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INDUSTRIAL AND ENGINEERING CHEMISTRY REPORTS ON THE CHEMICAL WORLD TODAY

Technology

IN INTRODUCING "I. & E. C. Reports on the Chemical World Today" as a monthly feature, a few words of explanation are perhaps necessary. I. & E. C. Editors are constantly circulating in chemical producing and chemical consuming industries, in Washington, in New York, in dozens of other cities and towns the length and breadth of the country; they are the recipients of considerable "behind-the-news" material unsuitable for publication as straight news items, yet of special value to I. & E. C. readers. The Report on the Chemical World Today is designed to provide a digested, interpretive, and chatty survey of the highlights of the news each month so that "he who runs may read" with profit and with a better understanding of the reasons underlying the moves currently being made on the chemical "chessboard".

Material will be grouped under such broad titles as Technology, Washington, Industry and Commerce, Markets, and Finance; but such classifications are open to change, additions, deletions, depending upon the trends in the news itself.

Future of Synthetic Rubber. This program and its vastness are too well known to our readers for extensive review here. The age-old argument of natural *vs.* synthetic has been given fresh impetus by the synthetic development, and the question of the day is, what about its permanence? An inkling in this direction is obtained from a recent speech of E. R. Weidlein at the dedication of the Goodyear Research Laboratory when he stated that government rubber plants had all been built with the appreciation that they would be obsolete in five years. Newsmen immediately assumed that he was talking about the end of war and the return of natural rubber production. Rather than that it is I. & E. C.'s opinion that he really meant the technical aspects of synthetic production and the fact that five years of experience in making this material would teach us so much that present "know-how" would be old fashioned.

This may or may not mean the abandonment of present equipment, depending entirely upon the extent of obsolescence and the participation of equipment builders in developing new processing techniques. In any event, the rubber program is not all cut and dried. Much is yet to be learned and countless improvements must be made. Whether natural is displaced or not, synthetic is due for changes.

To those who see only international discord and disaster for the economic status of the Far East if synthetic should, for all practical purposes, displace natural, the story of natural indigo should prove enlightening. Indeed it is not necessary to revert to past history beyond the story of the improvement in the position of those southern farmers who, in the last ten years, have heeded the advice of advocates of crop diversification as a profitable substitute for utter dependence upon cotton.

More Powerful Gasoline. It's well to be enthusiastic about our manufacture of high-octane gasoline, some of which is well over the standard of 100-octane. The job is not finished for one reason: The military wants to fly supplies to remote spots, and present fuel is not powerful enough to enable planes to go considerable distances with a military pay load. There must be intermediate spots for refueling, a serious drawback in military operations. One of the large oil companies has made a complete study of the subject which indicates that the huge flying ships of the future may be forced to land frequently.

Jerome Hunsaker of NABA predicts that land-based planes have a definite limit as to size. Factor is landing gear, as shock must be absorbed over a relatively small area of metal, and alloys are not yet in sight which will get around this bug. The flying boat, however, is something else again, for shock is taken along the entire hull.

Now that triptane is much in the news, it might be of interest to put on the record the story behind the title it now bears. In 1928 George Calingaert of Ethyl Corporation made all the heptanes so that their power outputs could be studied. Results were such that, when the need for a standard to test fuels of higher output than isooctane was beginning to be felt in 1934, the outstanding heptane of the 1928 experiments was considered. It was 2,2,3-trimethylbutane. To avoid the nomenclature confusion experienced with the octane standard, Calingaert decided to coin a name for the material and came up with the present name "triptane". The "tri" portion is easily understood, but the "ptane" ending is harder to trace. After considering the name "tribtane", it seemed more pleas-

(Continued on page 8)

An interpretative monthly digest for chemists, chemical engineers, and executives in the chemical producing and chemical consuming industries ing phonetically to Calingaert to use the present title. It's a dull story that has no sequel, but Calingaert is sorry to this day that he did not call the material "chazane", after his professor of organic chemistry, Chazanne, who, incidentally, was the first person to synthesize the compound.

Penicillin Magic. We have hopes that a successful synthesis will be developed soon. Until then the laborious method of growing mold in bottles will continue. The cost of the product varies with the telling, but the best figure obtained by I. & E. C. Editors is about $18,000 per pound. Even so, at this figure the cost of a dose is only $2.00.

It is anyone's guess where the research will go from here, and sometimes great doubt is thrown upon the speed with which its synthesis can be accomplished. Well to remember, though, is the record of the American chemists in synthesizing vitamin K, for only a few months elapsed from the first clue to its structure to the identification, and a few more months to its synthesis. One major difficulty in penicillin chemistry, however, is the fact that the material now being used is mostly impurities, and a lot of work needs to be done to obtain the pure active material, which will be quite unstable when it is obtained—meaning more trouble.

Most hopeful aspect of the penicillin picture now is the diverse points of view and talents of the companies authorized by WPB through special allocations to expand production of the drug. One would expect the old-line pharmaceutical houses to be in the list, but others listed too bring to the problem special skills in fermentation and biochemical techniques and essentially synthetic experience.

Obviously, the team is well assorted and entitled to our confidence of the earliest possible solution of the production problem. And problem it is; make no mistake about that! Laborious culture of the mold in multitudes of bottles is necessary at the present stage to ensure against contamination by ubiquitous wild molds and to provide the essential contact of medium and air required for mold growth. Partially successful experiments are reported with a not yet continuous process, analogous to the quick vinegar process. Enlarging units to a size comparable with other industrial fermenters involves changes in the surface-to-volume ratio which constitute a nice engineering problem not yet solved.

As we go to press a well-founded rumor is reported in Washington that Albert L. Elder, now head chemical advisor of WPB, will be appointed to the post of coordinator for penicillin. Thus a leaf has been taken from the book of experiences in the synthetic rubber program. Many pitfalls and delays are likely to be avoided by this action. As already mentioned, the penicillin program involves three distinct types of concerns—pharmaceutical houses, companies with special skills in fermentation and biochemical techniques, and outfits which have demonstrated over a period of many years outstanding technological knowledge of organic synthesis of complex chemicals. Elder as coordinator for penicillin can tie these efforts together much as did Jeffers on rubber, when the conflicting statements on sources of raw materials for butadiene production threatened to delay starting of the synthetic rubber program.

(Continued on page 10)

Chemical Output. Output of labor in the chemical field has always been high, but recent trends are toward a decrease in man-hour production. Reason for this trend, which the industry tries to avoid as a matter of efficiency, is found in the relative scarcity of automatic instruments and the influx of green and poorly educated help. The relations between labor and management have always been excellent and will probably continue so only as long as wages are above the average. It is plain that the chemical industry can no longer afford to lose trained personnel in plant or laboratory to the draft or to war industries (currently paying excessively high wages) without seriously hurting output. The industry must devise ways and means to hold present personnel—if necessary to fight to hold key men out of the draft. The machinery is available to do this, but it is industry's problem, not that of the local draft boards. One of the most disturbing features is found in recent figures of the Labor Department estimating that in the past summer, man power turnover reached 7.04 per 100 employed, which is higher than last year for the same period and is another high point on an upward trend.

Not "No Soap" but More Soap. Highly comforting is the recent action of the War Food Administration authorizing a 28 per cent increase in soap production, for it is a clear indication that the critical situation with respect to fats and oils is easing up. The increased production is being made possible by improved shipping conditions which permit importation of more foreign fats and oils, particularly from South American sources, and by the more general use of rosin and other domestic materials to replace a portion of customary soap oils and fats. Nevertheless, it is quite plain that the fat salvage campaign should continue to receive active support from industry and from the housewives of this country. Much still remains to be done in recovery of inedible fats in certain industrial fields, especially in meat-packing centers. Glycerol is still short and likely to continue so indefinitely.

Fortunately the drying oils situation also looks more encouraging. Domestic acreage and condition of the flaxseed crop are very favorable factors. However, any surplus of linseed offers distinct possibilities as a reserve food surplus, and it is doubtful that any full green light will be given until the picture on the other edible oils is more clearly defined.

Raw Material for Alcohol. The ultimate and highly desirable swing to greater use of molasses for production of industrial alcohol has been given definite impetus by the recent agreement reached between the Commodity Credit Corporation and the Cuban Sugar Stabilization Institute calling for minimum purchase of 4,000,000 short tons of the 1944 Cuban sugar crop. The new contract is the largest ever negotiated with Cuba. The deal emphasizes the improved shipping conditions prevailing on the Atlantic Coast and the desire of government officials to husband grain supplies for the inevitable feeding of Europe. The announced 1944 sugar purchase, however, does not mean much immediate swing away from grains, now largely wheat, for alcohol production. There is a time element, to be sure.

(Continued on page 12)

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

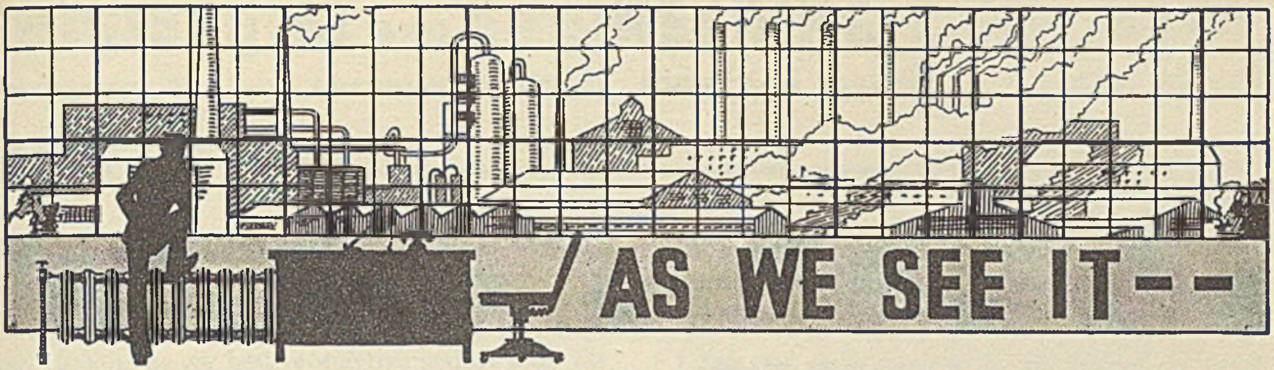
Industry and Commerce

Chemical Production Change. Production for war by the chemical industry is a source of great satisfaction to all connected with it. Recent reports emphasize the excellence of the production job and state that output is being reduced in some directions to prevent the accumulation of excessive stocks. Apparently, efficiency of operation of the chemical industry's plants which produce certain items has risen beyond expectation and has outstripped the ability of the armed forces to use such products. Output of TNT and smokeless powder, for example, has been thus reduced to fit needs, and other chemical products have from time to time been curtailed where certain programs have failed to keep pace.

New and highly efficient explosives have freed substantial stocks of ammonium nitrate, and production of this product is being allocated now to the fertilizer industry. Peculiar problems arise in utilizing ammonium nitrate in mixed fertilizers; its hygroscopic properties cause some trouble in storage and mixing, and its reputation as an explosive creates a certain fear in its handlers in a different industry. We are assured by members of the fertilizer industry that methods of handling ammonium nitrate (granulation and the addition of a diatomaceous earth and other materials) overcome its hygroscopic tendency which is, in fact, little more pronounced than that of several other fertilizer constituents. Fear of explosive danger from ammonium nitrate appears largely unfounded in view of its low sensitivity to ordinary shocks. Hence 1944 crops will get part of their nourishment from an ex-military explosive, which is also an excellent fertilizer.

Plywood and the Pacific Northwest. A trend that isn't particularly hard to predict is the future domination of plywood developments by the area known as the Pacific Northwest. The raw materials are all there. The great stands of Douglas fir can be made to yield at a rate of 6 billion board feet per year; the resin glues, necessary for the best bonding, can be made on the west coast, for phenol can come from petroleum. The immense power developments in that area almost ensure the new electronic method of setting plywood. The potential power to be obtained from the Columbia River project is staggering to the imagination. Boulder Dam and Niagara Falls are just about equal in the amount of electricity developed, but when the whole of the Columbia River project is complete, it will turn out about ten times as much as Boulder Dam. If Niagara Falls attracted a vast chemical industry because of its power, we can also expect the Northwest to be important in the future, more so because the airplane companies who, we think, will use great quantities of plywood in the postwar period, seem to be well entrenched there. And the power to make plywood, electrochemicals, and metals will be available in quantities begging to be used.

Low-Grade Iron Ore. The steel industry has, for over thirty years, been conducting experiments in using the low-grade iron ores that underlie the high-grade strata now being "exploited" by the steel companies. The reason behind this is to make sure that we have the know-how to use the stuff once the rich bodies are exhausted.



▶ Solvents in increasing variety and utility perform an ever widening service in modern industry and occupy places of growing importance in the output of chemical industry. Because this is a developing field, surveys of progress in it are particularly valuable in bringing together up-to-date information from diverse sources. Such a survey of available solvents and their properties features this issue.

▶ Coal Tar Solvents fall into three general classes, hydrocarbons, oxygen compounds, and nitrogen compounds, according to Cislak (page 1020), who provides descriptions of those most commonly used and of the wide range of their properties.

▶ Petroleum yields compounds of valuable solvent properties by separation of its constituents and by their chemical conversion. Toby (page 1044) discusses solvents obtained by physical means from crude oil and indicates their applications, present and future, as suggested by their properties.

▶ Pine Trees were sources of solvents in ancient times, but modern industrial developments have increased both the number and the usefulness of products derived from this common tree. Palmer (page 1023) describes both methods of production and the various products coming from this source.

▶ Nitroparaffins, comparative newcomers in the field, possess properties particularly adapting them to many solvent uses, according to Ericsson (page 1026).

▶ Alcohols are proving valuable in applications beyond those involving protective coatings and may indeed be considered primary tools in chemical processing. Park and Donlan (page 1030) give data on the industrially important solvent alcohols.

▶ Monochloropentanes yield a variety of important compounds containing no chlorine. Hunt (page 1048) describes amyl phenols, mercaptans, amines, and naphthalenes as produced in this way, as well as the processes used.

▶ Ketones owe their present wide use and availability to their strong solvent power for vinyl resins. Quarles (page 1033) presents the results of an extensive study of a variety of ketones as solvents for this purpose and gives the properties of the solutions formed.

▶ Wood Rosin, ordinarily of lower grade than gum rosin, can be substantially improved by refining with furfural, according to Humphrey (page 1062). Furfural possesses selective solvency for the dark colored constituents extracted from the wood and removes them from the extract.

▶ Film Coefficients of heat transfer useful in designing condensers and other equipment handling alcohols, esters, and ketons have been determined by Othmer and Berman (page 1068). Data on eighteen common solvents are given.

▶ Vapor Pressure Variations with temperature are cumbersome to calculate by the usual equations. Consequently, Miles (page 1052) has devised a slide rule to perform this arduous task quickly and simply.

▶ Scaling of Ferrous Alloys is often serious in their use of elevated temperatures required in many chemical processes. Day and Smith (page 1098) have devised an apparatus for measuring this factor for a number of specimens simultaneously and present results obtained with it in comparing steels of different compositions.

▶ Fouling of domestic oil burner systems through instability of furnace oils under conditions of normal storage has been investigated by Heisberger, Cowles, and Zieber (page 1104). A test method is described and results obtained with it are correlated with practice. Both refined and unrefined oils have been investigated.

▶ Builders added to laundry soaps affect both the detergency of the soap solution and whiteness retention. Vaughn and Vittone (page 1094) describe results obtained in tests of these factors with a variety of common builders.

▶ Viscosities of solutions of n-paraffins in n-hexane have been shown by Kemp and Peters (page 1108) to follow Staudinger's relation of specific viscosity to molecular weight of the solute.

▶ Asphalts in most uses are valuable for their surface properties rather than those in a mass, according to Knowles and McCoy (page 1118) who have devised a method of determining surface consistency of asphalt in thin layers.

▶ TNT Manufacture, now practiced on a huge scale, creates special problems in waste disposal since effluent from the plant contains both acid and organic matter. Schott, Ruchhoft, and Megregian (page 1122) present an exploratory report of this problem and the behavior of the waste under various sewage treatments.

▶ Lignin Esters with a number of mono- and dibasic aliphatic acids have been prepared by Lewis and co-workers (page 1113). A number of them appear likely to have important uses.

▶ Brandy is commonly treated with charcoal to improve its quality by removing objectionable constituents. Tolbert and Amerine (page 1078) have studied the effects of a variety of charcoals in removing nonethyl alcohol constituents.

