounds activated with litharge. For extreme heat service, however, it is advisable to substitute 2–3 parts of litharge for the zinc oxide to stabilize the polyvinyl chloride.

The preferred sulfur-accelerator ratios for general compounding are 1.2 parts of each per 125 parts of the mixture (Table II). Modifications of these ratios may be necessary for special compounds. Vulcanizates with good physical properties, particularly after aging, may be obtained with a cure employing tetramethylthiuram disulfide (3 parts) and mercaptobenzothiazole (3 parts). High-quality hard rubber products may be obtained with 35–40 parts of sulfur.

The use of the remaining compounding ingredients (softeners, pigments, etc.) in the mixture (Table II) have been dealt with in the previous section. By proper selection of softeners and pigments and by control of the cure, practically all of the possible varieties of compounds with Hycar OR-15 can be made with this mixture

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PIGMENT INCORPORATION IN *GR-S through Latex*

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The physical properties of GR-S stocks prepared by dispersing the pigment in the polymer in the latex stage appear definitely superior to those of corresponding stocks in which the pigment is incorporated on the mill. Thus carbon black stocks may be made which are stronger and more resistant to cut growth than those made by mill dispersion of filler. Insulating stocks, particularly white and colored ones, can be made which will have physical properties considerably above those obtainable by present methods. Zinc oxide compounds made by this process offer distinct possibilities for use in carcass stocks. The coagulum of polymer and pigment forms a fine crumb which should be easier to wash free of impurities and to dry than polymer alone which forms relatively large particles and tends to agglomerate when coagulated. There are other possible advantages, such as cleaner handling in the factory since there is no dusting of pigment when it is master-batched in polymer; for this same reason the shipping of pigments, particularly blacks, is made easier. Dispersion of pigments in GR-S latex may prove more economical than mill dispersion. The power consumption would be less, and the productive capacity of a factory unit should be greater due to the saving in time of milling. Offsetting this, of course, is the added cost of the latex pigmentation process.

THE physical properties of GR-S gum stock are decidedly inferior to those of natural rubber gum stock, and they have to be greatly enhanced for practical use of the elastomer. At present these physical properties are augmented to the greatest degree by compounding with reinforcing pigments, especially carbon blacks. Experience has shown, furthermore, that for a given pigment the reinforcement it affords is proportional to the degree to which it is dispersed in the elastomer. A thorough dispersion of pigment on the mill or in the Banbury mixer is not feasible with schedules which can be applied in the factory, particularly with those pigments which are more difficult to disperse.

A study of the relation between the characteristics of pigments used as fillers in GR-S and their reinforcing properties indicated that the particle size of the pigment was the predominant characteristic associated with reinforcing ability. The finer carbon blacks yielded the greatest reinforcement, as measured by ultimate tensile strength; also, a fine grade of magnesium oxide yielded compounds with tensile strengths approximately equal to stocks made with blacks of the same particle size. Stocks made from a coarser magnesium oxide were considerably lower in tensile strength, and zinc oxides and calcium carbonates fell roughly in the order of their particle sizes. The calcium carbonates, zinc oxides, and magnesium oxides had to be worked on the mill much more than the carbon blacks to develop maximum reinforcement; and even though well worked, the finest zinc oxide and calcium carbonate did not yield compounds with properties which their particle size indicated they should have. It was felt that this was due to inability to disperse these materials properly on the mill; thus their effective particle size in the compound was much greater than their ultimate size.

Accordingly, a better means was sought to disperse fillers in GR-S than that afforded by milling. It was known that excellent dispersions of pigments could be made in water with the aid of dispersing agents. It was also reported that the polymer particles in GR-S latex were very finely divided, less than one tenth the diameter of particles in natural rubber latex. If, then, a water suspension of well dispersed pigment was mixed with latex, and the filler and polymer were precipitated or coagulated simultaneously, it was thought that the pigment might be more thoroughly dispersed in polymer than it would be through dry milling; the physical properties of compounds made in this manner should then show improvement over those made on the mill.

INCORPORATION OF PIGMENTS IN LATEX

A practical method follows for incorporating reinforcing pigments in GR-S polymers while the latter is in the latex stage. A high degree of dispersion is attained which is reflected in compounds with physical properties well above those of identical compounds made on the mill:

The pigment is dispersed, with the aid of a colloid mill or ball mill, in water containing a suitable dispersing agent. The type of dispersing agent employed depends on the pigment to be dispersed. For example, the material known as Daxad No. 23 is excellent for dispersing zinc oxides or whitings, whereas Daxad No. 11 is a somewhat more effective dispersing agent for carbon blacks. A concentrated slurry is first prepared and then passed through the mill until the pigment is thoroughly dispersed. This slurry should contain 5 to 10 volumes of pigment per 100 volumes of water, depending on the fineness of the pigment; the finer the particle size, the smaller the volume of pigment. The thoroughness of dispersion is important and may be checked with an ultramicroscope or other convenient means.

This slurry is then diluted with an equal volume of water and thoroughly mixed with an amount of GR-S latex containing the weight of polymer which will yield the desired ratio of pigment to polymer.

The mixture is coagulated with dilute sulfuric acid (25 volumes of concentrated sulfuric acid plus 475 volumes of water) or 2% alum solution. As the coagulant is added, a porous mass of polymer and pigment will form which on continued addition of the reagent will break up into a fine crumb. Care must be taken to add sufficient coagulating agent, otherwise filtration will be difficult. The crumb is filtered and washed free of water-

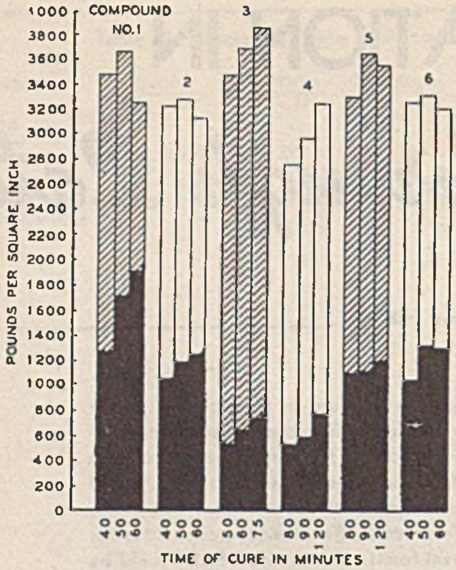


Figure 1. Stress-Strain Properties of Carbon Black Compounds

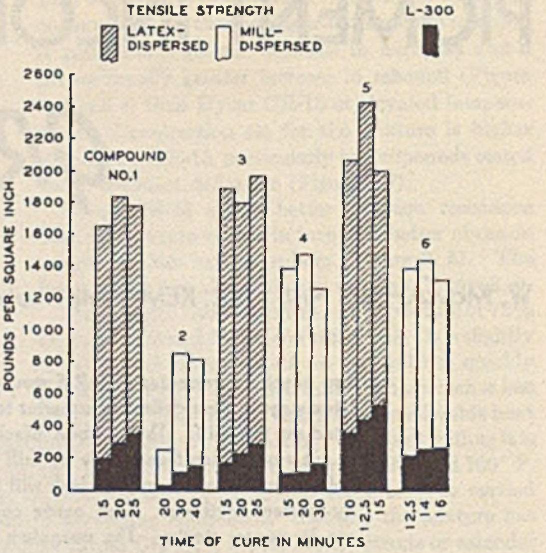


Figure 2. Stress-Strain Properties of Zinc Oxide Compounds

soluble impurities. The material can be repulped readily while wet and washed with hot water to aid in removing impurities.

The master batch may be dried in an air dryer at 70° C. and is then ready to be compounded with sulfur, accelerators, etc.

Table I. Physical Data on Carbon Black Compounds

Compound No.	1	2	3	4	5	6
GRS	100.00	100.00	100.00	100.00	100.00	100.00
EPC black (40 mμ)	50.00	50.00	50.00	50.00	....	....
Fine channel black (30 mμ)	....	....	....	....	50.00	50.00
Zinc oxide	5.00	5.00	5.00	5.00	5.00	5.00
Sulfur	2.00	2.00	2.00	2.00	2.00	2.00
Mercaptobenzothiazole	1.50	1.50	1.50	1.50	1.50	1.50
Softener (Bardol)	5.00	5.00	5.00	5.00	5.00	5.00
Softener (Turgum)	....	....	10.00	10.00	....	....
Filler dispersed:	In latex	On mill	In latex	On mill	In latex	On mill

	Cure at 293° F., Min.	Tensile Strength, Lb./Sq. In.	Stress at 300% Elongation, Lb./Sq. In.	Elongation at Break, %	Torsional Hysteresis, K
Compound 1	40	3460	1270	580	...
	50	3640	1680	510	0.148
	60	3230	1890	440	...
Compound 2	40	3200	1060	625	...
	50	3245	1160	580	0.164
	60	3115	1215	530	...
Compound 3[a]	50	3440	520	805	...
	60	3650	630	775	...
	75	3825	725	730	0.145
Compound 4[b]	60	2545	400	850	...
	80	2750	505	795	...
	90	2960	585	745	...
	120	3235	775	725	0.211
Compound 5	80	3285	1100	625	...
	100	3615	1100	635	0.224
	120	3540	1195	620	...
Compound 6	40	3250	1050	610	...
	50	3315	1320	550	0.183
	60	3200	1300	525	...

[a] Cut growth, inch (cycles): at 75-min. cure, 0.6 (30,000): at 90-min. cure, 0.66 (25,000).

[b] Cut growth, inch (cycles): at 50-min. cure, 0.91 (30,000): at 60-min. cure, 0.81 (25,000).

The process has been employed in this laboratory to make master batches of carbon blacks, zinc oxides, and calcium carbonates. Stocks have been prepared with these master batches and various properties have been measured.

CARBON BLACK COMPOUNDS

Compounds were prepared with a fine channel black and an easy-processing carbon. The physical data are given in Table I. Compounds of the same recipe which were made by dispersing the pigment on the mill are included for comparison. It is apparent in Figure 1 that the stress-strain properties of the latex-dispersed stocks are of a higher order than those of the mill-dispersed. The hysteresis values of compounds 1 and 3, compared with those of compounds 2 and 4, indicate that the heat build-up of these latex-dispersed stocks should be lower than that of mill-dispersed; this order is reversed for HPC black compounds 5 and 6. The comparison of cut growth of compounds 3 and 4 shows that the latex-dispersed compound is superior in this respect also.

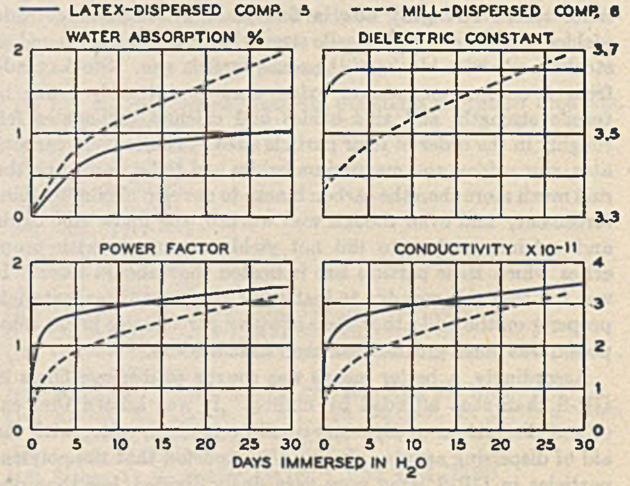


Figure 3. Electrical Properties of Zinc Oxide Compounds 5 and 6

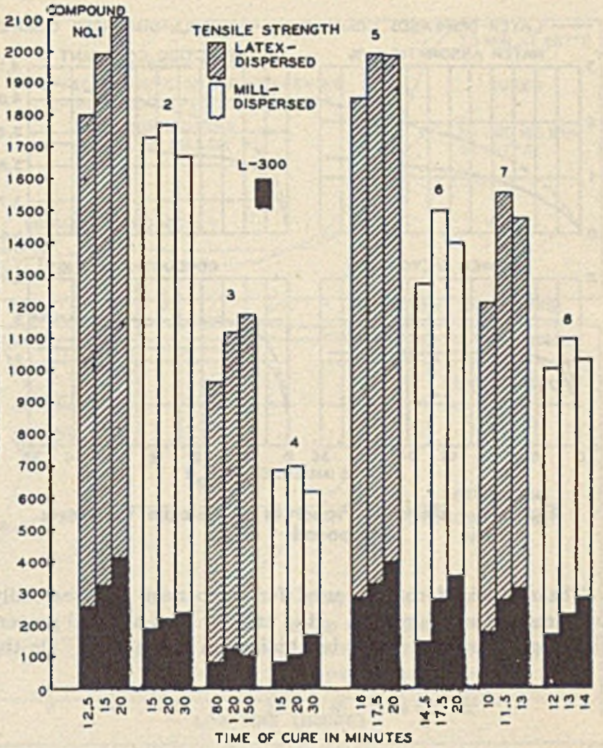
Table II. Physical Data on Zinc Oxide Compounds

Compound No.	1	2	3	4	5	6
GR-S	100.00	100.00	100.00	100.00	100.00	100.00
Coarse ZnO (350 mμ)	100.00	100.00	....	....	....	....
Medium fine ZnO (190 mμ)	....	....	100.00	100.00	....	....
Fine ZnO (120 mμ)	....	....	....	....	100.00	100.00
Stearic acid	2.00	2.00	2.00	2.00	2.00	2.00
Sulfur	2.00	2.00	2.00	2.00	2.00	2.00
2-Mercaptothiazoline	1.00	1.00	1.00	1.00	1.00	1.00
Aldehyde-amine	0.25	0.25	0.25	0.25	0.25	0.25
Filler dispersed:	In latex	On mill	In latex	On mill	In latex	On mill

	Cure at 282° F., Min.	Tensile Strength, Lb./Sq. In.	Stress at 300% Elongation, Lb./Sq. In.	Elongation at Break, %	Torisonal Hysteresis[a] *K*
Compound 1	15	1660	205	950	...
	20	1840	295	810	0.096
	25	1780	350	730	...
Compound 2	20	265	40	1475	...
	30	865	120	1030	[b]
	40	830	165	790	...
Compound 3	15	1900	190	895	0.096
	20	1790	240	765	...
	25	1960	300	740	...
Compound 4	15	1395	115	1015	...
	20	1480	125	855	0.122
	30	1280	185	695	...
Compound 5	10	2075	370	750	...
	12.5	2440	450	735	0.088
	15	2000	540	585	...
Compound 6	12.5	1395	220	780	...
	14	1440	260	735	...
	16	1325	265	665	...

[a] Method of Mooney and Gerke [*Rubber Chem. Tech.*, 14, 35 (1941)]. Determinations were made through courtesy of F. L. Holbrook, U. S. Rubber Company.

[b] Hysteresis of this cure could not be measured at 282° F. because its modulus was too low at that temperature.



↑ Figure 4. Stress-Strain Properties of Calcium Carbonate Compounds

Table III. Physical Data on Calcium Carbonate Compounds

Compound No.	1	2	3	4	5	6	7	8
GR-S	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Extra fine $CaCO_3$ (100 mμ)	95.00	95.00	....	....	125.00	125.00	....	....
Fine $CaCO_3$	....	....	....	....	....	....	125.00	125.00
Medium fine $CaCO_3$ (600 mμ)	....	....	91.00	91.00	....	....	....	....
Zinc oxide	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
Stearic acid	2.00	2.00	2.00	2.00	1.00	1.00	1.00	1.00
Sulfur	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
2-Mercaptobenzothiazole	1.00	1.00	1.00	1.00	....	....	....	....
Aldehyde-amine	0.25	0.25	0.25	0.25	....	....	....	....
Paraffin	....	....	....	....	2.00	2.00	2.00	2.00
Akroflex C	....	....	....	....	1.00	1.00	1.00	1.00
Agerite white	....	....	....	....	1.00	1.00	1.00	1.00
Heliozone	....	....	....	....	2.00	2.00	2.00	2.00
Softener (Turgum)	....	....	....	....	10.00	10.00	10.00	10.00
Ethyl selenac	....	....	....	....	1.00	1.00	1.00	1.00
Altax	....	....	....	....	1.50	1.50	1.50	1.50
Filler dispersed:	In latex	On mill	In latex	On mill	In latex	On mill	In latex	On mill

	Cure at 282° F., Min.	Tensile Strength, Lb./Sq. In.	Stress at 300% Elongation, Lb./Sq. In.	Elongation at Break, %
Compound 1	12.5	1800	260	855
	15	1995	325	830
	20	2110	415	755
Compound 2	15	1730	190	950
	20	1770	220	850
	30	1670	240	760
Compound 3	80	965	85	1060
	120	1120	125	895
	150	1175	105	915
Compound 4	15	690	85	870
	20	700	110	725
	30	620	170	630
Compound 5	16	1850	290	780
	17.5	1990	330	715
	20	1985	400	645
Compound 6	14.5	1270	145	930
	17.5	1500	280	635
	20	1400	355	540
Compound 7	10	1210	180	900
	11.5	1555	280	715
	13	1475	315	615
Compound 8	12	1010	170	875
	13	1100	235	725
	14	1035	285	615

ZINC OXIDE COMPOUNDS

Three different zinc oxides were used to make master batches—a fine, a medium fine, and a coarse grade. The physical properties of stocks made with these master batches and also those of compounds of the same recipe which were mill-dispersed are given in Table II. Figure 2 shows that the stress-strain properties of the latex-dispersed compounds are markedly higher than those of the mill-dispersed. The hysteresis of the former is lower than that of the latter, another indication that the heat build-up of the latex-dispersed stocks should be less than that of the mill-dispersed. The electrical properties of compounds 5 and 6 were measured and are shown in Figure 3. The mill-dispersed compound possesses better electrical properties initially, but during immersion in water they decline more rapidly than those of the latex-dispersed compound which, therefore, has the advantage of greater stability.

CALCIUM CARBONATE COMPOUNDS

To typify the improvement obtained by dispersing whitings in GR-S latex, a group of three particle sizes are cited—extra fine, fine, and moderately fine. Table III and Figure 4 show that a substantial improvement in stress-strain characteristics is obtained as compared with the mill-dispersed compounds. Furthermore, Figure 5 indicates that the electrical properties of a latex-dispersed whiting compound are superior in all respects to those of the same compound dispersed on the mill.

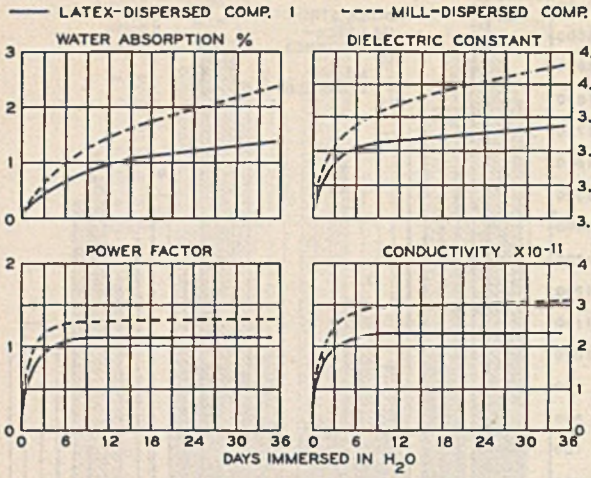


Figure 5. Electrical Properties of Calcium Carbonate Compounds 1 and 2

The mill-mixed controls used for comparison were carefully prepared in the laboratory. It is unlikely that physical properties as good as these would be obtained in the factory. On the other hand, a latex-dispersed master batch in which the pigment is already well dispersed should yield compounds in the factory with physical properties substantially as good as those of a laboratory-prepared stock; it is generally recognized that sulfur, accelerators, etc., are less difficult to disperse in polymer than is pigment. This is substantiated by a laboratory experiment in which two zinc oxide stocks were made with the same master batch. One was milled only 13 minutes and not refined; the other was milled 30 minutes and refined twice. The physical properties of the two compounds were substantially the same.

It is also practical to use a latex-dispersed master batch of high pigment loading and to cut back with polymer to make compounds of any desired loading. Compounds made in this manner may be slightly inferior to those made with master batches containing the desired loading for the compound which are not cut back. However, they are still greatly superior to the mill-mixed.

ACKNOWLEDGMENT

The authors gratefully acknowledge the invaluable aid of W. G. Straitiff, D. B. Herrmann, C. M. Hill, and J. B. Howard of these laboratories, and the cooperation of the group headed by G. S. Haslam of the New Jersey Zinc Company, which was designated by the Research Compounding Branch, Office of Rubber Director, to study this subject.

EFFECT OF ELASTOMER CRYSTALLIZATION ON Tests for Freeze Resistance

During long exposures to moderately low temperatures, Neoprene Type GN and rubber show a delayed stiffening that usually begins after 24 to 48 hours. This is caused by crystallization of the elastomer. The degree of crystallization under proper conditions is a function of the state of cure. The magnitudes of the increases in hardness are dependent upon the filler and softener content of the elastomer. Neoprene Type FR and GR-S do not show crystallization effects. Compounds of Neoprene Type FR containing certain softeners may undergo delayed stiffening. This is believed to be caused by plasticizer incompatibility at low temperatures. Some Neoprene Type GN compounds show the same effect. The effects of several plasticizers are summarized. This information should be helpful in selecting materials to improve freeze resistance as manifested by lower brittle temperatures or by reduced stiffening.

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At SUBZERO temperatures cured elastomers become stiff and may or may not become brittle. As stiffness increases, elasticity decreases and stress at any given elongation increases. Brittleness occurs when the elastomer reaches an inelastic state. Both time and temperature of exposure are important factors affecting these changes in properties. Under any given testing methods, the degree of stiffness and conditions of brittleness are intrinsic properties of the elastomers and their compounds. Summaries of these factors have been given by Liska (*6*) and Graves and Davis (*5*).

Crystallization, which explains some of the results to be described, has been known to occur in rubber for a long time. Factors influencing the crystallization of rubber were investigated by Bekkedahl (*2*). He concludes that the crystals formed during the freezing or the stretching of rubber are identical. It is believed that this is true for crystallizable elastomers.

Carothers and co-workers (*4*) and later Sebrell and Dinsmore (*8*) reported that the x-ray pattern of neoprene (polychlorobutadiene) crystals obtained upon stretching resembles those of rubber. Wood (*10*, *11*) showed that neoprene, like rubber, crystallizes at low temperatures. The most favorable temperature for Neoprene Type GM appears to be 0° C., and Neoprene Type FR shows no crystallization at low temperatures. Some properties of the latter at low temperatures were reported by Yerzley and Fraser (*12*).

Although considerable information on the properties of elastomers at low temperatures has been reported, few of the investigators have considered the possible effects of time of exposure. It was decided to study the changes that occur during long exposures at −17.8°, −28.9°, and −40° C. (0°, −20°, and −40° F.). Rubber, GR-S, Neoprene Type FR, and Neoprene Type GN

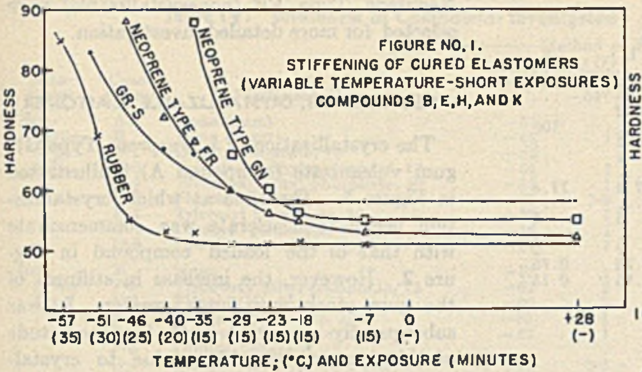
FIGURE NO. 1. STIFFENING OF CURED ELASTOMERS (VARIABLE TEMPERATURE-SHORT EXPOSURES) COMPOUNDS B, E, H, AND K

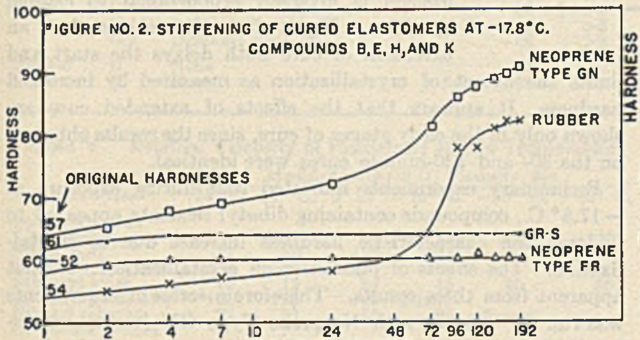
FIGURE NO. 2. STIFFENING OF CURED ELASTOMERS AT -17.8°C. COMPOUNDS B, E, H, AND K

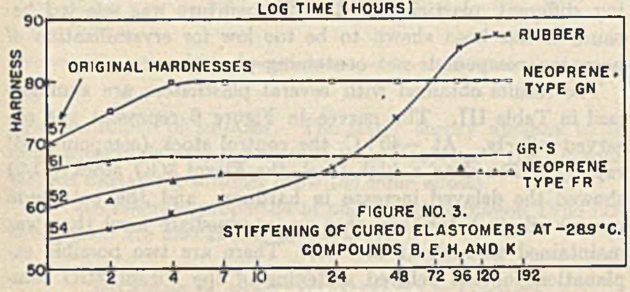
FIGURE NO. 3. STIFFENING OF CURED ELASTOMERS AT -28.9°C. COMPOUNDS B, E, H, AND K

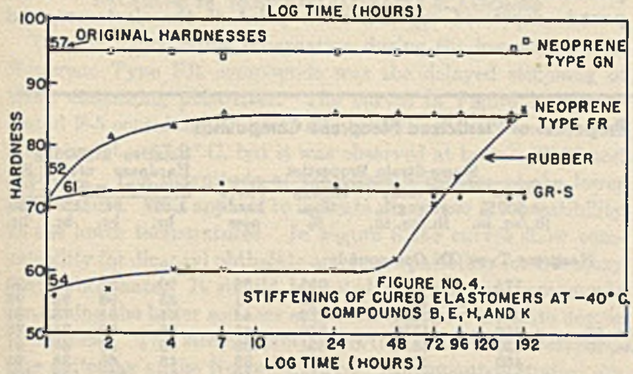
FIGURE NO. 4. STIFFENING OF CURED ELASTOMERS AT -40°C. COMPOUNDS B, E, H, AND K

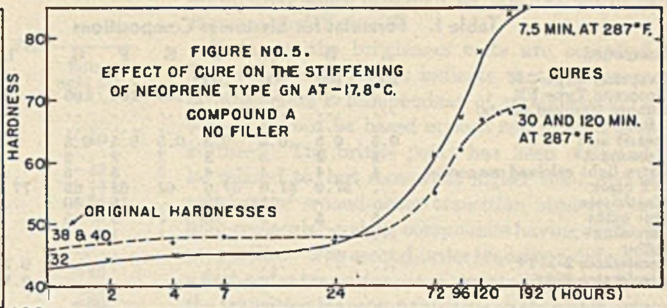
FIGURE NO. 5. EFFECT OF CURE ON THE STIFFENING OF NEOPRENE TYPE GN AT -17.8°C. COMPOUND A NO FILLER

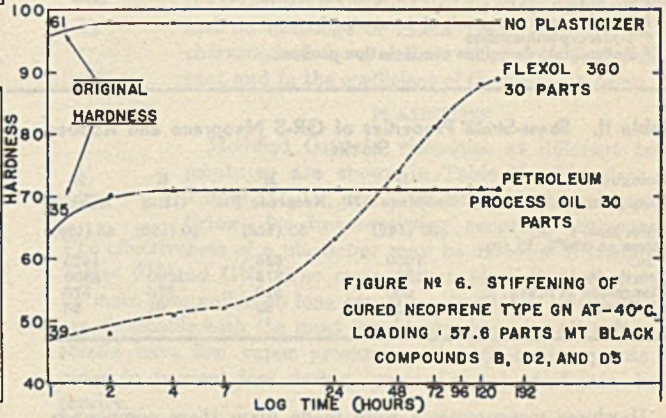
FIGURE No. 6. STIFFENING OF CURED NEOPRENE TYPE GN AT -40°C. LOADING : 57.6 PARTS MT BLACK COMPOUNDS B, D2, AND D5

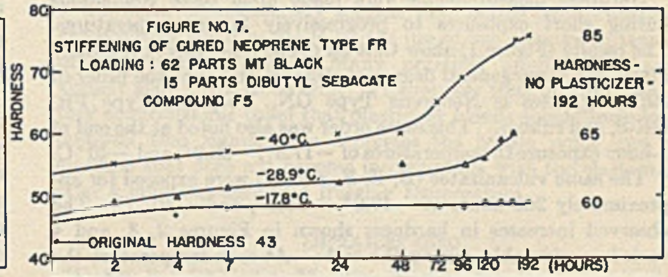
FIGURE NO. 7. STIFFENING OF CURED NEOPRENE TYPE FR LOADING : 62 PARTS MT BLACK 15 PARTS DIBUTYL SEBACATE COMPOUND F5

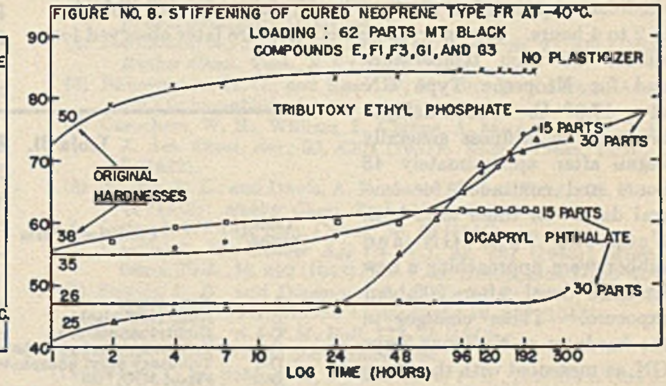
FIGURE NO. 8. STIFFENING OF CURED NEOPRENE TYPE FR AT -40°C. LOADING : 62 PARTS MT BLACK COMPOUNDS E, F1, F3, G1, AND G3

were selected, and the stiffening of their compounds was followed by observing changes in hardness.

The results show striking similarities between rubber and Neoprene Type GN and also between GR-S and Neoprene Type FR. Accordingly, the two neoprenes were selected for a more extensive study that included the effects of plasticizers on these polymers. This had the added advantage of providing data for the classification of the plasticizers for improving the freeze resistance of neoprene compounds.

Table I gives the formulas of the compounds studied. The stiffening of these stocks was measured with the apparatus described by Yerzley and Fraser (*12*). Readings were made after approximately 15 seconds, which corresponds to the suggestions of Taylor (*9*) for using the Shore durometer. The measurements were made at various times during long exposures to a given temperature or after short exposures to progressively lower temperatures. Brittleness tests were made by the methods of Martin (*7*) and Bimmerman and Keen (*3*) so that comparisons of stiffness with brittleness would be available. The viscosity measurements on the plasticizers were made in an Ostwald viscometer (*1*) immersed in a circulating coolant.

STIFFENING OF ELASTOMERS

To compare the stiffening of rubber, GR-S, Neoprene Type GN, and Neoprene Type FR, compounds B, E, H, and K (Table I) were prepared. Physical properties are shown in Table II.

Table I. Formulas for Elastomer Compositions

Compound	A	B	C	D	E	F	G	H	K
Neoprene Type GN	100	100	100	100	...	...	...	...	...
Neoprene Type FR	...	...	...	...	100	100	100	...	...
Rubber (smoked sheets)	...	...	...	...	...	...	...	100	...
GR-S	...	...	...	...	...	...	...	...	100
Stearic acid	0.5	0.5	0.5	0.5	0.5	0.5	0.5	1	...
Neozone A[a]	2	2	2	2	2	2	2	1	...
Extra light calcined magnesia	4	4	4	4	5	5	5	...	...
MT black	...	57.6	57.6	57.6	62	62	62	77.4	77.4
Plasticizers	...	...	15	30	...	15	30	...	...
Zinc oxide	5	5	5	5	5	5	5	5	5
Permalux[b]	...	...	...	...	1	1	1	...	...
Sulfur	...	...	...	...	...	...	...	2	2
Accelerator 2-MT[c]	...	...	...	...	...	...	...	0.75	0.75
Accelerator 808[d]	...	...	...	...	...	...	...	0.15	0.15

[a] Phenyl-α-naphthylamine.
[b] Di-o-tolylguanidine salt of decatechol borate.
[c] 2-Mercaptothiazoline
[d] Butyraldehyde-aniline condensation product.

Table II. Stress-Strain Properties of GR-S Neoprene and Rubber Stocks

Compound	B	E	K	H
Elastomer	Neoprene GN	Neoprene FR	GR-S	Rubber
Cure, min. (° C.)	30 (142)	30 (142)	90 (138)	45 (138)
Stress at 300%, lb./sq. in.	1050	825	..	1475
Tensile, lb./sq. in.	1675	1275	1700	3400
Elongation at break, %	600	510	270	570
Hardness	57	52	61	56

Hardness measurements were made upon these compounds during short exposures to progressively lower temperatures. The results (Figure 1) show that all of the elastomers eventually attain the same general degree of stiffness and that the order of stiffening rates is Neoprene Type GN, Neoprene Type FR, GR-S, and rubber. This same order was also noted at the end of 1-hour exposure to temperatures of −17.8°, −28.9°, and −40° C.