▶ Cellulose has been oxidized with periodic acid by Goldfinger, Mark, and Siggia (page 1083) in an effort to elucidate its structure. The kinetics of the reaction suggests the presence of two forms of cellulose of unequal rates of oxidation.

▶ Phosphate Rock in its crude form is unsatisfactory as a source of calcium and phosphorus for animal feeding, presumably because of its fluorine content. Fraser and his colleagues (page 1087) have tested fused phosphate and calcium metaphosphate in rat nutrition.

DHKilleffer

INDUSTRIAL AND ENGINEERING CHEMISTRY

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EDITORIALS

Let's Look Southward

CHEMICAL manufacturers are already looking southward toward the future. Latin America's potentialities as our best prospective market after the war awaken new interest as devastation spreads further through Europe. Already American chemical companies base their economic planning on a southern exposure. That has happened before as one economic factor or some series of thoughtless manifestations of a crude Yankee jingoism has nullified our best efforts. Now the scene seems set with an atmosphere unprecedentedly favorable to us. Lend-Lease has filled many of the gaps left by the withdrawal of European suppliers from the field. Our diplomacy of the good neighbor has opened the door to the cultivation of solid friendship and one can almost make out a "welcome" on the South American door mat. Let us be ever so sure that these advantages are not thoughtlessly wasted. Only the best men of the most mature judgment should be allowed to represent American industry in the cultivation of these vital commercial contacts.

Cooperate with Draft Boards

ONE of the serious difficulties encountered in holding chemists and chemical engineers in the production army, where they can be of the greatest practical value to the war effort, involves more or less complicated rules set up by certain organizations, mostly large ones, as to how deferments can be requested and how appeals can be made. A few organizations still have rules against asking for deferments or against making appeals. Others require that all such requests and appeals clear through one central office, usually in the hands of individuals who have only second-hand knowledge as to the needs for chemists and chemical engineers and the requirements which such men have to meet in order to do their work properly.

The important thing to remember is that the local board, or the appeal board, or the state Selective Service headquarters, shall be provided with facts in each individual case under consideration or review. In the final analysis these facts should be given by someone who knows them at first hand and who can properly swear to them as facts. In many instances it is very helpful for the individual who knows the most about a technically trained man in question to write a personal letter to the local board, the appeal board, or the state headquarters, stating that he is giving full particulars in the case to supplement any other information which they receive. The letter should be marked "personal" and it should close somewhat as follows:

> I, John Doe, am in charge of the unit in which the above registrant is working and do solemnly swear that the above facts are true.

This should, of course, be accompanied by the usual affidavit form for a notary public. Local boards naturally like to be supplied with information which they can regard as first hand. They are getting more and more suspicious of forms executed and sworn to by individuals who are far removed from the registrant.

Modified "No" to Civilians

ALLOCATION of chemical production, never a simple task, has taken on new complexities with the development of the war program. Whereas a year ago the simple answer to civilian demands for this or that product was a more or less blunt reply that no supplies were available, today many factors contribute to a general easing of the entire situation. Perhaps the most important of these is the success of production programs which quite generally have given a yield beyond expectation. In part this result comes from improvements in the efficiencies of processes and in part from safety factors cautiously included in original estimates and designs which have proved unnecessary. Only less significant has been the progressive change from the materials and tactics of World War I to others fitting the needs of the new air-borne and amphibious war of today. The combined effect of these and other factors has been to relax the stringency of many shortages. While surpluses have certainly not yet been created, numerous important civilian needs are being met to an increasing extent by the thoughtful exercise of considered judgment in making allocations. Fertilizer manufacturers and mixers find the burden of their expanding program considerably eased by more liberal allowances of sulfuric acid and ammonia. Increasing demands for certain plastics have required careful selection of civilian requirements to be met on the basis of their importance. Thus more liberal allotments of cellulose acetate, cellulose acetate butyrate, phenolic laminating varnishes, protective coating resins, certain phthalic alkyds, and various other synthetic resins have been made to essential civilian uses. Some of these remain in the class of substitutes for metals, as in certain plumbing parts, and some are still restricted to fractions of the requests. Yet the entire picture is perceptibly brightening. Much arduous labor of both production and planning remains to be done before the civilian outlook can be considered clear. It is as if we had passed from the pitch blackness of a cloudy night to the bright starlight of a radiantly clear sky. For that relief we should be duly thankful to the unraveling of intricate chemical and commercial relationships through the painstaking efforts of the Chemicals Division of WPB.

The Gift Horse's Mouth

SOME forty thousand United State patents and applications, formerly owned by nationals of enemy and enemy-occupied countries, have been placed at the disposal of American industry by the Alien Property Custodian. The cost to those who wish to utilize these patents is negligible, having lately been reduced to a flat fifteen dollars per patent in lieu of all royalty. Copies of applications for patents may be had without restriction at 10 cents each. The subject matter covered is extremely broad and its usefulness substantial. But neither industries nor individuals appear eager to seek licenses, much to the disappointment of workers in the Office of Alien Property Custodian who have labored to collect and collate this valuable material.

The reasons for this reluctance are not difficult to understand. Although the Alien Property Custodian makes a great point of the restrictions imposed on American industry by the foreign owners of these patents in the past, it is obvious that his strictures fall upon deaf ears. Conditions now are clearly different from those of the corresponding period in World War I. Our industry, particularly our chemical industry, has a roundness conspicuously lacking a quarter century ago. Industry is unaware of onerous proscriptions of its activities by foreign holders of patents. Indeed, the extraordinary speed with which we reached huge production of synthetic toluene, synthetic rubber, and aviation gasoline (touted as alien developments) when necessity required, clearly denies restrictions in these fields. Obviously, hamstringing of our industry by patents is a chimera.

Through its peculiar nature the patent grant acquires value from the right of the patentee to prevent others from practicing his invention. This is a restrictive and not a permissive value. Thus, a license from the Custodian confers no permission on the licensee, but rather relieves him of one form of restriction. That, quite naturally, suggests to the prospective licensee that he consider carefully whether avoiding the restrictive rights of the vested patents creates a field broad enough for him to operate freely. American industry already possesses broad patent rights in the fields covered by the vested patents which any newcomer must consider carefully before depending on licenses from the Custodian alone for his protection.

The present form of license offered by the Custodian is a simple and generally innocuous document, free from objections to its earlier forms, as we have previously noted. But it still contains a perfectly proper provision which, by interpretation, has become alarming. No one would question the right of the Government to cancel the granted license when the national interest requires, were it not for the repeated emphasis placed by the Office of Alien Property Custodian on "patents will be at the peace table". While the license is granted for the life of the patent, this gratuitous injection of peace negotiations into the matter by authorized spokesmen suggests that diplomatic maneuvering at the conclusion of this war may create a national interest to cancel all such licenses. Should that prove to be the case, a license useful now might easily become a serious liability to the licensee if and when the patents themselves revert to their former owners at the peace settlement.

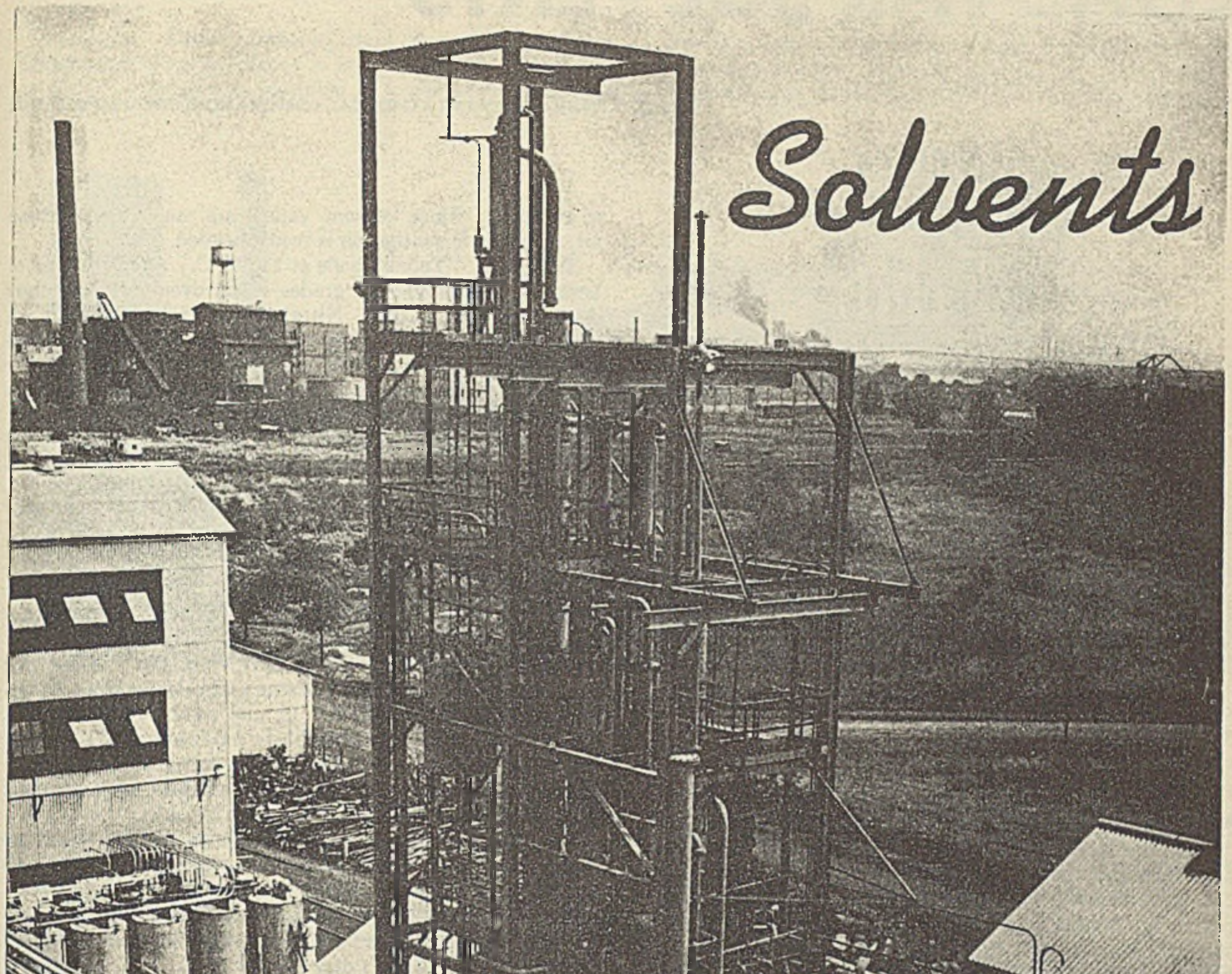
Obviously, then, industry has reason to look carefully into the wisdom of licensing in each particular case. While the vast labors of the Office of Alien Property Custodian in presenting these patents to industry are unquestionably valuable, one must in prudence examine the gift horse's mouth.

Alcohol

THE recent action of WPB in banning a two-week holiday for whisky distillers to replenish supplies of beverage alcohol was dictated by several factors. First and foremost was the present over-capacity of the synthetic rubber plants. As Rubber Director Dewey indicated at the Pittsburgh meeting of the AMERICAN CHEMICAL SOCIETY, most of the plants will produce about 20 per cent more than originally expected. New demand by the rubber office for 40,000,000 more gallons of alcohol is just about 20 per cent of the original alcohol butadiene-rubber plan. This over-capacity will enable the petroleum plants to cut down their production of butadiene and transfer the hydrocarbons to the making of larger quantities of aviation-grade gasoline, of utmost importance now that the timetable of operations against the Axis has been pushed ahead by the exit of Mussolini and the entrance of Italy as an ally of the United Nations.

Another reason suspected by the editors is that the political dynamite of allowing whisky to be made in time of war, with the uncertainty of how much food will be needed for Europe, and the hocus-pocus about the corn and wheat surpluses or shortages make for a policy of building up surpluses now, to prevent reverberations later. By using all our present facilities, we will be in a better position later to switch food to Europe should it be necessary.

Solvents



The papers on pages 1020 to 1077 were presented before the Division of Industrial and Engineering Chemistry at the 105th Meeting of the AMERICAN CHEMICAL SOCIETY, Detroit, Mich.

The crude reaction product obtained on vapor-phase nitration of propane is fractionated in this tower to yield the four nitroparaffins (page 1026).

COAL TAR SOLVENTS

F. E. Cislak, REILLY TAR & CHEMICAL CORPORATION, INDIANAPOLIS, IND.

Coal tar solvents are composed of neutral, acidic, and basic cyclic compounds characterized by the presence of a six-membered ring in the molecule. They are all soluble in most of the common organic solvents. Some are insoluble in water; others are miscible with water in all proportions. They may conveniently be grouped into three classes—hydrocarbons, oxygen-containing compounds, and nitrogen-containing compounds.

TO MANY, the term "coal tar solvents" calls to mind benzene, toluene, and xylene. While these are important, there are other coal tar materials which, as their properties are becoming better appreciated, are increasing in importance. In this paper attention will be called to some of the not-so-well-known coal tar solvents. A broader meaning of the term "coal tar solvents" will be used. It will include not only those materials obtainable as such from coal tar but also solvents which are prepared from coal tar materials by simple chemical reactions, such as hydrogenation or alkylation.

HYDROCARBONS

The hydrocarbon class of coal tar solvents includes benzene, cyclohexane, toluene, methylcyclohexane, xylenes, isopropylbenzene, Decalin, Tetralin, methylnaphthalenes, dimethylnaphthalenes, amylnaphthalenes, and mixtures of these compounds. They include solvents having boiling points as low as 80° C. and those distilling well above 300° C.

BENZENE. Commercially called "benzol", it has a boiling point of 80.1° C. and a melting point of 5.4° C. (it should be protected from freezing). Commercial grades of benzene distill over varying ranges, depending upon the purity required; e. g., nitration pure benzol has a 1° C. boiling range, industrial pure benzol has a 2° C. boiling range, and industrial 90 per cent benzol distills over a range between 78.2° and 120° C. with at least 90 per cent distilling under 100° C.

Benzene is insoluble in water but soluble in most common organic solvents. It is used as a diluent in quick-drying lacquers, in paint and varnish removers, in rubber cements, etc.

The vapors of benzene are very toxic. Even small amounts of the vapors breathed over a period deplete the blood in both white and red corpuscles and greatly lower the resistance to infection. It should be used only when sufficient ventilation is available. Since benzene vapors are much heavier than air, down-draft ventilation is recommended.

TOLUENE. "Toluol" boils at 110.5° C. As in the case of benzene, the commercial grades distill over varying ranges depending upon purity. Nitration pure toluol has a 1° C. boiling range, including the temperature 110.6° C.; industrial pure toluol has a 2° C. boiling range.

Toluene is insoluble in water but is soluble in all common organic solvents. Because solutions of nitrocellulose and of cellulose esters can be diluted with large amounts of toluene without causing precipitation, toluene finds extensive use as a diluent for nitrocellulose or cellulose ester lacquers. Toluene is a solvent for many natural resins, such as dammar, copal ester, and mastic, but it does not dissolve shellac or copals. It is also a good solvent for most synthetic resins and an excellent solvent for chlorinated rubber.

While toluene possesses narcotic properties, it is not so dangerously toxic as is benzene.

CYCLOHEXANE AND METHYLCYCLOHEXANE. These are hydrogenation products of benzene and toluene, respectively. Cyclohexane boils at 80–81° C. and methylcyclohexane at 100–103° C. They are insoluble in water but soluble in most organic solvents. They are used as solvents for oils, fats, waxes, crude rubber, bitumens, nitrocellulose, ethylcellulose, and other resins.

XYLENES. Commonly referred to as xylols, these are commercially available in several different grades; some have a distillation range of only 3° C., and others distill over a range of more than 20° C. The purer grades of xylol consist essentially of mixtures of the three isomeric xylenes, *o*-xylene boiling at 144° C., *m*-xylene at 139.3° C., and *p*-xylene at 138.5° C. The most common commercial grades of xylenes are the 5° xylol which distills entirely between 137° and 143° C. and the 10° xylol which distills entirely between 135° and 145° C.

The xylenes are insoluble in water but are soluble in most of the organic solvents. While the xylenes are not solvents for nitrocellulose, they can be used as diluents for the slower-drying nitrocellulose lacquers. They are solvents for ester gum, copal esters, dammar, and mastic, but do not dissolve copals or shellac.

The higher flash point (80° F.) of the xylenes makes them of special interest in certain applications.