The same vulcanizates (B, E, K, and H) were exposed for approximately 200 hours at −17.8°, −28.9°, and −40° C. The observed increases in hardness shown in Figures 2, 3, and 4 varied considerably during the tests. At each temperature the elastomers appeared to reach an equilibrium degree of stiffening in 2 to 4 hours. However, large changes were later observed for rubber at each temperature and for Neoprene Type GN at −17.8° C. These delayed increases in stiffness generally began after approximately 48 hours and continued for several days. In these tests both Neoprene Type GN and rubber were approaching a new hardness level after 200-hour exposure. These changes in the hardness of Neoprene Type GN as measured with the Shore durometer are in close agreement with the changes in Young's modulus with time as reported by Liska (*6*).

Investigation of the literature (*2*, *4*, *6*, *8*, *11*) indicated that this effect was probably due to crystallization. Although the optimum temperatures (0° C. for Neoprene Type GN and −22° C. for rubber) were not represented, those used were within the crystallization range. Accordingly, Neoprene Type GN (crystallizable) and Neoprene Type FR (noncrystallizable) were selected for more detailed investigation.

NEOPRENE GN, CRYSTALLIZABLE ELASTOMER

The crystallization of a Neoprene Type GN gum vulcanizate (compound A) is illustrated in Figure 5. The time at which crystallization began to accelerate was commensurate with that of the loaded compound in Figure 2. However, the increase in stiffness of the gum stock was much greater. It was subsequently observed that the magnitude of this increase in stiffness due to crystallization is inversely proportional to loading by filler. Figure 5 further shows that an extension of cure both delays the start and limits the extent of crystallization as measured by increased hardness. It appears that the effects of extended cure are shown only in the early stages of cure, since the results obtained on the 30- and 120-minute cures were identical.

Preliminary experiments indicated that during exposure at −17.8° C., compounds containing dibutyl sebacate appeared to undergo the characteristic hardness increase due to crystallization. The effects of plasticizer on crystallization were not apparent from these results. Therefore a series of experiments was run at −40° C. with Neoprene Type GN stocks containing different plasticizers. This temperature was selected because it has been shown to be too low for crystallization of neoprene compounds not containing plasticizers.

The results obtained with several plasticizers are summarized in Table III. The curves in Figure 6 represent the observed effects. At −40° C. the control stock (compound B) rapidly stiffened to a high level, the Flexol 3GO stock (D-2) showed the delayed increase in hardness, and the petroleum process oil stock (D-5) reached an intermediate level that was maintained throughout the test. There are two possible explanations for the delayed stiffening of the Flexol 3GO compound—depressed crystallization point of the elastomer, and

Table III. Properties of Plasticized Neoprene Compounds

Compound[a]	Plasticizer, Parts	Stress-Strain Properties: Stress at 300% lb./sq. in.	Stress-Strain Properties: Tensile strength, lb./sq. in.	Stress-Strain Properties: Elongation, %	Stress-Strain Properties: Shore hardness	Relative Stiffening as Hardness after Exposure at −40° C. for: 1.58[b] hr.	24 hr.	120 hr.	200 hr.
	Neoprene Type GN Compounds								
A	None (gum)	175	3450	995	38	90	93	93	93
B	None (MT black)	1050	1650	540	61	85	98	98	98
C-1	Dibutyl sebacate, 15	600	1625	770	44	61	61	78	81
C-2	Tributoxy ethyl phosphate, 15	550	1750	640	45	66	69	75	78
D-1	Tributoxy ethyl phosphate, 30	350	1550	655	36	46	56	89	91
D-2	Flexol 3GO,[c] 30	450	1600	820	39	48	60	86	91
D-3	Tricresyl phosphate, 30	400	1575	730	40	85	100	100	100
D-4	Dicapryl phthalate, 30	450	1650	800	44	51	54	57	64
D-5	Petroleum process oil,[d] 30	450	1825	875	35	49	71	71	71
	Neoprene Type FR Compounds								
E	None	850	1250	485	50	72	82	84	84
F-1	Tributoxy ethyl phosphate, 15	325	1300	975	35	56	58	68	75
F-2	Flexol 3GO,[c] 15	475	1250	940	39	55	57	65	71
F-3	Dicapryl phthalate, 15	350	1250	980	38	55	60	62	62
F-4	Tricresyl phosphate, 15	450	1650	1010	40	65	76	78	78
F-5	Dibutyl sebacate, 15	400	1300	1100	43	..	...	...	...
G-1	Tributoxy ethyl phosphate, 30	125	1225	1160	25	42	46	69	73
G-2	Flexol 3GO,[c] 30	225	1125	1095	27	40	51	60	73
G-3	Dicapryl phthalate, 30	225	1100	1075	26	43	47	47	48
G-5	Dibutyl sebacate, 30	250	1075	1055	27	41	77	81	89
G-6	Dibenzyl ether, 30	275	1350	1050	30	39	49	55	65

[a] All stocks cured 40 min. at 153° C. except those of compound A cured 30 min. at 142° C.; C and D series based on compound B; F and G series based on compound E.
[b] Exposed to progressively lower temperatures down to −40° C. (Figure 1 gives time cycle).
[c] Triethylene glycol di-2-ethyl hexoate.
[d] Circo process oil.

Table IV. Brittleness of Compounds Investigated

Elastomer	Compound	Plasticizer, Parts	Method of Test: Bent loop (7) Temp., ° C.	Method of Test: Bent loop (7) Days at −54° C.	Method of Test: Solenoid (3), ° C.
Neoprene type GN	A	None (gum)	−51	..	..
	B	None (gum)	−46	1	−40
	C-1	Dibutyl sebacate, 15	−62	..	..
	C-2	Tributoxy ethyl phosphate, 15	−51	1	−43
	D-1	Tributoxy ethyl phosphate, 30	−62	1	−48
	D-2	Flexol, 3GO, 30	−62	>3	−54
	D-3	Tricresyl phosphate, 30	−57	1	−40
	D-4	Dicapryl phthalate, 30	−46	1	..
	D-5	Petroleum process oil, 30	−57	1	..
Neoprene type FR	E	None	−57	1	−45
	F-1	Tributoxy ethyl phosphate, 15	−62	2	−60
	F-2	Flexol 3GO, 15	−62	2	−60
	F-3	Dicapryl phthalate, 15	−57	1	..
	F-4	Tricresyl phosphate, 15	−57	1	−45
	F-5	Dibutyl sebacate, 15	..	..	..
	G-1	Tributoxy ethyl phosphate, 30	−68	>3	..
	G-2	Flexol 3GO, 30	−68	>3	−70
	G-3	Dicapryl phthalate, 30	−68	>3	..
	G-5	Dibutyl sebacate, 30	−68	>3	..
	G-6	Dibenzyl ether, 30	−68	>3	..
Rubber GR-S	H	None	−62	..	..
	K	None	Below −62	..	..

Table V. Relative Viscosity of Plasticizers at Low Temperatures

Plasticizer	Modified Ostwald (1) Viscosity, Sec. 25° C.	15° C.	0° C.	−10° C.	−20° C.	−40° C.
Tributoxy ethyl phosphate	29	41	90	168	306	>1200
Flexol 3GO	37	60	131	275	692	>1200
Tricresyl phosphate	233	980	>1200	[a]		
Dibenzyl ether	12	15	30	46	80	390
Dicapryl phthalate	124	270	918	>1200	[a]	
Dibutyl sebacate	21	31	55	89	Frozen	
Petroleum process oil	200	450	>1200	[a]		

[a] Too viscous.

incompatibility of softener. The latter theory appears to be more acceptable since noncrystallizable Neoprene Type FR compounds containing softener show the same effects.

The stress-strain properties of plasticized Neoprene Type GN compounds are also shown in Table III.

NEOPRENE FR, NONCRYSTALLIZABLE ELASTOMER

The most interesting observation during the investigation of Neoprene Type FR compounds was the delayed stiffening of those containing plasticizer. The curves in Figure 7 on compound F-5 containing 15 parts dibutyl sebacate show no delayed stiffening at −17.8° C. but it was observed at both −28.9° and −40° C. The magnitude of the effect is greater at the lower temperature. This appears to indicate plasticizer incompatibility at the lower temperatures. In Figure 8 the curves show compatibility for dicapryl phthalate and incompatibility for tributoxy ethyl phosphate. It should be noted that the two compounds containing the latter softener approach the same ultimate degree of stiffness. The stress-strain properties and the low-temperature stiffening of the Neoprene Type FR compounds studied are summarized in Table III.

BRITTLENESS

None of the compounds exposed to −40° C. for 200 hours became brittle in the Martin apparatus (*8*). When the compounds were tested once daily during 72-hour exposure to −54° C., all of the neoprene stocks containing 15 parts of softener became brittle before the end of the experiment. With 30 parts of softener the Neoprene Type GN compound (Flexol 3GO) and all of the Neoprene Type FR stocks were flexible after 72 hours.

Brittle points were also determined after short exposures to low temperatures. The results obtained by a slight modification of A.S.T.M. Designation D736–43T (*8*) are generally lower than those obtained by the method of Bimmerman and Keen (*3*).

Data on the brittleness tests are compiled in Table IV. The results indicate that this property of elastomers is independent of crystallization and that it cannot be based upon a measured degree of stiffness. The brittle point has been observed to be related to, but somewhat higher than, the temperature of second-order transition observed in all high-molecular-weight compounds having rubberlike properties. The second-order transition differs from a first-order transition—e.g., crystallization—in that the transition is accompanied by no change in volume and no exchange of latent heat. However, it is characterized by a definite change in the specific heat and in the coefficient of thermal expansion.

PLASTICIZERS

Modified Ostwald viscosities at different temperatures are shown in Table V. The data in Tables III, IV, and V are helpful in selecting plasticizers for freeze-resisting neoprene compounds. The effectiveness of a plasticizer may be different in Neoprene Types FR and GN. The more viscous plasticizers appear to be more compatible on long exposures, but lower brittle points are obtainable with the most limpid plasticizers. All softeners should have low vapor pressures and high boiling points in order to prevent loss during processing at moderate heat service.

The data on plasticizers suggest that better freeze-resisting compositions could be made by the use of one or more softeners in the same compound. Many practical applications have already shown this to be true. Preliminary tests in this laboratory confirmed our belief that plasticizer blends should include a material that significantly depresses the brittle point and a material that does not become incompatible with the elastomer after a long exposure to a freezing temperature.

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Effect of Solvents on Sludge Digestion

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Laboratory experiments on the effects of solvents used in industrial processes show that relatively small quantities influence the rate and degree of sludge digestion. The different solvents have various effects on volatile matter destruction and gas production. Small quantities of methyl, ethyl, butyl, and isoamyl alcohols produce greater volumes of gas but slightly retard volatile matter destruction. Ethyl ether stimulates gas production but has no effect on volatile-matter reduction. Acetone increases liquefaction of volatile matter without affecting gas production. Toluene and carbon tetrachloride, in smaller quantities, aid gas production but do not materially affect volatile matter destruction. Larger quantities retard or inhibit digestion. Xylene is toxic to liquefying and gas-producing organisms. Ethylene dichloride is extremely toxic. Even 1 to 2 parts per million ethylene dichloride in the sludge liquor retards gasification, whereas 10 p.p.m. reduces gas production over 50%. Plant experience indicates that small batches of spent solvent cause fluctuation in gas production and repeated discharges retard greatly or may inhibit the sludge-digestion processes.

VARIOUS types and differing amounts of solvents are used in industrial processes. Small quantities of solvents escape or are discharged regularly or intermittently. Some solvents have been used for a considerable time, whereas others are relatively new or are replacing those which have been in use. As an example may be cited the rather extensive use of ethylene dichloride as a substitute for carbon tetrachloride. The effect of various solvents on biological sewage treatment processes and particularly on sludge digestion has not been studied in detail. With the exception of information published some years ago on the effect of chloroform, ether, and alcohols on the bacterial activities in sewage (*1*) and a few tests on digestion of sludge (*2*), no information appears to be available.

During a study of the effect of different types of industrial wastes (acids, alkalies, poisons) on a sewage treatment plant receiving industrial wastes, suspicion was aroused regarding certain solvents present in small quantities. Sludge digestion was unaccountably retarded and gas production reduced at intervals. The decrease in gas production, amounting to 10–80%, lasted for several days or even weeks, in spite of the fact that there were no appreciable changes in the wastes. Laboratory studies on the portion of the work dealing with certain solvents are reported here.

FRESH solids and ripe sludge collected from plants receiving domestic wastes only were incubated at 70° F. and various quantities of solvents added. The solvents used were acetone, ethyl, methyl, butyl, and isoamyl alcohols, benzene, ethyl ether, ethylene dichloride, carbon tetrachloride, toluene, and xylene.

The studies were divided into series, and all sludge mixtures used were based upon a 2:1 fresh-solids ripe-sludge volatile matter basis. Percentages of volatile matter reduction and total gas production were chosen as indices of the effect of solvents on digestion. The quantities of solvents used are indicated in Table I.

The total solids concentrations used for the mixtures varied from 6.62 to 6.63% and the ash content from 39.1 to 40.0%. The volatile matter reduction of the control mixtures after 36-day digestion averaged 32.0%, with a greatest variation of 3.0% and a deviation of the means of 2.0%. The average amount of gas produced by the control mixtures was 515 cc. per gram volatile matter added; the greatest variation was 4.5% and a deviation

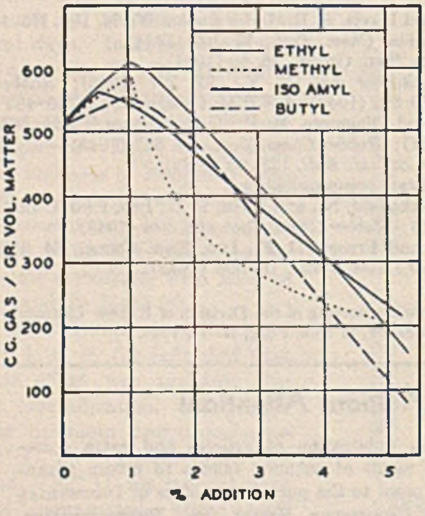

Figure 1. Effect of Alcohols on Gas Production

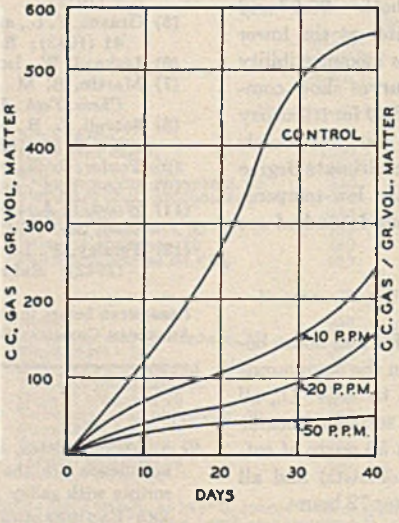

Figure 2. Effect of Ethylene Dichloride on Gas Production

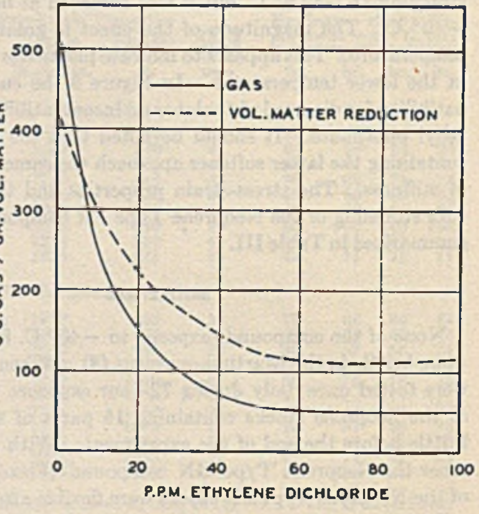

Figure 3. Effect of Different Concentrations of Ethylene Dichloride on Gas Production and Volatile Matter Reduction

TABLE I. VOLATILE-MATTER REDUCTION AND TOTAL GAS PRODUCTION PER GRAM VOLATILE MATTER ADDED AFTER 36-DAY DIGESTION

Solvents	Added by Volume, %	Volatile Matter Reduction, %	Gas, Cc.	% Increase* or Decrease from Av. Controls: V. M. reduction	% Increase* or Decrease from Av. Controls: Gas
Control 1	...	31.6	504	...	...
Control 2	...	31.7	512	...	...
Control 3	...	32.6	528	...	...
Methyl alcohol	0.1	26.7	582	16.6	13.0*
	0.2	23.6	356	26.2	30.9
	0.5	13.6	206	57.5	60.9
Ethyl alcohol	0.1	29.0	612	9.2	15.7*
	0.2	26.9	531	15.8	3.0*
	0.5	16.9	165	47.1	68.0
Butyl alcohol	0.1	28.4	554	11.2	7.5*
	0.2	28.7	489	10.3	5.0
	0.5	5.5	101	82.8	80.4
Isoamyl alcohol	0.05	29.0	567	9.3	10.0*
	0.1	30.0	542	6.1	5.5*
	0.2	27.2	470	14.9	8.6
	0.5	11.5	217	44.1	57.8
Ethyl ether	0.2	31.2	594	2.5	15.2*
	0.5	30.7	554	4.0	7.6*
Acetone	0.1	30.5	518	4.5	0.5
	0.2	35.2	528	10.0*	2.5*
	0.5	37.2	535	16.0*	4.2*
Benzene	0.1	16.4	452	48.7	12.2
	0.2	12.0	97	62.4	81.1
	0.5	7.5	9	76.6	99.3
Toluene	0.02	33.0	550	3.0*	6.6*
	0.05	32.9	570	2.8*	10.6*
	0.1	22.8	440	28.8	14.5
	0.2	10.1	69	68.3	86.6
	0.5	4.5	18	86.0	95.5
Xylene	0.1	24.7	453	22.7	12.0
	0.2	7.6	155	76.3	69.8
	0.5	3.0	17	93.5	96.7
Carbon tetrachloride	0.05	31.7	566	1.0	10.0*
	0.1	32.5	502	1.5*	2.5
	0.2	18.0	262	43.8	45.2
	0.5	7.0	30	78.2	82.8
Ethylene dichloride	0.001	17.3	227	45.9	55.9
	0.002	17.2	148	46.2	71.2
	0.005	11.3	52	64.7	90.0
	0.01	8.7	47	72.8	90.5
	0.02	11.0	36	66.7	96.3
	0.05	9.5	22	70.3	97.7

of the mean of 2.5%. Increases or decreases in volatile matter reduction and gas production caused by the addition of the solvents must be greater than 5% before they become significant. For comparison the results obtained are condensed in Table I, where volatile matter reduction and total gas production are given, together with increase or decrease in volatile matter reduction and gas production in relation to the results of a set of control mixtures.

All solvents added affected the rate and degree of digestion more or less. In general, the depressing or retarding effect of the solvents was more uniform on volatile matter destruction than on gasification. In most cases, however, the degree of gasification was more extensively affected than volatile matter destruction. The different solvents had various effects. Addition of smaller quantities of methyl, ethyl, butyl, and isoamyl alcohol produced greater volumes of gas per gram volatile matter, but slightly retarded volatile matter destruction. The amount of gas produced per gram volatile matter destroyed in the mixtures with 0.1% alcohol was materially higher as indicated by the following figures:

	Gram Volatile Matter per Liter Destroyed	Cc. Gas per Gram Volatile Matter Destroyed
Controls	13.05	973
Methyl alcohol	10.85	1220
Ethyl alcohol	11.76	1325
Butyl alcohol	11.52	1230
Isoamyl alcohol	11.76	1210

Probably most of the additional gas was the result of the destruction of the different alcohols. When increasing quantities of the various alcohols were added, volatile matter destruction and gas production decreased. The increased and decreased gas production is graphically shown in Figure 1.

ETHYL ether in the quantities added did not affect volatile matter reduction and stimulated gas production slightly.

Acetone in smaller quantities had no appreciable effect on volatile matter reduction or gas production, but increasing quantities stimulated volatile matter reduction without affecting gasification. The increased liquefaction of the solids, without subsequent gasification, is of considerable interest for the explanation of interrelated digestion processes. Similar results may be caused by milk wastes and certain acids.

Toluene and carbon tetrachloride in small quantities appeared to aid gas production but did not materially affect volatile matter destruction. Larger quantities of these solvents retarded or inhibited digestion.

Xylene appeared to be toxic to liquefying and gas-producing organisms. Larger quantities prevented volatile matter destruction and gasification.

Ethylene dichloride was very poisonous and caused a marked reduction in gas formation. As little as 10 p.p.m. in the sludge liquor caused more than 50% reduction in gas reductions (Figure 2). Ethylene dichloride ($CH_2Cl\text{—}CH_2Cl$), a colorless oily liquid with a rather pleasant odor and sweet tastes, is used as a solvent for fats, oils, waxes, gums, resins, and particularly for rubber, and has been replacing other solvents in industry. The material is nonflammable and is assumed to be only slightly toxic to man. With a more widespread use, there seems to be some evidence that concentrations of 100 p.p.m. in the air affect the worker. The chemical, made from ethylene and chlorine, is miscible with alcohol, chloroform, and ether, and is soluble in about 120 water, or to the extent of about 8000 p.p.m. The toxic action appears to be most pronounced on the methane-producing organisms. As little as 1 p.p.m. added to an actively digesting sludge concentration of 5% solids exerts a depressing influence. The effect of ethylene dichloride in quantities of 1 to 100 p.p.m. on gas production and volatile matter reduction is shown graphically in Figure 3. The indicated volatile matter reduction in the digesting mixtures is based on the assumption that no further destruction of ripe sludge took place.

Intermittent discharge of even small quantities of ethylene dichloride may cause temporary reduction in gas production. Since the chemical is soluble to a much greater extent than is required to exert a retarding action, and a few parts per million present in the sludge liquor are sufficient to affect gas production, this particular solvent should be kept out of the sewer if the sewage is biologically treated.

It is clear from the brief description that the effect of the various solvents on sludge digestion differs and that the limits of tolerance are not the same. The allowable quantities of solvents are in nearly all cases larger than would be expected to be present in industrial wastes treated in conjunction with sewage.

No appreciable effect would be expected, except when batches of spent solvent are discharged. Ethylene dichloride seems to be in a special class, however. Because this solvent is appreciably soluble in water, a small batch discharged may result in a sufficiently high concentration of a few parts per million in the sludge liquid and cause material fluctuations in gas production. Repeated discharges of relatively small batches may inhibit the entire digestion process. Digestion plant operation experience appears to substantiate this conclusion.

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Adsorption of Riboflavin by Lactose

INFLUENCE OF TEMPERATURE

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This work follows a study previously reported (*1*) on the influence of concentration. A knowledge of the influence of temperature furnishes the most adequate basis for the production of adsorbates (milk sugar containing adsorbed riboflavin) as by-products in the manufacture of the milk sugar of commerce. To utilize the productive capacity of existing milk sugar plants for the manufacture of adsorbates, it is necessary to establish conditions for the controlled preparation of these adsorbates. The purpose of this paper is to furnish data to operators for the establishment of these conditions. The range of concentrations and temperatures studied include those which would be encountered in the manufacture of adsorbates from grain curd casein whey and are applicable to a wide range of operating conditions. Although the data are considered primarily from the standpoint of their practical application, a number of problems of both theoretical and practical interest are considered.

IN THE present commercial process for the manufacture of lactose, grain curd casein whey is neutralized and boiled to coagulate proteins and insoluble salts. The filtrate is then concentrated under vacuum to approximately 70% solids, and the sugar is permitted to crystallize under conditions facilitating the establishment of the proper grain size. Under these conditions even if all of the riboflavin present in whey were adsorbed, a weak adsorbate would be obtained, inasmuch as the ratio between the quantity of lactose crystallizing from whey and the quantity of riboflavin in whey is large. Actually all of the riboflavin is never adsorbed. Furthermore, experiments in this laboratory indicate that the quantity adsorbed may prove variable.

To obtain concentrated adsorbates in good yields and under controlled conditions, it is necessary to modify the present commercial process in such a way that the crystallization operation is conducted in two steps: in the first only insignificant quantities, and in the second the greater quantity of riboflavin would be adsorbed. The phenomenon underlying the conduct of the first step lies in the existence of a critical concentration of riboflavin below which adsorption does not occur. This critical concentration is a function both of lactose concentration and temperature. If crystallization of lactose can be carried out under such conditions that the critical concentration is not exceeded until a considerable portion of lactose has crystallized, then the first step of the crystallization operation may be effected.

To ascertain the limits of lactose and riboflavin concentration under which this first step in the crystallization operation can be carried out, it is necessary to generalize and extend considerably the data previously recorded (*1*), to apply not only to Cheddar cheese whey (*2*) but also to grain curd casein whey, and not only at one temperature, 5° C., but over a range of temperatures (*3*). The critical concentration increases markedly with temperature; consequently, by choosing a temperature sufficiently high, it is possible to crystallize a considerable portion of lactose free of riboflavin. Then by lowering the temperature it becomes possible to crystallize another batch of lactose containing adsorbed riboflavin in good yields. Tables are given from which the operator may choose at his discretion operating conditions with respect to concentration and temperature. These conditions would then determine the concentration and the yield of the adsorbate.

EXPERIMENTAL TECHNIQUE

The technique was essentially the same as that previously reported (*1*). A stock solution was prepared from mother liquor obtained in the manufacture of milk sugar from grain curd casein whey. This liquor was stirred at 5° C. to remove excess lactose and treated with decolorizing carbon to remove riboflavin. The resulting stock solution had a pH of 4.6 and contained 0.14 gram of lactose per ml. and 31.8% solids. To 15-ml. samples, lactose and synthetic riboflavin were added to yield solutions of varying concentration. Sealed 22 × 175 mm. tubes containing these solutions and shielded from light by foil were rotated in a thermostat, the temperature of which was maintained constant within 0.2°. Temperatures ranged from 5° to 63° C. Riboflavin determinations were made fluorimetrically by a Duboscq nephelometer with the following accessories: a General Electric type H3, 85-watt, mercury vapor lamp; Corning glass filters No. 511 (to limit wave length band of incident light) and No. 352 (to limit wave length band of fluorescent light). The contents of the various tubes were filtered rapidly (within 5 seconds), and the lactose was washed well with 70% alcohol. The quantity of adsorbate recovered was weighed directly. The results checked well with polarimetric determinations of lactose. Blanks run at the higher temperatures indicated that no significant quantity of riboflavin was lost.

EFFECT OF COMPLETE CRYSTALLIZATION

Adsorption results under conditions of complete crystallization are given in Tables I and II and Figure 1. Riboflavin concentration is expressed as the number of micrograms contained initially in 1 ml. of solution just saturated with lactose at the temperature indicated. In Table I concentrations are referred to solutions just saturated with lactose at 5° C. In Table II concentrations are expressed in terms of solutions saturated at 5°, and at the temperatures indicated. Crystallization in these experiments proceeded to the point at which solutions were saturated with lactose.

The results in Figure 1 indicate that, as the concentration of riboflavin increases, only traces of riboflavin are adsorbed until a critical concentration is exceeded. The degree of adsorption then rises sharply and increases linearly at 5° and 28° C. with increasing concentration. Even at 50.8° C. the increase appears to be linear, but the data have not been sufficiently extended to decide this point. There are then, two definite stages in the adsorption process as it relates to the influence of riboflavin concentration; in the first stage only traces of riboflavin are adsorbed, and in the second, the degree of adsorption increases with increasing concentration, linearly, at 5° and 28° C. and perhaps even at higher temperatures. At high temperatures the transition between the two stages is more gradual than at lower temperatures.

The linear relation was stressed previously (*1*). The empirical formula,

$$a = (c - 2.5)/s \qquad (1)$$

where c = initial riboflavin concentration, γ/ml.
a = degree of adsorption, γ/gram
s = excess lactose at 5° C., grams/ml.
2.5 = minimum riboflavin concentration at 5° below which adsorption does not occur, γ/ml.

derived to apply to the solutions studied previously, did not apply generally to the solutions of the present investigation. At 5° C. a minimum critical concentration of 2.5 was found, which agrees favorably with the value previously obtained. However, the measured values of residual riboflavin, unlike the values established previously, were not equal to the minimum concentration nor independent of the concentration of riboflavin. Formula 1 may be generalized to apply, within certain temperature limits, to all of the solutions studied. Thus,

$$a = k-(c-c_t)/(s - s_t) \qquad (2)$$

where k = a constant
c_t = critical concentration below which adsorption does not occur at temperature t
s = initial lactose concentration, grams/ml.
s_t = solubility of lactose at t

From data obtained here and previously reported, it appears that at low supersaturation levels with respect to lactose there is a range of lactose concentration within which k in Equation 2 may be taken as unity. Within this range of concentration, at 5° and 28° C. and probably within the range 5–28.0° C., k does not differ significantly from unity. For highly supersaturated solutions k is less than unity. This point is brought out strikingly in curves 1, 1′, 2, and 2′ of Figure 1. The lines representing adsorption at 28° from solutions containing, respectively, 0.56 and 0.20 gram of excess lactose per ml., converge to a point on the horizontal axis representing 7.5 micrograms per ml. The respective values of k deduced from the slopes of these lines and from the quantities of lactose recovered are 0.84 and 1.0. Similarly, the values of k deduced from the slopes of curves 1 and 1′ (representing adsorption at 5° from solutions containing 0.63 and 0.20 gram excess lactose) are 0.88 and 1.0, respectively.

The value of k cannot exceed unity as long as conditions are such that c_t remains invariant; that is, the measured or extrapolated values of c_t, the critical concentration, can be less than but cannot exceed the measured value of residual riboflavin concentration for any given initial value of c. From a practical standpoint the observation that k can be less than but cannot exceed unity indicates that the equation,

$$a(s_i - s_t) = c - c_t \qquad (3)$$

may be employed to calculate the maximum quantity, $a(s_i - s_t)$, of riboflavin which, given the temperature and the initial riboflavin concentration, can be adsorbed. This maximum quantity is independent of the initial lactose concentration.

The relation between adsorption on growing crystals and temperature has received little notice in the past. The decrease in the degree of adsorption on growing lactose crystals with increasing temperature might be reasonably anticipated from the known behavior of insoluble adsorbents. However, the decrease attending adsorption on the growing crystals can be attributed, under conditions in which k is equal to unity, only to the decrease with increasing temperature in the value of the critical concentration below which adsorption does not occur. Under these conditions, once adsorption begins, the rate at which the degree of adsorption changes with riboflavin concentration becomes independent of temperature.

The manner in which the critical concentration decreases with increasing temperature is shown in Table II. The critical values corresponding at the various temperatures to the values for the degree of supersaturation are given in the third and fourth columns. The critical concentration is a function of temperature and is greater, the higher the temperature. Because it was deemed desirable to establish these critical concentrations with a minimum of extrapolation, the concentration range studied did not extend much beyond the highest evaluated critical concentration. At relatively low temperatures this concentration range included a sufficient number of points to determine the relation between the degree of adsorption and riboflavin concentration. At higher temperatures, however, only the critical concentration values could be ascertained satisfactorily. Ascertained definitely at all temperatures was the region of transition between the first and second stages of adsorption. Because of the more gradual nature of the transition at 50.8–63° C., the critical values of the minimum were less clearly defined than at lower temperatures. The minimum values established at these temperatures were those at which the degree of adsorption fell below one microgram per gram.

EFFECT OF VARIATION IN DEGREE OF CRYSTALLIZATION

Tables I and II show in detail the progress of adsorption at various temperatures as a function of the degree of crystallization. The previous paper (*1*) indicated that the critical riboflavin concentration is a function of the instantaneous concentration of lactose, and that this critical concentration decreases as the degree of supersaturation with respect to lactose decreases, and approaches a final minimum value as the point of saturation is approached. These critical values were not established over a sufficiently wide range of temperatures and lactose concentration to satisfy practical requirements. One purpose of the present study was the tabulation of data necessary to establish these values. The tables are drawn up to emphasize the practical significance of the phenomenon. From a practical standpoint, the residual riboflavin recoverable following the first stage of lactose crystallization is important. These values are given in the last column of Table I as the maximum percentage of riboflavin initially present which can be recovered at 5° C., under conditions of crystallization such that k is equal to unity. These values were calculated by the formula:

$$\frac{(c_r - 2.5)}{c_r} \times 100 = \text{max. \% riboflavin recoverable}$$

where c_r = residual riboflavin concentration.

Consider, for example, a solution containing 32.4 micrograms of riboflavin per ml. and 0.77 gram or more of lactose per ml. The last three columns of Table I*B* indicate that, if crystallization proceeds to the point at which 0.45 gram of excess lactose remains

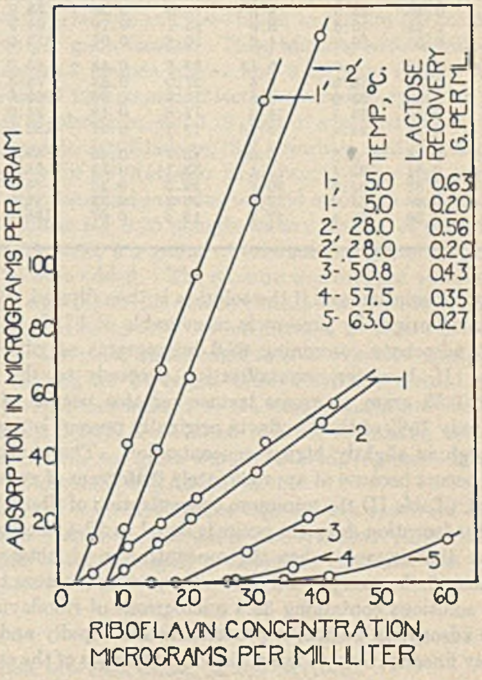

Figure 1. Relation between Degree of Absorption and Riboflavin Concentration at Various Temperature Levels

Table I. Adsorption as Lactose Crystallizes at Various Temperatures, Yields, and Degree of Adsorption on Residual Lactose at 5° C.

Initial Riboflavin Concn., γ/Ml.	Lactose Separated, Gram/Ml.	Riboflavin Adsorbed on Lactose, γ/gram	Total Flavin Adsorbed, γ/ml.	Final Flavin Concn., γ/ml.	Residual Lactose Separable at 5° C.[a], Gram/Ml.	Max. Calcd. Adsorption at 5° on Residual Lactose, γ/Gram	Max. Calcd. Yield of Riboflavin Adsorbate, %
A. Adsorption at 5° C.							
5.4	0.23	0.10	0.023	5.4	0.40	7.3	53.7
	0.50	1.5	0.75	4.7	0.13	16.9	40.7
	0.63	3.2	2.0	3.4	0.00	...	..
10.8	0.25	0.18	0.05	10.8	0.38	21.8	76.8
	0.30	0.8	0.24	10.6	0.33	24.5	75.0
	0.53	12.5	6.6	4.2	0.10	17.0	15.7
	0.63	11.6	7.3	3.5	0.00	...	..
16.2	0.17	0.40	0.07	16.1	0.46	29.6	84.0
	0.26	2.0	0.52	15.7	0.37	35.1	81.5
	0.34	13.4	4.6	11.6	0.29	31.4	56.1
	0.53	21.3	11.3	4.9	0.10	24.0	14.8
	0.63	18.4	11.6	4.6	0.00	...	..
21.6	0.09	0.15	0.01	21.6	0.54	35.4	88.3
	0.27	12.5	3.4	18.2	0.36	43.6	72.7
	0.31	27.0	8.4	13.2	0.32	33.5	49.6
	0.53	31.3	16.6	5.0	0.10	25.0	11.6
	0.63	26.3	16.6	5.0	0.00	...	..
32.4	0.13	0.80	0.10	32.3	0.50	59.6	92.0
	0.19	22.0	0.42	32.0	0.44	67.1	91.0
	0.26	37.5	9.8	22.6	0.37	54.3	62.0
	0.31	49.0	15.2	17.2	0.32	45.9	45.3
	0.53	52.5	27.8	4.6	0.10	21.0	6.5
	0.63	43.5	27.4	5.0	0.00	...	..
43.2	0.11	0.80	0.08	43.1	0.53	76.6	94.0
	0.22	33.5	7.1	36.1	0.41	82.0	77.8
	0.28	68.4	19.1	24.1	0.35	61.7	50.0
	0.30	70.0	21.0	22.2	0.33	59.7	45.6
	0.53	66.3	35.1	8.1	0.10	56.0	13.0
	0.63	55.8	35.1	8.1	0.00	...	..
B. Adsorption at 28° C.							
5.4	0.56	0.15	0.08	5.3	0.07	40.0	51.8
10.8	0.24	0.1	0.02	10.8	0.39	21.3	76.8
	0.33	0.3	0.1	10.7	0.30	27.3	75.9
	0.40	0.5	0.2	10.6	0.23	35.2	75.0
	0.45	1.4	0.6	10.2	0.18	42.7	71.3
	0.56	4.0	2.2	8.6	0.07	82.2	56.4
16.2	0.19	0.08	0.02	16.2	0.44	31.2	84.5
	0.30	0.3	0.1	16.1	0.33	41.2	84.0
	0.38	3.0	1.1	15.1	0.25	50.4	77.8
	0.44	9.4	4.1	12.1	0.19	50.5	59.2
	0.56	12.5	7.0	9.2	0.07	95.7	41.3
21.6	0.23	0.25	0.06	21.5	0.40	47.5	87.8
	0.31	0.50	0.16	21.4	0.32	59.0	87.5
	0.38	12.0	4.6	17.0	0.25	58.0	67.1
	0.44	15.6	6.9	14.7	0.19	64.2	56.4
	0.56	20.0	11.2	10.4	0.07	113.0	36.6
32.4	0.20	0.75	0.15	32.2	0.43	69.0	91.6
	0.30	18.0	5.4	27.0	0.33	74.3	75.6
	0.38	25.0	9.5	22.9	0.25	81.6	63.0
	0.45	32.5	14.6	17.8	0.18	85.0	47.2
	0.56	34.4	19.3	13.1	0.07	152.0	32.8
43.2	0.18	2.8	0.50	42.7	0.45	89.3	93.0
	0.31	32.5	10.1	33.1	0.32	95.6	70.8
	0.37	55.8	20.7	22.5	0.26	76.9	46.3
	0.45	51.0	23.0	20.2	0.18	98.3	40.9
	0.56	49.4	27.7	15.5	0.07	186.0	30.1
C. Adsorption at 50.8° C.							
5.4	0.32	0.05	0.02	5.4	0.31	9.4	53.7
	0.36	0.05	0.02	5.4	0.27	10.7	53.7
	0.43	0.05	0.02	5.4	0.20	14.5	53.7
10.8	0.31	0.05	0.02	10.8	0.32	25.9	76.8
	0.46	0.075	0.03	10.8	0.27	30.7	76.8
	0.43	0.075	0.03	10.8	0.20	41.5	76.8
16.2	0.36	0.12	0.04	16.2	0.27	50.6	84.6
	0.37	0.12	0.04	16.2	0.26	52.5	84.6
	0.43	0.12	0.05	16.1	0.20	68.0	84.0
21.6	0.13	0.07	0.01	21.6	0.50	38.2	88.3
	0.24	0.09	0.02	21.6	0.39	49.0	88.3
	0.35	0.12	0.04	21.6	0.28	68.3	88.3
	0.38	0.60	0.23	21.4	0.25	75.7	87.4
	0.43	0.55	0.24	21.4	0.20	94.5	87.4
32.4	0.06	0.22	0.01	32.4	0.57	52.4	92.4
	0.23	1.7	0.39	32.0	0.40	73.7	91.2
	0.35	7.5	2.6	29.8	0.28	97.5	85.0
	0.43	6.3	2.7	29.7	0.20	136.0	84.7
43.2	0.01	0.52	0.05	43.2	0.62	65.7	94.2
	0.13	3.6	0.47	42.7	0.50	80.4	93.1
	0.23	8.0	1.8	41.4	0.40	94.7	90.1
	0.39	17.5	6.8	36.4	0.24	141.0	78.4
	0.43	17.5	7.5	35.7	0.20	166.0	76.9
D. Adsorption at 57.5° C.							
21.6	0.30	0.13	0.04	21.6	0.33	57.9	88.3
	0.35	0.20	0.07	21.5	0.28	68.2	88.0
32.4	0.19	0.1	0.02	32.4	0.44	67.9	92.3
	0.22	0.1	0.02	32.4	0.41	73.0	92.3
	0.32	0.5	0.16	32.2	0.31	95.9	91.7
	0.35	0.7	0.25	32.1	0.28	106.0	91.4
43.2	0.13	0.4	0.05	43.1	0.50	81.2	93.8
	0.24	2.5	0.60	42.6	0.39	103.0	92.7
	0.32	5.0	1.60	41.6	0.31	126.0	90.5
	0.35	5.0	1.75	41.4	0.28	139.0	90.0
Adsorption at 63° C.							
32.4	0.27	0.3	0.08	32.3	0.36	82.8	92.0
43.2	0.27	0.3	0.08	43.1	0.36	114.0	93.8
52.0	0.27	1.8	0.49	51.5	0.36	138.0	94.3
74.5	0.27	16.0	4.3	70.2	0.36	200.0	90.8

[a] Solubility of lactose at 5° C., — 0.14 gram/ml.; initial lactose concentration, 0.77 gram/ml.

per ml. of solution and if the solution is then filtered, 91% of the riboflavin originally present is recoverable at 5° C. in the form of an adsorbate containing 68.6 micrograms of riboflavin per gram. If, however, crystallization proceeds to the point at which 0.33 gram of excess lactose remains per ml. of solution, then only 75% of the riboflavin originally present is recoverable, although in slightly higher concentration. The sharp drop in yield occurs because at approximately 0.45 gram of excess lactose per ml. (Table II) the minimum concentration of riboflavin below which adsorption does not occur is equal to 32.4 micrograms per gram; that is, only when the concentration of lactose becomes less than 0.45 gram per ml. does adsorption on lactose take place from solutions containing 32.4 micrograms of riboflavin per ml. Once adsorption begins, it proceeds rather rapidly and approximately linearly, only to fall off in the late stages of the crystallization process.

Adsorption from highly supersaturated solutions proceeds in three phases—a lag phase in which crystallization takes place without significant adsorption, an adsorption phase in which crystallization is attended by rapid adsorption, and a saturation phase in which crystallization approaches completion with practically no further adsorption.

At high temperatures the transition between the first and second phases is not so sharp as the transition at lower temperatures. The approximate location of the points of transition at 5° and 28° for given initial values of c is given in Table II. These points represent the lactose concentrations at which lactose will just begin to adsorb from a solution containing c micrograms riboflavin per ml. These points were located by extrapolation of the points on the adsorption phase of curves plotted (from the data of Table I*A* and *B*) of the relation between the quantity of riboflavin adsorbed and the quantity of lactose crystallized at the various levels of initial riboflavin concentration indicated in the last column of Table II. These points were located only approximately but with sufficient accuracy for practical purposes.

DISCUSSION

The data presented are intended to apply principally to grain curd casein whey processed for the removal of proteins and calcium salts as in the manufacture of milk sugar. There is no reason to assume, however, that the data are not equally valid or at least approximately valid for various types of cheese whey.

The relation,

$$a = k(c - 2.5)/(s - s_0)$$

applies at 5° C. equally well for the solutions described here and for solutions originating from Cheddar cheese whey (*1*). The stock solution used previously (*1*), exclusive of its lactose content, possessed approximately the same concentration of total solids and the same pH as the one employed in the present study.

Although the differences in composition probably existed, they were insufficient to affect the general relation between adsorption and concentration. Of practical significance was the difference in the rate of crystallization. It was previously reported that crystallization under the condition of seeding and stirring employed was complete in 3 to 5 weeks. In the present investigation crystallization under comparable conditions of concentration was complete within 3 days.

Table II. Critical Riboflavin Concentration Values at Various Lactose Levels and Temperatures

Temp., ° C.	Supersatn. with Respect to Lactose[a], Gram/Ml.	Critical Concn. of Riboflavin[a], γ/Ml.	Critical Concn. of Riboflavin[b], γ/Ml.
5.0	0.0	2.5	2.5
	0.20	5.4	5.4
	0.30	10.8	10.8
	0.35	16.2	16.2
	0.40	21.6	21.6
	0.50	32.4	32.4
	0.55	43.2	43.2
28.0	0.0	7.5	7.8
	0.20	10.3	10.8
	0.25	15.5	16.2
	0.30	20.7	21.6
	0.45	31.0	32.4
	0.50	41.3	43.2
50.8	0.0	19.0	21.8
57.5	0.0	27.0	32.9
63.0	0.0	37.5	48.9

[a] Referred to solution saturated with lactose at temperature indicated in first column.

[b] Referred to solution saturated with lactose at 5° C.

The value of *k* may be dependent on the rate of crystallization, and this may account for the lower values obtained at the higher lactose levels. If this condition obtains, maximum yield can be obtained only when the rate of crystallization is sufficiently low.

The yield values given in the last column of Table I are idealized and are results of calculations based upon the assumption that it is possible to realize conditions of crystallization in which *k* is equal to unity. Although this is not always the case, in the preparation of concentrated adsorbates, conditions are met under which *k* is equal to unity.

The values in Table II relating critical riboflavin concentration with lactose concentration obtain when the initial lactose concentration is equal to 0.77 gram per ml. It is not possible without further experimentation to say whether these values are independent of the initial lactose concentration. The data plotted in Figure 1 indicate that, for equilibrated lactose solutions, the critical concentration is independent of initial lactose concentration; consequently it might be reasonable to assume that for supersaturated solutions the critical values at various lactose levels are also independent of the initial lactose concentration.

In the manufacture of milk sugar from grain curd casein whey, operating conditions are such that the initial lactose concentration exceeds 0.77 gram per ml. On theoretical grounds it is plausible to assume that the degree of adsorption is a function of relative diffusion rates, and consequently that increases in lactose concentration at the same riboflavin level should result in a lowering in adsorption values. Such a lowering might be reflected in a lowering of critical values; on the other hand, it might be reflected merely in a decrease in the rate of adsorption, once adsorption begins.

The maximum values cited in the next to the last column of Table I for the degree of adsorption were calculated by the formula,

$$a = (c - 2.5)/(s - 0.14)$$

These values may be exceeded in practice by dilution of the mother liquor in which the second stage of crystallization is effected.

APPLICATION OF DATA

Pilot plant investigations on the application of the data to the preparation of concentrated adsorbates from whey and from related riboflavin-containing liquors will be reported separately. However, an example is given here which illustrates an operable process and the operations involved.

Example. The steps involving neutralization, heat coagulation of proteins and insoluble calcium salts, decantation, and filtration were identical with those employed commercially (*4*) in the manufacture of lactose from grain curd casein whey. Care was used to shield the hot liquor from light. The 400 pounds of clarified whey obtained as a result of these operations contained 6.0% solids, 4.8% lactose, and 1.0 microgram riboflavin per gram. This liquor was concentrated in a vacuum pan to contain 64.4% solids, 52.4% lactose, and 11.0 micrograms riboflavin per gram. Just before draining, the concentrate was brought to approximately 60° C. The concentrated liquor (36.5 pounds) was mixed in a jacketed mixer equipped with agitators mounted concentrically and geared to rotate in opposite directions. The temperature of crystallization was maintained approximately at 55–60° C. After 4 hours the warm mixture was filtered by a centrifuge. The wet unwashed crude milk sugar (14.8 pounds) recovered in this manner contained 13.6 pounds solids, 12.6 pounds crystalline lactose, and 3.4 micrograms riboflavin per gram solids. Calculation showed that each gram of sugar had adsorbed 0.5 microgram riboflavin. The disposition of this wet crude is identical with the disposition of the wet crude obtained in normal practice (*4*).

The residual liquor or sirup (21 pounds) flowing from the centrifuge contained 45.3% solids, 29.5% lactose, and 19 micrograms riboflavin per gram. It was well seeded and stirred at 5–10° C. for 24 hours; as a result, a second lot of lactose crystals containing adsorbed riboflavin crystallized. A 2.7-pound yield of wet crystals was obtained by centrifuging. These wet crystals analyzed 93% lactose and were found to contain 112 micrograms riboflavin per gram lactose. Thus, starting with clarified whey containing 19.2 pounds lactose and 0.18 gram riboflavin, there were obtained 12.6 pounds of lactose as crude lactose, 2.5 pounds of lactose as adsorbate, and 0.13 gram of adsorbed riboflavin, representing yields of 65% lactose, 13% adsorbate, and 72% riboflavin.

Preparation of Refined Adsorbate. The wet crude adsorbate was dissolved in water to yield a solution containing 2.5 pounds lactose per 8.25 pounds water; 25 ml. of concentrated hydrochloric acid, 3.5 grams of calcium oxide, and 15 grams of Filter-Cel were added. The mixture was brought to boiling and filtered. The pH of the cooled filtrate was then adjusted with sodium hydroxide to 5.6. Crystallization at 5–10° C. was permitted to take place under conditions of vigorous agitation and copious seeding for 24 hours, after which the formed crystals were separated and washed with a small quantity of cold water. Nine tenths pound of air-dried crystals containing 280 micrograms riboflavin per gram were recovered, representing a yield of 36% lactose and 90% riboflavin.

All first-run wash and mother liquors were combined with the second-run feed liquor entering the vacuum pan. However, the mother liquor belonging to the crude adsorbate was recycled only once.

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Crystallization of Binary and Commercial SOAP SYSTEMS

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Although the short spacings of x-ray diffraction patterns have proved most suitable for identification of at least four crystalline modifications of sodium soap, it is necessary to turn to the long spacings in order to ascertain the crystallization behavior of the individual fatty constituents of mixed and commercial soaps. The present study, based on long-spacing data, indicates that fractionation into the constituent single soaps is completely absent when anhydrous binary systems crystallize from isotropic melt. Fractional crystallization may occur when there is a sufficient difference in chain length between the two components, but even here the fractions are solid solution phases and not pure components. It appears to be the general rule that commercial soap crystallizes as a solid solution. No evidence of fractional crystallization has been observed in commercial soap.

A PREVIOUS paper (*3*) showed that x-ray diffraction patterns reveal the existence of at least four crystalline forms of soap. A scheme of identification was outlined, based on the short spacing rings which for each modification are practically constant over a wide range of fatty composition and of moisture content of the soap. (A discussion of deviations from pattern constancy is given in the footnote to citation *1*.) Although this constancy of ring diameter is of great value for identifying the crystalline modification, it seriously restricts the usefulness of the short spacings in other connections, particularly in determining the chemical compositions of the individual soap phases. For this purpose it is desirable to examine also the long-spacing rings, which depend upon the number of carbon atoms in the soap molecule as well as on the modification present, as indicated in the related work of Slagle and Ott (*4*) on fatty acids.

Thus in the whole field of research on solid forms of soap, our experience indicates that it is of the utmost importance to concentrate attention on the short spacings for identification of the crystal modification and on long spacings for considering questions of fatty composition. Much of our work in this field has been concerned with crystallization of soap mixtures, which in general have been found to yield solid solutions. Fractional crystallization may occur within certain limits of composition, but separate crystallization of the soap of a single constituent fatty acid from any typical soap has not been observed. The purpose of the paper is to present a sufficient cross section of the experimental work to support these conclusions, together with a partial interpretation of the observed patterns in terms of crystal structure.

The single soaps used in the experimental work were prepared from Eastman fatty acids (*3*) by alcoholic saponification, followed by oven drying at 150° C. Binary systems of the dry single soaps were made up by homogenizing the appropriate mixtures at 300–320° C. for one hour in a sealed glass tube contained in a rolling autoclave. At this temperature range the anhydrous samples exist as isotropic melt. Following the heat treatment the systems were allowed to cool slowly to room temperature over about 4 hours. When rapidly cooled samples were desired for comparison, a portion of the slowly cooled sample was placed in a small glass tube, heated to isotropic melt, and then quenched in ice water.

Mechanical mixtures of the anhydrous soaps which, as will be shown, are readily distinguishable from the homogenized samples by x-ray analysis, were prepared by grinding the pure dry soaps together in an agate mortar.

To avoid confusion introduced by differences in crystal modification, the anhydrous soaps used were those which could be obtained in the omega condition. The results given below for binary systems refer, therefore, to the omega type of structure alone.

The method of obtaining the diffraction patterns was described in the previous paper (*3*); in the present work the distance from soap sample to film was increased to 10 cm. to facilitate measurement of the long-spacing rings. Each long spacing reported here is a weighted average of the spacings derived from measurements of four, and usually five, orders of the long-spacing reflection.

ANHYDROUS BINARY SOAP SYSTEMS

A background for the crystallization behavior of blended commercial soaps is best developed by considering the simplified relations in binary systems of anhydrous soaps. Accordingly, crystallization phenomena observed in three binary systems are described below, and some of the related crystallization properties characterizing the commercial soaps will be elaborated in a later section.

SODIUM MYRISTATE–SODIUM PALMITATE SYSTEM. If a mechanical mixture of anhydrous sodium myristate and sodium palmitate is examined by x-ray diffraction analysis, the pattern will be found to exhibit two sets of long-spacing rings—one set characteristic of the myristate, the other characteristic of the palmitate. If heated to isotropic melt and then cooled either slowly or rapidly, this same mixture will exhibit only one set of long-spacing rings, with diameters intermediate between the values for the two original components.

All compositions of myristate and palmitate behave in the same manner, the values for long spacing showing a nearly linear relation with composition (Figure 1*A*). The behavior of this system is thus consistent with the formation of a continuous series of solid solutions.

If, during the cooling from liquid condition, the individual components had crystallized separately, the diffraction pattern would be expected to exhibit two sets of long-spacing rings characteristic of the single soaps; experiment has shown that as little as 5% palmitate can be detected in mechanical mixtures of laurate and palmitate (Figure 4). The pattern of a mechanical mixture is compared with patterns of the components and with typical solid solution patterns in Figure 2.

The crystalline modification in which the solid solution phase crystallizes is determined by the short spacings, and particularly by one or two identifying rings in the diffraction pattern (*3*).

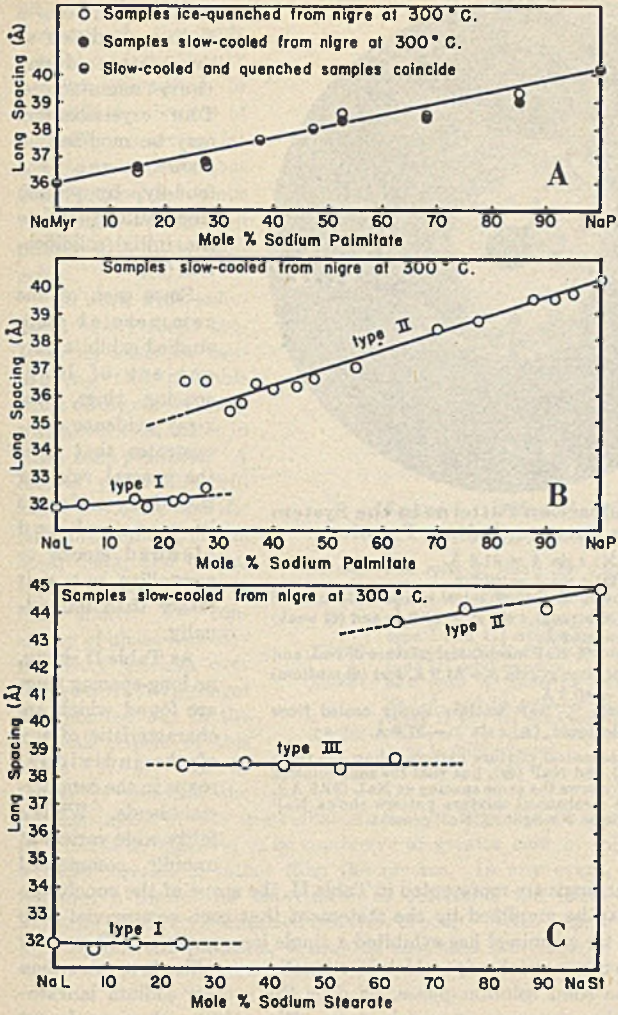

Figure 1. Variation of Long Spacing with Composition in Anhydrous Sodium Soap Systems

A, myristate-palmitate; *B*, laurate-palmitate; *C*, laurate-stearate

SODIUM LAURATE–SODIUM PALMITATE SYSTEM. When mixtures of the components of this system are heated to melting and slowly cooled, two types of solid solution may result, each continuous in long spacing with one of the pure components and depending on the proportions of the two original components. Type I solid solution is continuous in long spacing with the shorter component (sodium laurate), and type II solid solution is continuous in long spacing with the longer component (sodium palmitate). Figure 1*B* illustrates the variation of long spacing with composition in this binary system. (The dotted extensions in *B* and *C* indicate possible limits of two-phase regions.) There is no evidence for fractionation into the pure components, even though the solid solutions at high laurate and high palmitate composition exhibit long spacings almost identical with the pure components, because as little as 5% of a minor constituent can be detected if present as a single soap. This is shown in Figure 3 where the long-spacing rings of sodium palmitate can easily be detected in a mechanical mixture of sodium laurate and palmitate containing 5% palmitate.

At about 25 mole % palmitate, slowly cooled samples contain both types of solid solution phase; rapidly cooled samples do not, within the limits studied (Table 1*A*). Figure 3 compares the patterns of the pure components, two mechanical mixtures, and a typical solid solution in the system.

SODIUM LAURATE–SODIUM STEARATE SYSTEM. The components of this system differ by six CH_2 groups, and cooling from the melt gives rise to the more complex behavior illustrated in Figure 1*C*, involving the formation of three different types of solid solution. Type I, continuous with the shorter-chain component, exists alone in the composition range up to a maximum of about 23 mole % stearate. There is no appreciable increase in long spacing over that of pure sodium laurate. However, no rings characteristic of sodium stearate appear in the pattern; and since as little as 5% palmitate can be detected in laurate-palmitate mechanical mixtures, as indicated in the preceding section, it seems clear that the crystal phase is a solid solution.

Type II solid solution, continuous with pure sodium stearate, exists alone down to a minimum of about 63 mole % stearate. Type III solid solution, which is characterized by an almost constant spacing of 38.5 Å., exists alone in the intermediate region from a minimum of about 23 to a maximum of about 63 mole % stearate.

Types I and III are present together in samples over a range from possibly 15 to 35 mole % stearate; types II and III can coexist from possibly 53 to 75 mole % stearate. Ice-quenched samples, however, at these compositions exhibit only one set of long-spacing rings. Hence fractionation in this region is repressed by rapid cooling, as would be expected under conditions inimical to attainment of equilibrium. Diffraction patterns of variously prepared samples are shown in Figure 4. Numerical data are given in Table I*B*.

NATURE OF SOLID SOLUTIONS. The nature of the solid solutions occurring in these binary systems of mixed chain lengths is probably substitutional. Thus in the first system discussed above, where the difference in chain length is only two CH_2 groups, the evidence shows a continuous curve approaching linearity when composition is plotted against long spacings (Figure 1*A*). A spread of four CH_2 groups, as in the sodium laurate–sodium palmitate system, leads to two separate solid solutions, both of the same crystalline structure (as deduced from short spacings). In the type I solid solution phase, probably the substitution of one longer chain for two shorter leads to large holes in the structure, which accordingly soon breaks down when only about 25% of the longer component is present. In the type II solution, substitution of one shorter for one longer chain leads

TABLE I. VARIATION OF LONG SPACING WITH COMPOSITION IN ANHYDROUS SODIUM SOAP SYSTEMS

A. Na Laurate–Na Palmitate			*B.* Na Laurate–Na Stearate		
	Long Spacing, Å.			Long Spacing, Å.	
Mole % NaP	Ice-quenched from isotropic melt	Slowly cooled from isotropic melt[a]	Mole % NaSt	Ice-quenched from isotropic melt	Slowly cooled from isotropic melt[a]
0.0	31.9	31.9	0.0	31.9	31.9
5.0	....	32.0	7.5	31.9	31.7
7.5	31.9	....	15.0	32.0	31.9
14.5	31.9	32.2	23.5	37.1	31.9 (*m*); 38.4 (*s*)
16.8	....	31.9	35.0	38.0	38.5
18.4	32.0	....	42.2	38.5	38.4
21.5	....	32.1	52.5	38.6	38.4
22.7	36.1	....	62.5	40.9	38.7 (*s*); 43.7 (*w*)
23.7	36.2	32.2 (*w*); 36.5 (*s*)	75.0	43.2	44.2
25.0	36.3	....	90.0	43.5	44.2
27.5	36.3	32.6 (*w*); 36.5 (*s*)	100.0	44.9	44.9
32.0	....	35.4			
34.3	36.5	35.7			
36.8	....	36.4			
40.0	36.3	36.2			
44.3	36.3	36.3			
47.5	....	36.6			
55.0	36.8	37.0			
65.0	37.8	....			
70.0	....	38.4			
77.5	39.3	38.7			
87.5	....	39.5			
91.5	39.5	39.5			
95.0	....	39.7			
100.0	40.2	40.2			

[a] Letters in parentheses indicate: *w* = weak, *m* = medium *s* = strong.

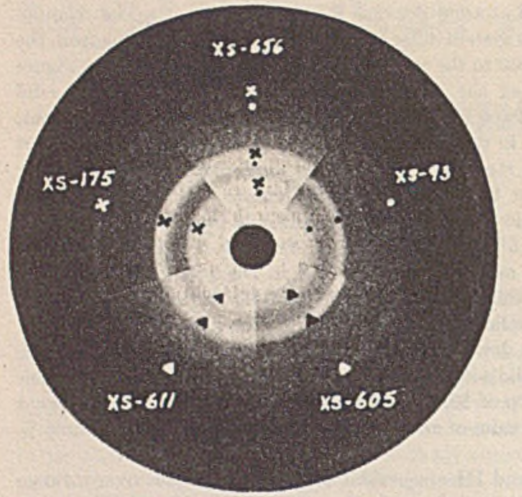

Figure 2. Diffraction Patterns in the System Sodium Myristate–Sodium Palmitate

XS-175	NaMyr, (×) $c \sin \beta = 36.0$ Å.
XS-93	NaP, (●) $c \sin \beta = 40.2$ Å.
XS-656	47.3 mole % NaP in mechanical mixture of NaMyr and NaP, (×) $c \sin \beta = 36.0$ Å and (●) $c \sin \beta = 40.2$ Å.
XS-605	47.3 mole % NaP mixture slowly cooled from isotropic liquid, (▲) $c \sin \beta = 38.0$ Å.
XS-611	47.3 mole % NaP mixture, ice-quenched from isotropic liquid, (▲) $c \sin \beta = 38.0$ Å.

Note that the rings for NaMyr (×) and NaP (●) are both found in the mechanical mixture pattern (XS-656), but the rings in the solid solution patterns (▲) are intermediate in diameter between those of NaMyr and NaP.

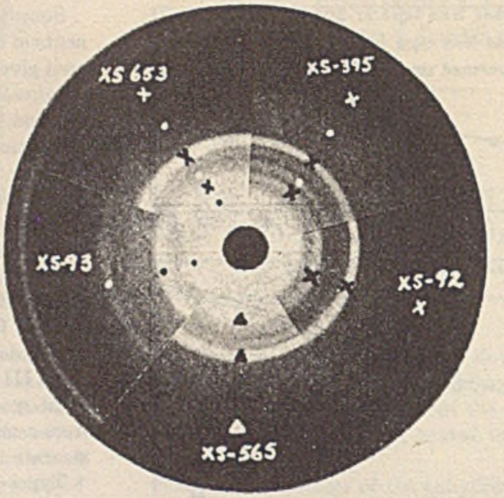

Figure 3. Diffraction Patterns in the System Sodium Laurate–Sodium Palmitate

XS-92	NaL, (×) $c \sin \beta = 31.9$ Å.
XS-93	NaP, (●) $c \sin \beta = 40.2$ Å.
XS-653	5 weight % NaP mechanical mixture of NaL and NaP, (× strong) $c \sin \beta = 31.9$ Å. and (● weak) $c \sin \beta = 40.2$ Å.
XS-395	20 weight % NaP mechanical mixture of NaL and NaP, (× strong) $c \sin \beta = 31.9$ Å. and (● medium) $c \sin \beta = 40.2$ Å.
XS-565	16.8 mole % NaP mixture slowly cooled from isotropic liquid, (▲) $c \sin \beta = 31.9$ Å.

Note that the mechanical mixture patterns show the rings of both NaL (×) and NaP (●), but that the solid solution pattern (XS-565) shows the same spacing as NaL (31.9 A.), even though the mechanical mixture pattern shows NaP rings with as little as 5 weight % NaP present.

to a structure stable over a wider range. Accommodation by the structures grows more restricted as the difference in chain lengths of the constituent soaps increases. Thus in the system sodium laurate–sodium stearate there are three solid solution phases. The intermediate phase (type III) is probably a structure in which a mixed double molecule (laurate-stearate) dominates.

The soaps prefer to form the intermediate solid solution rather than exist as a two-phase system over a wider range. Although the two-phase region is limited, each of the three types can apparently accommodate excess longer or shorter molecules over a considerable composition range.

While the foregoing study is deliberately confined to the omega structure, it demonstrates the capabilities of the x-ray study of long spacings and indicates what types of crystallization behavior may be expected in soaps. It thus provides a suitable background for the study of other soap structures and commercial soaps.

COMMERCIAL SOAP CRYSTALLIZATION

The evidence from x-ray diffraction studies of the binary anhydrous soap systems points definitely to the conclusion that fractionation into the single-constituent soaps does not occur when the systems are cooled from a melted condition. Fractionation, when it occurs at all, yields solid solution phases. It is important to recall that such fractionation in the binary systems seems to occur only over rather restricted composition ranges, and that it is influenced in part by rate of cooling of the system. While the behavior becomes more complex as the chain length spread between components is increased, no crystallization of the pure single constituents has been observed in any of the binary systems studied.

Turning to the far more complex compositions which make up commercial soaps, a similar crystallization behavior is found, as will be inferred from the results in Table II. It should be recalled that commercial bar soaps all undergo crystallization and solidification from a molten condition at some stage during their manufacture. The crystallization may be modified, in some cases profoundly, by process steps subsequent to the initial solidification (*3*).

Since each of the commercial soaps studied exhibits only one set of long-spacing rings, this x-ray evidence demonstrates that it is the general rule for the mixtures of soaps in natural and blended stocks to crystallize as a unit rather than individually.

As Table II shows, no long-spacing rings are found which are characteristic of any of the individual soaps in the commercial blends. While a fairly wide variety of unbuilt commercial bar soaps are represented in Table II, the scope of the conclusion may be amplified by the statement that each commercial soap so far examined has exhibited a single long spacing. There may be commercial soaps which fractionally crystallize into more than one solid solution phase, as does the system sodium laurate–sodium stearate at certain compositions, but such soaps do not

Table II. Long Spacings of Typical Commercial Soaps

Type of Soap	% H_2O	Phase	Long Spacing, Å.	Mol. Weight	
				From long spacing	By chem. analysis
Milled	14.0	β	42.7	282	281
Framed	27.2	$\omega + \delta$	42.0	288	285
Agitated	18.5	β	43.0	285	282
Agitated	22.4	β	43.4	288	283
Agitated	15.8	ω	42.0	289	282
Agitated	15.0	ω	41.9	289	283

Table III. Long Spacings of Tallow-Coconut Soaps in Omega Phase

Mole % Tallow Soap	Long Spacing, Å.	Mol. Weight	
		Calcd. from long spacing	Detd. chemically
0.0	34.8	242	236
44.1	38.0	263	266
54.0	38.8	268	267
75.9	40.6	280	281
100.0	43.8	300	300

Table IV. Long Spacings of Coconut–Red Oil Soaps in Omega Phase

Mole % Red Oil Soap	Long Spacing, Å.	Mole % Red Oil Soap	Long Spacing, Å.
0.0	34.8	54.0	40.8
7.9	35.8	64.5	42.5
16.3	36.5	75.6	43.6
25.0	37.6	87.6	44.2
34.2	39.2	100.0	45.2
44.4	40.7		

seem to be common. Because of the wide variety of molecule lengths represented in the graded mixtures of naturally occurring fat stocks, it appears that most commercial soaps form solid solution phases with little difficulty.