SOLVENT NAPHTHAS. The coal tar solvent naphthas are mixtures of higher-boiling aromatic hydrocarbons. They are available in several grades, of which two are most common: light solvent naphtha, distilling between 130° and 160° C., and high-flash solvent naphtha, distilling between 150° and 200° C.

The coal tar solvent naphthas are insoluble in water and are not solvents for cellulose esters, copals, or shellac. They are excellent solvents for ester gum, copal esters, dammar, mastic, pitches, asphalts, chlorinated rubber, alkyd resins, phenolic varnish resins, etc.

Raw wool scouring operations, bronzing liquids, baking enamels, metal protective coatings, marine finishes, soap manufacture, dry cleaning solvents, and thinner for insulating varnishes and finishes are a few of the applications of coal tar solvent naphthas.

The light solvent naphthas have flash points about 75–85° F.; the high-flash naphthas have flash points not lower than 95° F.

Tetralin. Tetrahydronaphthalene is made by the hydrogenation of naphthalene; it boils at 200° C. and freezes at 25° C. Tetralin is insoluble in water but mixes with practically all organic solvents. It dissolves a wide range of oils, gums, resins, and waxes. It is used in detergents and soaps for textile purposes. Tetralin absorbs oxygen from the air, hence it can be used in the formulation of rapid-drying varnishes.

Decalin. Decahydronaphthalene boils over a range of 186–196° C. The solvent properties are similar to those of Tetralin.

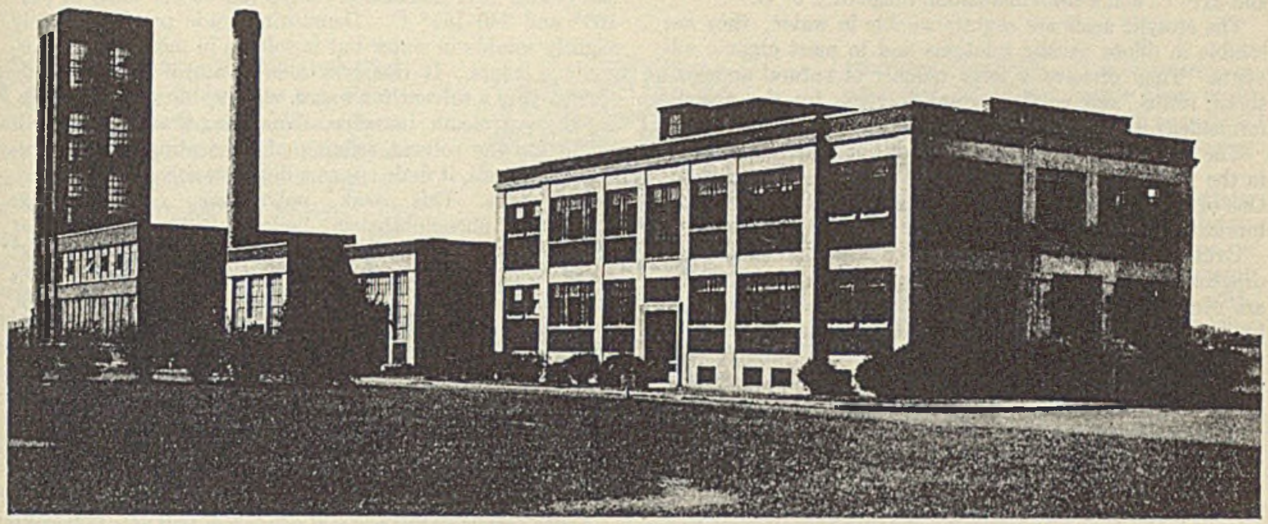
Methylnaphthalene. This mixture of the two isomeric methylnaphthalenes, alpha- and beta-methylnaphthalene, has a distillation range of 239.5° to 242° C. It is insoluble in water but is soluble in all common organic solvents including alcohols, ethers, ketones, esters, etc. It is a solvent for a large number of oils, gums, waxes, and pitches.

The high boiling point of methylnaphthalene and its extreme stability at the boiling point make it suitable for use in formulation of certain types of printing inks, baking enamels, high-temperature solvent extractions, and in refining operations. Its high solvency properties suggest its use in detergents and soaps for the textile trade. It may also be used as a rubber softener and tackifier for both natural and synthetic rubbers.

Dimethylnaphthalene. This mixture of the isomeric dimethylnaphthalenes has a distillation range of 255° to 270° C. It is a solvent for a wide variety of natural and artificial resins, pitches, gums, oils, and waxes. It is soluble in all common organic solvents, such as alcohols, esters, ketones, and aliphatic and aromatic hydrocarbons, but is insoluble in water.

The properties of dimethylnaphthalene—i. e., its high boiling point, stability at the boiling point, and high solvency—suggest its use in formulation of stoving lacquers, printing inks, as a rubber softener, as a semiplasticizer, in detergents, and in wool degreasing. Its toxicity to fungi and insects makes dimethylnaphthalene a desirable constituent in the formulation of insecticides and fungicides. The ease with which it forms stable oil-in-water emulsions makes it a valuable ingredient of emulsion-type cleaners.

Amylnaphthalenes. Made by the alkylation of naphthalene, these are mixtures of monoamyl-, diamyl-, and polyamylnaphthalenes. These high-boiling mixtures have distillation ranges varying from 279–320° C. for the monoamyl- to 353–393° C. for the polyamylnaphthalenes. Because of their high boiling points the amyl naphthalenes are more useful as plasticizers than as ordinary solvents. They are used with rubber resins, such as Pliolite, with vinyl resins, etc.



Research Laboratory of Reilly Tar & Chemical Corporation

OXYGEN-CONTAINING COMPOUNDS

Phenols, cresols, their hydrogenation products, and xylenols are representative of the oxygen-containing class of coal tar solvents. Phenol, cresol, and xylenols are tar acids; their hydrogenation products, cyclohexanol, methylcyclohexanol, cyclohexanone, and methylcyclohexanone, are neutral compounds.

Phenol. This solid melts at 40° and distills at 182° C. It is available in several commercial grades. The 40° and the 39° C. freezing point materials are the purer commercial forms. The 90–92 per cent and the 82–84 per cent grades contain varying amounts of ortho-, meta-, and para-cresol.

The addition of 10 per cent water to phenol converts it into a liquid at room temperature; it also dissolves in about 15 parts of water at room temperature. At elevated temperatures phenol is soluble in water in all proportions; it is soluble in all proportions in dilute caustic solutions. Phenol is soluble in all common organic solvents. It is a solvent for copals, copal ester, mastic, and shellac. It also dissolves many synthetic resins, even the thermosetting phenol-formaldehyde type. It is a solvent for cellulose esters and ethers and for ethylcellulose. One of the large solvent uses of phenol is in the solvent refining of lubricating oil.

Phenol is used as a solvent recovery agent, in mercerizing cotton, in degumming silk, etc.

Cresols. There are three isomeric cresols: *o*-cresol boiling at 190.8°, *m*-cresol at 202.8°, and *p*-cresol at 202.1° C. Each of them is available as a pure compound. For solvent purposes, however, they are used as liquid mixtures called "cresylic acids" which, in addition to the three cresols, contain varying amounts of phenol and xylenols; the composition varies with the distillation range of the particular cresylic acid. Many different grades of cresylic acid are available, but there are three common ones. For cresylic acid No. 1, the point at which 50 per cent distills over is between 204° and 206° C.; cresylic acid No. 2 has a 50 per cent distillation point between 206° and 210° C.; and cresylic acid No. 3 has a 50 per cent distillation point between 210° and 211° C. and a total distillation range over 9° C.

The cresylic acids are slightly soluble in water; they are soluble in dilute caustic solutions and in most organic solvents. They dissolve a large number of natural and synthetic resins, and are important solvents for the phenol-formaldehyde resin varnishes used for wire coating.

The cresylic acids are used as solvent recovery agents and in the formulation of wetting agents for mercerizing cotton. One of the important solvents used in the solvent refining of lubricating oils is cresylic acid.

CYCLOHEXANOL AND METHYLCYCLOHEXANOL. These hydrogenation products of phenol and cresols, respectively, are cyclic alcohols which are only slightly soluble in water but are miscible in all proportions with organic solvents, fats, and oils. Cyclohexanol distills at about 160° C., and methylcyclohexanol over a range of 170–190° C. The properties of these compounds are so similar that they are used interchangeably in most cases.

They are characterized by their ability to act as solubilizers and homogenizers. They are used as components of textile soaps, in lacquer formulas, enamels, etc.

XYLENOLS. These liquid mixtures consist essentially of the isomeric xylenols. Several grades are available commercially, distilling at about 215° and 220° C.

The xylenols are only slightly soluble in water; they are soluble in dilute alkali solutions and in most common organic solvents. They are solvents for many resins, both synthetic and natural, for waxes, and oils.

NITROGEN-CONTAINING COMPOUNDS

In the nitrogen class of coal tar solvents are pyridine, picolines, lutidines, hexylpyridines, aniline, quinoline, and higher coal tar bases. They are basic compounds which react with acids to form water-soluble salts.

PYRIDINE. This coal tar base boils at 115.5° C. The commercial 97.5 per cent pyridine has a 2° C. distillation range. It forms a constant-boiling mixture with water, distilling at 93° C.

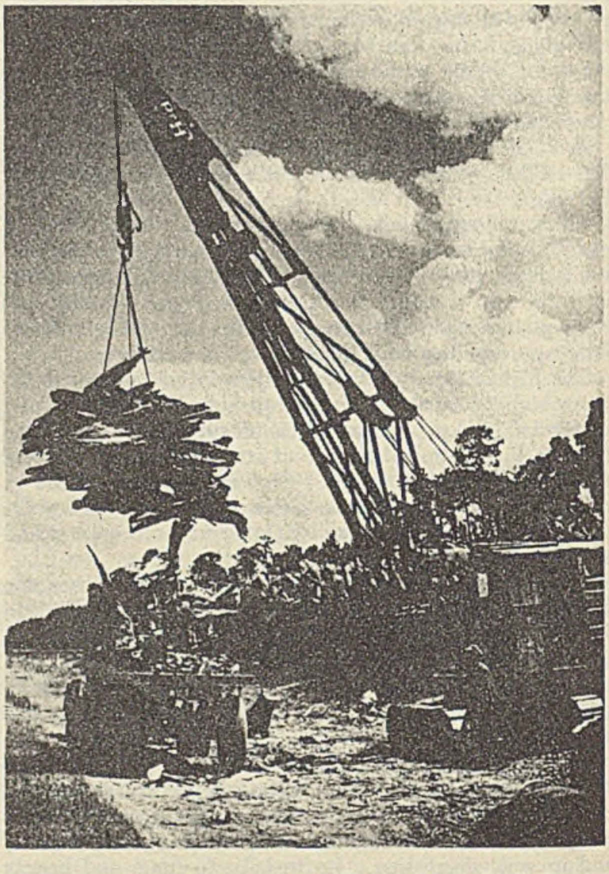
Pyridine is soluble in water in all proportions. Many substances are more soluble in pyridine-water mixtures than in either liquid alone; there are a few substances which are less soluble in the pyridine-water mixture than in either liquid. Pyridine is an important coupling agent for water-like solvents and oils. Most of the common organic solvents dissolve pyridine. Pyridine dissolves most natural and synthetic resins, and swells rubber.

Because of its ability to dissolve rayon, pyridine is used to produce pattern effects in woven goods by removing rayon threads from rayon-cotton fabrics. Pyridine is a solvent for many inorganic salts; it is used as a solvent in the manufacture of anhydrous inorganic salts. Because of its remarkable stability toward oxidizing agents, pyridine is an excellent solvent medium for oxidation reactions. It can also be used as a solvent in the reduction of nitro compounds, being particularly advantageous when the nitro compound is sparingly soluble in alcohol.

α-PICOLINE. 2-Methylpyridine boils at 129.3° C. It forms a constant-boiling mixture with water which boils at about 93° C. It is soluble in water in all proportions. The α-picoline-water mixtures possess solvent properties quite similar to the pyridine-water mixtures. The solvent properties of α-picoline are similar to those of pyridine; it is miscible with most common organic solvents, and dissolves a wide variety of resins, waxes, and oils. It differs from pyridine in that it is not stable toward oxidizing agents and hence cannot be used as a solvent for oxidation reactions.

DENATURING-GRADE PYRIDINE. This is essentially a mixture of picolines and lutidines; the two common commercial grades have distillation ranges (50–90 per cent) of 140–160° and 140–165° C. Denaturing-grade pyridine is only slightly soluble in water but is soluble in most common organic solvents. It dissolves many natural and synthetic resins; it is a solvent for waxes, rubber, bitumens, and oils. In the petroleum industry, denaturing-grade pyridine is useful for the solvent refining of lubricating oils. In organic synthesis, it finds use as a directive solvent.

QUINOLINE. This weak, polynuclear, coal tar base (neutral to phenolphthalein) boils at 238° and freezes at −22.6° C. It is moderately soluble in cold water but readily soluble in hot water. It is soluble in dilute aqueous acid solutions and is miscible in all proportions with alcohol, ether, acetone, and carbon disulfide, and is soluble in most common organic solvents. Quinoline dissolves many natural and synthetic resins. It is an important directive solvent in organic synthesis. It dissolves sulfur, phosphorus, arsenic trioxide, and many inorganic salts, as well as hydrogen peroxide.



Courtesy, Hercules Powder Company

Pine Stump Wood Being Hauled to the Mill for Solvent Extraction

SOLVENTS FROM PINE

R. C. Palmer, NEWPORT INDUSTRIES, INC., PENSACOLA, FLA.

PRODUCTS from the pine tree rival those from petroleum as the oldest solvents known to the arts. The ancient Egyptians and even earlier civilizations undoubtedly employed crude turpentine or oleoresin as we know it today. The use of this material as a vehicle for the natural earth colors in decorating and perhaps as a binder for various constructional purposes constitute the early counterparts for the use of terpenes and related products in the modern paint, varnish, and plastic industries.

METHODS OF PRODUCTION

Four different processes are used in this country in producing solvents from the pine tree. Until recently, the method that was first in volume was the time-honored collection of oleoresin from the living tree. The gum is gathered periodically during the spring, summer, and early fall months from containers fastened onto the tree. Until recent years the resin was refined in equipment near the forest. The apparatus was a simple still, heated by direct fire to vaporize the oil and connected to a cooling worm and receiver to condense and collect the turpentine. This method has been replaced lately to an appreciable extent by more modern engineering methods in large central refineries. Here the oleoresin is first treated in various ways to remove foreign matter, and the volatile oil is then separated from the resinous portion by steam and fractional distillation.

Another method, now first in the quantity produced, is the solvent extraction of the wood. This industry had its beginning about thirty years ago; it was based largely on the premise, since proved erroneous, that the living tree would soon cease to be a commercial source of terpenes. It was recognized that the enormous tonnage of pine stumps and other waste from lumbering operations contained a potentially great quantity of turpentine and rosin. This industry has become well established within the last fifteen years. The method of extracting the products was necessarily based on a central chemical plant and an efficient process, both as to engineering and chemistry, in order to survive. It was therefore natural that, after fundamental problems were solved, attention was turned to developing many secondary solvents and chemicals. It is of interest to note that in the last decade alone some 10,000,000 tons of forest waste have been reclaimed by a dozen or more plants using the extraction process.

For the production of primary materials from the pine tree, useful as solvents, four important methods are employed. The collection of oleoresin from the living tree still produces a substantial quantity of turpentine oil; this system is now adopting modern methods in large central refineries. First in volume of initial products is the solvent extraction of dead wood; this branch has grown rapidly in recent years and made progress in developing derivatives which have important chemical uses. A large potential source of terpenes is the pine pulp and paper industry; a large quantity of fatty acids and rosin and other by-products should be available from this origin. The destructive distillation of pine wood is an old process and is the fourth important method of yielding solvents as well as chemical by-products. Alpha-pinene is the only substance common to the four methods and is the starting chemical for many possible derivatives.

The fundamental process of extraction is a two-stage operation. After being ground into small chips, the stumps or other dead wood are placed in metal vessels or retorts and extracted with a petroleum or coal tar solvent. The terpene oils dissolved in the solvent are then separated by fractional distillation; the solvent is re-used and the terpenes are further refined into turpentine and other terpenes which occur only in old wood. The nonvolatile residue from the extract is the rosin. The second phase of the operation is pressure steaming of the chips for additional solvent recovery for reuse. The chips are used principally as fuel, although at one operation extracted wood is conveyed to an adjacent plant for conversion to a building and insulating board.