The work with anhydrous binary soaps provides no basis for estimating the probable effect of the considerable quantities of water in many soap products. A related paper (*2*) will show, however, that the moisture content of the beta, delta, and omega structures may vary over finite limits. The constancy of phase-identifying short spacings over wide moisture ranges was pointed out in the previous papers of this series (*1*, *3*). In so far as it concerns the crystallization of the individual soaps, the presence of moisture might be expected to be conducive to greater ease of solid solution formation, rather than the reverse. In any event, it becomes a matter for experiment to determine the effect of moisture on the crystallization behavior of soap. With respect to final commercial products, it may be said that the presence of water does not in general bring about the formation of fractionally crystallized components.

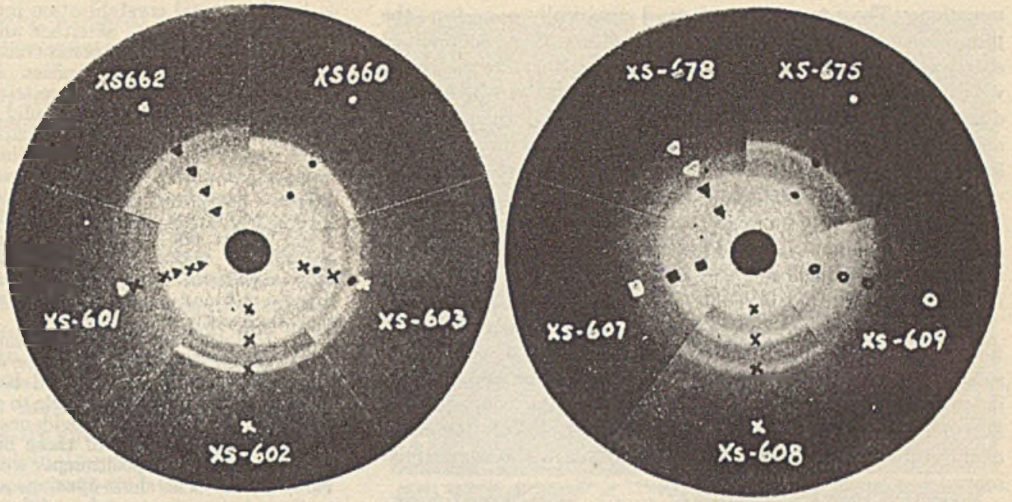

Figure 4. Diffraction Patterns in the System Sodium Laurate–Sodium Stearate

Slowly Cooled

XS-660	15.0 mole % NaSt, (●) $c \sin \beta$ = 31.9 A.; type I solid solution
XS-603	23.5 mole % NaSt, (● medium) $c \sin \beta$ = 31.9 Å. and (× strong) $c \sin \beta$ = 38.4 Å.; type I and III solid solutions
XS-602	42.2 mole % NaSt, (×) $c \sin \beta$ = 38.4 Å.; type III solid solution
XS-601	62.5 mole % NaSt, (× strong) $c \sin \beta$ = 38.7 Å. and (▲ weak) $c \sin \beta$ = 43.7 Å.; types II and III solid solutions
XS-662	75.0 mole % NaSt, (▲) $c \sin \beta$ = 44.2 Å.; type II solid solution

Ice Quenched

XS-675	15 mole % NaSt, (●) $c \sin \beta$ = 32.0 Å.; type I solid solution
XS-609	23.5 mole % NaSt, (○) $c \sin \beta$ = 37.1 Å.; long spacing intermediate between type I and III solid solutions
XS-608	42.2 mole % NaSt, (×) $c \sin \beta$ = 38.5 Å.; type III solid solution
XS-607	62.5 mole % NaSt, (■) $c \sin \beta$ = 40.9 Å.; long spacing intermediate between types II and III solid solutions
XS-678	75.0 mole % NaSt, (▲) $c \sin \beta$ = 43.2 Å.; type II solid solution

In Tables II and III molecular weights of commercial soaps determined from long-spacing data are compared with those derived from the conventional "saponification value" deter-

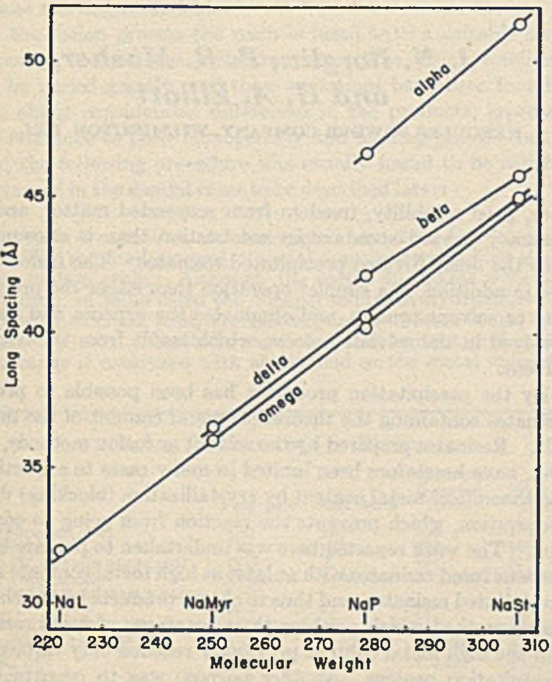

Figure 5. Variation of Long Spacing with Molecular Weight in Anhydrous Soaps

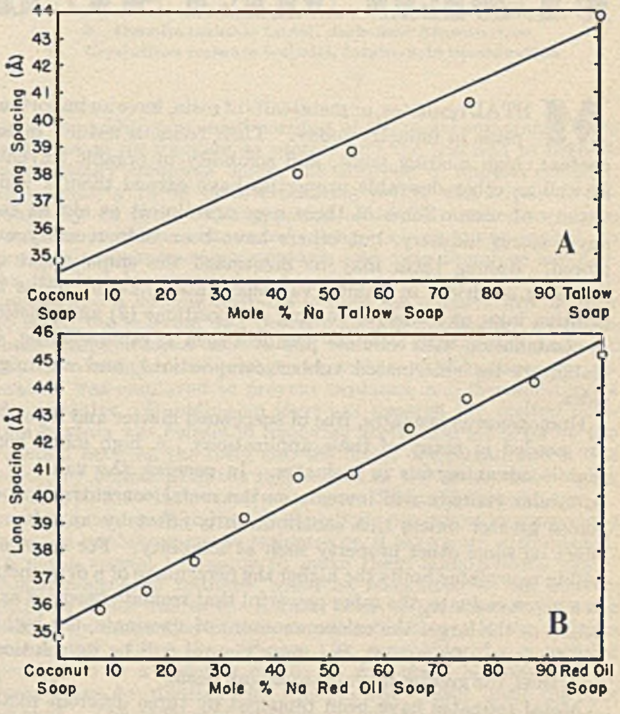

Figure 6. Variation of Long Spacing with Composition in Soap Mixtures

A. Coconut-tallow. *B.* Coconut-red oil mination. The x-ray value is derived empirically—i.e., from the proper curve in Figure 5; since modification of the commercial soap was deduced by the identifying short spacings, the molecular weight corresponding to the observed long spacing is read off directly. Thus for the second soap of Table III, which is in the omega structure (from short-spacing data), the long spacing is 38.0 Å. corresponding to a molecular weight of 263 as compared with the chemically determined value of 266. In preparing Figure 5, the slightly more accurate values (because of improvements in technique) were used for the long spacings of the omega structure of the single soaps as shown in Figure 5 and Table I instead of those listed in Table VII of the previous paper (*3*).

While the agreement is less marked in some other examples, it appears that the long spacings of the commercial soaps correspond, in general, to the values which would be predicted by interpolating from the curves for saturated single soaps (Figure 5), even though the determination by x-rays neglects the effect of unsaturated chains known to be present in the commercial soaps.

Thus, commercial soaps exhibit an almost linear relation between long spacing and fat formula (Figure 6). Soaps made up of mixtures of coconut oil and tallow or of red oil and coconut oil (Tables III and IV), resemble more closely the binary mixtures of adjacent, even homologs (e.g., sodium myristate–sodium palmitate), than the more widely separated homologs. In spite of the range embraced within the fat composition of a typical commercial soap, the proportion of each homolog is such that the intricate assortment of chain lengths is blended into a single solid solution phase.

CONCLUSIONS

From a study of the long spacings, the following conclusions can be drawn relating to the nature of crystalline phases in the solidified soap systems:

1. Fractional crystallization into the single-constituent soaps is completely absent, as either anhydrous binary soap systems or the more complicated commercial soap systems crystallize.
2. Fractional crystallization into different solid solution phases can occur in certain restricted composition ranges, as in binary systems, but only one solid solution phase has been found in typical unbuilt commercial soap systems.
3. In the typical anhydrous binary system sodium myristate–sodium palmitate, where the components are even-numbered adjacent homologs, a continuous series of solid solutions occurs, with nearly linear variation of the long spacing with composition.
4. Where the components differ by four CH_2 groups, as in the system sodium laurate–sodium palmitate, the behavior is more complex. A laurate-rich solid solution separates at the laurate end and a palmitate-rich solid solution separates at the palmitate end of the system.
5. In a system in which the components are even further separated by six CH_2 groups, as in the system sodium laurate–sodium stearate, a still more involved behavior is found. Here three different solid solutions are able to exist.
6. While no detailed evidence is included here, the short-spacing x-ray patterns of these binary mixtures are essentially independent of composition, as would be expected from our previous work. The short spacings are thus uniquely useful in detecting changes in crystal modification over wide ranges of fatty composition. Their value in the complicated mixtures involved in commercial soaps needs scarcely be emphasized.

ACKNOWLEDGMENT

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FUSED METAL RESINATES

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METAL resinates, or metal salts of rosin, have an important place in industry today. Their resinous nature, metal content, high melting point, and solubility in organic solvents as well as other desirable properties have earned them a wide variety of uses. Some of these uses are almost as old as the naval stores industry, but others have been only recently explored. Among them may be mentioned the employment of resinates as driers in paints, varnishes, and inks, as resins in printing inks, as resins for coating compositions (*2*) and plastics in combination with cellulose products such as ethylcellulose, as stabilizers for chlorinated rubber compositions, and as fungicides.

Homogeneous resinates, free of suspended matter and crystals, are needed in many of these applications. A high metal content is advantageous in resinates. In general, the value of a particular resinate will increase as the metal concentration becomes greater unless this contribution is offset by an adverse effect on some other property such as solubility. For example, within reasonable limits the higher the percentage of a drier metal in a given resinate, the more powerful that resinate becomes as a drier; or the larger the calcium content of a resinate, the higher will be its melting point, the more viscous will be its solutions and, thus, the greater its value as an ink resin.

Metal resinates have been prepared by three different methods—precipitation process, solvent process, and fusion process. Resinates prepared by either the fusion or solvent process are similar in nature, and have the advantages of resinous appearance, good solubility, freedom from suspended matter, and less tendency toward spontaneous combustion than is encountered with the finely divided precipitated resinates. The fusion process, in addition, is a simpler operation than either the precipitation or solvent process, and eliminates the expense and hazard, involved in the solvent process, which result from the use of a solvent.

By the precipitation process it has been possible to produce resinates containing the theoretical metal content of the neutral salt. Resinates prepared by the solvent or fusion methods, however, have heretofore been limited in many cases to a fraction of the theoretical metal content by crystallization (blocking) during preparation, which prevents the reaction from going to completion. The work reported here was undertaken to prepare homogeneous fused resinates with at least as high metal contents as the precipitated resinates, and thus to obtain products by the cheaper fusion method which combine the advantages of fused resinates and the high metal content previously reached only through the precipitation process. Another purpose was to prepare resinates of a variety of metals from both regular and modified rosins and to compare their properties.

Homogeneous metal resinates, prepared by the fusion of refined wood rosin, disproportionated wood rosin, commercial hydrogenated rosin, and commercial polymerized rosin with metal diacetates, are found to have the following maximum metal contents: 6% calcium, 19% cobalt, 8–9% copper, 29–40% lead, 6–8% manganese, or 18–23% zinc. The pronounced "blocking" (crystallization) tendency of cobalt, manganese, and zinc resinates during preparation is overcome by using temperatures as high as 285–330° C. to keep the resinate molten and by adding enough calcium acetate to supply about 0.5–2% calcium in the resinate. No blocking is encountered with the resinates of polymerized rosin. Cobalt, lead, and zinc resinates are prepared with higher metal content than their corresponding metal diabietates, possibly due to the formation of salts of the metal acetate-abietate type. The homogeneous resinates are amorphous resins and are higher melting than the original rosins. Calcium resinates increase in melting point 20–22° C. for each 1% calcium; lead and copper resinates increase only 2–4° C. for each 1% metal. Cobalt, lead, and manganese resinates have intermediate melting point rise with metal content. At metal contents which approach the theoretical value, based on acid number of rosin, most of the resinates are completely soluble in organic solvents. Zinc resinates are soluble at metal contents of approximately twice this theoretical value.

◆ ◆ ◆

This paper is limited to a report on the successful preparation and the properties of calcium, cobalt, copper, manganese, lead, and zinc resinates produced by the fusion method and having a high metal content and homogeneity. They were prepared from the following rosins and modified rosins which were chosen as typical of the classes represented: wood rosin of N color grade representing a typical refined wood rosin; Staybelite (*3*, *4*), representing commercial hydrogenated rosin; Poly-pale (*1*, *5*, *6*), representing commercial polymerized rosin; and disproportionated wood rosin. Table I gives comparative analyses of these starting materials.

In the fusion process the rosin is fused with a suitable metal compound to form the metal resinate. The fusion conditions may be varied greatly, and these variations have been found to bring about considerable differences in the products, especially with reference to their homogeneity and melting point. In this work, the following procedure was usually found to be satisfactory except in the special cases to be described later:

The rosin was melted and heated to about 250° C. with agitation. The required amount of metal diacetate was added slowly to the molten rosin. Although the metal diacetates were generally used, in some cases the cheaper oxides or hydroxides such as those of calcium, lead, manganese, and zinc were found to be satisfactory over a limited range of metal content and over a wider range if catalyzed with acetic acid or the metal diacetate. After the addition of small portions of the metal compound, time was allowed for foaming to subside and the reaction to become substantially complete before the addition of another portion. In general, a 15–90 minute addition period was required, followed by an extra cooking period of 15–60 minutes to ensure complete reaction. Excessively long cooking times tended to produce nonhomogeneous products and were therefore avoided. As the metal compound and rosin reacted, the viscosity increased and it became desirable to raise the temperature in order to speed the reaction and prevent excessive foaming. A maximum temperature of 285° to 295° C. was usually sufficient. A neutral atmosphere of nitrogen or carbon dioxide above the reactants was employed to prevent oxidation and discoloration of the resinates. Bubbling an inert gas through the molten reaction mixture was helpful in removing acetic acid given off by the reaction between the rosin and the metal diacetates, and it was especially beneficial in the preparation of the resinates of higher melting points which were very viscous during the preparation.

Table I. Analyses of Rosins

	Poly-pale	Staybelite	Disproportionated Rosin	N Wood Rosin
Saponification No.	160	167	166	172
Acid No.	150	162	160	166
Color (U. S. rosin standard)	WG	X	WG	N
Color (Lovibond)	27 amber	10 amber	27 amber	38 amber
Ring and ball softening point, ° C.	94	69	74	75
Drop melting point (7), ° C.	101	75	81	83
Refractive index, n_D^{20}	1.5440	1.5270	1.5382	1.5453
Sp. gr., d_4^{20}	1.073	1.045	1.056	1.067
Bromine No.	102	80	69	138
Thiocyanogen No.	68	24	18	90
Sp. rotation (7/8-in. cube)	−3°	....	+50°	+6°

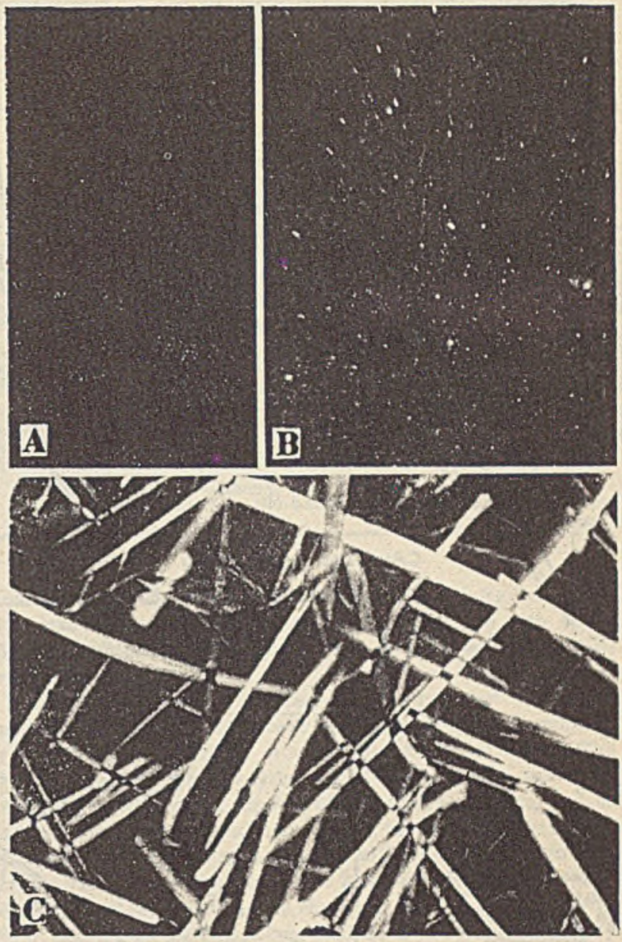


Figure 1. Photomicrographs of Resinates (×500)

A. Homogeneous resinate (manganese), dark-field illumination
B. Opaque resinate (zinc), dark-field illumination
C. Crystalline resinate (cobalt), bright-field illumination

It was necessary to modify the above procedure in some cases to avoid nonhomogeneous resinates or, if they were encountered, to use a special technique to make them homogeneous again. Nonhomogeneous resinates could be recognized by an opacity which was not due to the natural color of the resinate but was caused by suspended matter or crystallization. If the resinate was of the opaque type (Figure 1*B*), consisting of a suspended precipitate in a resinlike matrix, it was made homogeneous in most cases by diluting the resinate with rosin until the mix cleared. The success of this remedy indicated that the precipitate was probably unreacted salt or oxide. After this precipitate had reacted with the excess of rosin, the metal content could be increased again just as if the mix had never been in two phases.

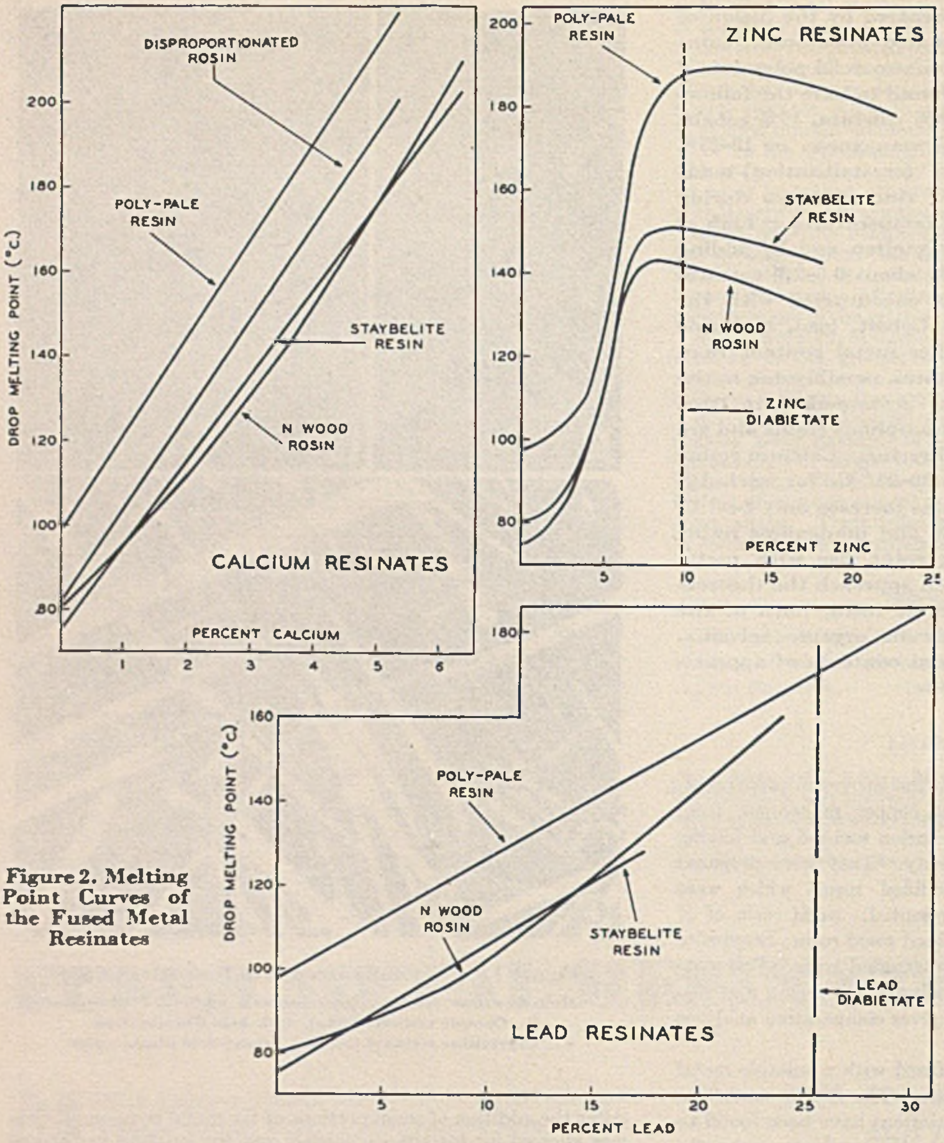


Figure 2. Melting Point Curves of the Fused Metal Resinates

This opaque type of resinate resulted from adding more metal salt than would react with the rosin or from cooking the resinate too long at high temperatures. The copper resinates had a special tendency to form this type of nonhomogeneity and had to be prepared at temperatures below 200° C. with special care to prevent local overheating in order to avoid the formation of a reddish-brown precipitate.

The second type or crystalline nonhomogeneity (Figure 1*C*) gave a blocked resinate consisting of a crystalline phase in an amorphous resinlike matrix. It was overcome by raising the temperature of the reaction mixture to 285–320° C. to keep the resinate fluid and by adding enough calcium acetate to supply about 0.5 to 2.0% calcium in the resinate. The latter was often unnecessary, however, since zinc and cobalt resinates which ordinarily block in the range of about 3–12% metal could be prepared with more than 12%, provided the temperature was maintained. Manganese resinates also exhibited this blocking tendency at metal concentrations above approximately 3%. A decided advantage was found in the use of Poly-pale which did not block in resinate preparation.

PROPERTIES OF RESINATES

Appearance. Homogeneous fused resinates were amorphous resinlike solids. Their colors varied widely. Calcium, lead, and zinc resinates resembled the refined wood rosins in color, and manganese resinates resembled the darker grades of rosin. Copper resinates were deep green and cobalt resinates were bright purple.

Metal Content. The approximate maximum metal contents of the homogeneous resinates are given in Table II. Taking into account the small variations in the acid numbers of the rosins, the maximum metal content was found to be substantially the same for resinates of a particular metal from different rosins; the exceptions were the zinc resinate of Poly-pale, which had a higher maximum metal content, and the lead resinate of Poly-pale, which had a somewhat lower value. The resinates with metal contents considerably higher than the theoretical value for their diabietates were probably complex metal salts of the acetate-abietate type. This possibility was indicated by the presence of appreciable combined acetic acid in resinates with greater than theoretical metal content. Below theoretical metal content the acetic acid content was negligible.

Solubility. All the metal resinates showed good solubility in organic solvents if the metal content was not too high, as indicated in Table III. Zinc resinates had exceptional solubility; resinates were soluble which contained almost twice as much zinc as the diabietate did theoretically. Lead res-

Table II. Approximate Maximum Metal Content of Homogeneous Resinates (Fusion Process)

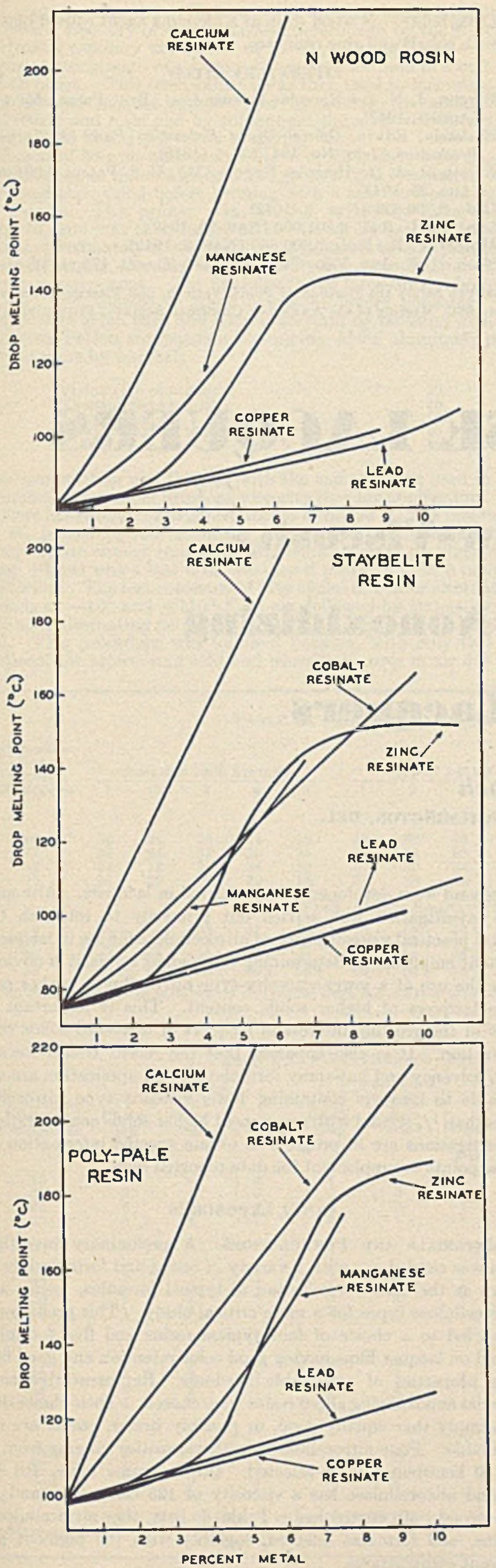
Metal	Theoretical Metal Content of Diabietate	Poly-pale	Disproportionated Rosin	Staybelite	N Wood Rosin
Calcium	6.2%	6%	6%	6%	6%
Cobalt	8.9	19	19[a]	19[a]	19[a]
Copper	9.6	8	..	8	9
Lead	25.5	29	40	40	40
Manganese	8.4	8	..	>6[a]	>7
Zinc	9.8	23	18	18[a]	18[a]

[a] Special technique required to prevent blocking (temperatures of 285–330° C. and addition of small amounts of calcium acetate).

Table III. Solubility of Fused Metallic Resinates

Metal	Theoretical Metal Content of Diabietate	Approx. Max. Metal Content of Resinate[a] Made from: Poly-pale	Staybelite	N wood rosin
Calcium	6.2%	5–6%	6%	4–5%
Cobalt	8.9	9–10	9	9
Copper	9.6	7–8	7–8	7–8
Lead	25.5	29	5–10	5–10
Manganese	8.4	8	>6	>7
Zinc	9.8	17–18	18	18

[a] Resinates completely soluble in xylene, toluene, or Varsol at 40% concentration.



← **Figure 3. Melting Point Curves of Fused Resinates of Various Rosins**

Table IV. Blending of Fused Resinates with Rosins (1:2 Ratio of Resinate to Rosin)

Rosin	% Metal	Poly-pale[a]	Stay-belite[a]	N Wood Rosin[a]
Poly-pale	9.5 Co	C	C	I
Staybelite	9.0 Co, 2.0 Ca	C	I	I
N wood	9.0 Co	C	C	C
Poly-pale	25 Pb	C	C	C
Staybelite	30 Pb	C	C	C
N wood	25 Pb	C	C	C
Poly-pale	7.5 Mn	C	C	C
Staybelite	6.0 Mn, 2.0 Ca	C	C	C
N wood	5.0 Mn, 2.0 Ca	C	C	C
Poly-pale	17 Zn	C	C	I
Staybelite	18 Zn	C	I	I
N wood	18 Zn, 1.0 Ca	C	C[b]	I
N wood	9.4 Zn, 0.6 Ca	C	C	I

[a] C = compatible; I = incompatible.
[b] Blend had hazy appearance which suggests approaching incompatibility.

inates of Poly-pale were completely soluble at high lead contents; the lead resinates of regular rosin and Staybelite with above 5–10% lead tended to precipitate from solution and to form gels, respectively.

Melting Points. The Hercules thermometer bulb drop method (7) was used to determine melting points of resinates, prepared by the reaction of metal diacetate and rosin. The melting point of a metal resinate is dependent upon the metal used, the rosin used, the amount of metal in the resinate, and, to a lesser extent, the procedure by which the resinate is prepared. Resinates of identical metal content and from the same rosin have shown variations as great as 10° to 25° C. in melting point when conditions of preparation were changed. All the resinates, however, had higher melting points than the rosins from which they were prepared.

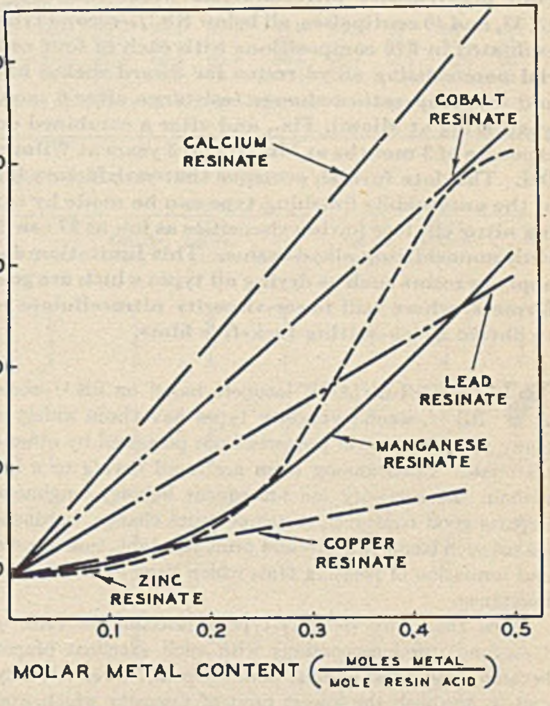


Figure 4. Melting Point Curves of Fused Resinates of Poly-pale Resin (Molar Basis)

Figure 2 shows that differences in the melting point of modified rosins were in general carried over to their resinates. Figure 3 indicates the correlation between the melting points of resinates and their metal contents for three of the rosins used. Plotting on a molar basis, as in Figure 4, was useful in comparing these melting points.

Compatibility and Blocking. Some resinates could not be blended by fusion with some rosins without blocking (Table IV). Resinates of lower metal content should be more compatible, as the dilution with rosin would tend to lower the metal content to a point below the blocking range. All the resinates could be blended with Poly-pale without blocking. All the resinates except the cobalt and zinc resinates of Staybelite were compatible with Staybelite. N wood rosin as a blending agent caused blocking with cobalt and zinc resinates.

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NITROCELLULOSE LACQUERS

Evaluation of Low-Viscosity Nitrocelluloses in Nonoxidizing Alkyd Resin Lacquers

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Four low-viscosity nitrocelluloses with viscosities of 19, 27, 33, and 40 centipoises, all below RS $^1/_4$-second type, were evaluated in five compositions with each of four commercial nonoxidizing alkyd resins for Sward rocker hardness and for temperature-change resistance after 6 months of weathering at Miami, Fla., and after a combined outdoor exposure of 3 months at Miami and 3 years at Wilmington, Del. The data furnish evidence that satisfactory lacquers of the automobile finishing type can be made by combining nitrocellulose having viscosities as low as 27 centipoises with nonoxidizing alkyd resins. This limitation does not apply to resins such as drying oil types which are good film formers, where still lower-viscosity nitrocellulose is used to obtain quick-setting tack-free films.

NITROCELLULOSE lacquers based on RS $^1/_2$-second and RS $^1/_4$-second viscosity types have been widely used for many years because of properties not possessed by other coating materials. Chief among them are rapid drying to a hard film without the necessity for subsequent baking, toughness which imparts good resistance to temperature change, hardness which makes such lacquers scuff- and print-resistant, ease of refinishing, and formation of pleasing films which have excellent weathering resistance.

Since these low-viscosity-type nitrocelluloses (RS $^1/_2$- and $^1/_4$-second) produce coatings with such excellent properties, it became of practical interest to develop still lower-viscosity types, and to establish the lowest limit of viscosity which would still retain the good qualities exhibited by RS $^1/_2$- and $^1/_4$-second types. Consequently, a series of viscosity types below RS $^1/_4$-second were developed and evaluated in lacquers. Although this investigation was carried out primarily to establish the lowest practical viscosity type of nitrocellulose for use in lacquers, without emphasis on determining the highest solids, it is obvious that the use of a lower-viscosity-type nitrocellulose makes possible lacquers of higher solids content. This is important in view of the growing interest in lacquers of increased solids concentration. It is also apparent that the recent trends toward high solvency and hot-spray formulation and application are applicable to lacquers containing lower-viscosity-type nitrocelluloses than $^1/_4$-second with consequent higher-solids concentration. Investigations are in progress to obtain specific information on these points to supplement the data reported here.

PANEL EXPOSURES

Materials and Formulations. A preliminary investigation was carried out with a variety of resins and formulations to serve as the basis for selection of typical formulas, resins, and nitrocellulose types for a more critical study. This preliminary work led to a choice of four typical resins and five formulas, based on lacquer films having good color retention and good buffing properties of reasonable hardness. Representative commercial nonoxidizing alkyd resins were chosen. Their choice does not imply that equally good, or possibly better, resins are not available. Four nitrocelluloses with viscosities ranging from 19 to 40 centipoises were selected. On the same scale, RS $^1/_2$-second nitrocellulose has a viscosity of 125 centipoises and RS $^1/_4$-second, 50 centipoises. Table I lists the nitrocelluloses, resins, and formulas selected, together with the pigment and solvent compositions.

Lacquers and Test Panels. All lacquers were formulated to have a viscosity of 40 centipoises (determined by the Hercules horizontal capillary viscometer at 25° C., *2*) when sprayed. The pigment was ground in a nitrocellulose-base solution in a ball mill for 48 hours. This base solution was then used to formulate the five selected lacquer compositions by adding the appropriate plasticizer and resin and by subsequent thinning with solvent to the selected viscosity level for spraying,

Panels of 20-gage auto body steel, 6 × 12 inches, were cleaned with toluene to remove oil, sanded, given a final cleaning in toluene, and then dried before priming with a standard commercial oil primer. The primer was allowed to air-dry after being sprayed, and was then baked at 70° C. for 24 hours. Lacquer films approximately 3 mils thick were built up by spraying three coats of lacquer, allowing each to air-dry before application of the next successive coat. The final films were force-dried 2 hours at 70° C., and allowed to stand overnight before polishing. All panels were given edge and back protection by painting with the following Parlon composition containing Alcoa aluminum powder (in parts by weight):

Parlon (120 centipoises)	20
Thermolyzed tung oil	10
Alcoa aluminum	10
Hi-Flash solvent naphtha	40
Xylene	40

This composition was thinned with the same solvent used in the formulation to proper brushing viscosity for easy application.

Test Methods. The Sward rocker hardness (*1*) was measured on all panels by the standard method without modification. Temperature-change resistance data were obtained on films of all compositions which had been weathered previously for 6 months in Florida. The test consisted of fifty cycles of 2-hour alternating periods at −15° and +110° F. in air, followed by sixteen cycles of 2-hour alternating periods at +110° in air and −15° F. in glycerol. This procedure was followed because, with only two exceptions, the alternating cold and warm exposures in air did not cause any failure. To obtain additional information, a more severe (rapid) change in temperature was considered necessary. Consequently, the panels which had survived the fifty cycles in air were given additional temperature-change exposure by plunging the warm panels at +110°, directly into glycerol at −15° F. This direct contact with a liquid coolant was more effective in revealing differences in temperature-change resistance.

All panels exposed to outdoor weathering were placed at an angle of 45° with the vertical, facing south, both at Wilmington, Del., and Miami, Fla. One set was exposed 6 months in Florida and then given the temperature-change resistance test described. Another similar set was exposed 3 months in Miami, followed by an additional 3 years at Wilmington. The latter set was observed after the 3 months in Florida for chalking, dirt collection, and gloss after repolishing, The panels were then given an arbitrary rating based on visual inspection: on a scale of 1 to 5, inclusive, 1 was good and 5 very bad. This same set of panels was inspected periodically during the additional 3-year exposure at Wilmington for rusting, cracking, blistering, and chalking.

Table I. Formulations and Materials Used (Parts by Weight)

Formulation No.	1	2	3	4	5
Nitrocellulose[a]	10	10	10	10	10
Resin (solid)[b]	7.5	7.5	10	10	15
Dibutyl phthalate	2	4	1	3	1
Pigment[c]	7.8	8.6	8.4	9.2	10.4

[a] RS 19-, 27-, 33-, 40-centipoise types were used. Viscosity determined on 12.2% (by weight) solutions of nitrocellulose in Hercules horizontal capillary viscometer at 25° C., using a solvent composed of: 25% denatured No. 1 alcohol; 20% ethyl acetate; 55% toluene (by weight).

[b] Resins used: Beckosol 1308, Glyptals 2471 and 2477, Rezyl 99.

[c] Composed of: titanium dioxide, 100 parts; antimony oxide, 100; lampblack, 2.

Lacquer Solvent: 10% ethyl acetate; 20% butyl acetate; 10% denatured ethyl alcohol; 7% butanol; 25% toluene; 28% xylene (by weight).

Table II. Hardness and Temperature-Change Resistance of Films

Nitrocellulose Viscosity, Centipoises	Beckosol 1308 Formulas					Glyptal 2471 Formulas					Glyptal 2477 Formulas					Rezyl 99 Formulas				
	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
Sward Rocker Hardness																				
19	32	26	36	24	18	42	28	30	28	18	38	32	34	26	24	44	32	50	34	34
27	36	24	32	20	24	36	34	36	26	28	36	26	36	26	22	40	36	44	34	32
33	34	18	34	24	22	40	30	42	20	34	38	30	36	20	26	44	34	50	30	28
40	34	22	32	22	18	34	28	34	24	24	36	22	40	20	32	42	36	46	38	32
Temp.-Change Resistance after 6-Month Exposure in Florida[a]																				
19	66+	58	58	57	58	66	66	66+	66	20	66+	66+	66+	66+	66+	66+	66+	20	66+	66
27	66+	66+	66+	66+	66+	66	66+	66+	66+	66+	66+	66+	66+	66+	66+	66+	66+	66+	66+	66+
33	66+	66+	66+	66+	66	66+	66+	66+	66+	66+	66+	66+	66+	66+	66+	66+	66+	66+	66+	66
40	66+	66+	66+	66+	66+	66+	66+	66+	66+	66+	66+	66+	66+	66+	66+	66+	66+	66+	66+	66+

[a] 66+ indicates those tests where no failures occurred. Other numbers tell the total number of cycles passed before failure by cracking or checking.

Table III. Weathering Data[a] on Panels Exposed 3 Months in Florida

Nitrocellulose Viscosity, Centipoises	Formula 1			Formula 2			Formula 3			Formula 4			Formula 5		
	Chalking	Dirt collection	Gloss[b]	Chalking	Dirt collection	Gloss[b]	Chalking	Dirt collection	Gloss[b]	Chalking	Dirt collection	Gloss[b]	Chalking	Dirt collection	Gloss[b]
With Beckosol 1308															
19	5	4	2	4	1	1	4	2	1	5	4	1	5	4	4
27	5	4	2	5	2	1	5	4	2	5	2	1	5	4	4
33	5	1	2	5	2	1	5	2	1	4	2	1	5	4	1
40	5	4	1	5	1	1	4	1	1	5	4	1	5	4	1
With Glyptal 2471															
19	3	4	1	4	4	2	4	1	2	3	4	1	3	5	1
27	1	4	1	1	2	1	3	2	1	1	2	1	3	5	1
33	1	2	1	3	4	1	1	2	1	4	5	2	3	5	1
40	1	4	2	3	4	1	1	4	1	1	4	1	3	5	1
With Glyptal 2477															
19	4	2	1	3	2	1	3	4	1	4	2	2	4	4	1
27	4	2	1	3	4	1	3	2	1	4	4	1	3	2	1
33	4	2	1	3	2	1	3	2	2	4	4	1	4	4	1
40	4	2	2	4	2	1	3	4	1	1	2	1	3	2	1
With Rezyl 99															
19	3	2	2	4	4	1	1	2	1	1	4	1	1	2	1
27	1	4	1	3	2	1	1	1	1	3	4	1	1	4	1
33	1	2	1	3	2	1	1	1	1	1	4	1	1	2	2
40	3	4	1	4	4	1	4	4	2	3	2	1	3	4	1

[a] 1 = good, 2 = fair, 3 = medium, 4 = bad, 5 = very bad.

[b] After polishing.

INTERPRETATION OF DATA

The Sward hardness data in Table II demonstrate that the viscosity of the nitrocellulose has no direct bearing on the hardness of the lacquer films. On the other hand, both formulation and the nature and quantity of resin influence hardness. In general, lacquers with hardness ratings in the range of 19 to 30 had the best buffing characteristics.

The temperature-change resistance results given in Table II show that ten of the thirteen failures were with 19-centipoise nitrocellulose. Since this test was considered relatively severe, the results should serve as an indication that lacquers with good temperature-change resistance can be made with any low-viscosity nitrocellulose having a viscosity of 27 centipoises or higher. Formula 5, with a ratio of 1.5 parts of resin to 1 part nitrocellulose, produced more than twice as many failures as any of the formulas containing a higher proportion of nitrocellulose. This indicates that the toughening action imparted by nitrocellulose is reduced somewhat when the proportion of nitrocellulose to resin is reduced from 1:1 to 1:1.5. Different resins also have a bearing on the temperature-change resistance.

Table IV. Combined Ratings from Data in Table III (Lowest Numbers Are Best)

Rating by Viscosity Type of RS Nitrocellulose				Rating by Resin				Rating by Formula			
Centipoises	Chalking	Dirt collection	Gloss	Type	Chalking	Dirt collection	Gloss	No.	Chalking	Dirt collection	Gloss
19	68	61	28	Beckosol 1308	96	56	30	1	50	47	22
27	60	60	25	Glyptal 2471	47	72	24	2	57	40	17
33	61	54	24	Glyptal 2477	68	54	23	3	43	38	20
40	58	65	23	Resyl 99	40	58	23	4	49	53	18
								5	52	50	23

Table V. Weathering Data for Panels Exposed 3 Years at Wilmington, Following 3 Months in Florida

Nitrocellulose Viscosity, Centipoises	Formula 1, Months		Formula 2, Months		Formula 3, Months		Formula 4, Months		Formula 5, Months	
	To first rusting	To complete failure[a]	To first rusting	To complete failure[a]	To first rusting	To complete failure[a]	To first rusting	To complete failure[a]	To first rusting	To complete failure[a]
					With Beckosol 1308					
19	6	26	..	3(cr)	.	6(cr)	3	26	15	27
27	.	27	..	27(bl)	7	37	..	37	27	27
33	7	37	27	27	6	27	..	26	15	27
40	6	37	6	27	31	37	..	26	..	37
					With Glyptal 2471					
19	..	3(cr)	..	4(cr)	..	3(cr)	..	3(cr)	..	3(cr)
27	6	37	6	37+	5	37	6	37	..	27
33	12	27	6	37	27	37	..	3(cr)	..	27
40	15	27	..	37+	6	37+	6	37	32	37
					With Glyptal 2477					
19	16	26	4	17	..	27(cr)	..	27	..	27
27	6	37	Not exposed		4	37	..	37	27	37
33	..	37	6	26	Not exposed		..	37+	18	37+
40	..	27	31	37+	7	37+	32	37+	3	27
					With Resyl 99					
19	..	3(cr)	6	17	..	3(cr)	6	26	..	4(cr)
27	7	37	27	27	6	25	6	37	27	27
33	6	37	6	17	..	37	27	27	..	3(cr)
40	6	37	6	25	31	37	6	37	6	37

[a] By chalking. Letters in parentheses indicate failure by cracking (cr) and by blistering (bl) instead of by chalking. Values followed by + sign indicate good condition and satisfactory coatings even after 37 months of outdoor weathering.

A visual rating of the panels, after exposure for 3 months in Florida, for chalking, dirt collection, and gloss after repolishing is recorded in Table III. A regrouping and totaling of the numerical ratings in Table III is shown in Table IV. With this compilation it is easier to make a general comparison of the effects of the three variables—nitrocellulose viscosity, resin, and formulation. The numbers indicate the degree of failure, with the lowest totals representing the best results.

Chalking and gloss after repolishing appear to be slightly poorer for 19-centipoise nitrocellulose than for the three higher-viscosity types tested, with little difference between 27-, 33-, and 40-centipoise types. No correlation appeared to exist between nitrocellulose viscosity and dirt collection. The choice of resin has a direct bearing on chalking, dirt collection, and gloss after repolishing. Formula 2, which contains most plasticizer, and formula 5, which contains most resin, chalked most. Formulas 4 and 5, with more resin than the others, collected most dirt. Gloss after repolishing was affected slightly by formulation.

Following the 3-month exposure in Florida, the panels were exposed for an additional 3 years at Wilmington (Table V). Although the results are not entirely consistent, a large majority of the early failures occurred with 19-centipoise-type nitrocellulose, and these failures were largely due to cracking, an indication of embrittlement. With these exceptions, failure of a majority of the films was due to chalking. Rusting appeared on a number of the panels during the exposure period, but there was no correlation between rusting and any of the variables studied.

Since a majority of failures by cracking occurred in the lacquers containing 19-centipoise nitrocellulose, and essentially no difference appeared in the higher viscosities, it may be concluded that, with the particular formulas used, the low limit of viscosity of nitrocellulose for good weathering properties is in the neighborhood of 27 centipoises. There appears to be little choice among the resins. Considering formulation, the trend appears to be toward more rapid chalking as the resin concentration is increased.

The data showing that many of the lacquers afforded protection to the metal for 3 months in Florida plus an additional 3-year continuous exposure in Wilmington is believed ample evidence that satisfactory lacquers of the automobile finishing type can be made by combining low-viscosity nitrocelluloses within the 27- to 40-centipoise range with nonoxidizing alkyd resins. Attention is drawn to the fact that the conclusions reached are limited at present to this type of formulation. There is no conclusive evidence available at this time to indicate any viscosity limitations on low-viscosity nitrocelluloses in combination with oxidizing-type alkyds or with mixtures of oxidizing and nonoxidizing types. Investigations are now being carried out which may furnish information on these points.

ACKNOWLEDGMENT

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Chemical Composition of REDWOOD BARK

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Redwood bark is separated commercially into two fractions, "bark fiber" and "bark dust". The former is used for insulation and is blended with various fibers for textile and related purposes. Bark fiber is inherently a cellulose fiber. After delignification it swells with cuprammonium solution as does a wood fiber. In its raw state the cellulose appears to be combined with lignin by a linkage which is resistant to splitting by caustic soda or by phenol and acid. Part of the lignin appears to be closely related structurally to sprucewood lignin. One other compound appears to be associated with the fiber in its raw state—a low-methoxyl phenolic acid; a second may be present, which closely resembles lignin but contains a definite percentage of carboxyl groups. The first of these is readily soluble in alkali; the second is somewhat more difficultly soluble. Small amounts of catechol-type tannins and phlobaphenes and a carbohydrate gum are also present in the fiber. Bark dust represents a heterogeneous mixture of broken fibers and parenchyma cells, together with a large amount of the low-methoxyl phenolic acid found in the fiber. This substance probably makes up 70–80% of the hark dust. The carbohydrate gum present in the fiber is also present in the dust to the extent of 8–9%. It is soluble in hot water and precipitated with alcohol, and at least half of it is peptic acid. Small amounts of catechol-type tannins and phlobaphenes are likewise present in the dust.

◆ ◆ ◆ ◆ ◆

LARGE amounts of redwood and redwood bark wastes normally result from lumbering operations in the West. The present paper is the third in a series (*2*, *3*) presenting results of research on the possibilities of developing chemical and fibrous by-products from these wastes.

The bark of the redwood tree—at least of that part brought in from the woods for conversion into lumber—is a dense, somewhat fibrous material ranging in thickness from an inch or less up to 10 inches or more. The thickness of the bark depends upon the age of the tree, upon conditions during the growing years, such as forest fires, lightning, and storms, and upon denseness of growth, etc.

A botanical description of redwood bark was published by Isenberg (*2*). The bark, as separated and converted commercially, is a complex tissue made up of a number of cell types including sieve cells, phloem parenchyma, phloem fiber (better known as redwood bark fiber), and phloem ray parenchyma, as well as cork cells formed when the cells of the phellogen layer mature. Of these, the sieve cells and parenchyma cells in the living phloem served to conduct elaborated food products; the fibers, on the other hand, are sclerenchyma tissue (adapted for mechanical strengthening because of their thick lignified walls). As the tissues die, the thin-walled sieve cells and parenchyma cells may compress or distort, whereas the fibers remain essentially the same in shape and composition. As a result, more than 25% of the weight of dead bark represents fiber, in contrast to the much smaller percentage (by weight) of fiber in the living bark. The cork cells appear to be partially filled with a dark, reddish-brown, alkali-soluble material which will be described later; the same material also appears within the ray cells of the outer bark and as a thin deposit on the walls of the other cells in the dead outer bark.

SEPARATION OF STRUCTURAL ELEMENTS

In any structure as complex as redwood bark, a clear-cut physical separation of the various types of cells is practically impossible. In the dead bark the possibility is even less because, with the exception of the bark fiber and the cork cells, the cell structures no longer show any tendency to adhere, and the materials forming the walls, together with the reddish compounds lining them, separate when the bark is run between milling rolls to form an amorphous powder, termed by the redwood lumberman "bark dust". Another term sometimes used, particularly in the patent literature, is "bark sand".

However, a satisfactory technical process has been developed for isolating the bark fiber from the smaller cork cells, cell wall fragments, and other amorphous material. The first step consists in running the bark slabs from the peeling plant through milling rolls to loosen the bark structure, with the subsequent formation of large matted fibrous bundles. This heterogeneous product is then subjected to a textile cleaning and carding operation; a large percentage of the fiber is obtained as a loose fill insulation in fairly clean fiber bundles possibly 1 to 2 inches long; these bundles still retain some of the original bark structure and composition. The remainder of the fibers is separated from the bark dust as cleaned textile fiber approximately $^{1}/_{4}$ to $^{3}/_{4}$ inch in length, with the fiber bundles well separated into what appear to be isolated fibers; each filament, however, consists of several ultimate bark fibers intertwined into a characteristic corkscrew structure. The greater share of the bark dust is taken from the condensers during the textile operation and at the present time is burned for lack of a better use. At least half of the weight of the bark is lost as dust in this stage of the operation.

For the following investigations, 225 pounds of specially clean fiber were used in all the work on fiber; bark dust, ground to a product called "bark flour", was used in the work on bark dust.

COMPOSITION OF BARK FIBER BY PULPING METHODS

The chemical investigation of textile bark fiber was carried out as follows:

One part of the fiber was washed with water in a beater to break down the fiber bundles and to remove loosely bound bark dust, and then air-dried; the dry product was tested for extractives and the extracted fiber was analyzed (Table I). A second portion of the original fiber was used for a study of the lignin and high-molecular-weight organic acids by cooking with alkali, precipitating lignin and insoluble acids by acidification of the black liquor, and purifying these from carbohydrate material. The nature and number of the hydroxyl groups were determined by the lignin technique of methylation with diazomethane, with dimethyl sulfate in alkaline solution, and again with diazomethane.

The results of solubility tests are given in Table I. Alcohol solubilities were run for 8 hours with 95% alcohol; hot water solubilities, for 3 hours at reflux temperature, and 1% caustic for 1 hour, also with refluxing. Additional extractions were then run successively with ether in a Soxhlet apparatus, with alcohol in the same extractor, and finally with hot water. The relatively small solubility in ether (0.6%) indicates the presence of a low content of fatty substances. Of the ether extract, 42% was soluble in petroleum ether and benzene, leaving a hard brittle brown mass as a residue.

The alcohol extract after ether extraction was investigated for its tannin and phlobaphene content. In one case (a 12-hour extraction) the extracted material contained 6.1% tannin and 42% phlobaphene; the remainder was alcohol-soluble reducing sugars, salts, and substances giving dark precipitates with lead acetate. The tannins gave a pronounced green-black color with ferric chloride and a tan precipitate with bromine water, tests which usually indicate a catechol-type tannin.

Hot water extraction of ether and alcohol-extracted fibers removed only 4.6% of the fiber, the extract being largely a carbohydrate gum. The same gum is also present in much larger amount in the bark dust, and will be characterized later.

The extractive-free fiber was analyzed for lignin, using the 72% sulfuric acid method, 41.1% of insoluble material being found. In connection with bark analyses, it should be stressed that the conditions followed in the lignin determination may leave as a residue not only lignin but other high-molecular-weight acidic substances and may also bring about condensations with certain types of carbohydrate degradation or oxidation products with resultant insolubility. The above lignin residues differ somewhat from redwood lignin isolated by the same process, in that they are partly soluble in caustic and the solutions have a reducing action on Fehling solution. The sulfuric acid lignin was found to contain only 0.2% pentosan; therefore, this was not the cause of the reducing action. Redwood lignin is almost insoluble in Fehling solution.

The filtrate from the lignin determination contains the carbohydrate fraction of the fiber hydrolyzed by the acid to low-molecular-weight sugars. The filtrate was tested for reducing value and for component sugars. In addition, extracted bark fiber was found to contain 0.3% ash and 8.3% pentosans (Table I).

The simple sugars present in the hydrolyzate from the lignin determination were estimated by microbiological methods. The solutions used for the final tests were prepared by neutralizing an aliquot of the filtrate with barium carbonate, filtering the precipitated barium sulfate, concentrating the solution of barium uronate and sugars, treating with alcohol to precipitate the insoluble barium uronate, and distilling off the alcohol. The residue was dissolved in a known volume of water, and 10-cc. portions were used for inoculation and fermentation. One portion was tested for total reducing sugar (A). Mannose (B) was determined as the phenylhydrazone. Another portion was fermented with *Saccharomyces cerevisiae* to destroy all hexoses; residual pentoses (C) were then determined as reducing sugars in the fermented solution; by subtracting from the original reducing value ($A - C$), the value (D) for glucose, mannose, and galactose was obtained. Still another portion was fermented with *Torula dattila*, which destroys mannose and glucose and leaves only galactose (E). Subtraction of mannose (B) and galactose (E) from total hexoses (D) gives glucose (F). The residual solution after fermentation with *Saccharomyces cerevisiae* was sterilized, and separate portions were inoculated with organisms 19 and 36 (University of Wisconsin), respectively. The first organism ferments arabinose, the second xylose. The inoculate from organism 19 was titrated for xylose, and that from organism 36 for arabinose. The results of these tests follow:

Sugar	% Based on Total Reducing Sugar	% Based on Extractive-Free Fiber
Mannose	13.4	8.8
Glucose	71.4	46.9
Galactose	Absent	Absent
Xylose	15.5	9.9
Arabinose	Absent	Absent
Total reducing	..	65.6

Of particular interest is the close check between the pentosan content of the extracted fiber determined as the phloroglucide of furfural (8.3%), and by the biochemical method which gave 9.9% xylose or 8.7% xylan, with arabans not present.

Because a complete separation of bark fiber from other cellular and amorphous material is not achieved by the technical process used, these fiber samples as analyzed contain much of the bark dust fraction. It is evident that the extracted fiber is composed largely of two chemical types, one related to lignin, the other to the polysaccharides; that the main polysaccharide is cellulose is indicated by the large percentage of glucose in the hydrolyzate.

Table I. Composition of Redwood Bark Fiber

	Calcd. to Original Fiber, %	Calcd. to Extractive-Free Fiber, %
Separate extractions		
Alcohol	3.1	...
Hot water	15.5	...
1% NaOH	40.7	...
Successive extractions		
Ether	0.2	...
Alcohol	2.6	...
Hot water	4.6	...
Extracted fiber	92.6	100.0
Ash	0.3	0.3
Pentosans	7.7	8.3
Lignin	37.9	41.1
Pentosans in lignin	..	0.2
Reducing sugar after hydrolysis (as glucose)	60.4	65.6

Table II. Chemical Data on Redwood Bark Fiber Cooks

	Original Fiber	Soda Cooks					Sulfite Cook, 6
		1	2	3	4	5	
Pretreatment	...	None	None	Recook of No. 1	Prechlorination	Alcohol-extd.	...
Cooking conditions							
Temp., ° C.	...	160	180	160	160	160	135
Time, hr.	...	1	1.5	1	1	1	5
NaOH, %	...	10	20	22	14	12.5	[a]
Pulp yield, %	100	50.7	41.3	96.5	42.2	65.5	51.0
Screenings, %	...	9.1	1.6	...	5.0	8.6	17.0
Lignin in pulp, %	41.8	31.9	21.6	28.1	25.4	30.9	31.8
OCH_3 in lignin, %	10.0	13.3	14.0	14.6	...	...	10.4

[a] Commercial sulfite liquor with 5.8% total and 4.5% free SO_2.

BARK LIGNIN AND HIGH-MOLECULAR-WEIGHT ACIDS

Because there is a relatively large background of information in the literature regarding alkali lignin, the alkali cooking process was used to separate lignin and the high-molecular-weight organic acids from the fibrous cellulose. Following the cook, the resulting alkali black liquor was acidified, which precipitated the dissolved bark alkali lignin and acids. After purification, these were characterized by determining their alcoholic and phenolic hydroxyls and carboxyl groups. The lignin remaining in the pulp was condensed with phenol, and the product was studied in the same way.

Before the solutions for lignin isolation were prepared, a number of cooks (Table II) was made with the bark fiber. Two of these (1 and 2) were made by cooking with alkali directly, a third represented a recook of the pulp of cook 1, a fourth was an alkaline cook following prechlorination, a fifth an alkaline cook of alcohol-extracted bark fiber, and the sixth was a sulfite cook.

A preliminary cook was made to study the pulping characteristics of the bark fiber, using the conditions for cook 1. The raw pulp was screened with the laboratory size Valley screen. The washed pulp was analyzed by conventional methods, and the results are summarized in the following table:

Cross & Bevan cellulose, %	66.2
Apparent α-cellulose in pulp, %	95.9
"Lignin" in α-cellulose, %	30.3
α-Cellulose corrected for lignin, %	65.6
α-Cellulose in C. & B. cellulose, %	89.6
C. & B. cellulose viscosity, centipoises	3.1
Lignin in pulp, %	31.1
Methoxyl in lignin, %	13.5
Permanganate number of pulp	54.1
Chlorine consumption of pulp, %	36.3

The pulp was bleached with hypochlorite, and swelling experiments were carried out on the bleached fibers with cuprammonium solution. The swelling behavior proved to be identical with that of bleached wood fibers, suggesting a somewhat similar ultimate fiber structure. It should be emphasized that these values are largely empirical. Bark lignin and bark alpha-cellulose might differ considerably from the wood analogs. The particular point of interest is the large percentage of alpha-cellulose in the Cross and Bevan cellulose and the extremely low viscosity of this fraction.

The great resistance of the residual lignin in the pulp to delignification by the alkaline pulping solutions is apparent in the slight pulping action on recooking pulp 1. The yield of pulp in cook 3 was 96.5% of pulp 1, and this pulp still had a lignin content of 28.1%. This lignin had a methoxyl content of 14.6%, almost identical with that of redwood alkali lignin. Apparently a stable lignin-carbohydrate linkage exists in redwood bark, which is different from that present in the wood.

Two of the black liquors were further investigated. The one from the recook of cook 1 represented a less alkali-soluble lignin, because the more soluble lignin would have been removed in the first cook. The second was the black liquor from the alcohol-extracted fiber (cook 5). In the latter case the material in the black liquor would represent the more soluble "lignin", because the alcohol extraction removes only about 3% of the total fiber content.

The processes followed with each black liquor were approximately the same; therefore, only the operations used in the treatment of the black liquor 3 will be described in detail:

"Lignin" was isolated from the black liquor by acidifying with a slight excess of hydrochloric acid; the brown, flocculent precipitate was centrifuged and washed with distilled water, and as much water as possible was removed by filtration on a Büchner funnel. The moist precipitate was then dialyzed toward distilled water until the precipitate appeared to be free of hydrochloric acid (5 to 7 days). As the electrolytes were removed, a portion of the lignin formed a colloidal solution; hence, it was necessary to recentrifuge the lignin suspension. The lignin thus recovered was dissolved in dioxane. The supernatant aqueous solution (after removal of the lignin) was evaporated under reduced pressure, and the residual lignin was dissolved in dioxane and added to the dioxane solution of the main portion of the lignin.

"Lignin" was isolated from the dark red-brown dioxane solution, after drying over sodium sulfate, by dropping the solution into ether with vigorous stirring. The product separated as a brown, finely divided powder which was washed several times with dry ether and petroleum ether, and finally dried under reduced pressure at 100° C. The average methoxyl content of the precipitated lignin was 11.6%. Spruce alkali lignin prepared in exactly the same manner contains 14.9% methoxyl.

The alkali-insoluble redwood bark lignin remaining in the pulp after the alkaline cook was separated by the action of 72% sulfuric acid and contained 14.3% methoxyl. Apparently, either some methoxyl splits off during the alkali cook and the partly demethylated lignin thus formed goes into solution, or there are at least two lignins differing from each other in methoxyl content.

The lignin in the waste liquor of cook 5 was similarly isolated but was purified by dropping its solution in anhydrous pyridine into anhydrous ether. The methoxyl content of this product was 2.7%, indicating the presence in the bark fiber of a relatively large amount of material with a low methoxyl content which is easily removed by the alkaline cooking liquor.

These experiments demonstrate that a mixture of substances is present in the bark fiber which may appear as lignin in the analysis. One is similar to sprucewood lignin as measured by its methoxyl content; the second has very little methoxyl and is much more soluble in alkaline solutions and, hence, is probably much more acidic. The products were purified from any contaminating carbohydrates by dissolving in dioxane, in which the carbohydrates are insoluble, pouring the dioxane solution into ether, and thus precipitating the lignin.

The lignins from the black liquors of cooks 3 and 5 were methylated with diazomethane and dimethyl sulfate, and acetylated with acetic anhydride in pyridine by conventional lignin methods (*1*). Diazomethane in ether methylates only the acidic hydroxyls (such as phenolic or carboxylic hydroxyls); dimethyl sulfate with caustic methylates all hydroxyls except those whose methyl derivatives are saponified by the caustic solution (carboxylic hydroxyls); acetic anhydride in pyridine reacts with all phenolic and alcoholic hydroxyls. By carrying out the appropriate calculations, it is possible to determine the percentage of different types of hydroxyls in a "lignin" derivative and, hence, to characterize it. No attempt will be made to describe these reactions in detail, because the methods have been widely used in published lignin researches.

TABLE III. DISTRIBUTION OF METHOXYL GROUPS INTRODUCED IN VARIOUS "LIGNIN" DERIVATIVES

Methoxyl Group Distribution, %	Lignin from Cook 3	Lignin from Cook 5	Sprucewood
In alkali lignin (*A*), %	11.6	2.7	14.9
In diazomethane-methylated lignin (*B*), %	22.6	23.5	22.2
In methyl-sulfate-methylated lignin (*D*), %	20.0	19.6	31.4
In methyl-sulfate- & diazomethane-methylated lignin (*E*), %	29.5	27.4	31.5
Due to methylation of phenolic acid and carboxyl (*F*), %	11.0	20.8	7.3
Added Methoxyl Groups			
Due to carboxyl $(E - D)$ (G)	3.5	7.8	0.1
Due to phenolic hydroxyl $[(F - G)\ (H)]$	7.5	13.0	6.6
Due to alcoholic hydroxyl $[(D - A) - (H)\ (I)]$	6.9	3.9	9.9

By a series of calculations from the analytical data for the various lignin derivatives, it is possible to determine the percentage of methoxyl reacting with phenolic hydroxyls, alcoholic hydroxyls, and carboxyl groups, and to calculate the percentage (calculated to the lignin) of the various types of free hydroxyl groups in the lignin before methylation. These are given in Table III. From these figures, calculations may also be made of the percentage (calculated on the lignin) of the various types of free hydroxyl groups in the lignin before methylation:

Group	Lignin from Cook 3	Lignin from Cook 5	Sprucewood Alkali Lignin
Methoxyl, %	11.6	2.7	14.9
Carboxyl, %	2.0	4.4	0.4
Phenolic, %	4.2	7.8	3.6
Alcoholic, %	3.9	2.1	5.5

The data used in the calculations on sprucewood alkali lignin were reported by Marshall, Brauns, and Hibbert (*4*).

Apparently, then, there are at least two types of materials in redwood bark fiber which dissolve in the alkaline cooking liquor and which appear by analysis as lignin; and these are significantly different from the alkali lignin from sprucewood. One of them, the product dissolving first and almost completely in the alkaline cooking reagent used with cook 5, is present in the fiber in large amounts. It contains little if any methoxyl, but significant percentages of free carboxyl and phenolic hydroxyl groups. It is easily soluble in dilute alkaline solutions, as are its derivatives, in which all alcoholic and phenolic hydroxyls are methylated. The second is the product dissolved when the once-cooked pulp is recooked (cook 3). Assuming the removal of all acid in the first cook, a product is found in the black liquor of the recook which still appears to contain a certain amount of carboxyl groups and possibly a smaller methoxyl content than the original lignin. It is more probable that this is a mixture of lignin and the carboxy acid removed in the first cook. Thus, it appears that redwood bark fibers contain large quantities of high-molecular-weight phenolic acids related to lignin. These acids resemble humic acids in many ways. They are not present in the living bark, but are present in the parenchyma and cork cells of the dead bark and appear to fill the latter. They are also present on the surface of the cell walls of the bark fiber. There is evidence also for the existence of a substance more closely related to lignin but containing carboxyl groups—what might be termed a "lignin acid".