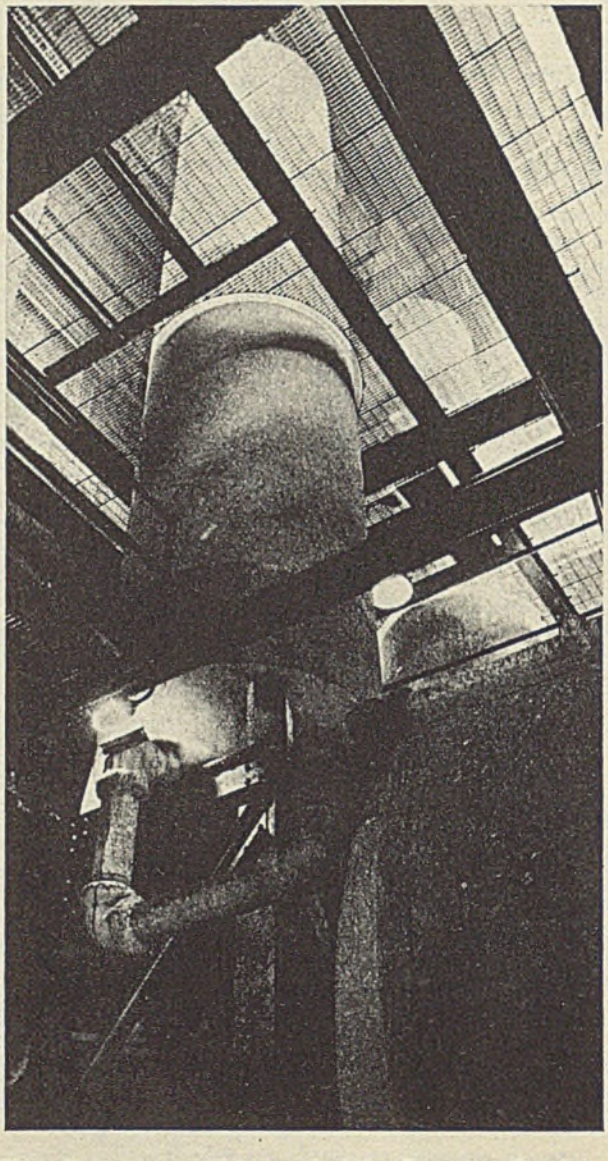
Sulfate pulp cooking of southern pine has long been considered a potential source of terpenes and related by-products, and ranks third in volume of production. The recovery of these materials from the paper industry in the southern Atlantic and Gulf Coast states has not kept pace with the expansion in the kraft paper production, but in the last three or four years there has been a notable increase in the separation of these by-products. The primary process involves the condensation of volatile terpene oils in the blowoff of the digesters, and the separation of crude fatty acid oils by gravity after acidification of the alkaline black liquors. A number of methods have been devised for refining these materials since they are not very useful in the crude state. Sulfate turpentine, as the terpene oil from this process is known commercially, requires considerably more than simple refining to free it completely of the characteristic odor associated with the sulfate pulping process. This has been largely solved, however, and the best quality sulfate turpentine is now being used for most purposes formerly employing only fresh natural turpentine or the highest quality steam-distilled wood turpentine.

The fourth method is the oldest of all—the destructive distillation industry. The manufacture of pine tar from fat pine wood for use in treating cordage and in caulking wooden ships was one of the earliest industries established in continental America, and the present naval stores industry acquired its name from these uses. The modern version of the process consists in heating the pine wood, both stumps and other forest waste, in closed retorts at a sufficiently high temperature to bring about destructive distillation. The more volatile terpene oils distill off without much change, but the rosin and wood fiber are largely broken down by the process.

TURPENTINE

Each of these major sources yields some products distinctive to the process. The most widely distributed of all the terpenes, α-pinene, is the only solvent common to the four methods and is the principal constituent of oil of turpentine recovered from the living tree. α-Pinene is also the predominating constituent of the oils obtained in the extraction process. β-Pinene, the other bicyclic terpene which composes between 30 and 35 per cent of natural turpentine oil, is not present in wood turpentine, but the latter contains a number of other terpenes not found in the natural oil. Chemically the pulp by-product turpentine contains both α- and β-pinene in about the same ratio as the oil obtained from gum oleoresin.

The use of turpentine as a solvent in the paint and varnish industry is so common that it is generally believed to be the principal use. Statistical information published by the U. S. Department of Agriculture does not confirm this idea. It was probably true, however, at the beginning of the last decade, but the use of turpentine as a thinner by paint and varnish manufacturers has been largely replaced by petroleum solvents. Recent data compiled by the Government indicates that at present not more than 30 to 40 per cent of the total turpentine produced is consumed in this country as a solvent in the manufacture of paint, varnish, and lacquer. Fortunately, the true worth of this oil in painting and decorating is still recognized and substantial quantities are still being used for this purpose; this use will no doubt continue for many years. Industrial, furniture, floor, and shoe polishes and creams consume a good deal of turpentine, which are also solvent uses.



Thirty-Plate Vacuum Columns Used for Separating Petroleum Solvent, Pinene, Dipentene, and Pine Oil

Chemical Uses. The decline in the use of this oil in the manufacture of shelf goods and industrial paints has led to the search for and discovery of other uses. Many of these new applications, however, like coal tar and many petroleum solvents, are more properly considered chemical as well as solvent uses. For instance, the large chemical use for α-pinene as the raw material for the synthesis of camphor is indirectly a solvent application, since the camphor is largely employed as a plasticizing solvent for nitrocellulose in the manufacture of celluloid and many related products. The entire requirements of camphor in this country, including the expanded war purposes as well as other uses, are being supplied by synthetic camphor. α-Pinene derived from oil of turpentine is the principal raw material employed, although a portion of the synthetic camphor, chiefly U. S. P. grade, is obtained from another terpene source.

Other uses include conversion to pharmaceuticals, such as terpin hydrate. A recent development which many believe will eventually rank as a leading chemical use for turpentine is the manufacture of neutral resins from β-pinene by catalytic polymerization. The latest data on the consumption of turpentine in the United States showed that more than half was used under the heading "chemicals and pharmaceuticals", an indication of how this old industry is turning to new fields.

DIPENTENE TERPENES

Much attention has been given the other oils besides α-pinene recovered from the dead pine wood. These oils are properly grouped into two classes: (1) monocyclic terpenes, principally dipentene together with the isomeric terpinenes and terpinolene, and (2) a group of oils called "pine oil". The latter is principally a mixture of tertiary and secondary alcohols and a small amount of a terpene oxide and a phenol ether, methylchavicol. The hydrocarbons of the first group are difficult to separate by distillation and are sold commercially under the name "dipentene", as well as numerous trade names.

One of the more recent chemical applications of the monocyclic terpene hydrocarbons is the conversion to the corresponding aromatic dehydrogenation-hydrogenation products. One commercial process subjects dipentene, terpinene, or terpinolene to a liquid-phase catalytic disproportionation to obtain *p*-cymene and *p*-menthane. The cymene is further treated by liquid-phase oxidation to yield a *tert*-tolyl-carbinol which is then dehydrated to the α-methyl-*p*-methyl-styrene. During this step a portion of the alcohol is dehydrated to the styrene which is oxidized in the process to *p*-methylacetophenone. An interesting by-product of this process is cumic acid (isopropylbenzoic acid). It was expected that if acids were produced they would be by the oxidation of the isopropyl group rather than the attack on the *p*-methyl position. Cumic acid is, however, not yet available commercially.

These dipentene oils are finding many uses in connection with the war. Besides providing the necessary solvents for a number of Army, Navy, and other specification paints and varnishes, this type of terpene is of special value as a penetrating and softening solvent in rubber reclaiming. They are also the base for the manufacture of terpene ethers which are finding an important application as insecticides.

When these monocyclic terpenes were first made, there was no market for them, and the development of uses was the subject of intensive chemical research. As indicated above, that work has been attended by considerable success; it may even be necessary to convert α-pinene to the monocyclic hydrocarbon by isomerization in order to supply the demand.

PINE OIL

The pine oil recovered from dead wood, composed primarily of tertiary and secondary alcohols, was in much the same position when this industry was established as were the dipentene oils. One of the earliest uses developed for pine oil was as a frothing solvent in the then new flotation process for reclaiming low grade copper-, lead-, and zinc-bearing ores. The mining industry is still probably the largest single user of this oil. The high solvent properties of pine oil, together with the polar character of the tertiary alcohols, has resulted in the large use of this material as a solvent and wetting agent in a variety of textile manufacturing and also as solvent lubricant in synthetic fiber production. The pine oils are also widely used as an important ingredient of many disinfectants, insecticides, and deodorants.

The natural constituents are recovered by chemical separation and have many important uses. Considerable pine oil is thus processed to produce the "β-terpineol" of commerce which is used not only as solvent but as a perfume base principally for soaps. The process includes the step of dehydrogenating the secondary alcohols, fenchol and borneol, to obtain their corresponding isomeric ketones, fenchone and camphor. Liquid fenchone is a powerful plasticizing solvent just as is the familiar solid, camphor. The phenol ether, methylchavicol, present in the natural oil is converted to its isomer, anethole, which is largely used because of its licorice flavor.

The pine oil manufactured at the present time by the extraction of pine wood has not been sufficient to meet the demand, and in recent years a synthetic pine oil has been produced from turpentine. Chemical pine oil resembles natural oil closely in composition; so here also because of the growing demand the basic terpene oil, α-pinene, is finding a chemical market as the raw material for pine oil.

FATTY ACIDS

The other by-products obtained from southern pine kraft consist principally of fatty acids comprising both oleic acids and small amounts of other, more unsaturated vegetable acids, such as linolenic and linoleic, and also rosin acids. These crude vegetable fatty acids and rosin are available in the wood in considerably larger quantity than the terpenes and, with the growing demand for all fats, could make a substantial contribution to the much needed supplies of fatty oils. This product is sold commercially under the name "tall oil"; that being manufactured at present is, for the most part, only partially refined. A large amount of these crude fatty acids was produced by the paper mills last year, including the rosin acids which make up about 40 per cent of the total; if they had all been refined and separated from the rosin acids, a huge quantity of liquid fat would have become available for use as soaps and possibly as paint and varnish vehicles and many other uses. Edible fats now being used solely for industrial purposes would thus have been released.

DESTRUCTIVE DISTILLATION PRODUCTS

In the destructive distillation process the natural oils and decomposition products of the rosin acids, cellulose, and lignin are recovered as a crude oil. This tar oil is then separated by chemical treatment and fractional distillation into several light solvent oils and light and heavy pine tars. The solvent oils are further refined into various fractions, such as toluene and xylene containing solvents, as well as turpentine, dipentene, and finally pine oils. These terpene oils have certain characteristics which usually identify them with this process. All of the oils have a large number of uses as solvents in a number of industries, including paint, varnish, lacquer, and rubber reclaiming. The pine oils and lighter pine tar oils were among the first to be employed in the solvent ore-flotation development, and a considerable amount is still used for that purpose. These oils are also widely used because of their medicinal, disinfectant, and deodorant properties. Pine tars occupy an important position in the rubber industry where they have been used for many years as a plasticizing antioxidant component of natural as well as reclaimed rubber goods.

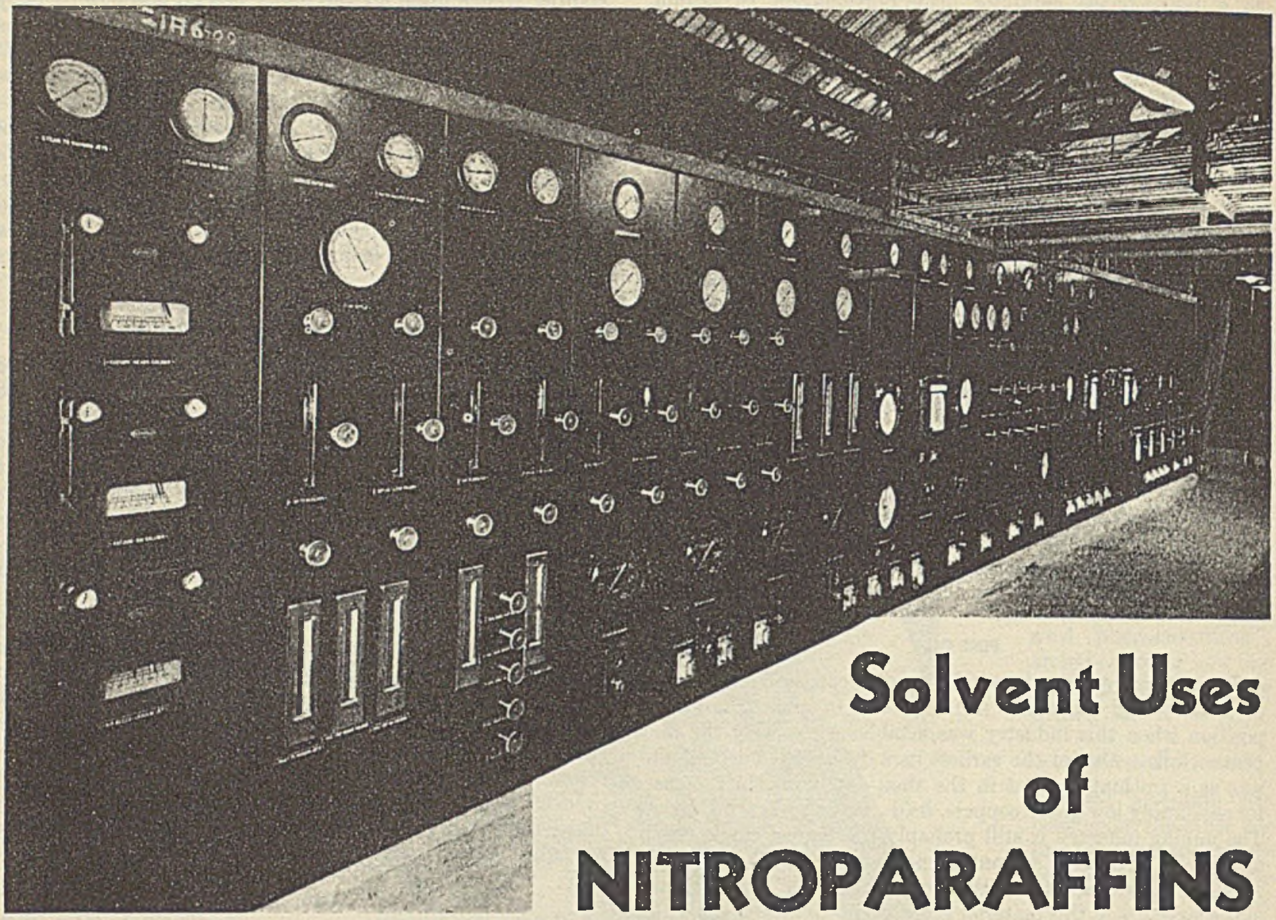
ROSIN OILS

The resin base, rosin, from which the solvent turpentine oil has been separated, cannot be disregarded when solvents from the pine tree are being considered. An old and important use for rosin is in the manufacture of rosin spirits and oils by destructive distillation; these oils have a wide variety of application as solvents and lubricants and for special paints and other compounds of particular importance now in shipbuilding. Recent figures on the production of these oils in this country show the quantity produced annually as nearly equal to the amount of turpentine consumed industrially in paint and varnish.

ISOPRENE

Any discussion of the role of terpenes in solving important chemical problems of the war would hardly be complete without at least mention of the fact that substantial amounts of isoprene are being produced from terpenes. The extent of this development is not available as public information. The importance of isoprene to the chemical rubber program has been described elsewhere and need not be re-emphasized here. Incidentally, some unsaturated solvents which largely boil in the toluene-xylene range, as well as some film-forming solvent materials, will probably be available as by-products from the isoprene operation.

It has been possible to give only a limited survey of the production and uses of solvents from the pine tree. The total quantity of the primary products discussed is relatively small compared to the total volume of solvents produced by the petroleum, coal tar, and fermentation industries, but the wide variety of applications has indicated the importance of the contributions being made by this industry to the over-all prosecution of the war.



The Entire Operation of the Nitroparaffin Plant Is Supervised from This Central Control Station

Solvent Uses of NITROPARAFFINS

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MANY reports have been made on the usefulness of the nitroparaffins (*1*, *3*, *6*, *10*, *15*, *16*). This paper will recapitulate some of the recorded information on the solvent applications of the nitroparaffins and will bring it up to date in the light of research carried out during the past year.

The nitroparaffins now in commercial production comprise the four lowest members of the series: nitromethane, nitroethane, 1-nitropropane, and 2-nitropropane. They are made by the vapor-phase nitration of propane (*8*). These compounds have medium boiling points ranging from 101° for nitromethane to 131° C. for 1-nitropropane. At room temperatures their evaporation rates lie between those of butyl acetate and toluene. They are nonhygroscopic and, as might be expected, have relatively low mutual solubilities with water which decrease with increasing molecular weight. Table I lists the physical properties of these four nitroparaffins.

The nitroparaffins are solvents for a wide variety of materials. Practically all of the cellulose esters and many of the resins used for coating purposes are easily dissolved by the nitroparaffins. The nitroparaffins are also powerful solvents for fats, oils, dyes, and many other organic materials. The mere fact that a given material is a solvent for a wide variety of substances does not necessarily mean that it can be used industrially. Solvency may be a factor of prime importance, but the other properties of a solvent or the combination of its properties make it valuable. In other words, before a solvent can find a major industrial application, a thorough examination of both its properties and its limitations must be undertaken; very often the limitations are what make a solvent industrially important. Obviously, a solvent which will dissolve every constituent of a complex mixture such as crude oil or coal tar will have little value in resolving such mixtures into their components. For example, one of the large industrial uses for solvents is in separating the aromatic from the paraffinic constituents of mineral oil. Since 1-nitropropane and 2-nitropropane are good solvents for both types of hydrocarbon, they offer few possibilities as selective solvents in this application. Nitromethane, on the other hand, dissolves aromatic hydrocarbons but is practically immiscible with paraffinic or naphthenic hydrocarbons. This compound has therefore been the subject of a considerable amount of work in solvent extraction, and its use as a selective solvent in the refining of petroleum is covered by patents (*5*, *14*).

Where large-scale uses of solvents are undertaken, it is desirable from an economic standpoint to recover as much of the solvent as possible. Recovery is doubly important when the solvents are not only high priced but scarce. It has been found that conventional carbon recovery systems are not wholly satisfactory for recovering the nitroparaffins, (*a*) because recovery efficiency is not high, and (*b*) because the carbon appears to be very sensitive to moisture, rapidly losing its adsorptive capacity for the nitroparaffins when insufficiently dried after steaming or when the solvent vapors contain moisture. Methods of recovering the nitroparaffins have been under active investigation for some time, and it is expected that detailed instructions for their recovery may be published in the near future.

The nitroparaffins are subject to a slight thermal decomposition during distillation, particularly when the liquid or vapor comes in contact with certain metals. The decomposition is least when the nitroparaffins are distilled in glass. Somewhat greater decomposition occurs in stainless steel while the use of aluminum equipment accelerates the rate of decomposition even further. The decomposition of the nitroparaffins when distilled in the presence of metals is greatly reduced if the distillation is carried out under reduced pressure. For all practical purposes, this thermal decomposition of the nitroparaffins can be inhibited by adding 0.1 to 1.0 per cent boric acid, hydrolyzable esters of boric acid, or salts such as aluminum borate, zinc borate, or lead borate (*2*) to the still charge. Where fractionation at high reflux ratios is employed, decomposition in the column can be prevented by arranging for continuous addition of stabilizer at the top of the column.

The nitroparaffins form azeotropes with water having the boiling points and compositions shown in Table II.

Since these compounds contain a nitro group, the safety of the nitroparaffins for large industrial applications is occasionally questioned. The flash points of the four nitroparaffins (Table III) are much higher than those of the common hydrocarbons, ketones, and esters having the same boiling points. Exhaustive attempts have been made to detonate pure nitroparaffins with blasting caps (*7*). These attempts were unsuccessful except for nitromethane, which could be detonated only under very special conditions (*13*). Therefore from the standpoint of fire or explosion hazard, the nitroparaffins present no particular problem when the usual precautions are observed. Because of their higher flash points, they are far less hazardous than hydrocarbon solvents having the same boiling range.

A word of caution should be inserted here. The nitroparaffins are weak oxidizing agents, particularly at elevated pressure and temperature, and unexpectedly violent reactions may take place especially in the presence of readily oxidizable organic matter. Therefore, high-temperature and high-pressure applications of the nitroparaffins should be treated as hazardous until they are proved to be safe.

TABLE I. PROPERTIES OF PURE NITROPARAFFINS

Name	Nitromethane	Nitroethane	1-Nitropropane	2-Nitropropane
Formula	CH_3NO_2	$CH_3CH_2—NO_2$	$CH_3CH_2—CH_2NO_2$	$CH_3CH—NO_2CH_3$
Molecular weight	61.04	75.07	89.09	89.09
Specific gravity, d_{20}^{20}	1.139	1.052	1.003	0.992
Lb. per U. S. gal. at 20° C.	9.48	8.75	8.35	8.24
Melting point, ° C.	−29	−90	−108	−93
Boiling point, ° C.	101.2	114.0	131.6	120.3
Flash point (Tag open cup), ° F.	112	106	120	103
Vapor pressure, at 20° C., mm.	27.8	15.6	7.5	12.9
Surface tension at 20° C., dynes/cm.	37.0	31.3	30.0	30.0
Refractive index at 20° C.	1.3818	1.3916	1.4015	1.3941
pH 0.01 *M* aqueous soln. at 25° C.	6.4	6.0	6.0	6.2
Evapn. rate by wt., (*n*-butyl acetate = 100)	180	145	100	124
Solubility at 20 °C.				
Ml. solvent in 100 ml. water	9.5	4.5	1.4	1.7
Ml. water in 100 ml. solvent	2.2	0.9	0.5	0.6

The nitroparaffins are used by the protective coatings industry in formulating lacquers based on cellulose acetate and acetate butyrate. Data are presented to show the improved evaporation and flow characteristics obtained when one of the nitroparaffins is substituted for the commonly used rapidly evaporating solvents. The nitroparaffins are also useful as solvents for the Vinylite VY resins. High proportions of diluent (toluene) may be used and low viscosities can be readily obtained if a nitroparaffin is the solvent. Another important solvent use for the nitroparaffins is in certain types of synthetic rubber, notably Hycar OR. Hycar cements and coating compositions in which a nitroparaffin is the solvent are being used in the fabrication of waterproof textiles.

Another factor which must be taken into account when considering a new solvent is its toxicity. Hass (*7*) and Machle and their respective associates (*11*, *12*) have indicated that the toxicity of the four nitroparaffins is of the same order as that of ester-type solvents having approximately the same evaporation rates. Thus, the ordinary care exercised in handling the common lacquer solvents suffices in respect to the nitroparaffins.

USE IN LACQUERS

The coating industry is one of the largest consumers of solvents; and because the nitroparaffins are such powerful solvents for most of the coating materials, they have been thoroughly examined for use by this industry. It is not within the scope of this paper to discuss lacquer solvent formulation but it seems pertinent to mention briefly some of the factors which must be taken into consideration when the nitroparaffins are used for this purpose.

The conventional lacquer based on cellulose nitrate has been under intensive investigation for roughly twenty years. Constant improvements, made possible by a better understanding of the variables influencing both the application of the film and its durability, have brought cellulose nitrate lacquers to such a state of perfection that their films now often outlast the article they are designed to protect or beautify. The solvents available for use with cellulose nitrate are satisfactory; and although the nitroparaffins are strong solvents for cellulose nitrate, they do not promise sufficient improvement to warrant their widespread use in conventional cellulose nitrate lacquers. However, a number of specialty lacquers have been formulated in which the nitroparaffins are used because of their mild nonpersistent odors and the fact that they do not hydrolyze, or because they impart some unusual property to the lacquer.

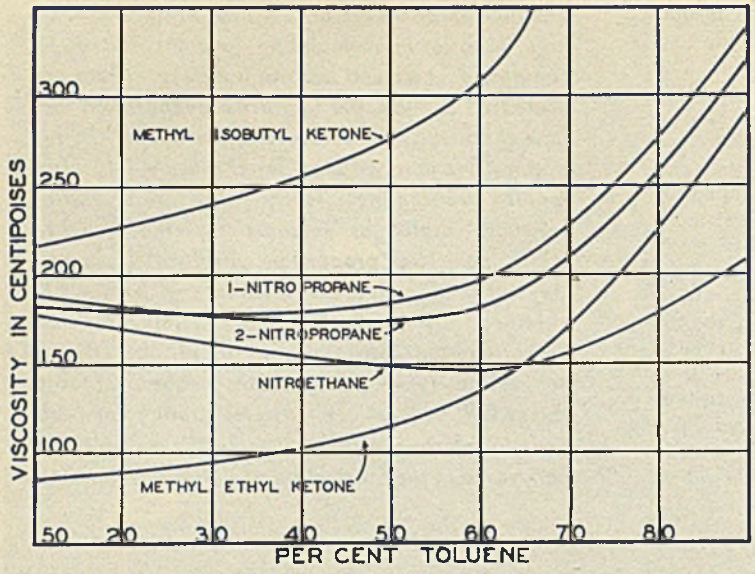

Figure 1. Effect of Toluene on Viscosity of Vinylite VYHF in Various Solvents (Concentration, 20 Grams per 100 Ml.)

Many other cellulose esters have been proposed as coating materials on which to base lacquers. The search has been primarily for a cellulose derivative that is nonflammable and, to a lesser extent, for one having better resistance to sunlight than cellulose nitrate. Flammability is not a factor where the lacquer is applied to metal surfaces or heavy furniture but it is a matter of prime importance to the aircraft, coated paper, and textile industries. Aircraft manufacturers in particular have been anxious to obtain a nonflammable coating material; within the past ten years cellulose acetate, triacetate, acetate butyrate, and acetate propionate have been developed and used with varying degrees of success. Acceptance of such esters by the lacquer industry has been greatly retarded by the lack of satisfactory medium-boiling solvents since those hitherto available were either very rapid or very slow evaporating.

Table II. Composition and Boiling Points of Nitroparaffin-Water Azeotropes at 760 Mm.

Nitroparaffin	Boiling Point of Azeotrope, ° C.	Nitroparaffin in Azeotrope, % by Wt.
Nitromethane	83.6	77.1
Nitroethane	87.1	73.6
2-Nitropropane	88.4	73.1
1-Nitropropane	91.2	64.5

CELLULOSE ACETATE BUTYRATE

The nitroparaffins have awakened much of the latent interest in the whole group of cellulose esters, and the reason should be apparent from an examination of Table IV which lists the solvents for cellulose acetate butyrate together with their evaporation rates.

The coating industry has not found it practical to use dioxane because of its hygroscopicity and relatively high toxicity. The chlorinated hydrocarbons must also be eliminated because of their toxicity. The remaining solvents are either very rapid evaporators which cause the lacquer to have poor flow and tendencies to blush, or very slow evaporators which greatly delay final hardening of the film. It is therefore apparent that the only practical solvents for cellulose acetate butyrate in the desirable medium evaporation range are the nitroparaffins.

It has been previously shown that the use of the nitroparaffins with cellulose acetate butyrate often permits the addition of as much toluene as is customarily used in nitrocellulose lacquers (*7*). Bogin and Wampner recommended a solvent mixture for cellulose acetate butyrate lacquers consisting of the following: 1- or 2-nitropropane 25 per cent, butyl alcohol 10, ethyl alcohol 15, toluene 50. In formulating this lacquer, a solvent-rich mixture is used to dissolve the cellulose ester, and the concentrated solution is thinned to spraying viscosity with a mixture containing the bulk of the diluent and as little as 5 per cent of solvent. The entire solvent power of the mixture is contributed by the nitropropane.

It is often desirable to formulate solvent mixtures for cellulose acetate butyrate in which only part of the solvent power is contributed by the nitropropane and the remainder is obtained from solvents such as ethyl acetate and from latent solvents such as butyl acetate. When such changes are made, alcohols must be eliminated from the formula since cellulose acetate butyrate is much more likely to blush than are the other coating materials and, of course, alcohols have blush-promoting properties.

The importance of producing a smooth surface on military aircraft needs no elaboration, and a considerable improvement in smoothness can be obtained when the nitroparaffins are used in formulating the solvents for aircraft dopes based on cellulose acetate butyrate. Their medium evaporation rates and powerful solvent properties are also advantageous in the formulation of "hot" lacquers and dopes (*9*). The application of lacquers and dopes at elevated temperatures is a new departure which has lately been shown to make rather remarkable economies in aircraft finishing time possible.

CELLULOSE ACETATE

Cellulose acetate lacquers, as previously indicated, have been limited in application by much the same solvent problems that affected the general acceptance of cellulose acetate butyrate. Table IV lists the solvents for the usual grade of cellulose acetate. With the exception of nitromethane and nitroethane, there are no true solvents for this cellulose ester in the evaporation range approaching that of butyl acetate. Table V lists the latent solvents for this coating material which are activated by the nitroparaffins, and it is apparent that mixtures of 1- or 2-nitropropane with alcohols are

Table III. Boiling and Flash Points of Nitroparaffins Compared with Common Hydrocarbons, Ketones, and Esters

	Boiling Point, ° C.	Flash Point (Tag Open Cup), ° F.
Nitromethane	101.2	112
Nitroethane	114.0	106
2-Nitropropane	120.3	103
1-Nitropropane	131.6	120
Toluene	110.8	56
Naphtha, high-boiling	103–142[a]	<70
Dioxane	101.5	69
Methyl ethyl ketone	79.6	66
Methyl isobutyl ketone	116.0	98
Butyl acetate	126.5	102

[a] Distillation range.

effective solvents for cellulose acetate. Tables IV and V also show that only with the nitroparaffins is it possible to formulate solvent mixtures which will have the medium evaporation rates necessary for good flow and smooth films without sacrificing rapid drying. Most of the work on the solvent uses of the nitroparaffins has been confined to 1-nitropropane and 2-nitropropane since these solvents are available in larger quantities than are nitromethane and nitroethane.

TABLE IV. SOLVENTS FOR CELLULOSE ACETATE BUTYRATE[a] AND CELLULOSE ACETATE[b]

Cellulose Acetate Butyrate		Cellulose Acetate	
Solvent	Evapn. rate[c]	Solvent	Evapn. rate[c]
Acetone	720	Methyl acetate	1040
Ethylene dichloride	575	Acetone	720
Ethyl acetate	525	Ethyl acetate	525
Methyl ethyl ketone	465	Methyl ethyl ketone	465
Dioxane	215	Dioxane	215
Nitromethane	180	Nitromethane	180
Nitroethane	145	Nitroethane	145
2-Nitropropane	124	Mesityl oxide	87
1-Nitropropane	100	Tetrachloroethane	75
Tetrachloroethane	75	Methyl Cellosolve	55
Ethylene chlorohydrin	45	Ethylene chlorohydrin	46
Diacetone (acetone-free)	15	Methyl Cellosolve acetate	40
		Methyl lactate	29
		Ethyl lactate	22
		Diacetone (acetone-free)	15

[a] Acetyl content 31%, butyryl content 10%.
[b] Acetyl content 37–42%.
[c] Butyl acetate = 100.

Neither butyl nor ethyl alcohol is a true solvent for cellulose acetate, but each of them is activated by the nitropropanes which are themselves not true solvents. Because of the difference in the evaporation rates of these liquids, it is essential that the nitropropanes and the alcohols be used in such proportions that maintenance of the proper solvent balance is assured throughout the drying of the film. For example, if ethyl alcohol and nitropropane were used alone, the alcohol would leave the film before all of the nitroparaffin had evaporated and, because of the resultant loss of solvent power, the film would become cloudy or precipitated and have poor adhesion. On the other hand, if butyl alcohol and nitropropane were used alone, part of the butyl alcohol would remain behind after the nitroparaffin had evaporated; and since butyl alcohol is not a true solvent for cellulose acetate, a faulty film would again be obtained.

TABLE V. LATENT SOLVENTS FOR CELLULOSE ACETATE, ACTIVATED BY NITROPARAFFINS

Latent Solvent	Evapn. Rate (Butyl Acetate = 100)
Methyl alcohol	370
Isopropyl alcohol	205
Ethyl alcohol	203
sec-Butyl alcohol	115
Isobutyl alcohol	83
Butyl alcohol	45
sec-Amyl alcohol	42
Cellosolve	40
Amyl alcohol (from fusel oil)	33
Butyl Cellosolve	10
Cyclohexanol	9

It is apparent, then, that mixtures containing nitropropanes, ethyl alcohol, and butyl alcohol are entirely satisfactory solvents for lacquers based on cellulose acetate. Fortunately the proportion of each alcohol required is not critical. For example, a typical solvent mixture might contain 35 per cent nitropropane, 35 per cent toluene, and 30 per cent alcohols. The alcohol portion of this mixture may consist of ethyl alcohol–butyl alcohol in ratios of 1 : 4 to 5 : 1. As the richness of the solvent mixture decreases (i. e., as the proportion of toluene increases), the permissible ratio between the alcohols narrows somewhat but is still far from critical.