RESISTANT REDWOOD BARK LIGNIN

In addition to the products studied above, there remains in the bark pulp a relatively large amount of material which can be isolated as lignin in the Klason lignin determination with 72% sulfuric acid. This residual lignin contains 14.3% methoxyl—i.e., in the range 14–15% generally obtained for the methoxyl content of softwood alkali lignins. An extensive investigation was made of this lignin by the techniques described in the litera-

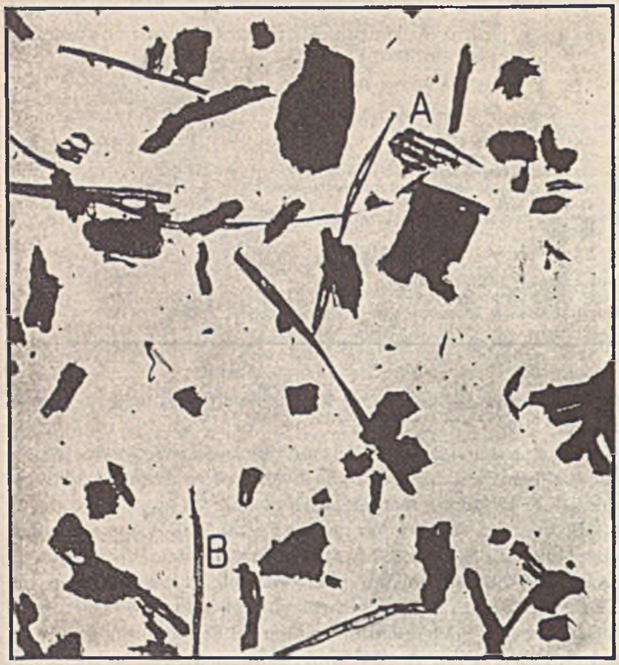

Figure 1. Photomicrograph of Redwood Bark Dust (×30)
A, cell structure; *B*, phloem fiber

ture for producing phenol lignin. For some reason it is not easily removed from the fiber by either the soda or sulfite process, but it does combine with phenol in much the same way as spruce lignin. It may be concluded that ether-insoluble bark phenol lignin is much the same as ether-insoluble spruce phenol lignin.

The difficulty of removing the phenol lignin from the bark pulp suggests again the possibility that the lignin in the bark fiber is combined in some form of stable chemical union with the carbohydrate constituent of the fiber. Such a bonding is much more stable than similar linkages in wood.

The value for the methoxyl contents of the phenol lignin and its methyl derivatives has been calculated to indicate the distribution of the methoxyls introduced among alcohol and phenol hydroxyls and carboxyls. The data are included in Table IV. These values for methoxyls were calculated as percentage hydroxyls in the ether-insoluble alkali phenol lignin:

	Redwood Bark Pulp	Sprucewood
Phenolic hydroxyls, %	5.4	6.4
Alcoholic hydroxyls, %	4.0	4.0
Carboxyls, %	0.2	0.1
Methoxyls, %	11.1	10.3
Free hydroxyls covered by methoxyls, %	6.4	5.9
Total free and potential hydroxyls in phenol lignin, %	15.8	15.3
Percentage of above methylated	40.6	38.5

As far as these methods for indicating structural relations in the lignin field permit, it may be concluded that a large part of the residual lignin in redwood bark pulp is similar to the lignin in sprucewood. At least the above values for ether-insoluble phenol lignin appear to be checks within experimental error. The method will not differentiate between isomeric or polymeric compounds. Later work carried on with redwood lignin showed close checks between spruce and redwood lignins; hence, we may conclude that at least a portion of the lignin in the bark is similar to the lignin in the wood.

The quantities of various derivatives described above may be roughly estimated from the pulp studies. In cook 1, in which the original fiber was cooked with caustic, the "lignin" which dissolved at first proved to be largely low-methoxyl acid material. Of the original 41.8 grams of "lignin" per 100 grams of bark fiber, only 16.2 grams remain in the pulp (cook 1); 25.6 grams or about 60% have dissolved in the alkaline liquor. After cook 3, 13.7 grams of the original lignin remain in the pulp; hence, 2.5 grams or 6% have dissolved. This lignin was found to have a somewhat smaller percentage of methoxyl than the regular alkali sprucewood lignin. To these "lignins" may be added: (*a*) normal lignin, represented by the lignin which combines with phenol to form an ether-insoluble phenol lignin closely analogous to sprucewood phenol lignin; (*b*) resistant lignin remaining in the fiber even after the alkali cook and phenol condensation; and (*c*) soluble phenol lignin derivatives removed as water-soluble compounds when the crude lignin derivatives are precipitated from their alkaline aqueous solutions or when the crude phenol lignin is precipitated by water.

The bark fiber pulp after the two alkaline extractions (cook 3) contained 13.7 grams of residual lignin. This was extracted with phenol. From the original 48.9 grams of pulp, 11 grams of phenol lignin were obtained; two thirds was ether-insoluble phenol lignin containing approximately 75% lignin or 5.5 grams. Similarly the 3.7 grams of ether-soluble phenol lignin are only about one third lignin, or about 1.2 grams. Thus the 13.7 grams of "lignin" remaining in the pulp contain 5.5 grams of lignin forming ether-insoluble phenol lignin and 1.2 grams forming ether-soluble phenol lignin, or a total of 6.7 grams.

The residue from the phenol extraction weighs 34.2 grams. It is largely cellulose, but it still contains 8.0% or 2.7 grams of a lignin resistant to alkali and phenol delignification. The sum of the normal lignin (6.7 grams) and resistant lignin (2.7 grams) amounts to 9.4 grams. The 48.9 grams of pulp contained 13.7 grams of material testing as lignin; hence, the difference (4.3) must be accounted for. It may have remained in the aqueous solution on precipitation of the crude phenol lignin into water or changed by the action of phenol into a material no longer appearing as "lignin" by analysis:

Distribution of Lignin Bodies	Grams	
Bark lignin in 100 grams bark fiber		41.8
Low methoxyl, high acid	25.6	
Lower acid, higher methoxyl	2.5	
Normal lignin	6.7	
Resistant lignin	2.7	37.5
Not for accounted		4.3

COMPOSITION OF BARK DUST

Fifty per cent of the bark as separated commercially is recovered in the operation as a dust. It is made up of broken fibers, small cells, and the powdered walls of dead parenchyma cells and sieve cells, together with the dried contents of these and the cork cells. Figure 1 is a photomicrograph of a typical bark dust field. Inasmuch as the origin of the dust is much the same as that of a portion of the bark fiber, we might expect dust and fiber to contain similar components.

Eighty-eight per cent of the dust dissolved quickly in 4% caustic at 160° C.; the solution gave no precipitate with carbon

TABLE IV. DISTRIBUTION OF METHOXYL GROUPS INTRODUCED INTO PHENOL LIGNIN BETWEEN PHENOLIC AND ALCOHOLIC HYDROXYLS AND CARBOXYLS

	Redwood Bark Pulp Phenol Lignin		Sprucewood Phenol Lignin	
Methoxyl Group Distribution, %	Ether insol.	Ether sol.	Ether insol.	Ether sol.
(*A*) In diazomethane-methylated phenol lignin	21.0	20.5	21.6	22.8
(*B*) In phenol lignin	11.1	6.8	10.3	5.3
(*C*) Due to methylation of phenolic OH and COOH	9.9	13.7	11.3	17.5
(*D*) In diazomethane- and methyl-sulfate-methylated phenol lignin	27.7	..	28.4	..
(*E*) In methyl-sulfate-methylated phenol lignin	27.3	..	28.2	..
(*F*) Due to COOH ($D - E$)	0.4	..	0.2	..
(*G*) Due to phenolic OH ($C - F$)	9.5	..	11.1	..
(*H*) Due to aliphatic OH [$(D - B) - G$]	7.1	..	7.0	..

dioxide, which is in direct contrast to the behavior of wood lignin in alkaline black liquors. On acidification with hydrochloric acid, a voluminous brown precipitate was formed. Thus the dust contains a product which behaves in much the same manner as the material dissolved from the bark fiber by the cooking liquor in cook 5. The methoxyl content of the dust was only 0.08%. The "lignin" content of the dust by analysis with 72% sulfuric acid was 60%. This "lignin" differed from the residual bark lignin in that it did not react with phenol in the presence of acid catalysts.

In view of the probable relation between the material in the dust (reacting as lignin) and that portion of the fiber dissolved as lignin in cook 5, an attempt was made to isolate and purify the alkali-soluble material reacting as "lignin" in the bark. The dust was extracted by cooking under pressure at 110° C. with three separate charges of 1% sodium hydroxide for 1 hour. The "acid lignin" was precipitated from the alkaline solution by acidifying with hydrochloric acid. The precipitate was removed in the centrifuge, and the inorganic content was dialyzed against distilled water. As the excess hydrochloric acid was removed, the "acid lignin" formed a colloidal solution; at this point the product was filtered by suction as dry as possible, and the remaining water was removed on a porous plate. The product was dissolved in dioxane, and the dried solution in dioxane was concentrated under reduced pressure and poured into ether. The precipitate (a dark brown powder) was washed with dry ether and petroleum ether and dried in a desiccator.

Such "acid lignin" still has an ash content of 0.81%. The "lignin" contained 57.1% carbon and 5.0% hydrogen. The yield of the purified product (calculated on the bark dust) was 22.5%. The low yield results from incomplete precipitation with acid and the difficulty in handling the product. This "acid lignin" as recovered is representative of at least half of the "lignin" compounds in the bark. The purified product was then methylated by the methods used for bark fiber lignin, with the result shown in Table V.

It is apparent that the purified "acid lignin" is somewhat related to the crude "lignin" removed from the bark fiber in cook 5. It may be considered as a high-molecular-weight phenolic acid having alcoholic and phenolic hydroxyl groups.

We must keep in mind that, with a natural product of this type, we are not dealing with a uniform, chemically pure compound but rather with a polymerized product, which is probably changed in composition during isolation. In view of this, it is impossible to say much about a building unit or molecule size. Similarly, we cannot say too much about definite numbers of reactive groups. The data permit our assuming a ratio of aliphatic hydroxyls, phenolic hydroxyls, and carboxyls of 2:4:3; from this ratio we can establish, as minimum molecular weights, a value of 750 from the aliphatic hydroxyls, 835 from the phenolic hydroxyls, and 1000 from the carboxyls. These values are in the range assumed for alkali spruce lignin.

TABLE V. METHOXYL VALUES OF PURIFIED AND METHYLATED "ACID LIGNIN" FROM BARK DUST

Methoxyl Group Distribution, %	Lignin from Cook 5	Bark Dust Acid Lignin"
In alkali lignin (*A*)	2.7	0
In diazomethane-methylated lignin (*B*)	23.5	23.3
In methyl-sulfate- and diazomethane-methylated lignin (*E*)	27.4	29.9
In methyl-sulfate-methylated lignin (*D*)	19.6	22.3
Due to methylation of phenolic OH and carboxyl [(*B* − *A*) (*F*)]	20.8	23.3
On carboxyl [(*E* − *D*) (*G*)]	7.8	7.6
On phenolic OH [(*F* − *G*) (*H*)]	13.0	15.7
On alcoholic OH [(*D* − *A*) − *H*] (*I*)	3.9	6.6

Successive extractions were made with ether, alcohol, and hot water. Ether removed 0.9%, alcohol 1.5%, and hot water 9.6% from the dust. The extractive-free sample thus prepared gave 61% "lignin" by the 72% sulfuric acid method. A pentosan calculation was made from the pentose content of the hydrolyzate resulting from the lignin determination; it amounted to 3.1% of the extractive-free dust. The hydrolyzate was analyzed for sugars by the fermentation procedure outlined above. The results follow:

Sugar	% Based on Total Reducing Sugar	% Based on Extractive-Free Fiber
Mannose	11.4	4.5
Glucose	79.4	30.0
Galactose	Absent	Absent
Xylose	9.2	3.5
Arabinose	Absent	Absent
Total reducing	..	38.0

Of the extractive-free dust, 61% is the low-methoxyl phenolic acid which appears in the analysis as "lignin", and 38% appears as total reducing sugar in the acid filtrate. Thus, extractive-free dust is made up almost entirely of the complex phenolic acid and carbohydrates, of which 80% is cellulose (or some other substance insoluble in hot water and yielding glucose on hydrolysis).

BARK DUST EXTRACTIVE

Because of the small amount of ether-soluble material present in the dust, no attempt was made to investigate it. The alcohol extract contains 57.2% phlobaphene, 12% tannin, 17% ash, and 12% "humic acid". Fusion of the residue from the alcohol extract with potassium hydroxide gave protocatechuic acid, suggesting a catechol-type tannin. Since the total amount of alcohol extract was only 1.5%, the actual amount of these various materials was relatively small.

Extraction of the dust with hot water for 3 hours following the ether and alcohol extraction resulted in the solution of 9.6% of the dust. From the solution 83.0% could be precipitated with alcohol as a white or tan powder which contained 5.5% ash. After hydrolysis of the powder with 3% hydrochloric acid, the solution contained 52.3% reducing sugar and 9.0% of an insoluble material resembling lignin. A similar carbohydrate material was found in much smaller amount in the hot water extract of the fiber. The filtrate remaining after the alcoholic precipitation contained 0.5% ash, 2.9% reducing sugar, and 10.0% "humic acid".

The gum, present in the bark dust to the extent of 8.0%, may be purified until it is colorless. The component present in greatest amount (58.3%) is uronic acid anhydride. Oxidation with 25% nitric acid yielded mucic acid; hence, galactose or a derivative is present, and the uronic acid is a galacturonic acid which classes the material as a pectin. A pentosan determination gave a value of 26.2%, a portion of which comes from the uronic acid. Norman (*5*) found that, during a pentosan determination, uronic acid anhydrides liberate 16.6% of their weight as furfural; this value (calculated to pentosan) is equivalent to 22.8% uronic acid anhydride. Thus, 13.3% of the total pentosan determined came from the uronic acid anhydride, and the actual pentosan content was 12.9%. The sum of the uronic acid anhydride and pentosan (58.3 + 12.9) is equivalent to 71.2% of the bark gum. Apparent lignin amounts to 11.2% and ash, 6.2%, accounting for 88.6% of the gum. Half of the gum may be obtained after hydrolysis with 1% sulfuric acid as reducing sugar and half is fermentable with yeast (a hexose). About 5% of the reducing sugar is mannose as determined by isolation as the hydrazone.

Further experiments were carried out in these laboratories by Ernest Anderson with the crude hot-water extract. A sample weighing 47 grams was powdered in a mortar and dissolved in 2 liters of hot water, and the solution was filtered from a small amount of insoluble material. After cooling, the solution was treated with liquid bromine, during which the dark color changed to a pale red. After standing 3 hours, the solution was mixed with six times its weight of 95% alcohol which precipitated a pale cream-colored product. The mixture (after standing overnight) was centrifuged, washed with alcohol and ether, and dried in vacuo. The cream-colored product weighed 22 grams.

It was further purified by solution in 250 cc. of water and a small amount of ammonium hydroxide; dilute hydrochloric acid was added to slight acidity, and liquid bromine was again added. This solution yielded a white precipitate weighing 21 grams. This material contained 76% uronic acid (19% carbon dioxide), 25.9% pentosans, and 0.53% methoxyl. The rotation in 2% ammonium hydroxide was 233°. The data agree satisfactorily with similar values for pectic acid. The acid was further characterized as its calcium salt. Thus, at least half of the hot water extract in redwood bark is pectic acid, similar to that isolated from other woods.

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SOLVENT SELECTIVITY FOR HYDROCARBONS

Measured by Critical Solution Temperature

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Critical solution temperatures have been determined for over a hundred solvents of various types with ten representative hydrocarbons, two straight-chain paraffins, a branched-chain paraffin, two olefins, two naphthenes, paraffin wax, and two commercial oils. Aromatic hydrocarbons are too miscible with these solvents to observe the critical solution temperature. The difference in C.S.T. for the same solvent with different hydrocarbons is taken as a measure of the relative affinity or selectivity of the solvent for the two types of hydrocarbon. Selectivities for olefins, naphthenes, branched chains, type of oil, and molecular weight are calculated and plotted against each other to show their extent of interrelation. Effects of substituent groups in the solvents are estimated. The methyl and phenyl groups usually lower C.S.T. about 40° C. The nitro and carboxyl groups raise it over 100° C.

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THE choice of solvents for selective extraction of hydrocarbon mixtures depends upon several factors, including cost, availability, ease of recovery from the hydrocarbons, stability, selectivity for the desired or undesired type of hydrocarbon, and suitable degree of solubility at a convenient temperature. This investigation is concerned primarily with the last two factors. (Other factors which may become important are freezing point, boiling point, density, viscosity, water solubility, toxicity, interfacial surface tension, and refractive index.)

Ferris and co-workers (*20*) tested many solvents with lubricating oil. Their criterion of selectivity was the difference in viscosity-gravity constant of the extract and raffinate. They determined miscibility temperature of solvents with two lube oil stocks but not with any pure hydrocarbon. Correlations of type of hydrocarbon with affinity of solvents and with the desired properties for hydrocarbon mixtures aid in consideration of further extension of solvent refining.

Solvent refining of lube oils produces a raffinate of higher viscosity index (V.I.) because of selective removal of molecules containing a larger proportion of rings, aromatic or naphthenic, which are known to be lower in V.I. than more paraffinic molecules. Much of the former empiricism has been removed by the work of Mikeska (*43*) and by investigations at the Pennsylvania State College (*11*, *18*, *50*, *51*). In the case of the lower hydrocarbons, some incomplete data (*5*, *17*, *33*) seem to indicate that olefins are slightly higher and branched-chain paraffins slightly lower in V.I. than straight-chain paraffins.

In gasoline the antiknock values are in the descending order aromatics, olefins, naphthenes, normal paraffins; but branches increase the antiknock value of paraffins so much that three of them (as in iso-octane) produce more effect than the introduction of a double bond or of a cyclic structure (naphthenes). High ignition quality in Diesel fuel seems to be directly opposite to antiknock value with respect to type of hydrocarbon.

Affinity for various solvents is sometimes considered to be opposite to V.I. and, probably, to high ignition quality in Diesel fuel, and therefore to be parallel to antiknock value. This paper will show that the last supposition is not always true.

This investigation was made to estimate the relative affinity of several solvents for the various types of hydrocarbons. Critical solution temperature (C.S.T.) was chosen as a measure of affinity; the reason is illustrated in Figure 1. The solubilities in aniline of three typical hydrocarbons of different classes are plotted as functions of temperature. These three hydrocarbons boil at almost the same temperature, so that they cannot be separated readily by fractional distillation. The actual separation of two of these three hydrocarbons with the same solvent has been studied (*60*). In solvent extraction the hydrocarbons form approximately ideal mixtures, so that the amounts extracted by a solvent are nearly proportional to the separate solubilities. Since the three curves have almost exactly the same shape except for vertical displacement, the solubilities are related simply to the C.S.T. (tops of curves). Other solvents (e.g., sul-

Table I. Literature Survey of C.S.T. of Solvents with Individual Nonaromatic Hydrocarbons

Solvent	References
Acetic acid	*30, 38A*
Acetic anhydride	*2, 32, 38B*
Acetone	*29, 57*
Acetonitrile	*10, 38C*
Acetophenone	*22*
Aniline	*4, 15, 51*
Anisidines	*2*
Benzyl alcohol	*3, 42, 47*
n-Butanol	*37*
o-Chloroaniline	*22*
Cresols	*22*
β,β-Dichloroethyl ether	*63*
Diphenylamine	*8, 29*
Ethanol[a]	*28, 29, 36, 37, 38B, 65*
Ethyl sulfate	*47*
Ethylene chlorohydrin	*10, 38C*
Ethylenediamine	*10, 38C*
Eugenol	*22*
Formic acid[b]	*38C, 39, 53*
Methanol (see Table IV)	*10, 19, 24, 28, 29, 31, 36, 37, 38, 38B, 38C, 39, 40, 44, 48, 49, 52, 53, 57, 64*
Methyl Cellosolve[c]	*10, 38C*
Methylene iodide	*29, 57*
Nitrobenzene (see Table IV)	*13, 16, 22, 29, 38, 38B, 38C, 42, 45, 53, 57, 58, 59, 63*
Nitromethane	*47*
Nitronaphthalene	*9, 38*
o-Nitrotoluene	*22, 27, 38C, 53, 57*
m-Nitrotoluene	*13, 27, 38B, 38C, 53*
Phenetidines	*2*
Phenol	*9, 29, 38, 53, 62*
Propanols	*37*
Propionitrile	*26, 29, 53, 57*
Pyridine	*10, 38C*
Stannic iodide	*14*
Sulfur dioxide	*29, 38A, 38B, 38C, 41, 53, 54, 57*
o-Toluidine	*26, 53, 55*
m-Toluidine	*13, 29, 38B, 53, 55, 57*

[a] From Kuenen's results (*36*) it is doubtful if his ethanol was anhydrous.

[b] The low C.S.T. of formic acid–*n*-pentane, 28° C., is very improbable in view of the well-supported higher temperature for formic acid–benzene, 73.2–74.15° C. (*29, 38A, 38B, 38C, 58*).

[c] Ethylene glycol monomethyl ether.

fur dioxide) exhibit curves (*38, 54*) with shapes different from those of aniline; but those for different hydrocarbons with the same solvent are similar.

Another reason for choosing C.S.T. as a criterion of selectivity is that a determination can be made usually in a few minutes, and requires only about 1 ml. each of solvent and hydrocarbon. These considerations were important since it was necessary to make a large number of observations, and the quantities of some solvents available were limited. Another use for C.S.T. is the quick analysis of binary mixtures (*22, 28, 30, 31, 53*), especially percentage of water (*24, 28, 30, 31, 48, 53*) or analysis of multiple mixtures (*3, 16, 42*).

C.S.T. for a large number of hydrocarbons with aniline (or aniline point which is nearly the same) is recorded in the literature, and summarized by Doss (*15*) and by Ball (*4*). Additional values are given by Schiessler (*51*). References to other previous observations of C.S.T. are listed in Table I. Additional observations are given in the literature for C.S.T. of solvents with lube oils (*20, 25, 61, 65*), gasoline (*1, 6, 35, 56*), and terpenes (*29, 38, 38C, 39*).

DETERMINATION OF C.S.T.

Most of the observations in this investigation were made in small test tubes. The reagents were introduced and stirred with a thermometer while the tubes were warmed gradually in a bath of water or glycerol or were cooled with ice or a bath of acetone and dry ice; the temperature of disappearance or reappearance of the cloud due to two liquid phases was read two or three times in each direction.

The use of equal volumes of solvent and hydrocarbon does not always give quite the C.S.T., as evidenced by the rise of the interface to the top of the system with rising temperature (assuming that the hydrocarbon is lighter than the solvent). In such cases it was necessary to add a relatively larger volume of hydrocarbon—e.g., 1.5 ml. to 1.0 ml. of solvent. If the final disappearance of the interface is near the middle of the liquid, the temperature observed is the maximum temperature of incomplete miscibility (C.S.T.).

Temperatures below −40° C. are less accurate because the pentane thermometer used was less precise, and because there may be supercooling with respect to C.S.T. when the liquids become viscious (*12*).

About nine hundred determinations of C.S.T. were made, including several which were below the freezing point of the solvent or hydrocarbon, and several which were above one of the boiling points. The former were observed by careful supercooling (with respect to crystallization, since there is apparently little tendency to supercool with respect to C.S.T. unless the viscosity is extremely high). C.S.T. up to about 60° C. above the boiling point of the mixture is observed by using cork stoppers pierced by the thermometer and wired in. Still higher C.S.T. determinations were made in sealed glass tubes attached to the thermometer with rubber bands; the tubes were agitated by tipping, using the thermometer as a handle. The upper limit in temperature reached was about 240° C. for the glycerol bath. The lower limit was −78° C., the sublimation point of dry ice.

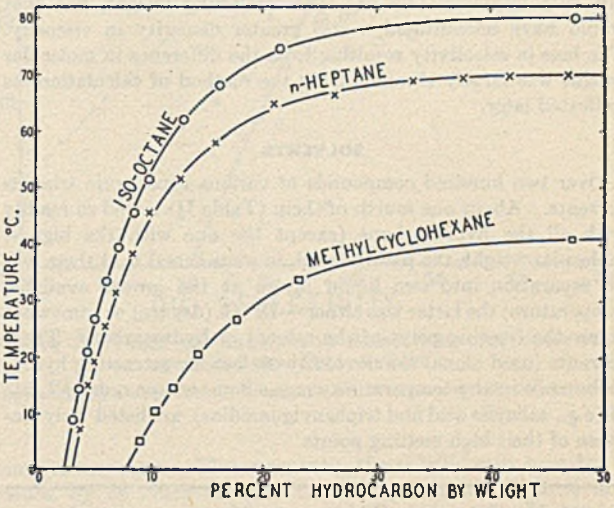


Figure 1. Solubilities of Hydrocarbons in Aniline

In several cases C.S.T. could not be reached even by supercooling (because of crystallization) or by superheating (because of decomposition or excessive pressure). In some of these cases an estimate of C.S.T. was made by extrapolation from determinations of ternary C.S.T. with the same solvent containing another hydrocarbon, or with the same hydrocarbon and another solvent similar in solubility characteristics. For example, several C.S.T. values for paraffin wax below 45° C. were found readily by adding a known amount of the paraffinic oil, which prevented crystallization. Similarly, the addition of a small percentage of methanol to acetic acid diminished its tendency to freeze and also raised the C.S.T. with *n*-hexane, cyclohexane, and di-isobutene sufficiently to permit observation. Jones' success in observing one of these points directly (*30*) was not duplicated.

HYDROCARBONS

The following individual hydrocarbons available in almost pure form were tested: *n*-hexane (from petroleum) and *n*-heptane (from Jeffrey pine), representative of straight-chain paraffins; iso-octane (2,2,4-trimethylpentane), a branched-chain paraffin; cyclohexane and methylcyclohexane, representative of naphthenes; 1-heptene, a straight-chain olefin, and di-isobutene, a branched-chain olefin, for comparison with their respective hydrogenation products, *n*-heptane and iso-octane.

The 1-heptene was made by the Grignard reaction following the directions of Kistiakowsky and co-workers (*34*). The purified product boiled at 93° to 93.5° C. and had a density of 0.6980 at 20° C.

The aromatics, benzene, toluene, and xylene, were tried in the most favorable cases, but they mixed completely at the lowest available temperature with practically all the solvents which gave a C.S.T. with any nonaromatic hydrocarbon. It may be assumed that any applicable solvent possesses a relatively great, but not necessarily uniform, selectivity for aromatic hydrocarbons. The C.S.T. of thirty-eight cyclic hydrocarbons with a different group of solvents (many of those in Table III) will be presented in a future paper.

To compare selectivities in the gasoline range with those in the lubricating oil range, three other hydrocarbon reagents were included. These were paraffin wax (melting at 53° C.) which consisted probably of straight-chain paraffins with molecular weight about 352; a solvent-refined highly paraffinic oil, S.A.E. 10 (V.I. 112, A.P.I. gravity 31.0, molecular weight about 470); and another commercial oil, S.A.E. 40 (V.I. 13, A.P.I. gravity 20.4, molecular weight about 412), which was probably highly naphthenic. It would have been preferable to select these two oils with approximately the same molecular weight, but that would have necessitated a still greater disparity in viscosity. The bias in selectivity resulting from the difference in molecular weight was largely eliminated by the method of calculation, as indicated later.

SOLVENTS

Over two hundred compounds of various types were tried as solvents. About one fourth of them (Table II) mixed so readily with all the hydrocarbons (except the one with the highest molecular weight, the paraffinic oil, in some cases) that there was no separation into two liquid layers at the lowest available temperature; the latter was either −78° C. (dry ice) or somewhat below the freezing point of the solvent or hydrocarbon. These solvents (used alone) are obviously useless for extracting hydrocarbon oils in any temperature range. Some compounds of Table II (e.g., salicylic acid and triphenylguanidine) are listed only because of their high melting points.

TABLE II. SOLVENTS COMPLETELY MISCIBLE WITH MOST HYDROCARBONS (AS LIQUIDS)

(Figures indicate C.S.T. with the paraffinic oil where determinable)

All hydrocarbons[a]
Halogen derivatives of hydrocarbons[b]
Monoatomic ethers[c]
Aliphatic monoatomic acids above propionic
Monohydric alcohols above amyl
Acetal, −16° C.
Acetyl chloride, 9° C.
sec-Amyl alcohol, −5° C.
tert-Amyl alcohol, −10° C.
Isoamylamine, −6° C.
Isoamylnitrite
p-*tert*-Amylphenol
Benzoyl chloride
Benzyl sulfide
Butyl Cellosolve[d], 7° C.
p-*tert*-Butylphenol
Carbon disulfide
Cinnamic acid
Cyclohexanol
o- & *p*-Cyclohexylphenol
Diamylhydroquinone
Dimethylaniline
Diphenyldisulfide
Ditolylthiourea
Ethyl abietate
Ethyl benzoate
Ethyl salicylate
Glyceryl oleate
p-Hydroxydiphenyl, 165° C.
Mesityl oxide, 0° C.
Methylanthranilic acid
Methylcyclohexanol, −16° C.
p-Nitrochlorobenzene
Phenyl salicylate, 34° C.
Phenyl stearic acid, −11° C.
Salicylic acid
Thymol
Triamylamine stearate
Triphenylguanidine, 151° C.
2,5-Xylenol
Higher homologs of the above

[a] Apparent exceptions in the literature are limonene–lube oil (*20*), and liquefied paraffin gases–aromatic oil (*47A*). Neither of these seems valid. The paraffinic lube oil of this paper is completely miscible with pinene (which closely resembles limonene) at all temperatures down to −78° C. The precipitated layer mentioned in the patent (*47A*) was probably due to asphalt, containing nonhydrocarbons. Evidence on this point was obtained with propane and naphthalene which, in some respects, seems to be the most aromatic hydrocarbon. These two hydrocarbons were completely miscible at temperatures above 51° C., the lowest temperature to avoid crystallization. More evidence will be presented in a later paper.

[b] Methylene iodide seems to be an exception (*29*, *57*).

[c] The system ether-chrysene (*7*, *29*, *57*) may not be an exception, although Büchner (*7*) gives a lower C.S.T. of 207° C. Since this is above the critical point of one component and below the melting point of the other, it may be the temperature of separation of the solution into solid and gas instead of into two liquid phases.

[d] Ethylene glycol monobutyl ether.

TABLE III. SOLVENTS WITH HIGH C.S.T. VALUES WITH NONAROMATIC HYDROCARBONS

Acetamide
Acetoacetanilide
Adipic acid
p-Aminoacetanilide
p-Aminoacetophenone
m-Aminobenzoic acid
p-Aminobenzophenone
p-Aminoethylacetanilide
o-, *m*-, & *p*-Aminophenols
p-Aminophenylacetic acid[a]
Antipyrine[b]
Benzidine
Catechol
Dianisidine
Diethanolamine
Diethylene glycol
Dimethyl sulfate
Dinitrobenzoyl chloride[a]
2,4-Dinitrochlorobenzene
2,4-Dinitrophenol
Ethanolamine
Ethylene diformate
Ethylene glycol
Formamide
Glycerol
Glyceryl α-chlorohydrin[a]
Hydrazobenzene[a]
Hydroquinone
o-Hydroxybenzyl alcohol
Lactic acid[a]
Maleic acid[a]
Maleic anhydride
Michler's ketone[c]
Monoacetin
p-Nitroaniline
o-Nitrobenzoic acid
m- & *p*-Nitrophenols
Nitroso-β-naphthol[a]
Oxalic acid
Phenylethanolamine
Phenylthiourea[a]
o-, *m*-, & *p*-Phenylenediamines
Propylene glycol
Resorcinol
Sebacic acid
Thiourea[a]
Tolidine
m-Toluylenediamine
Triethanolamine
Triethylene glycol
Water

[a] Decomposes below C.S.T. with hydrocarbons.

[b] 1-Phenyl-2,3-dimethylpyrazolone.

[c] Tetramethyldiaminobenzophenone.

Another group of solvents (Table III) formed two liquid layers with the hydrocarbons; but the mutual solubility was so low that they were not completely miscible at the highest available temperature, which was limited either to 240° C. in the glycerol bath, or in some cases to decomposition temperature (marked "a" in the table). Most of these solvents can be given little consideration as selective solvents for nonaromatic hydrocarbons because of low solubility.

Some basic relations of structure to miscibility are discernible from Tables II and III and also from Table IV. For example, an oxygen atom or a nitrogen atom not combined entirely with carbon atoms diminishes miscibility with hydrocarbons considerably unless its effect is counterbalanced by several carbon atoms. Two or more such atoms in the molecule usually prevent complete miscibility. Angelescu and co-workers (*2*) made somewhat similar observations.