As previously mentioned, it is necessary to use mixtures rich in solvents to dissolve cellulose acetate butyrate. The same is true when formulating lacquers based on cellulose acetate. Here again it is advisable to use the major proportion of the solvents to dissolve the cellulose acetate and then to add the toluene, mixed with a small proportion of solvents, when thinning the concentrated lacquer to spraying viscosity. When cellulose acetate lacquers are formulated with the nitroparaffins, it is possible to use as much as 40 per cent toluene in the final solvent mixture; with a more conventional formula containing acetone, ethyl acetate, methyl ethyl ketone, and ethyl lactate, no toluene can be used.

VINYL RESINS

The nitroparaffins are among the most powerful solvents for the vinyl copolymer resins, particularly those made from vinyl acetate and vinyl chloride. This is indicated by the fact that, at any given resin concentration, solutions made with nitroparaffins can be diluted with hydrocarbons to a far greater extent without causing gelling, precipitation, or a rapid rise in viscosity (*3*) than is possible if the solutions are made with methyl isobutyl ketone, for example. Figure 1 shows that a mixture containing 75 per cent toluene and 25 per cent 1-nitropropane yields a 20 per cent Vinylite VYHF solution having the same viscosity as one containing 40 per cent toluene and 60 per cent methyl isobutyl ketone at the same resin concentration. Stated another way, at any given concentration, when the same proportions of diluent are used, lower viscosities are obtained with the nitroparaffins than with methyl isobutyl ketone.

TABLE VI. TYPICAL SOLUBILITY CHARACTERISTICS OF NITROPARAFFINS

MATERIALS SOLUBLE IN 1- AND 2-NITROPROPANE

Most natural resins
Glyptal resins
Vinylite resins
Cellulose esters
Cellulose ethers
Liquid organic acids
Alkyl esters and ethers
Aryl esters and ethers
Alcohols
Ketones
Aldehydes
Alkyl amines
Aryl amines
Buna N type rubbers
Vegetable fats and oils
Animal fats and oils
All low-boiling hydrocarbons and chlorinated hydrocarbons

MATERIALS INSOLUBLE IN 1- AND 2-NITROPROPANE

Inorganic acids and salts
Metallic soaps
Solid organic acids
Sugars
Alkanol amines
Proteinlike materials
Natural rubber
Buna S type rubbers
High-boiling hydrocarbons

Figure 1 shows that methyl ethyl ketone yields lower viscosities than the nitroparaffins and that it may be diluted with toluene without encountering rapid viscosity increases. Two factors tend to limit the wide use of methyl ethyl ketone, however. The first is that its evaporation rate is roughly four times that of the nitroparaffins. This high rate of evaporation means that methyl ethyl ketone may be used only where Vinylite coatings are applied by dipping where the film is leveled mechanically or where film smoothness is not a consideration. The second is the fact that its rapid evaporation rate prevents its use with the slower evaporating toluene Obviously, a solvent mixture for Vinylite containing only methyl ethyl ketone and toluene will be unsatisfactory because the former will leave the film before the toluene, and since toluene is a nonsolvent for Vinylite, rough films having poor adhesion will be obtained.

MISCELLANEOUS

The nitroparaffins may be used advantageously with a large number of other coating materials. Cellulose triacetate, for example, is exceedingly resistant to attack by practically all solvents except the chlorinated hydrocarbons which have the disadvantages of being relatively toxic and corrosive. The nitroparaffins are latent solvents for cellulose triacetate and permit the formulation of solvent mixtures containing only small amounts of chlorinated hydrocarbons. Mixtures containing as little as 10 per cent of tetrachloroethane are excellent solvents for cellulose triacetate.

The nitroparaffins are also valuable in reducing the gelling tendencies of alcoholic zein solutions. They are perhaps the most powerful solvents for the synthetic rubber known as Hycar OR, and they have been found to be useful in cements made with this material. Certain nitroparaffin derivatives are also valuable antigelling agents while others are heat sensitizers for cements made from Hycar OR as well as from natural rubber (*4*).

Table VI is a list of the types of compounds soluble and insoluble in the nitroparaffins. This table indicates that the usefulness of the nitroparaffins as solvents lies in many different fields.

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ALCOHOLS OTHER THAN BUTYL

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The scope of this paper includes the saturated alcohols commercially and economically available to the protective coating and chemical industries. Since considerable information had been published on these products before the war, the present paper is confined to more recent developments. Also included in the discussion are the relative positions of the various alcohols with respect to the war effort. Some attempts are likewise made at predictions regarding their postwar status.

METHYL alcohol is now being produced commercially by three different processes—one old and two relatively new. The oldest source is the crude wood alcohol produced during the destructive distillation of wood in the manufacture of charcoal. Approximately 6 million gallons of methyl alcohol are obtained by this means. The output cannot be increased, however, since methyl alcohol thus made should be considered a by-product of charcoal which, in turn, is limited by the availability of proper hardwood and suitable labor to cut and collect the lumber. The value of the by-products obtained in the distillation of pyroligneous acid—namely, acetic acid, acetone, and methyl alcohol—becomes an asset to the operation if the price of and demand for charcoal justify the lumbering operation. In the event, however, that there is insufficient demand for charcoal, the cost of the solvents must pay for both the lumber and for the expense of their own distillation.

At present as in the past, the two main outlets for wood alcohol are in automotive antifreeze blends and ethyl alcohol denaturants. The crude alcohol contains a number of impurities which impart a strong odor to the material and thus make it specially suitable for these purposes. An additional distillation is required to render it satisfactory for other uses.

Wood-distillation methyl alcohol is in heavy demand at the present time, but its production cannot be greatly increased. The postwar position of this material will depend entirely on its ability to compete in cost of production with the synthetic product. As the manufacturing limitations of wood alcohol did not permit production to keep pace with demand, the manufacture of synthetic methyl alcohol, first prepared in this country in 1923, has steadily increased in volume.

The two outstanding processes for producing synthetic methyl alcohol are at present limited by difficulties in obtaining critically needed material. As an instance, the process in which carbon monoxide is partially reduced by hydrogen requires a pressure of 200 atmospheres at 450° C. with a zinc oxide–chromic oxide catalyst. Since high pressure equipment is practically unobtainable, this process cannot easily be expanded at this time. The second method, the catalytic oxidation of methane, requires 100 atmospheres pressure at

260° C. The methane is passed through copper tubes in a ratio of 9 parts methane to 1 of oxygen.

The chemical and physical properties of methyl alcohol make it an important product in industry. It finds extensive use as an industrial solvent for such products as wood stains, soaps, artificial leather, gums, celluloid cements, motor fuels, paint and varnish removers, shellac solutions, spirit varnishes, alcohol lamps, etc. In normal times the largest use, as previously mentioned, is in automobile antifreeze blends. Maximum antifreeze protection per gallon of the three water-soluble alcohols is given by methyl, and therefore it is probably the most economical to use. Data recently secured, however, tend to indicate that methyl alcohol loses sufficient volume in evaporation to reduce significantly its antifreeze protection.

The second major use for methyl alcohol is in the denaturing of ethyl alcohol. Both wood alcohol and a small amount of synthetic methyl alcohol are used for this purpose. It serves as a highly satisfactory denaturant owing to the difficulty in its separation from ethyl alcohol and the relative ease with which it can be detected.

Large quantities of synthetic methyl alcohol are used as the raw material in many chemical processes; the most important is the preparation of formaldehyde by mild oxidation of the alcohol. In recent years formaldehyde has become extremely important as a constituent of various synthetic resins, plastics, and explosive intermediates such as pentaerythritol. Heavy demands for explosives and other military requirements have resulted in a scarcity of methyl alcohol. Increased activity in certain plastics such as the methacrylates is also a contributing factor in the reduced availability.

Since synthetic methyl alcohol and ammonia are produced in the same type of equipment, increased production of methyl alcohol during the war period must necessarily be balanced by the military and agricultural requirements for ammonia. If the combined demand for these two products is in excess of the available supply, the least important civilian uses must be curtailed or replacement by less critical materials must be made. In the postwar period, however, the demand for methyl alcohol through its chemical derivatives may be expected to increase. There will be sufficient excess ammonia equipment in the country, and synthetic methyl alcohol should be readily available and in a favorable economic position. The basic cost for methyl alcohol should be figured in terms of ammonia since the value of the former can be calculated directly in ammonia displacement.

ETHYL ALCOHOL

Ethyl is the oldest of the alcohols. It is derived largely from the fermentation of sugar, cellulose, and related materials. Before the war practically all fermentation alcohol produced in this country was made from blackstrap molasses, but wartime difficulties in transporting molasses have increased and most of the ethyl alcohol today is being produced from grain. More recently, however, the fermentation of specially milled flour has been undertaken.

The fermented liquor, containing about 10 per cent crude alcohol, is concentrated by fractionation. The heads cut contains aldehydes and the tails a certain proportion of fusel oils. During the process of fermentation carbon dioxide is produced in quantities about equivalent to the weight of alcohol. This is recovered and merchandised as dry ice. The tails from molasses fermentation have been processed to produce cattle feed.

The synthesis of ethyl alcohol by hydrating ethylene is an increasingly important method for producing this valuable product. In the process ethylene is absorbed by sulfuric acid at slightly elevated temperatures; the ethyl hydrogen sulfate so formed is passed into water and is heated to hydrolyze the ester to ethyl alcohol. The product is characterized by its freedom from higher alcohols.

In normal times many industrial uses for ethyl alcohol are found. Production expanded enormously from the million-gallon output of the year 1907. A large part of this increase was due to the introduction of the closed car which permitted winter driving. The resulting antifreeze market consumed during one period almost 50 per cent of the total ethyl alcohol production. With its replacement in this field by methyl alcohol, ethylene glycol, and isopropyl-methyl alcohol blends, however, the volume of ethyl alcohol used today is only 25 per cent of the quantity produced; the balance goes into industry for other purposes.

The largest prewar consumption of ethyl alcohol was in the cellulose industry. Here it was used to dehydrate nitrocotton and prepare acetic anhydride, a starting component in the manufacture of cellulose acetate. Other large uses were in the preparation of shellac, lacquer, varnish, solvents, ethyl acetate, and toilet goods. The introduction of anhydrous ethyl alcohol greatly extended its uses owing to increased solvent power. It may be said that hardly an industry is without the need of ethyl alcohol during some phase of operation.

The greater part of the present gallonage goes into butadiene for synthetic rubber. Large quantities are also consumed in the preparation of smokeless powder and other military requirements, including medicinals. To meet this increased demand, the entire beverage industry of the United States is now utilizing its facilities to produce ethyl alcohol. After the war this industry will naturally return to its former business, and the production of ethyl alcohol will immediately be more than halved.

In 1939, 25 per cent of our ethyl alcohol was made synthetically. These facilities have been greatly expanded during the war so that at least 50 per cent of the country's normal production can be obtained from synthetic plants. Any discussion of the postwar synthetic rubber situation at the present time would be pure speculation. It is possible, however, that fairly large quantities of ethyl alcohol might be used to produce butadiene at that time. If new developments do not absorb the increased production, the demand will be largely drawn from the source having the lowest production cost. As approximately 2.5 gallons of blackstrap molasses or 0.4 bushel of grain is needed to produce a gallon of alcohol, the extent to which fermentation alcohol can compete with synthetic will depend entirely upon the postwar agriculture prices.

n-PROPYL AND ISOPROPYL ALCOHOLS

n-PROPYL. Originally obtained from fusel oil, this material is a constituent of the higher alcohol fraction in the production of synthetic methanol. The biggest market for the small amounts available is in its oxidation to propionic acid.

ISOPROPYL. Prepared in substantially the same manner as synthetic ethyl alcohol, isopropyl alcohol became available commercially in 1920; production figures have steadily increased. One of the largest present uses is the production of acetone and ketene by catalysis. Acetone can be made in this manner at a lower cost and probably in a purer form than that obtained by fermentation; the result is an increased demand for this product. Another large market for isopropyl alcohol is in antifreeze compositions. In combination with methyl alcohol it produced a particularly satisfactory antifreeze blend with properties not possessed by either alcohol alone.

As a result of war restrictions on the use of ethyl alcohol, isopropyl alcohol is now being employed as a satisfactory substitute in the toilet goods and cosmetic field. At present virtually all rubbing alcohol is made from isopropyl alcohol. Many other preparations such as after-shave lotions, toilet waters, etc., contain isopropyl alcohol. Certain types of perfume are now being blended with isopropyl alcohol as the carrying agent. The anhydrous grade displays solvency for certain essential oils in excess of that exhibited by the corresponding grade of ethyl alcohol. Since there has been a gradual improvement in the quality of isopropyl alcohol due to better manufacturing technique, perfumers are adjusting their blends to accommodate the new odor and improved solubility. It is believed that after the war many users will not return to ethyl alcohol.

Isopropyl alcohol is contributing to the war effort in such uses as fuselage cleaners, de-icing fluids, plywood impregnating solutions, shackle lubricants, shock absorber fluids, vitamin crystallization, lacquer thinners, etc. Increasingly large amounts are also being consumed in preparing isopropyl acetate, a nitrocellulose solvent finding wider uses within the past few years.

BUTYL ALCOHOLS

ISOBUTYL. Before the war isobutyl alcohol was obtained in large quantities as a by-product in the preparation of synthetic methyl alcohol. It exhibits typical reactions of the primary alcohols, except that the presence of a branched chain next to the carbinol group makes rearrangement unusually easy. An example is the reaction between isobutyl alcohol and hydrobromic acid to produce *tert*-butyl bromide rather than the iso compound. The commercial value of isobutyl alcohol is about halfway between normal and secondary butyl alcohol. Its use, therefore, has been limited largely to the production of the corresponding acetate, a satisfactory nitrocellulose solvent. Isobutyl alcohol has found some use as a lacquer cosolvent and as a constituent of brake fluids combined with castor oil. It is understood, however, that major producers are now using it in special war work which may find a definite position in industry after the war.

sec-BUTYL. This alcohol is becoming increasingly available due to improved manufacturing facilities. It is produced in substantially the same manner as ethyl and isopropyl alcohols—i. e., by hydrating the corresponding olefin. At present its two most important uses are in the preparation of *sec*-butyl acetate, an excellent intermediate-evaporating nitrocellulose solvent, and methyl ethyl ketone obtained by dehydrogenation of the alcohol.

Methyl ethyl ketone is a valuable solvent for vinyl resins, nitrocotton, and synthetic rubber. In the anhydrous state it presents solvent properties equal to that of acetone. Its evaporation rate, however, is definitely slower than acetone, a fact responsible for its high initial blush resistance in lacquer formulations. After the war the demand for this material should continue to increase, as special resins and synthetic rubbers, upon which its use is somewhat dependent, will continue to expand. Its superior nitrocotton solvency has been demonstrated. In this capacity it should replace ethyl and isopropyl acetates in many cases.

tert-BUTYL. This alcohol is readily obtained from the hydration of isobutylene. In the pure state, however, it freezes at 25° C., a property rendering its commercial use somewhat limited. It is employed as an alkylating agent in the preparation of such compounds as *tert*-butylphenol.

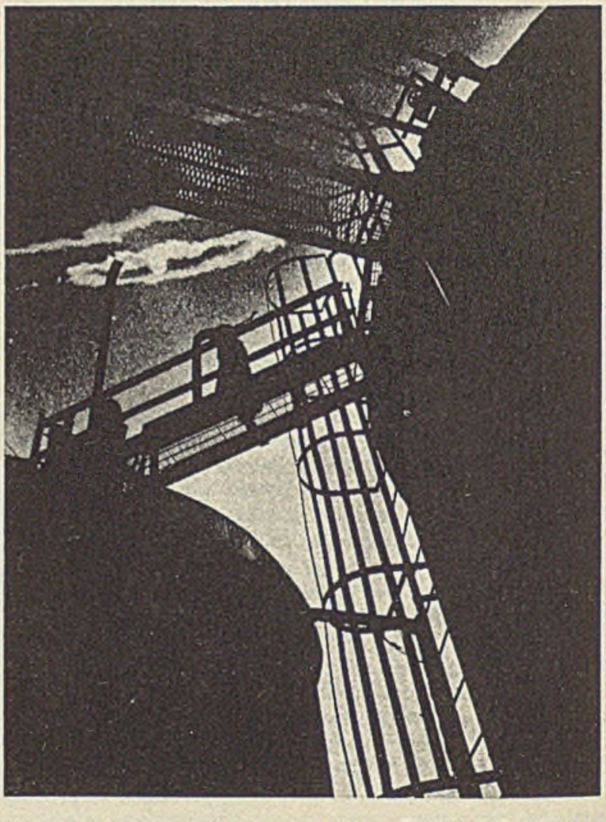
AMYL ALCOHOL

Originally amyl alcohols, both normal and iso, were obtained as by-products in the fermentation of grain. Little is apparently being produced at this time, probably owing to changes in manufacturing technique. The only additional amyl alcohol, other than that produced by chlorination, is *sec*-amyl alcohol. This material, prepared before the war by hydration of amylene, was used to make methyl *n*-propyl ketone, a dewaxing solvent. *sec*-Amyl acetate, derived from the alcohol, has found use in the lacquer trade.