There remained 102 compounds whose C.S.T. values could be determined with some or all of the ten hydrocarbons mentioned. These solvents were presumed to be substantially pure but were purified in some cases. Slight impurities would probably affect the C.S.T. with hydrocarbons almost uniformly and, consequently, not affect the selectivities. Some solvents which are miscible with water, and therefore hygroscopic, gave trouble in checking temperatures because a trace of water affects C.S.T. greatly. This may be one reason for the discrepant observations in the literature for C.S.T. of methanol with *n*-hexane and cyclohexane although those of nitrobenzene with hexane are no more concordant:

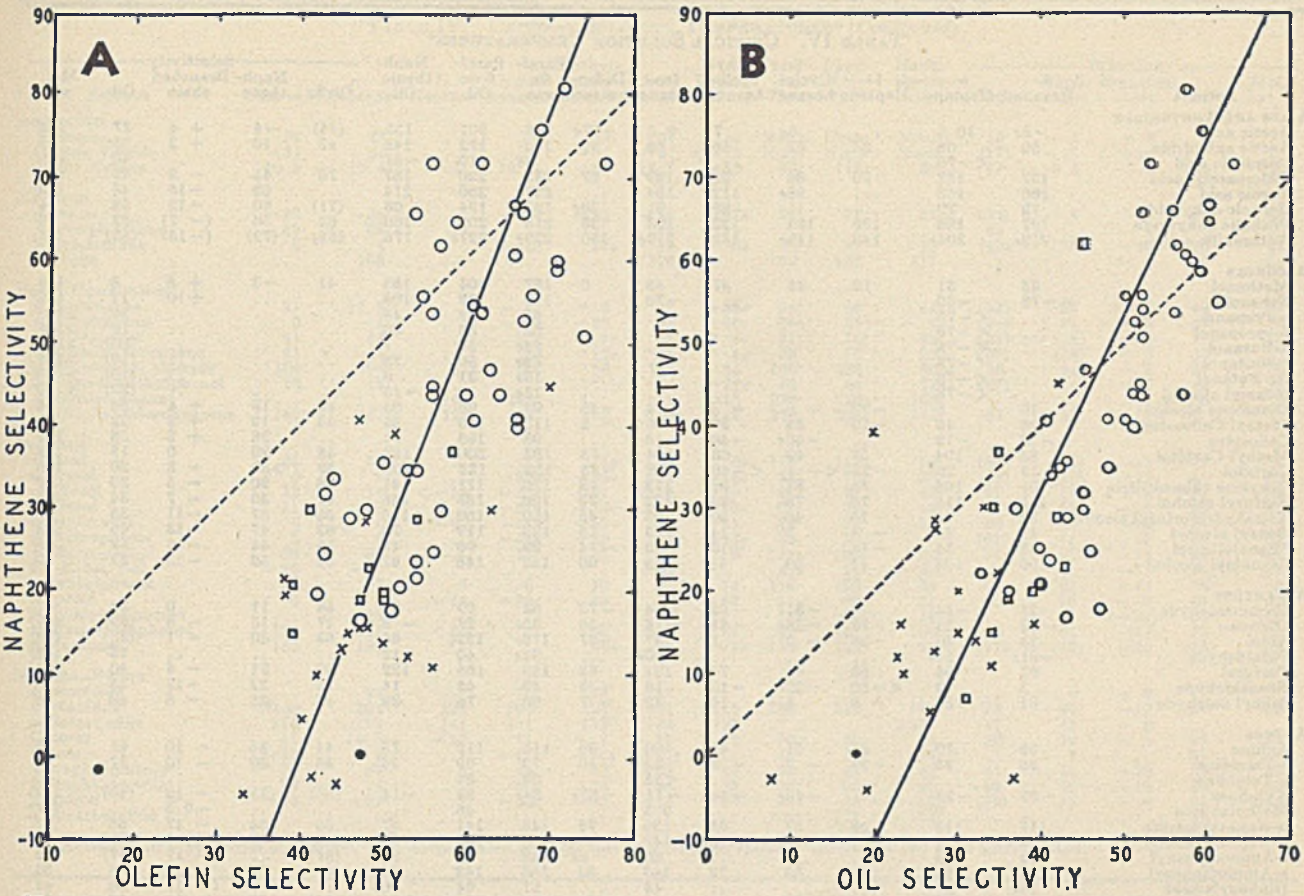
Temp., ° C.[a]	References
Methanol–*n*-Hexane	
42.8	*38*, *49*
42.6	*29*, *49*, *63*
43.8	*62*
42.2	*57*
36.55	*48*
42	*28*, *38B*, *63*
42.8	*64*
42.4	*19*
34.6	*24*, *38C*, *63*
33.6	*63*
32	*10*, *38C*, *63*
35	This paper
Methanol-Cyclohexane	
49.1	*38*, *40*
57.8[b]	*29*, *63*, *67*
49.1	*29*, *44*
47.2	*38C*, *39*
45.6	*31*, *38C*
45	*10*, this paper
Nitrobenzene–*n*-Hexane	
19.2	*68*
21.02	*29*, *38*, *68*
19	*13*, *38B*, *63*
10.40	*53*, *59*
14.8	*16*
21.3	*42*
20.2	*46*
21	*22*, this paper
20.60	*63*

[a] Arranged chronologically.

[b] Extrapolated.

C.S.T. with hygroscopic solvents may be less accurate than other C.S.T. values, which are believed to be within 1° or 2° C. of the true values.

Some commercial samples of Carbitol (diethylene glycol monoethyl ether) contain ethylene glycol, which boils at nearly the



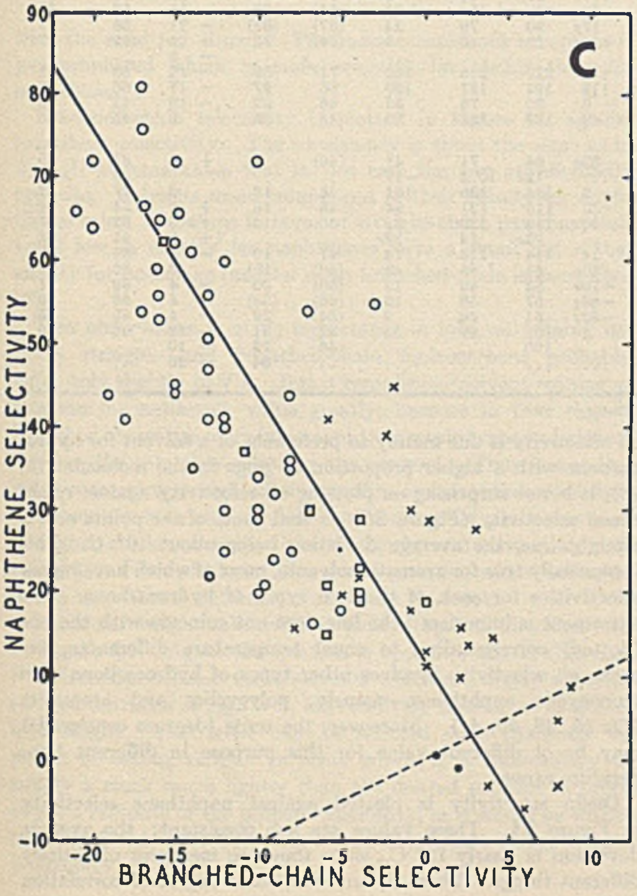


Figure 2. Plots of Naphthene Selectivities of Solvents against Other Selectivities

Solvents: ○ aromatic; ☐ heterocyclic; X aliphatic; ● inorganic

same temperature. This may raise the C.S.T. with a hydrocarbon by as much as 100° C. The points for Carbitol in Table IV were obtained with a special lot of glycol-free Carbitol.

SELECTIVITY DATA

The observations and calculations are recorded in Table IV. The selectivities with reference to paraffins are calculated from C.S.T. values as follows: C.S.T. for 1-heptene is subtracted from that of *n*-heptane, and that for di-isobutene from that for isooctane. The mean difference is considered as the olefin selectivity. Similarly, the selectivity for naphthenes is the mean difference between the C.S.T. of cyclohexane and *n*-hexane, and of methylcyclohexane and *n*-heptane, respectively. However, in the cases of five of the solvents, C.S.T. values with *n*-hexane are abnormally high (above 190° C.) because they are in the neighborhood of the critical temperature of that hydrocarbon, 235° C. In these cases only the C_7 difference is used. In one case (acetanilide) there is no C.S.T. with *n*-hexane because its critical temperature intervenes.

The selectivity for branched chains is found by subtracting the C.S.T. of iso-octane from that of *n*-heptane, since the two paraffins have almost the same boiling point. In a majority of cases, but not all, this value is negative. It is realized that the negative values in this column may not be primarily selectivities for normal over branched-chain isomers; but for some solvents as in the case of aniline points (*21*, *50*), they may be related to the densities of the isomers rather than to the numbers of branches. The positive branched-chain selectivities, which apply only to acyclic solvents, seem to be more nearly genuine (*25*).

TABLE IV. CRITICAL SOLUTION TEMPERATURES[a]

Solvent	*n*-Hexane	*n*-Heptane	1-Heptene	Cyclohexane	Methylcyclohexane	Isooctane	Di-isobutene	Paraffin wax	Paraffinic Oil	Naphthenic Oil	Selectivity				
											Olefin	Naphthene	Branched chain	Oil	Mol. wt.
ACIDS AND ANHYDRIDES															
Acetic acid	−5*e*	10.5	...	6*e*	7	6.5	−37*e*	178	201	153	(44)	−4	+ 4	37	168
Acetic anhydride	59	68	24	52	56	66	27	160	172	143	42	10	+ 2	23	92
Propionic acid	...	<−70	...	...	...	...	...	8*e*	10	−31	..	..	..	40	>78
Chloroacetic acid	137	137	70	86	98	139	67	238	220	187	70	45	− 2	42	101
Furoic acid	166	168	...	98*e*	112*e*	184	...	267*e*	250	214	..	62	−16	45	(99)
Benzoic anhydride	79	79	...	11*e*	28*e*	91	20*e*	123	124	66	(71)	60	−12	58	44
Phthalic anhydride	197	186	129	128	132	193	126	215	209	160	62	54	(− 7)	52	29
Anthranilic acid	219*e*	204*e*	149	118*e*	132	219*e*	150	229*e*	227*e*	175	(62)	(72)	(−15)	(53)	(25)
ALCOHOLS															
Methanol	35	51	12	45	47	43	0	187	204	188	41	−3	+ 8	8	136
Ethanol	<−78	−60	...	...	...	−70	...	112	128	108	..	..	+10	12	172
n-Propanol	...	<−78	...	...	...	...	...	65	82	48	..	..	..	26	>143
Isopropanol	...	<−78	...	...	...	...	...	68	83	60	..	..	..	16	>146
n-Butanol	...	<−78	...	...	...	...	...	25*e*	36	1	..	..	..	(30)	>103
Isobutanol	...	<−78	...	...	...	...	...	38*e*	50	28	..	..	..	(16)	>116
sec-Butanol	...	<−78	...	...	...	...	...	18*e*	31	9	..	..	..	(16)	> 96
Isoamyl alcohol	...	<−78	...	...	...	...	...	12*e*	18	−15	..	..	..	(30)	> 90
Diacetone alcohol	10	8	−32	− 6	− 5	4	−48	94	96	65	46	15	+ 4	30	86
Methyl Cellosolve	28	48	−10	25	26	46	− 2	115	119	95	53	12	+ 2	22	67
Cellosolve	−32	−12	...	−60*e*	−40	−15	...	98	106	74	..	28	+ 3	28	110
Methyl Carbitol	85	104	57	63	68	104	55	192	200	168	48	29	0	18	88
Carbitol	12	25	−25	<− 1	<−40	28	−25	125	133	109	52	>39	− 3	20	100
Ethylene chlorohydrin	101	108	74	81	89	113	72	170	171	141	38	20	− 5	30	62
Furfuryl alcohol	115	115	76	78	93	122	79	180	183	148	41	30	− 7	34	65
Tetrahydrofurfuryl alcohol	82	82	15	40	50	93	45	150	150	115	58	37	−11	35	68
Benzyl alcohol	49	60	− 8	2	14	73	15	123	119	76	63	47	−13	45	63
Phenylethanol	33	34	−14	...	−10	49	−14	99	98	47	56	44	−15	52	65
Cinnamyl alcohol	100	102	47	39	51	115	60	152	145	97	55	56	−13	52	50
ALDEHYDES															
Crotonaldehyde	−21	−14	...	−31*e*	−25	−14	−70	63	69	32	56	11	0	34	77
Dicroton	−22	−24	<−78	−36*e*	−41	−16	−56	35*e*	27	− 8	47	16	− 8	(39)	(59)
Aldol	23	36	−26	− 2	1	37	−27	116*e*	122*e*	86	63	30	− 1	(33)	(80)
Paraldehyde	−61*e*	−54*e*	...	...	...	−60*e*	...	34*e*	40	12	..	..	..	25	(88)
Furfural	92	95	56	69	76	101	62	159	165	122	39	21	− 6	40	64
Benzaldehyde	3	3	<−50	−22*e*	−15	16	−38	49	45	14	54	22	−13	33	46
Salicyl aldehyde	31	34	− 3	5	10	42	− 7	80	78	39	43	25	− 8	40	46
AMINES															
Aniline	69	70	26	31	41	80	36	116	115	75	44	34	− 10	41	46
o-Toluidine	25	25	−25	− 7	− 3	35	−10	72	69	34	48	30	− 10	37	47
p-Toluidine	...	...	...	...	...	<35	...	63	54	...	..	..	..	..	...
Xylidines	−22	−23	...	−49*e*	−46*e*	−11	−67*e*	34*e*	29	−14	(56)	(25)	− 12	(46)	(57)
Methylaniline	...	0	...	...	...	9.5	...	...	46	...	..	..	−9.5	..	(46)
α-Naphthylamine	117	113	58	57	65	130	74	145	141	87	56	54	− 17	56	32
β-Naphthylamine	143	131	...	65*e*	79*e*	147	88*e*	160	155	98*e*	(59)	65	− 16	(60)	29
o-Aminodiphenyl	45	43	...	...	...	60	3*e*	88	82	28*e*	(57)	..	− 17	(57)	45
p-Aminodiphenyl	134	125	70	63	72	140	82	155	142	93	57	62	− 15	56	30
Diphenylamine	23*e*	26*e*	...	...	...	43	...	67	64	10*e*	..	..	(− 17)	56	41
Diphenylethylenediamine	109	103	52	33*e*	48	118	62	139	134	85	54	66	− 15	52	36
Phenyl-α-naphthylamine	69	63	...	...	0*e*	84	17*e*	90	70	24	(67)	(63)	− 21	56	27
o-Chloroaniline	14	13	...	−25*e*	−17	26.5	−27*e*	50	46	6	(54)	35	− 14	42	37
p-Chloroaniline	...	80	...	...	...	86	...	...	...	...	..	..	− 6	..	...
o-Nitroaniline	233	206	...	133	147	222	151	227	216	163	71	59	− 16	59	21
3,4-Nitroaminotoluene	181	173	114	107	113	190	118	191	187	129	66	67	− 17	60	18
o-Phenetidine	26	28	−16	− 2	− 1	38	− 9	80	76	35	46	29	− 10	43	52
p-Phenetidine	81	83	41	46	54	92	48	139	131	90	43	32	− 9	45	56
ESTERS															
Ethyl formate	−40	−34	...	−48*e*	−36	−42	−82*e*	65	71	41	(40)	5	+ 8	27	99
Ethyl acetate	...	<−78	...	...	...	...	...	12*e*	10.5	−17	..	..	..	28	>90
Ethyl acetoacetate	32	43	− 2	24	26	43	−2	125	130	101	45	13	0	27	82
Ethyl lactate	8	21	−25	− 2	− 1	19	−30	115	121	94	48	16	+ 2	24	94
Ethyl oxalate	15	23.5	−26	5	5	21	−30	114	120	85	50	14	+2.5	32	91
Butyl oxalate	−58*e*	−55*e*	...	...	...	−58*e*	...	23*e*	14	−22*e*	..	..	(+ 3)	41	78
Methyl furoate	50	57	...	34	36	61	14	114	113	78	47	19	− 4	36	57
Ethyl furoate	16	20	...	− 1*e*	− 1*e*	20	−30*e*	85	85	49	(50)	(19)	0	36	65
n-Propyl furoate	−28	−24	...	−48*e*	−44	−20	−70*e*	53	49	12	(50)	20	− 4	39	77
n-Butyl furoate	−26	−22	...	−44*e*	−50*e*	−18	−66*e*	57	58	15	(48)	(23)	− 4	43	79
n-Amyl furoate	−36	−32	...	−56*e*	−70	−28	−82*e*	51	50	9	(54)	29	− 4	42	83
Methyl anthranilate	47	46	−13	16	15	58	3	101	99	55	57	31	− 12	45	55
Phenyl phthalate	...	135	79	41	63	145	...	190	...	...	50	72	− 10	..	45
Triphenyl phosphite	...	91	...	...	27	111	...	...	...	...	..	64	− 20	..	...

The "oil selectivity" results from subtracting the C.S.T. of the naphthenic oil from that of a paraffinic oil of approximately the same molecular weight. Although such an oil was not studied, its C.S.T. values were estimated from the mean of those with paraffin wax and the commercial paraffinic oil.

The affinity of solvents for hydrocarbons is affected also by the molecular weight of the latter, the lower hydrocarbons being more miscible; this effect varies with different solvents. It is calculated for convenience by subtracting the C.S.T. with *n*-heptane from that with paraffin wax, which is probably purely paraffinic. Selectivities involving C.S.T. below −40° C. and some requiring considerable extrapolation are enclosed in parentheses, as being less accurate.

PLOTS OF PAIRS OF SELECTIVITIES

These selectivities are somewhat arbitrary but are logical. As expected, they are not entirely independent. It is illuminating to plot some of them against each other in pairs. Since the oil selectivity is due mainly to preference of a solvent for hydrocarbons with a higher proportion of rings in the molecule (*18*, *43*), it is not surprising on plotting oil selectivity against naphthene selectivity (Figure 2*B*) to find most of the points near a straight line, the average deviation being about 10° C. This is especially true for aromatic solvents, most of which have higher selectivities for each of the two types of hydrocarbons. The agreement is imperfect; the line does not coincide with the one (dotted) corresponding to equal temperature differences, because oil selectivity involves other types of hydrocarbons than monocyclic naphthenes—namely, polycyclics and aromatics (*11*, *18*, *43*, *50*, *51*). Moreover, the units (degrees centigrade) may be of different value for this purpose in different temperature ranges.

Olefin selectivity is plotted against naphthene selectivity in Figure 2*A*. These values are less consistent; the average deviation is nearly 15° C., since they are measures of entirely different things. There is, however, some degree of correlation

Table IV. Critical Solution Temperatures[a] (*Continued*)

Solvent	*n*-Hexane	*n*-Heptane	1-Heptene	Cyclohexane	Methylcyclohexane	Iso-octane	Di-isobutene	Paraffin Wax	Paraffinic Oil	Naphthenic Oil	Selectivity: Olefin	Selectivity: Naphthene	Selectivity: Branched chain	Selectivity: Oil	Selectivity: Mol. wt.
Inorganic															
Ammonia	56	63	...	59	63	61	46	None	None	None	15	− 1	+ 2	..	...
Carbon dioxide	−61	−51	...	−37	−41	−61	<−78	None	None	None	(17)	−17	+10	..	...
Sulfur dioxide	10.2	19.4	−21	12.7	16	18.7	−35	95	113	86	47	0.5	0.7	18	76
Ketones															
Acetone	−39	−28	...	−29*e*	−30	−34	−67*e*	65	77	52	(33)	− 4	+ 6	19	93
Acetonylacetone	59	68	11	...	...	72	31	...	...	...	49	..	− 4	..	...
Acetophenone	3	4	...	−16*e*	−17*e*	14	−28*e*	51	47	13	(42)	20	−10	36	47
Quinone	...	108	...	...	...	116	...	162	152	117	..	..	− 8	40	54
Nitro Compounds															
Nitrobenzene	21	17.5	...	− 4	− 3	27	−25*e*	54	53	14	(52)	23	−9.5	40	37
o-Nitrotoluene	0	−1	...	−28*e*	−20	8	−46*e*	39*e*	35	− 4	(54)	24	− 9	41	(40)
o-Nitrophenol	41	43	...	25*e*	24*e*	48	− 3*e*	81	76	32	(51)	(18)	− 5	47	38
o-Nitrochlorobenzene	41	41	...	0*e*	12*e*	49	− 4*e*	78	73	28	(53)	(35)	− 8	48	37
p-Nitrobenzyl chloride	104	103	47	56	63	111	55	139	134	80	56	44	− 8	57	36
2-Nitro-4-methylphenol	18	18	...	...	...	25	−22*e*	56	54	12*e*	(47)	..	− 7	43	38
m-Dinitrobenzene	...	...	149	143	...	...	115	238	230	169	..	..	..	65	...
2,4-Dinitrochlorobenzene	199	187	127	124	132	190	128	218	206	151	61	55	(−3)	61	31
Phenols															
Phenol	51	53	...	...	11*e*	66	0*e*	117	112	74	(66)	(42)	−13	41	64
o-Cresol	5	9	...	−36*e*	−29*e*	21	−45*e*	82	76	28	(66)	(40)	−12	51	73
m-Cresol	12	14	<−52	−53*e*	−27	29.5	−39	94	93	43	67	53	−16	51	80
p-Cresol	11	12	...	−51*e*	−38*e*	28	−40*e*	97	98	48	(68)	56	−16	50	85
Cresylic acid	0	0	−60	−51*e*	−37	15	−45	74	74	23	60	44	−15	51	74
o-Chlorophenol	5	6	...	−44*e*	−27	18	−43*e*	58	50	6	(61)	41	−12	48	52
p-Chlorophenol	69	67	...	13	21	80	6	111	103	55	74	51	−13	52	44
2,4-Xylen-1-ol	−70	−60	...	...	...	−45	...	21*e*	27	(−30)	..	..	−15	(54)	(81)
o-Benzylphenol	65	67	3	0	10	81	14	116	108	54	66	61	−14	58	49
Eugenol	0	3	−44	−38*e*	−30	11	−42	64	63	21	50	36	− 8	43	61
o-Hydroxydiphenyl	...	28*e*	...	...	...	49	...	77	69	18	..	..	(−21)	55	(49)
m-Hydroxydiphenyl	134	121	< 56	...	60	138	67	162	156	100	69	61	−17	59	41
β-Naphthol	145	130	...	...	58*e*	150	73*e*	159	152	92*e*	(77)	(72)	−20	(63)	29
Miscellaneous															
Acetonitrile	...	84	...	76	78	81	...	...	...	...	..	6	+ 3	..	...
Acetanilide	None	204	134	103	123	221	145	233	232	176	73	81	−17	57	29
n-Butyramide	174	178	141	131	139	184	128	...	...	>231	47	41	− 6	..	...
Chlorex	11	15.5	−22	−11	− 7	19	−19	70	68	34	38	22	− 4	35	55
Dioxane	−13*e*	−4*e*	...	−17*e*	−14*e*	− 7*e*	...	45	45	14	..	7	..	31	49
α-Naphthonitrile	73	67	5	25	33	85	26	92	91	42	61	41	−18	50	25
β-Naphthonitrile	79	74	...	30	35	93	29	98	95	45	64	44	−19	52	24
Pyridine	−25	−21	...	−36*e*	−40	−15	−54*e*	23*e*	25	−10	(39)	15	− 6	34	(44)
Thiocarbanilide	...	...	...	...	...	...	...	179	177	153	..	..	..	25	...

[a] Selectivities in parentheses are derived from extrapolated or other less reliable observations; values marked *e* are extrapolated.

with the solid line drawn. The most conspicuous exception is *p*-chlorophenol which is more selective for olefins than for naphthenes.

Branched-chain selectivity is plotted in Figure 2*C* against naphthene selectivity. The consistency is about the same as in 2*A*. It is remarkable that in this case the two are distinctly opposite. Solvents most pronounced in their affinity for naphthenes reject iso-octane in favor of straight-chain paraffins; solvents low in affinity for naphthenes have a small but actual affinity for iso-octane (and for other branched-chain isomers also, *23*).

This observation is of no importance in lube oil refining because straight- and branched-chain hydrocarbons probably differ only slightly in V.I. But it complicates solvent refining of gasoline for antiknock value greatly, because in that respect branched chains are more important than naphthenes and olefins, and yet the solubility relations are reversed. Thus, a gasoline stock containing straight-chain paraffins and naphthenes, olefins, or aromatics with any applicable solvent would give an extract of higher antiknock value than the stock; one containing only straight and branched paraffins would give, with most solvents, an extract of lower antiknock value than the stock.

Molecular weight selectivity is plotted against oil selectivity in Figure 3*A*. Again the relation is opposite, but in this case it is desirable because those solvents which are highly selective for hydrocarbons of high V.I. are relatively indifferent to molecular weight. The latter can be selected more efficiently by means of boiling range. In other words, it is unnecessary to supply a stock much lighter than the desired product in order to get a raffinate of the proper consistency, as it would be with a solvent of high molecular weight selectivity, such as acetic acid or alcohols.

In Figure 3*B* the oil selectivity is plotted against the boiling point of the solvent. The concordance is rather better than in the other graphs, an indication that the higher the boiling point of the solvent, the more selective it usually is. This is unfortunate in solvent refining of lube or other heavy oils in which the boiling point of the solvent is limited by its ability to be recovered by distillation. In the case of gasoline this relation is advantageous, since it favors the choice of high-boiling solvents which are more easily separated by distilling off the gasoline.

Other pairs of selectivities could be plotted but would show no relations not given on Figures 2 and 3.

Another observation, not easily plotted, is that C.S.T. with paraffin wax is higher than that with paraffinic oil (in spite of the lower molecular weight), with the highly selective solvents and is lower with the less selective solvents. This indicates that even the paraffinic oil is far from 100% paraffinic. Probably no wax-free oil contains any large percentage of wholly paraffinic molecules. The term "highly paraffinic" as applied to lube oils means only that a high percentage (e.g., over 65%) of the carbon atoms are not members of rings.

Three inorganic liquefied gases are included as solvents. Sulfur dioxide, probably the original selective solvent for oils, is relatively poor in selectivity except for olefins (and probably aromatics). Its selectivity for oils is low and for naphthenes is negligible. This is shown also by Leslie (*41*). The selectivity of sulfur dioxide for cyclohexane over nonane-decane found by Moore, Morrell, and Egloff (*46*) may be related to the lower boiling point of the naphthene. Sulfur dioxide owes its use to its low cost and easy removal, and the fact that almost any solvent has adequate selectivity for aromatics.

Ammonia is still worse. It shows only a slight selectivity for olefins and, even, for aromatics. Carbon dioxide is likewise a poor selective solvent.

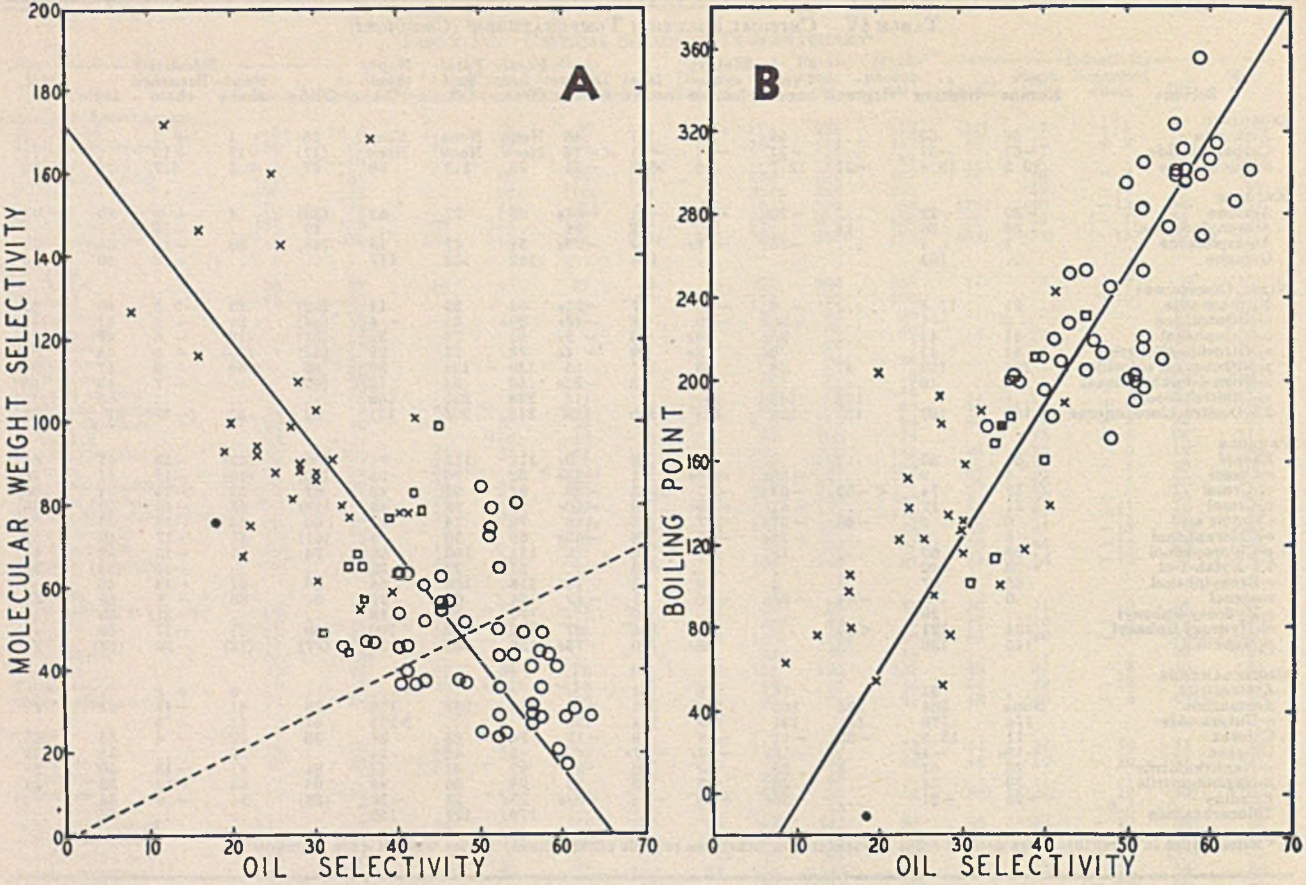


Figure 3. Plots of Oil Selectivities of Solvents

Solvents: ○ aromatic; □ heterocyclic; X aliphatic; ● inorganic

CONCLUSIONS

The following generalities may be noted with regard to selectivity of solvents:

1. Isomers and homologs differ little in selectivity although the individual C. S. T. values may differ greatly.
2. Monosubstituted benzene solvents differ only slightly in selectivity. Di-substituted derivatives are usually somewhat more selective, although higher melting points often complicate their use.
3. Aromatic solvents are more selective than aliphatics, as shown by Figures 2 and 3 and by the following average selectivities:

Selectivity Type	56 Aromatics	30 Aliphatics	11 Heterocyclics	SO_2
Olefin	59	47.5	47	47
Naphthene	47	18	26	0.5
Branched-chain	−13	0	−5	0.7
Oil	49	29	38	18
Mol. wt.	45	96	68	76

The effect of substituents on C.S.T. is summarized in Table V. The numbers are average differences in degrees centigrade, and are derived as shown by the following example (*o*-cresol under "Methyl Group"): The C.S.T. values of *o*-cresol with the several hydrocarbons are subtracted from those of phenol with the same hydrocarbons, respectively, in as many cases as possible, giving 46, 44, 40, 45, 45, 35, 36, and 46 (mean, 42). The figure is negative in Table V because the methyl group lowers C.S.T. in every case but two. (One of these may be in error because of an impurity in propyl furoate). The mean excludes the two positive values, and three large negative values, two of which are due to the formation of esters or "covering" of a free hydroxyl group of an acid. This effect might be still more pronounced if ethers could be compared with alcohols numerically. In a few cases the precursor (compound without the methyl group) is given in parentheses, where it is not evident from the structure.

The effect of the phenyl group is usually about the same as that of the methyl group since they both make the solvent somewhat more like a hydrocarbon in structure. In some cases the phenyl group raises C.S.T. Naphthalene derivatives are slightly less miscible with hydrocarbons than are the corresponding benzene derivatives.

The nitro group raises C.S.T. greatly except when it is *ortho* to a phenolic group and perhaps forms an intramolecular latent ester. The carboxyl group also diminishes solubility greatly, as expected. The effects of chlorine are sometimes positive and sometimes negative, depending on position. The acetyl group has a large positive effect except where it covers up a free hydroxyl group. The aldehyde group has a small negative effect in aromatic and positive effect in aliphatic solvents.

The effects of amino and hydroxyl groups are usually so great that they cannot be derived satisfactorily from the data of this paper alone.

The effects of position are summarized at the end of Table V The ortho isomers are much more miscible than the meta and para isomers, except in the cresols and toluidines where the effect is small. The distinction is probably due to the nonpolar character of the methyl group. There is little difference between alpha and beta derivatives of naphthalene.

Table V. Effects of Substituents in Organic Solvents on Critical Solution Temperatures with Hydrocarbons

	C.S.T., ° C.
Methyl Group (or $-CH_2-$)	
o-Toluidine	−44
p-Toluidine	−57
Xylidines (*o*-Toluidine)[a]	−45
Methylaniline	−70
o-Cresol	−42
m-Cresol	−32
p-Cresol	−31
Cresylic acid	−47
Xylenols (*o*- & *p*-Cresols)	−69
o-Nitrotoluene	−20
2-Nitro-4-methylphenol	−22
3,4-Nitroaminotoluene	−34
Ethanol	−91
Propanols	−52
Butanols	−44
Isoamyl alcohol	−19
Phenylethanol (Benzyl alcohol)	−24
Propionic acid	(−182)
Ethyl acetate (Ethyl formate)	−57
Methyl anthranilate	(−139)
Methyl furoate	(−118)
Ethyl furoate	−35
n-Propyl furoate	−40
n-Butyl furoate	(+3)
n-Amyl furoate	−11
Acetophenone (Benzaldehyde)	(+1)
Butyl oxalate (Ethyl oxalate)	4x−20
Cellosolve (Methyl Cellosolve)	−52
Mean	−40
Chlorine Atom	
o-Chlorophenol	−52
p-Chlorophenol	+4
o-Chloroaniline	−61
p-Chloroaniline	+8
o-Nitrochlorobenzene	+19
2,4-Dinitrochlorobenzene	−20
Ethylene chlorohydrin	+45
Chloroacetic acid	+90
Hydrogen Atoms	
Tetrahydrofurfuryl alcohol	4x−9
Furfuryl alcohol (Furfural)	2x+10

	C.S.T., ° C.
Phenyl Group	
Aniline (Ammonia)[a]	−3
Diphenylamine	−47
o-Aminodiphenyl	−29
p-Aminodiphenyl	+42
o-Hydroxydiphenyl	−35
m-Hydroxydiphenyl	+57
Phenyl-α-naphthylamine	−57
o-Benzylphenol (*o*-Cresol)	+47
Benzyl alcohol	−29
Phenylethanol	+22
C_4H_2 Group	
α-Naphthylamine (Aniline)	+33
β-Naphthylamine (Aniline)	+48
β-Naphthol (Phenol)	+63
Mean	48
Nitro Group	
o-Nitroaniline	+118
o-Nitrophenol	(−25)
m-Dinitrobenzene	+160
2,4-Dinitrochlorobenzene (*o*-Nitrochlorobenzene)	+135
3,4-Nitroaminotoluene (*p*-Toluidine)	+139
2-Nitro-4-methylphenol (*p*-Cresol)	(−18)
Mean	133
Acetyl Group	
Acetanilide	+109
Ethyl acetate	−114
Ethyl acetoacetate	+118
Acetic anhydride	+33
CHO Group	
Salicyl aldehyde	−22
Aldol (Isopropanol)	+35
Carboxyl Group	
Anthranilic acid	+116

Isomeric Effects

Para minus Ortho	
Cresols	11
Toluidines	12
Chloroanilines	60
Phenetidines	55
Aminodiphenyls	74
Chlorophenols	55

Meta minus Ortho	
Cresols	10
Hydroxydiphenyls	87
Beta minus Alpha	
Naphthylamines	15
Naphonitriles	5

[a] Names in parentheses are precursors.

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Recovery of Proteins from Wheat Mashes with Sulfite Waste Liquor

Sulfite waste liquor can be employed for the recovery of proteins from dilute solutions. A method is described for wheat mashes. For maximum recovery, protein hydrolysis should be avoided, and the acidity of the mash should be adjusted to a pH range of 1.5–2.5. Two parts of the sulfite waste liquor, calculated on the basis of its lignin content, are required to recover 5 parts of protein. During or after lignin addition, the mash is heated to at least 85° C. and is preferably cooled before filtration. Under these conditions 85 to 90% of the total mash protein (or 80 to 85% of the soluble protein) is readily recovered, and the filterability is markedly improved when compared with that of untreated mashes. The recovered protein shows promise as a feed, when properly supplemented.

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When cereals are used as the carbohydrate source in industrial fermentations, the protein content of the grain represents a valuable by-product. In view of the shortage of protein under wartime conditions, its recovery is important for the national economy. Furthermore, by such recovery the amount of wastes from fermentation industries will be reduced and stream pollution diminished. Various methods for protein recovery. such as screening, spraydrying of slops, the sulfite process (*1*), etc., are in use. A new method for protein recovery by precipitation with sulfite waste liquor is described here as applied to wheat mashes; it may be used with equal success for other cereals. The advantages are a high recovery of protein, low material and handling costs, and the use of conventional equipment.

The ability of some constituents of sulfite waste liquor to combine with protein is made use of in the tanning industry. It has been shown that the lignosulfonic acid effects a chemical combination with hide proteins (*3*, *7*). A study of the depressive effect of lignin upon the decomposition of proteins by bacteria showed that a complex is formed when lignin and gliadin (*5*, *6*), or casein, were allowed to interact. This lignin-protein complex possessed the various chemical, physicochemical, and biological properties characteristic of the major portion of the organic matter (humus) of the soil. Recently, proteins were used as a lignin precipitant in the purification of wood liquors (*2*).

In 1942 research was started in this laboratory on the production of glycerol from wheat by fermentation. Initially, second clears flour, and later, granular wheat flour, were employed. Since sizable quantities of nitrogenous matter interfere with the distillation of fermentation glycerol in various ways, experiments for the removal of proteins with sulfite waste liquor were undertaken for prepurification of the mash prior to fermentation. When the maximum amount of protein was removed by sulfite waste liquor treatment, it was found that distillation difficulties were substantially eliminated, the amounts of residue and solids in the distillations were reduced, and a greater purity of end products was obtained.

Initial experiments indicated that the quantity of protein removed by sulfite waste liquor is inversely proportional to the degree of its disaggregation. Therefore a method was employed by which the protein in the mash undergoes as little breakdown as possible prior to precipitation.

MATERIALS AND METHODS

The granular wheat flour used had the following analysis: moisture 11.0%, protein 10.3%, carbohydrates (calculated as glucose) 77.9%, ash 0.6%. The flour was converted into a fermentation mash with a minimum of proteolysis by the following method: A premalt was prepared by mixing 50 grams of high-diastatic malt with 500 ml. of water, stirring the mixture at 37° C. for 30 minutes to free the diastases for maximum activity, and then for an additional half hour at 60° C. to inactivate the proteases of the malt. One kilogram of granular wheat flour, suspended in 5 kg. of water, was liquefied by heating to 85° C. after addition of one fifth of the premalt. After liquefaction of the starch, the mash was cooled to 62° C., and the remaining four

TABLE I. COMPARISON OF PROTEIN-PRECIPITATING ACTION OF SAMPLES F AND M

Lignin Added, Mg.		Total N[b] in Filtrate of Lignin-Treated Sample, Mg.	% Sol. Protein Removed	% Total Sol. and Insol. Protein Recovered
Sample F	Sample M			
0	0	6.3	0	39
0.78 (3)[a]	...	5.61	9.5	44.9
1.56 (6)	...	4.72	25.0	54.2
2.6 (10)	...	4.66	26.0	54.8
...	3.9 (5.67)	4.17	33.5	59.5
5.2 (20)	...	3.45	45.0	66.0
...	7.8 (11.34)	2.99	52.5	71.0
7.8 (30)	...	2.39	62.0	76.8
10.4 (40)	...	1.22	80.5	88.1
...	15.6 (22.68)	1.32	79.0	87.2
20.8 (80)	...	1.12	82.0	89.1
...	31.2 (45.36)	1.23	80.5	88.1
31.2 (120)	...	1.10	82.5	89.3
41.6 (160)	...	1.07	83	89.6

[a] Figures in parentheses represent mg. of samples F and M used.
[b] Calculated after deduction of nitrogen present in amounts of samples F and M added (F = 0.86, M = 0.70 mg. N per gram).

fifths of the premalt was added with stirring. The mash was then malted for 2 hours at 62° C. and for an additional 2 hours at 52° C. The malting time is not critical and may be appreciably shortened. Instead of malt, other amylolytic materials, such as bacterial amylase, can be employed.

Two samples (F and M) of lime-neutralized, concentrated sulfite waste liquor were investigated with respect to their protein-precipitating action. Sample F was obtained as a concentrated liquid for which the following percentage analysis was submitted by the Farber Laboratories:

Water (as loss at 105° C.)		49.17
Sulfur (calcd. total)		2.71
As inorganic SO_3	2.55	
As SO_2	0.16	
Ash (as residue after ignition)		5.36
CaO	2.39	
MgO	0.75	
Al_2O_3	0.13	
SiO_2	0.002	
Fe	0.011	
Alkali metals (as Na)	0.09	
Organic matter (calcd. by difference)		45.47
SO_2 in organic compound sulfone	2.47	
Lignin	26	
Total sugars	11	
Acetic and formic acids	1.6	

Sample M was a dry powder with the following analysis (in per cent):

Manufacturer's Analysis (Marathon Paper Mills Co.)		Calculated Composition	
Moisture	6.24	$CaSO_4 \cdot {}^1/_2H_2O$	0.68
Oven-dry basis		Fe_2O_3	0.10
Total S	5.63	Sulfonic SO_3	13.70
Sulfate S	0.15	Sulfonic Ca	3.23
Fe_2O_3	0.10	Sulfonic Mg	0.12
Total Ca	3.42 (4.79 CaO)	Nonsulfonic Mg	0.23
Total Mg	0.35 (0.58 MgO)	Lignin	68.80
Total methoxyl	9.98	Nonlignin organic matter	13.14 (by diff.)
			100.00

Stock solutions of equal concentration with respect to lignin content were prepared from sample F (26%) and M (68.8%). The actual precipitating agent was lignosulfonic acid, expressed in terms of lignin in accordance with the common analytical terminology for sulfite waste liquors. A 7.5-gram portion of sample F was diluted to 25 ml. with distilled water; 1 ml. of this solution contained 0.3 gram of the sample—i. e., 0.078 gram of lignin, calculated on the basis of the above analysis. Sample M was made up to the same concentration on the basis of its lignin content after conversion into free lignosulfonic acid (a procedure suggested by the manufacturer).

To 22.675 grams of oven-dry sample M suspended in 100 ml. of water, 1.22 ml. (2.243 grams) of concentrated sulfuric acid (95.5%), diluted to 8 normal strength, were added under stirring. The mixture was heated to 85° C. and filtered, the precipitate was washed, and the combined filtrate and washings were made up to 200 ml. with distilled water. One milliliter of this stock solution corresponds to 0.078 gram of lignin, calculated on the basis of the manufacturer's analysis.

For a more general comparison of the protein-precipitating action of the two samples of sulfite waste liquor, sulfosalicylic acid was employed; as stock solution, 10 grams of this acid (reagent grade) were dissolved in distilled water and brought to a volume of 100 ml. (pH = 1). The semimicro-Kjeldahl method was used for the nitrogen analyses. The factor 6.25 was taken for the conversion of nitrogen into protein. The pH determinations were made with a Beckman meter.

Experiments were undertaken to determine the optimum conditions for the precipitation of proteins in the mash. When the malted wheat flour mash was acidified to pH 2.0, approximately the optimal pH for precipitation with sulfite waste liquor, 39% of the protein originally present was insoluble and could be removed by filtration with Celite 512. The action of sulfite waste liquor was studied on the soluble 61% of the protein.

VARIATION IN QUANTITY OF PROTEIN PRECIPITANTS

The malted mash was acidified to approximately pH 2.0, diluted to four times its original volume with distilled water, and filtered with Celite 512. Each 100 ml. of the clear filtrate used for the following experiments contained an equivalent of 6.25 grams of granular wheat flour (392 mg. of soluble protein).

One milliliter of solution, containing different amounts of samples F and M by appropriate dilution of their stock solutions, was added to 10 ml. of the filtrate. The mixture was heated to boiling, readjusted to the preboil weight with distilled water, and filtered with Celite 512. One milliliter of distilled water was added to 10 ml. of the filtrate as control, and the mixture treated in the same manner.

The percentage of soluble protein removed with the addition of varying amounts of the sulfite waste liquor samples, calculated on their lignin contents, is shown in Table I. The protein recovery rises to a maximum with the increase in the concentration of precipitating agent. The lignin content of the sulfite waste liquor samples is a satisfactory index of their protein-precipitating action.

The protein-precipitating action of the sulfite waste liquor samples was compared with that of sulfosalicylic acid. Five milliliters of varying concentrations of sulfosalicylic acid made by dilution of the stock solution with 0.1 *N* hydrochloric acid were added to 10 ml. of filtrate; the mixtures were left in the incubator for 40 minutes (*4*) and then filtered with Celite 512. As control, 5 ml. of 0.1 *N* hydrochloric acid were added to 10 ml. of filtrate, and the mixture was left in the incubator for 40 minutes.

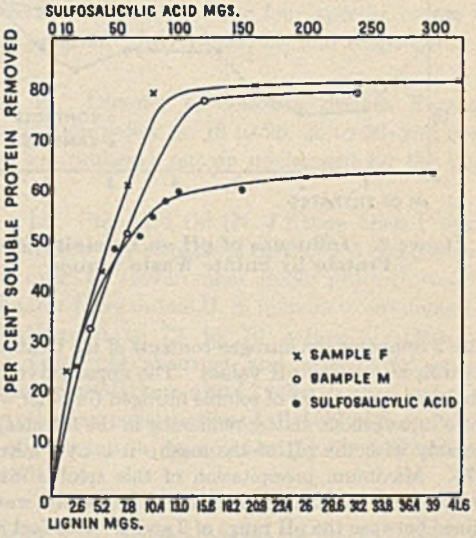

Figure 1. Comparison of Sulfosalicylic Acid and 2 Sulfite Waste Liquors (on Basis of Lignin Content) as Protein Precipitants

The percentage of soluble nitrogen removed from the mash filtrates with increasing amounts of sulfosalicylic acid and of the sulfite waste liquor samples in terms of their lignin contents are shown in Figure 1. These curves, which are representative of the experiments, indicate that sulfite waste liquor is a better precipitant for wheat proteins than sulfosalicylic acid; in order to achieve the same degree of precipitation, more than ten times as much sulfosalicylic acid was needed than lignin, and the maximal percentage of protein precipitated was considerably higher with the latter agent.

VARIATION IN pH

The effect of pH variation on the precipitation of protein was determined with the optimum addition of sample F. Samples of the mash used in the precipitation experiments were adjusted by addition of sulfuric acid or sodium hydroxide to the desired pH, made up to a final dilution of 1 to 4, and filtered with Celite 512. The pH values of the filtrates are shown in Figure 2. Ten milliliters of these filtrates were treated with 1 ml. of sample F containing 15.6 mg. of lignin. One milliliter of distilled water was added to 10 ml. of the filtrate in each case and used as control. The treated samples and controls were heated to boiling, cooled, brought to original weight with distilled water, and filtered with Celite 512.

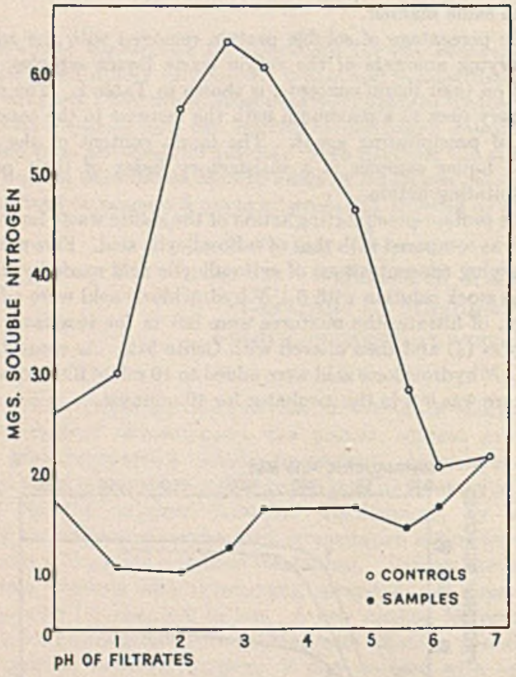

Figure 2. Influence of pH on Precipitation of Protein by Sulfite Waste Liquor

Figure 2 compares the nitrogen contents of the treated samples and controls at varying pH values. The upper curve (controls) indicates that the amount of soluble nitrogen (in other words, the amount of nitrogenous matter remaining in the filtrates) changes considerably with the pH of the mash; it is at a maximum at pH 2.75. Maximum precipitation of this soluble nitrogenous matter by addition of the optimum amount of sulfite waste liquor is obtained between the pH range of 2 and 4. This fact is derived from an examination of the lower curve (treated samples). The yield of precipitated protein calculated on the basis of the sum of soluble and insoluble nitrogen is greatest in the pH range of 1 to 3. Results of pH studies on sample M closely resemble those for sample F.

DISCUSSION

These studies on the precipitation of wheat proteins show that, with sulfite waste liquor, 80–85% of the soluble protein in a diluted mash is readily recovered. For experimental purposes, attention was directed chiefly to the soluble protein of the mash. However, when fermentation mashes of the usual concentrations containing insoluble as well as soluble protein were treated under optimal conditions for the recovery of soluble proteins, not only was 85–90% recovery realized, but also the filterability of the fermentation mash was greatly improved. The fermentation was not affected by this treatment.

To recover 85–90% of the protein from a fermentation mash, the acidity was adjusted to a pH value in the range 1.5–2.5. Sulfite waste liquor in an amount equal to 2 parts of lignin for every 5 parts of protein was added to the adjusted mash. The treated mash was heated to 85–90° C. for 10 minutes with thorough mixing. For the highest recovery of protein, it is preferable to filter after cooling the mash to room temperature. If desired, the filter cake can be washed free of sugar and the wash water used for subsequent mashings. The protein-lignin cake can readily be converted to a dry form following the usual precautions for drying such materials.

Proteins may be recovered by this method either from mashes prior to fermentation or from fermentation slops, such as slops from alcohol distilleries. If used for alcohol slops, the method not only provides for the recovery of a material high in protein but also leads to a considerable purification and thereby a lowering of the B.O.D. and solids content of the effluent.

Preliminary tests on the feeding of the dried protein-lignin to rats indicated that this material is a satisfactory source of protein, provided the diet is supplemented by the essential amino acids known to be lacking in wheat protein. With such a supplement the rats maintained satisfactory growth rate.

While the process described was developed for the recovery of wheat proteins, it may also be applied to proteins from other vegetable sources such as corn and potatoes. Yields for the latter are of the same order as those for wheat.

SUMMARY

1. A method is described for the recovery of protein by the addition of sulfite waste liquor to hot, acidified wheat mashes. By this method 85–90% of the protein is readily recovered and filtration of the mash is greatly improved.

2. Studies with two different sulfite waste liquor samples indicate that the protein-precipitating action is a function of lignin (lignosulfonic acid) content. For the precipitation of soluble wheat proteins, the optimum ratio of lignin to protein is 1 to 4.

3. The effectiveness of lignosulfonic acid for the precipitation of soluble wheat protein was compared to that of sulfosalicylic acid. The relative activity of lignosulfonic acid was more than ten times as great as that of sulfosalicylic acid. Further, the maximum amount of precipitation achieved by lignosulfonic acid was considerably higher.

4. The optimal range of acidity for maximum precipitation of soluble protein is pH 2 to 4.

5. With fermentation mashes containing both soluble and insoluble protein, approximately 2 parts of sulfite waste liquor, calculated on the basis of its lignin content, are required to recover 5 parts of protein. The optimum pH range for this precipitation is 1.5 to 2.5.

6. Preliminary tests indicate that the recovered protein is suitable for feed purposes, when properly supplemented.

ACKNOWLEDGMENT

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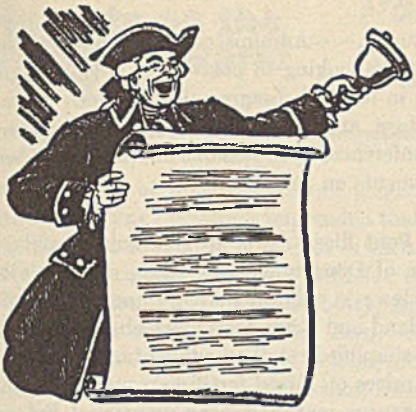

JULY'S HEADLINES

Events during the Month, of Interest to Chemists, Chemical Engineers, Executives

Reviewed by the Editors

¶ July 1. President Roosevelt signs bill outlining procedure for war contract termination.~~Germans in Normandy reported operating vehicles on producer gas because of acute oil shortage.

¶ July 2. Successful use of penicillin by Navy doctors to combat tuberculosis complication reported.~~Du Pont, at Government request, makes available to Russia details for building and operating neoprene plants.~~War Production Board adopts standard forms for terminating contracts, designed to cause minimum dislocation during transition.~~War Food Administration eliminates restrictions on fertilizers other than edible oilseed meals.

¶ July 3. WPB authorizes 7,000,000 pounds of aluminum during next 3 months for "experimental" manufacture of cans for specified purposes.

¶ July 4. Diamond Alkali begins construction of addition to chromate division at Painesville, Ohio.

¶ July 5. War Department regulation places rigid patent infringement risks on contractors.~~Senate subcommittee hits minerals control, and says haphazard handling of industry fomented disputes.~~President Roosevelt refuses to overrule Inter-Agency Committee on Deferments barring draft deferments for premedical students after July 1.~~American Potash & Chemical, under control of Alien Property Custodian since 1942, to be offered at public sale[1].

¶ July 6. Army and Navy attempt to block WPB plans to permit civilian use of aluminum and to prepare industry for reconversion.~~Domestic tung oil prices set by Office of Price Administration, effective July 11.~~Chemicals Bureau, WPB, to increase sharply small-order exemptions for urea- and melamine-aldehyde resins.~~Dow Chemical extends technical and distribution facilities of Fumigant Division to cover eastern territory.~~Spreckels Sugar to construct $200,000 unit for glutamic acid production.

¶ July 7. Open Facilities Section of WPB to survey plant facilities available for reconversion[2].~~Mercury and mercury-bearing ores freed of final wartime restrictions by lifting of import barriers.~~WPB tightens control on carbon black and eases aluminum paint regulations.

¶ July 10. War Mobilizer Byrnes orders WPB to hold up plans for plant reconversion.~~Sale of Government's war plants and surplus real estate will be handled jointly by Reconstruction Finance Corp. and Defense Plant Corp.~~Benzene, toluene, and xylene placed under price control at March, 1942, levels, OPA announces.~~Douglas Fir Plywood Assoc. reveals acquisition of sizable stands of timber to assure sources of raw material.~~Ansco Div., General Aniline & Film, acquires Binghamton, N. Y., land and 6 buildings from DPC.

¶ July 11. Compromise reached between WPB Chairman Nelson and armed services on reconverting industry to civilian production. War Mobilizer Byrnes reported making final decision. Dates set for four specific orders in reconversion program—July 15, 22, 29, and August 15.

¶ July 12. Director of Selective Service Hershey states that induction policy on 18 to 26, 26 to 30, and over-30 age groups will probably remain unchanged for the duration.

¶ July 13. Standard Oil (N. J.) sues Alien Property Custodian for recovery of patents costing $35,000,000 which were turned over to Government under protest[1].~~Petroleum Coordinator Ickes orders U. S. refiners to cut civilian gasoline specifications from 72 to 70 octane.~~Department of Justice postpones antitrust and price-fixing suits against 4 chemical manufacturers and 7 officials until end of war.~~WPB authorizes construction of allyl chloride and allyl alcohol plant at Houston, to be operated by Shell Chemical Div. of Union Oil Corp.

¶ July 14. Producers of cotton linters, beginning August 1, must set aside 80% of output that is acceptable for chemical use for delivery to Commodity Credit Corp. to meet military requirements for smokeless powder and rayon tire cord.~~Alien Property Custodian denies statement of Standard Oil (N. J.) president that custodian's office confiscated valuable property belonging to American citizens[1].~~Ethyl Corp. announces tetraethyllead production for military needs exceeds that used in motor fuel by Allied Nations in 1940.~~General Electric begins manufacture of chemical raw materials for expansion into postwar plastic field.

¶ July 15. WPB frees aluminum and magnesium for production of civilian goods for first time since early 1942.

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[1] *Chem. Eng. News*, 22, 1194 (July 25, 1944).
[2] *Ibid.*, 22, 1203 (July 25, 1944).

¶ July 16. U. S. Chamber of Commerce at midsummer meeting offers program for reconversion and economic development.∼∼WPB places further limitations on alkyd resins.∼∼S. B. Penick & Co. purchases firm of Compagnie Duval.∼∼Carbide & Carbon announces production of Navy requirements for polyethylene at 600% of plant's designed capacity[3].

¶ July 17. U. S. Rubber develops new flameproof rubber-coated cloth.∼∼Army Medical Corps reports only 3-day supply of vials available for penicillin and blood plasma, due to week-old strike of AFL workers at Vineland, N. J., plant of Kimball Glass Co.[4]∼∼Hercules Powder plans 60% expansion of ethylcellulose plant at Hopewell, Va.∼∼Waterproof match that strikes anywhere developed by Quartermaster Corps, Bureau of Standards, Diamond Match Co., Ohio Match Co., and Universal Match Corp.

¶ July 18. WPB removes most restrictions on use of glass containers for packing foods, drugs, and health supplies.∼∼U. S. will participate in late July and early August rubber parley with Great Britain and Netherlands in London.

¶ July 19. Federal Trade Commission announces investigation under Export Trade Act to determine whether Phosphate Export Assoc. (New York) and Florida Hard Rock Phosphate Export Assoc. (Savannah) have entered into illegal agreements and engaged in practices in restraint of trade.

¶ July 20. WPB cuts many chemical allocations as July list reveals severe shortages in phthalates, vitamins, and drugs.∼∼More alcohol "holidays" declared unlikely for several months by Walter G. Whitman, Chemicals Bureau, WPB, appearing before Industrial Alcohol Advisory Committee of WPB.

¶ July 21. Beaverbrook, Lord Privy Seal, arrives in Washington with British delegation for Anglo-American conference on international oil policies.∼∼Shell Oil will establish $599,000, 142-acre agricultural laboratory in Salida, Calif., first of its kind in the West.

¶ July 22. Forty-four nations approve International Monetary Fund, bank pacts, etc., as Bretton Woods, N. H., conference ends.

¶ July 24. Twentieth Century Fund announces plans for study of role postwar America can assume about trends toward monopoly in domestic business and cartels in international trade.∼∼Stauffer Chemical acquires Front Royal, Va., site for $500,000 carbon disulfide plant.∼∼Issuance of Directive 17, tightening control over high-octane gasoline and its components by Petroleum Administration for War and Aviation Petroleum Products Allocation Committee, announced by Deputy Petroleum Administrator Davies.

¶ July 25. In unprecedented move, Bradley Dewey resigns as Rubber Director, suggests liquidation of Rubber Director's Office, and reports output of synthetic now reaches rate of 836,000 tons annually.∼∼Administration's tentative plans for international talks looking to postwar commodity agreements strike snag in form of disagreement between Department of Agriculture and other federal departments.∼∼Anglo–U. S. oil conferences open sessions in Washington seeking postwar agreements on petroleum.

¶ July 26. Du Pont files answer to civil suit brought by Antitrust Division of Department of Justice, denying violation of antitrust laws in relations with Imperial Chemical Industries of England and other companies abroad.∼∼OPA issues nationwide simplified retail schedule of uniform dollars and cents ceiling prices on mixed fertilizers, superphosphate, potash, and nitrogenous materials.∼∼Commercial Solvents reports $0.539 per share for first half compared to $0.463 in same period of 1943.

¶ July 27. Standard Oil of Louisiana and Standard Oil of New Jersey will consolidate at end of 1944.∼∼Commerce Secretary Jesse Jones cautions prospective purchasers of government-financed war plants not to expect bargains but assures them of fair prices.∼∼United Nations agree on World Food Commission.∼∼Secondary offering of 850,000 shares of four Standard Oil stocks for account of John D. Rockefeller, Jr., declared a success.∼∼Fourth cut in price of Hycar synthetic rubber announced.∼∼Air Reduction's half-year sales total $48,744,595, but net earnings decline to $2,862,623.∼∼Freeport Sulphur reports $0.83 per share in June quarter as compared with $1.08 a year ago. First half of 1944 totals $1.58 per share.∼∼Truman Committee releases report on Canol Oil project.∼∼Union Carbide reports earnings for second quarter at $0.98 a share against $1.04 a year ago.

¶ July 28. Whisky distillers announce goal of 40,000,000 gallons during August "holiday".∼∼Newspaper reports indicate that Antitrust Division of Department of Justice is seeking help from the President to override opposition of military services against pressing antitrust suits at this time.∼∼Ben W. Lewis appointed chairman of Patents Contracts Committee in Office of Alien Property Custodian.

¶ July 29. WPB orders termination of production at Dow Chemical plant at Marysville, Mich., and reduction in output at 4 other magnesium plants; action trims over-all magnesium output to 7,517,000 pounds a month.∼∼Du Pont sales for first 6 months ($303,390,223), excluding federal plants, compare with $275,978,230 in same period of 1943; net also is higher.∼∼OPA will grant relief to chemical and drug manufacturers whose plant costs have advanced to point where many products cannot be sold at frozen March, 1942, prices.

¶ July 30. Office of War Information reports that disposal of surplus war property is expected to bring 50–100 billion dollars by end of war.∼∼Controls for placement of orders for maintenance, repair, and operating supplies by chemical producers liberalized by WPB under new revision of order P-89, which assigns rating for MRO materials for chemical industry.

¶ July 31. OPA appoints a Gum Naval Stores Industry Advisory Committee.∼∼General Aniline reports net sales for 6 months ended June 30 of $36,756,000, as compared with $28,668,000 for same period of 1943.

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[3] *Chem. Eng. News*, 22, 1216 (July 25, 1944).

[4] *Ibid.*, 22, 1195 (July 25, 1944).

"many billions of dollars worth of goods from the United States". It was Johnston's impression that long-term credits were involved to finance purchases in such amounts.

China presents another vast field for the trader, for her industrialization is a definite possibility, especially since plans specify China as one of the Big Four. Added to the machinery market that will develop from industrialization will be the need for such items as textiles, shoes, drugs, building materials, and farm implements. Little can be done in foreign trade without government assistance in stabilizing the money market, especially if there is a prolonged period, between the fall of Germany and the fall of Japan, when business credit and Lend-Lease supplies run concurrently. It would be risky for a company or group of bankers to extend credit to a country that might collapse financially when the shooting and Lend-Lease stop.

Some companies that formerly maintained offices in foreign countries exclusively for sales are now planning to use these branches also as export and raw material purchasing centers; they will count on the heavily increased flow of raw materials from foreign countries to maintain reasonable credit balances.

For our Government to be interested in international monetary matters is wise. Questions of postwar finance are so complex that they can be answered only by governments speaking for all their people. Further, although it appears that the United States may once again become "Uncle" to the world, the good that can come from a well-managed, realistic, world-wide finance is worth the risk. The catch for us and the rest of the world is making certain we do get a well-managed, realistic program.

Postwar Merchandising. That we will witness startling changes and, perhaps, innovations in merchandising of chemicals following the war seems inevitable. Few will deny that there is room for improvement in many directions. Emphasis now on production must, of necessity, shift to creation of new markets. The producer who is not well fortified with a top-flight market development department and staffed with keen-minded merchandisers will be left at the post.

Indicative of what one relatively small fertilizer manufacturer has done to improve his postwar outlook is the adoption of what he calls the Three-Point Protective Service. He is selling seed fumigants, fertilizers, insecticides, and fungicides. In a booklet entitled "Plant Food for Thought", prepared for the company's agents or dealers, the idea is summarized as follows: "While fertilizers are our business, we admit that fertilizers alone are not enough. A farmer must prepare his land, choose good seed, treat his seed, inoculate and finally protect his crop from pests. We, therefore, offer, in addition to our complete list of fertilizers, the following supplies and materials which we carry in our regular stock."

By doing just that, this fertilizer manufacturer is not only keeping his salesmen busy most of the year, but is also slowly developing them into a staff sufficiently technically informed to find a warm welcome from his dealers and their customers any time during the year.

Last-Minute Flashes
FROM THE EDITOR'S DESK

Some easement can now be looked for in huge Army backlogs which have been creating a squeeze on chemical suppliers. A major change in procurement policy calls for curtailment of so-called future goals. Previously Quartermaster Corps officers set up a program which would give them a certain quantity of material witnin a certain time. Now contracts are to be prepared restricting orders "to the practicable minimum both as to time and quantity".

★ Office of Price Administration is coming out of the clouds. A recent announcement on plans for the future reports that the agency considers the job of bringing commodities under control as completed. It will, therefore, concern itself less with ceilings from now on but will concentrate on enforcement, with emphasis on the treble-damage angle.

★ What's wrong with Sovprene? For years, Soviet Russia has had a chloroprene rubber; yet through the good offices of Rubber Director Dewey, it has prevailed upon Du Pont to furnish patents and technical assistance for the manufacture of neoprene. Du Pont has responded generously, furnished everything asked for, and invited Soviet technologists to come over and see how it is done at their Deepwater and Louisville neoprene plants.

★ Glycerol is no longer the problem child it was in the earlier stages of the war. This does not mean that stocks are accumulating rapidly, but the pressure has been relieved. It is still imperative that the fat salvage campaign be continued, but emphasis now is on maintenance of soap production rather than the by-product glycerol. At last the Office of War Information is giving the public the real facts; it had little choice, for housewives have questioned why they were being urged to save fats while lard and some meats are ration-free.

★ Although many items formerly in the extremely scarce category are showing improvement, this is far from true of containers generally. Nor is there much likelihood of appreciable improvement while pulp continues in short supply. With the munitions program now being increased and larger quantities of pulp being diverted to making containers for shells, the outlook for the next several months is a pessimistic one.

★ Industrial alcohol producers are getting a "half holiday" during August. This does not mean that the plants will close, but is merely another way of bringing to your attention that War Production Board has released 50% of their production from war purposes. It will go into beverage channels, swelling the alcohol produced during the "liquor holiday" by some 20,000,000 gallons. Do not look for another holiday until Germany is defeated. Then the pressure will be off the petroleum industry on aviation gasoline so that it can step up butadiene production and, in turn, relieve the pressure on alcohol production for butadiene.

★ Despite the fact that half the Italian mercury mines are now in "liberated" territory, the price is expected to continue around 100 dollars a flask, according to one authority. The market is looked upon as fairly well stabilized at the current level, with neither runaways nor slumps, notwithstanding the fact that the government stockpile includes a normal two-year supply.

★ WPB lists 15 of about 120 chemicals in a really stringent situation, led by acetone, benzene, and phthalate plasticizers. Two vitamins, A and B complex, are being sharply curtailed as far as civilian consumption is concerned.