Amylene, the raw material from which *sec*-amyl alcohol was made, now possesses a greater war value than that of the alcohol itself. The production of the alcohol, therefore, has dropped to almost nothing.

CONCLUSION

During the past twenty years the alcohol and solvent business has grown from infancy to maturity, but it found its place more in the protective coating field than in other industries. The war, however, has increased the outlets for these alcohols, so that today virtually all of the major chemical industries are consumers of one or more of the alcohols or their derivatives. While the release of the greater part of these new developments is now restricted because of military necessity, we may generalize to the extent of saying that aside from the protective coating industry itself, these alcohols, either as solvents or intermediates, will play a leading part in the postwar development of textiles, resins, rubber, and chemical intermediates, and, due to reduced cost, will contribute greatly to a better postwar standard of living.



Courtesy, du Pont Company

Equipment for Making Formaldehyde from Methyl Alcohol and Air

KETONES as Solvents for VINYL RESINS

Richard W. Quarles
MELLON INSTITUTE, PITTSBURGH, PENNA.

The use and production of ketones as solvents have grown enormously in the last decade concurrently with the development of the vinyl resins. In part the demand for these strong solvents for vinyl resins has accelerated the growth, but the ketones have made solution coatings of resins with high vinyl chloride content practical. Noncyclic ketones are adequate solvents for the vinyl chloride-acetate resins of 88 per cent vinyl chloride content and having an apparent molecular weight of 10,000, but ketones of stronger solvent power, such as isophorone, are more practical with the high-chloride resins and with the vinyl chloride polymers. Solvent studies, by the viscosity–phase diagram method, have been used to evaluate a number of ketone solvents with Vinylite resin VYHH. The marked effect of temperature on the solutions has been studied. With certain solvents, particularly cyclic ketones, solutions of minimum viscosity are obtained with solvent-diluent mixtures. The results are interpreted as indicating selective solvation of resin by the active solvent. The order in which solvents of a mixed thinner contact the resin has a marked effect on the viscosity of the resulting solution of the higher-molecular-weight vinyl resins.

THE remarkable combination of circumstances which marked the concurrent development of the pyroxylin lacquers and the butyl solvents has been duplicated on a smaller scale during the past decade by the evolution of the vinyl resin coatings and the ketone industry. Although it has been almost a century since Williamson recognized the nature of the carbonyl group and its functional relation to the ketones, nevertheless, a score of years ago acetone was the only ketone available in quantity. The past ten years, however, have been marked by the introduction of a number of new ketones to the solvent industry, and the availability of these compounds has contributed greatly to the development of practical coatings based on the vinyl resins. Conversely, the demand for ketones with a greater range of properties for use in vinyl resin coatings has led to the commercial production of a number of ketones which are finding wide application in other types of surface coatings. Today, acetone, methyl ethyl ketone, methyl isobutyl ketone, and diacetone alcohol are being used extensively as solvents. To a lesser extent, a large number of other ketones are available, such as diethyl ketone, dipropyl ketone, mesityl oxide, methyl amyl ketone, cyclohexanone, methyl cyclohexanone, isophorone, diisobutyl ketone, phorone, fenchone, methyl hexyl ketone, and acetonyl acetone. In addition, some of the higher ketone homologs of isophorone are being offered as plasticizers.

The same period that saw the development of diversified ketone solvents was characterized by the commercial utilization of the vinyl resins. During the past few years the production of these vinyl polymers has increased at a rapid rate so that today they have become one of the important families of synthetic resins. A large proportion of these vinyl resins are applied as adhesives and coatings from solutions in organic solvents, and four main types are used—vinyl acetate polymers, vinyl butyral polymers, vinyl chloride polymers, and vinyl chloride–vinyl acetate copolymers. The ketones find their widest application as solvents for the vinyl resins in solutions of the last two resins but are employed to a small extent with the others.

The vinyl acetate resins are the most soluble of the vinyl resins and dissolve in a wide variety of organic solvents. Nevertheless, there are many instances where the ketones are useful as solvents for the vinyl acetate resins. One application consists in lowering the viscosity of solutions of vinyl acetate resins in weaker solvents. In other cases acetone is employed as the sole solvent for the resins in adhesives because of the high concentration of resin obtained at low viscosity and also because of the rapid evaporation rate of this solvent.

The vinyl butyral resins, which have been widely used in safety glass, are now being utilized extensively for cloth coatings; many of them are being applied from solution. The solubility of this type of resin is largely dependent upon the ratio of butyral to alcohol groups. As a result, the viscosity of the solution is quite sensitive to the composition of the resin and to the solvent balance of the thinner. One of the more common resins of this type is Vinylite XYNC, an alcohol-soluble product. Despite the fact that this resin is an alcohol-soluble type, nevertheless mixtures of ketones and alcohols yield solutions of lower viscosity than do alcohols alone, due to the property of the ketones of solvating groups of widely different types.

The vinyl chloride-acetate polymers are the most widely used of all the vinyl resins. They are divided roughly into two solubility types determined by the percentage of vinyl chloride in the polymer, although the degree of polymerization influences the solubility of the borderline members. The resins containing 91–92 per cent vinyl chloride or less are, in general, readily soluble in the simple aliphatic ketones, such as acetone, methyl ethyl ketone, and methyl isobutyl ketone. The resins of higher vinyl chloride content, including polyvinyl chloride, require solvents of a more powerful type, such as the unsaturated and alicyclic ketones. For example, mesityl oxide, isophorone, and cyclohexanone are prominent among the solvents for such resins, with the aromatic solvents and the aliphatic ketones as diluents. In the subsequent discussions of solubility, Vinylite VYHH is chosen as

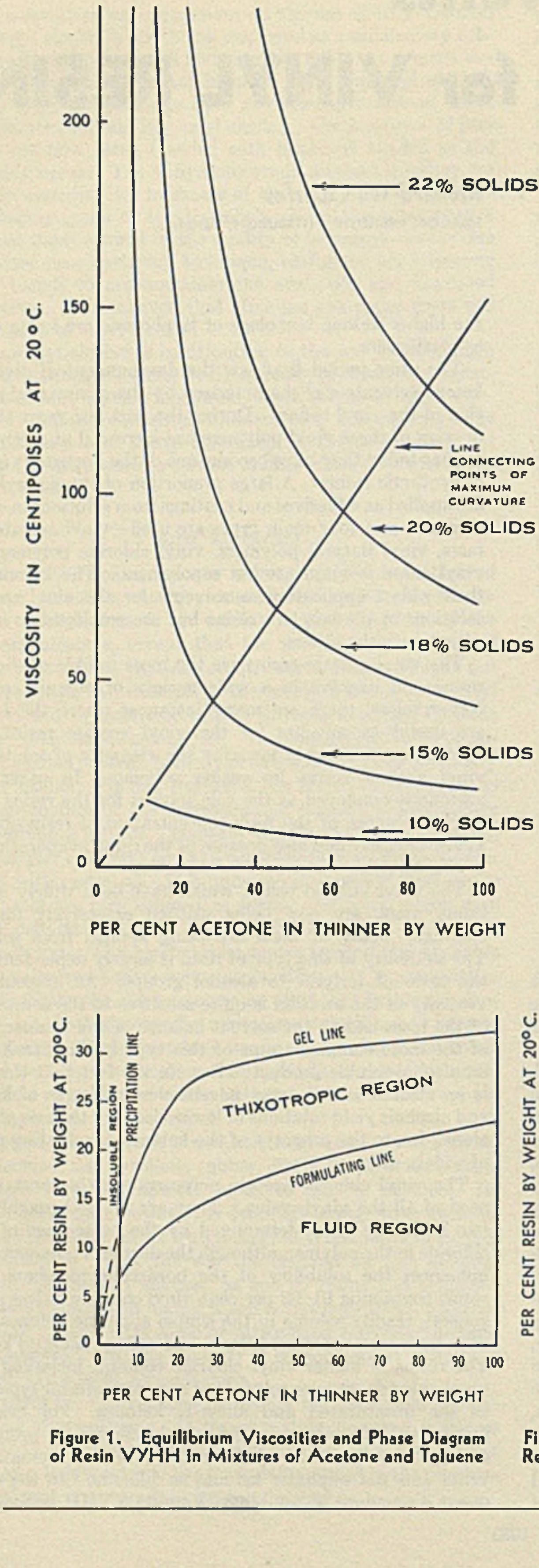


Figure 1. Equilibrium Viscosities and Phase Diagram of Resin VYHH in Mixtures of Acetone and Toluene

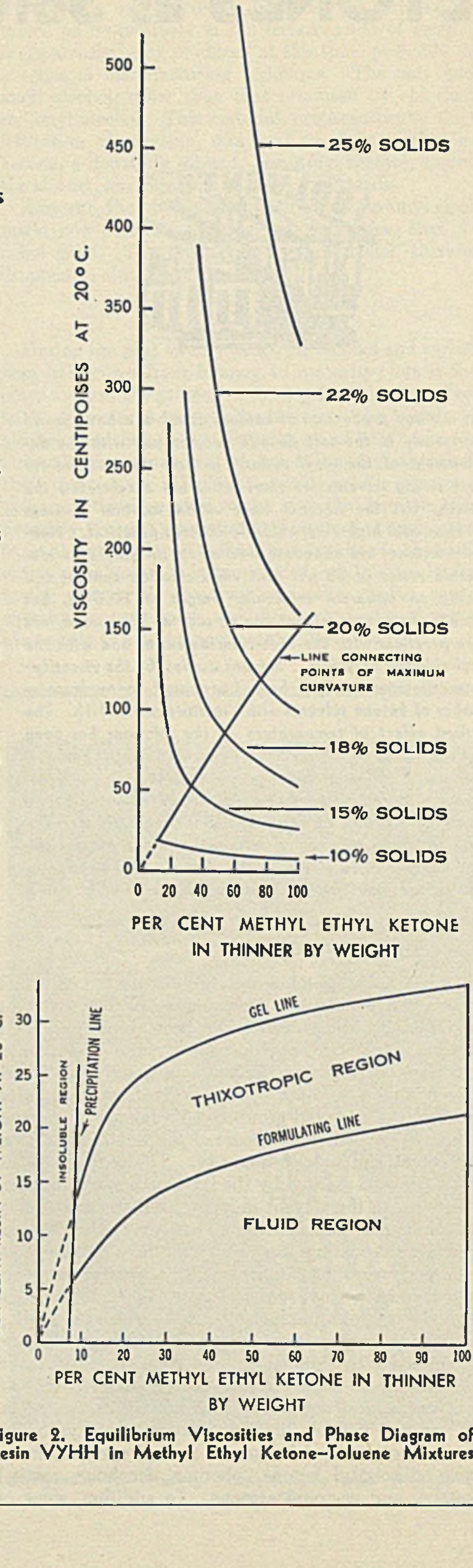


Figure 2. Equilibrium Viscosities and Phase Diagram of Resin VYHH in Methyl Ethyl Ketone–Toluene Mixtures

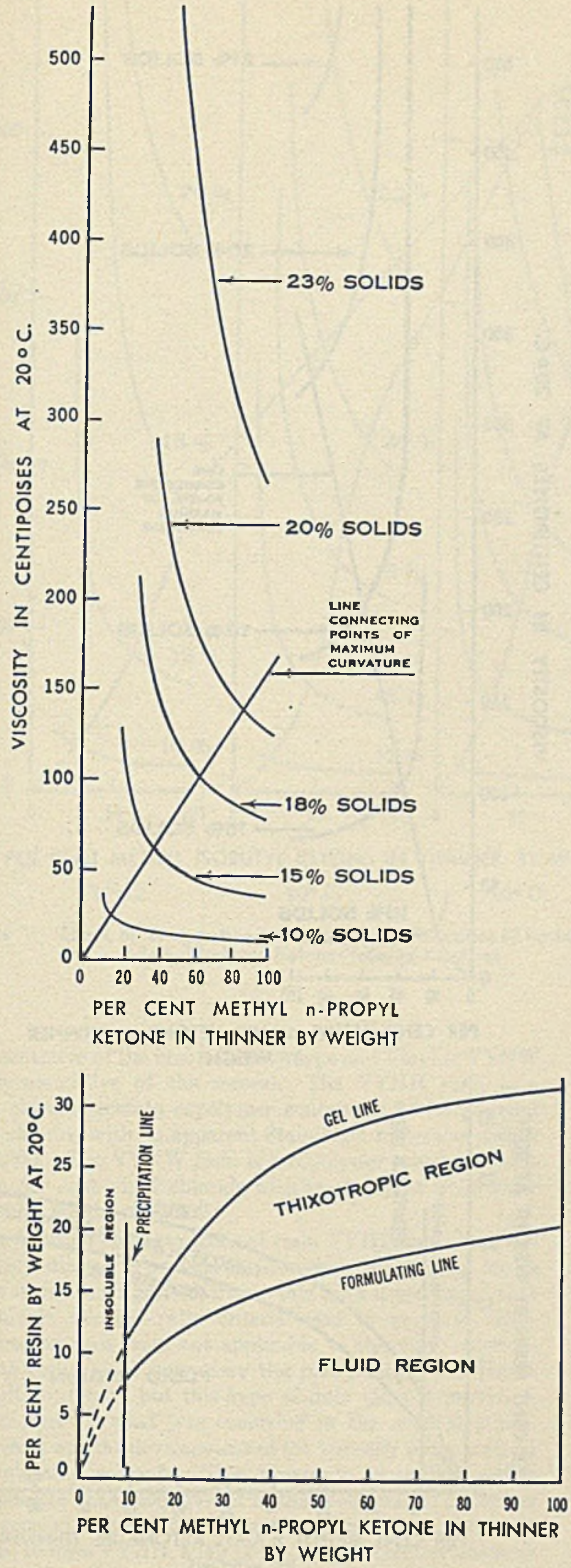


Figure 3. Equilibrium Viscosities and Phase Diagram of Resin VYHH in Methyl *n*-Propyl Ketone–Toluene Mixtures

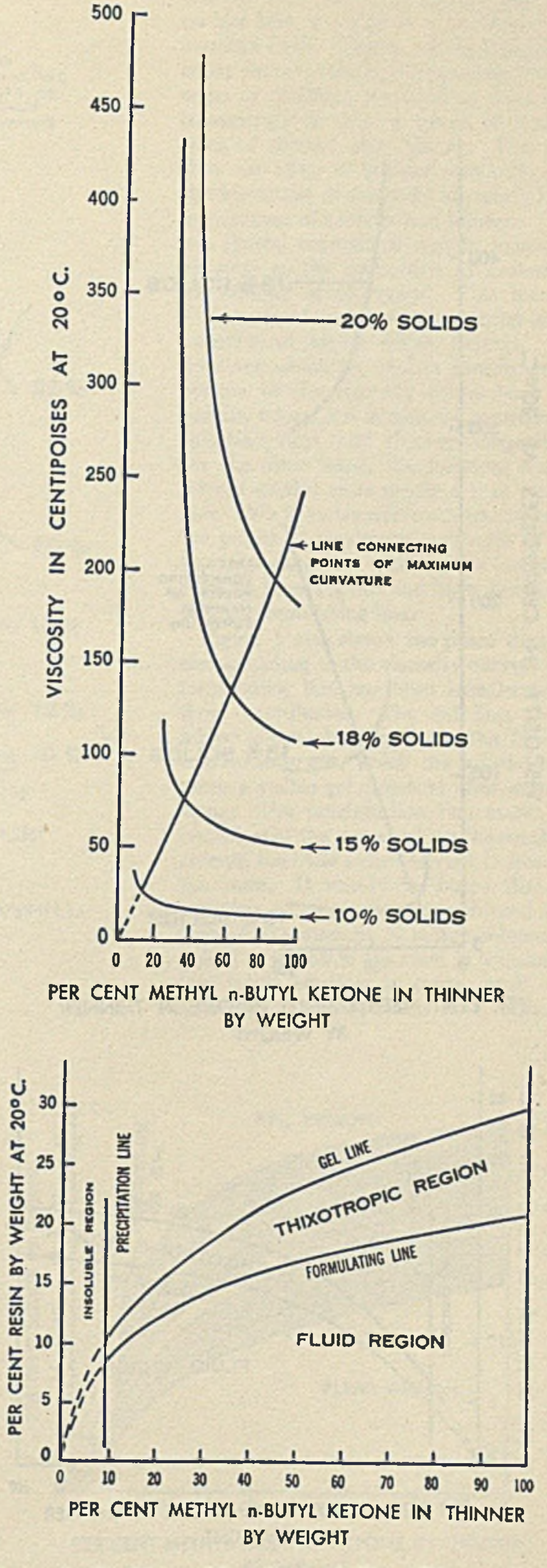


Figure 4. Equilibrium Viscosities and Phase Diagram of Resin VYHH in Methyl *n*-Butyl Ketone–Toluene Mixtures

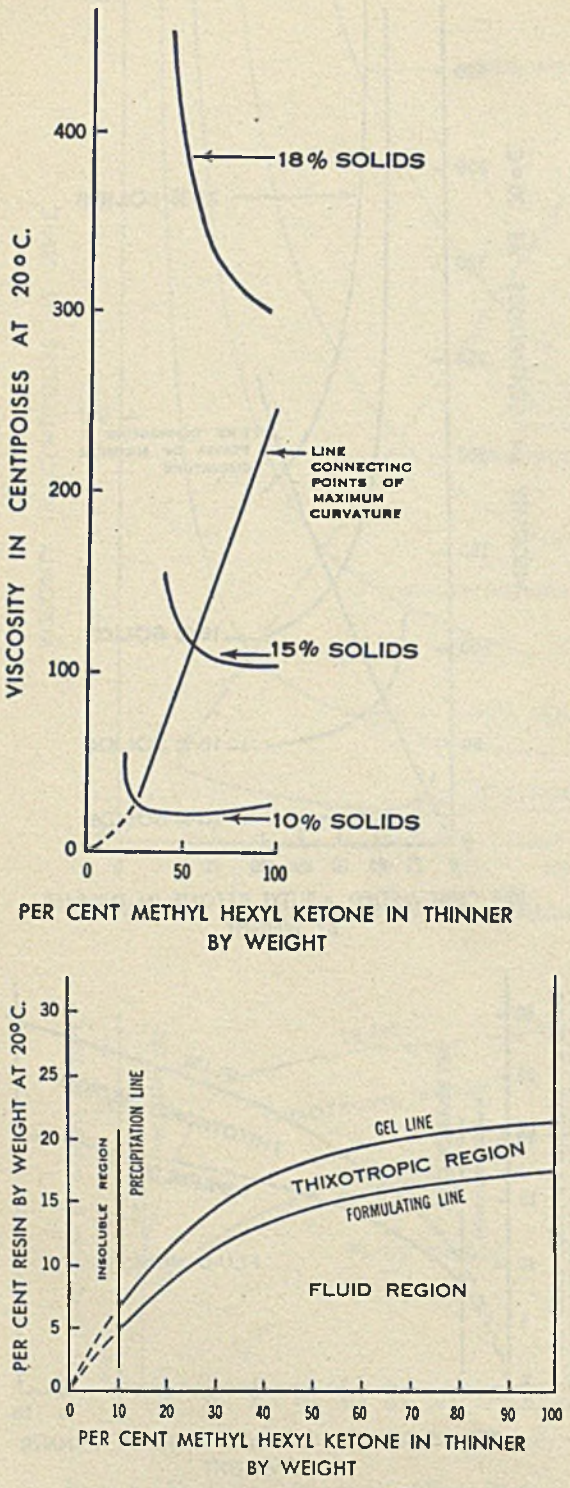


Figure 5. Equilibrium Viscosities and Phase Diagram of Resin VYHH in Methyl Hexyl Ketone–Toluene Mixtures

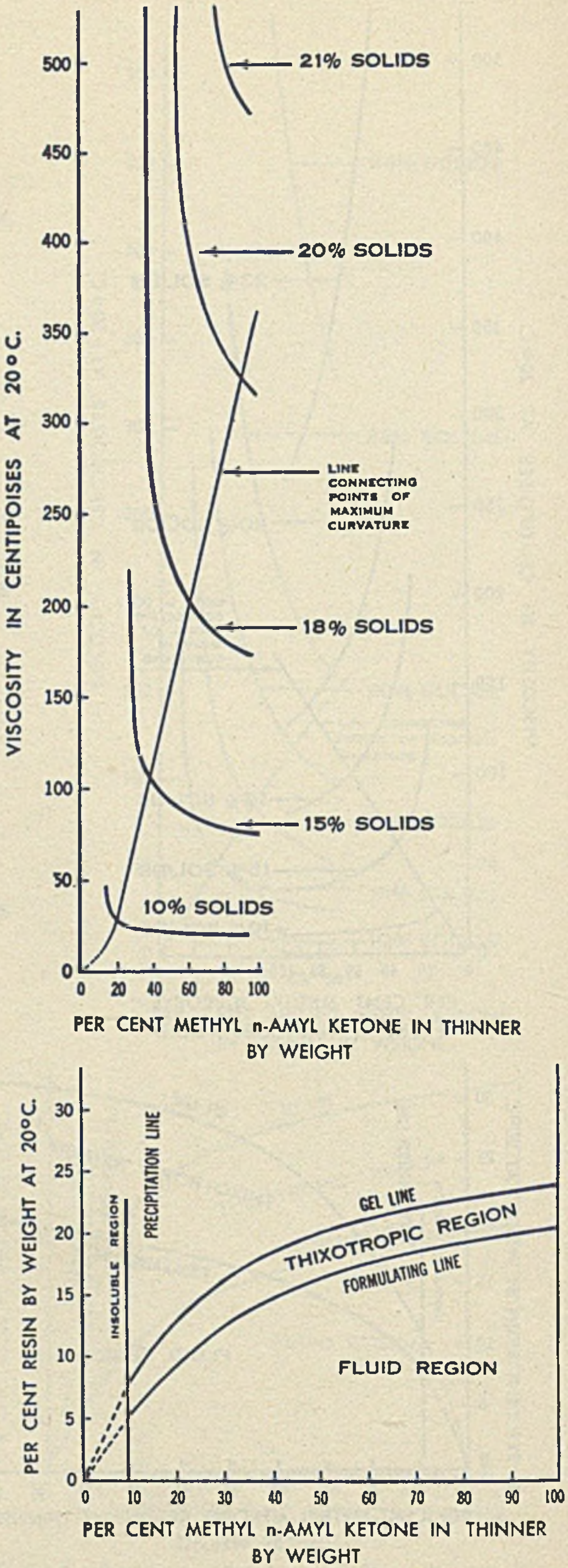


Figure 6. Equilibrium Viscosities and Phase Diagram of Resin VYHH in Methyl *n*-Amyl Ketone–Toluene Mixtures

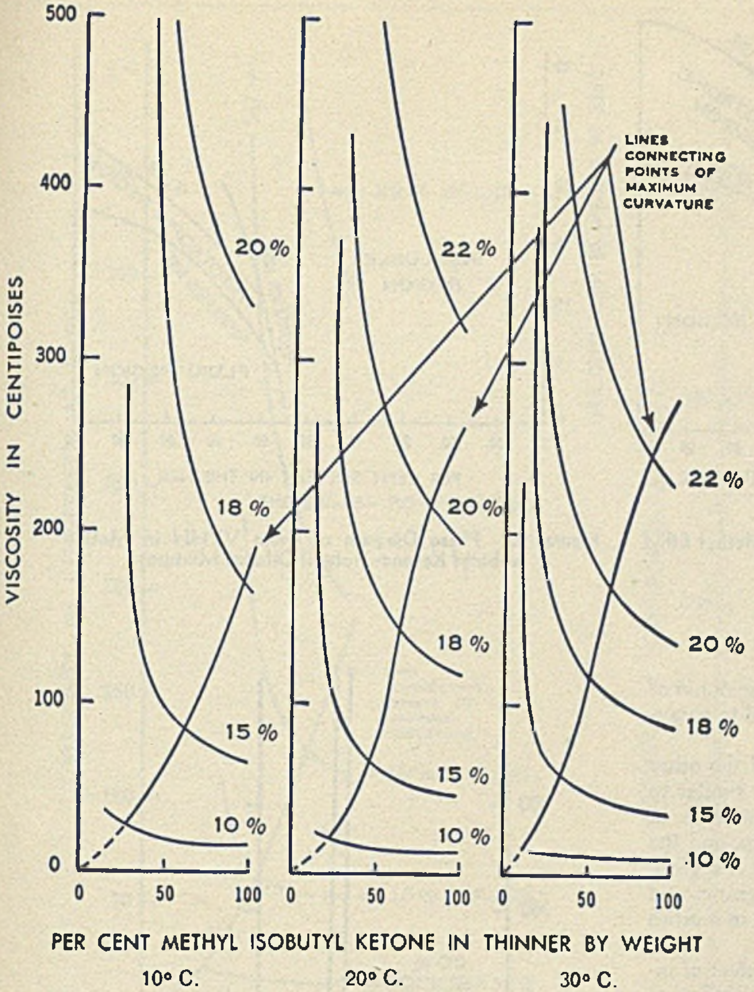


Figure 7. Effect of Temperature on Equilibrium Viscosities of Resin VYHH in Methyl Isobutyl Ketone–Toluene Mixtures

representative of the first solubility type and Vinylite VYNW as representative of the second. The VYHH resin is a vinyl chloride-acetate copolymer containing 85–88 per cent vinyl chloride with an apparent Staudinger molecular weight of 10,000. The VYNW resin is a copolymer which contains 93–95 per cent vinyl chloride with an apparent Staudinger molecular weight of 24,000.

The solution characteristics of resin VYHH have been extensively studied to provide the necessary background for its use in surface coatings. Early in this work it was found that the simple dilution ratio criteria used to evaluate nitrocellulose solvents were not applicable to the vinyl chloride-acetate resin. Not only were the precipitation end points difficult to obtain, but this type of data did not provide a true picture of what was occurring in the resin solutions. The result was the development of the viscosity phase method of evaluating solvents. This procedure, described earlier by Doolittle[1], has been applied to the evaluation of a number of nitrocellulose solvents. A continuation of that work as it applied to resin VYHH, a few of the many solvent evaluations made, and an interpretation of some of the effects obtained will be described here.

THE equilibrium viscosities were obtained with a precision Hoeppler viscometer after the solutions had been aged no less than 3 weeks in a constant temperature bath. Figure 1 gives typical viscosity curves obtained by measuring several series of solutions prepared at fixed resin concentrations over a range of proportions of solvent and diluent. The data show the effect of thinner composition on the viscosities of solutions of resin VYHH in mixtures of acetone and toluene. This is a typical example of rapidly increasing viscosity as the proportion of acetone in the thinner is decreased. This increase is more rapid and more pronounced in the solutions of higher solids content. The solutions which lie on the rapidly rising portion of the viscosity curves have viscosities which are extremely sensitive to agitation, heat, and thinner composition. On the other hand, the solutions rich in solvent exhibit more nearly a true viscous flow. We have therefore arbitrarily taken the points of maximum curvature of the viscosity curves as marking the boundary between these regions and have designated this the formulating line.

Figure 1 also shows the phase diagram corresponding to the viscosity curves; the formulating line has been transferred to these coordinates. The gel line, determined separately, represents the limiting concentrations at which the solutions develop a visible gel structure after suitable aging. The precipitation line marks the boundary of the region where the solutions contain too little active solvent to disperse the resin. It should be noted that, in solutions of copolymer resin diluted with toluene, the amount of active solvent required to maintain the resin in solution at low solids content is quite small. By and large this fact means that, although

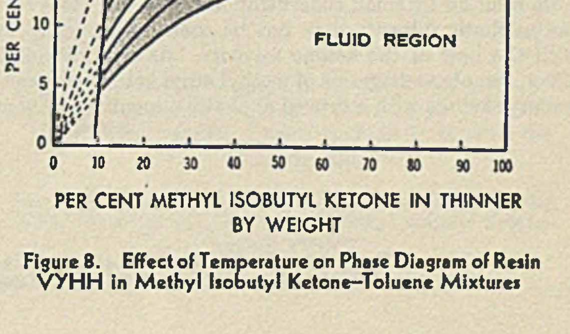


Figure 8. Effect of Temperature on Phase Diagram of Resin VYHH in Methyl Isobutyl Ketone–Toluene Mixtures

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[1] Ind. Eng. Chem., 30, 189–203 (1938).

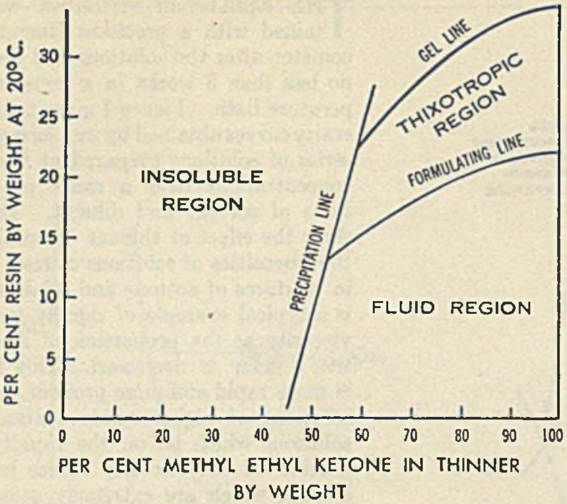

Figure 9. Phase Diagram of Resin VYHH in Methyl Ethyl Ketone–Troluoil Diluent Mixtures

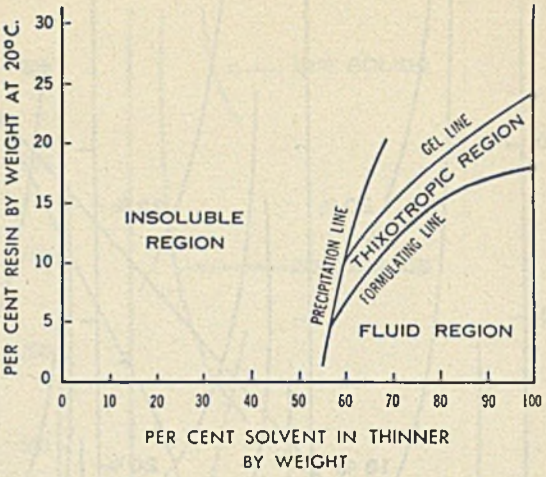

Figure 10. Phase Diagram of Resin VYHH in Methyl Isobutyl Ketone–Troluoil Diluent Mixtures

solutions prepared for storage must contain large amounts of active solvent, these same solutions may be thinned to spraying viscosities with diluent alone.

In general, the viscosity and phase diagrams of the other lower aliphatic ketones with toluene or xylene are similar to the acetone diagram. There is a progressive increase in viscosity as we ascend the series of methyl ketones, and the amount of resin carried in solution at the gel point is slightly lowered. Figures 2 to 6 present the phase diagrams and equilibrium viscosities of solutions of resin VYHH in a series of the methyl ketones, diluted with toluene.

The viscosity curves in Figure 7 illustrate the effect of increased temperature in lowering the equilibrium viscosity of the resin solution. Because solutions of vinyl resins rise slowly to their true equilibrium viscosity as the temperature is lowered, this characteristic is often employed to effect a certain amount of solvent economy where solutions are not subjected to storage. The corresponding effect of temperature on the phase diagrams is shown in Figure 8. The decrease in the concentration of resin at the gel line at lower temperatures gives a measure of the extent to which the solutions must be enriched with solvent for low-temperature storage.

THE previous diagrams represent the results obtained when aromatic hydrocarbons are used as diluents in the resin solutions. The various aromatic hydrocarbons can be substituted for one another without any important differences in the shape or position of the various curves. On the other hand, the vinyl polymers are particularly sensitive to the presence of aliphatic hydrocarbons and are precipitated from solution by small concentrations of them. As a result, the aliphatic diluents may not be used economically even with the best of the ketone solvents. As examples of this effect, the phase diagrams of methyl ethyl ketone and methyl isobutyl ketone with a typical aliphatic diluent are presented

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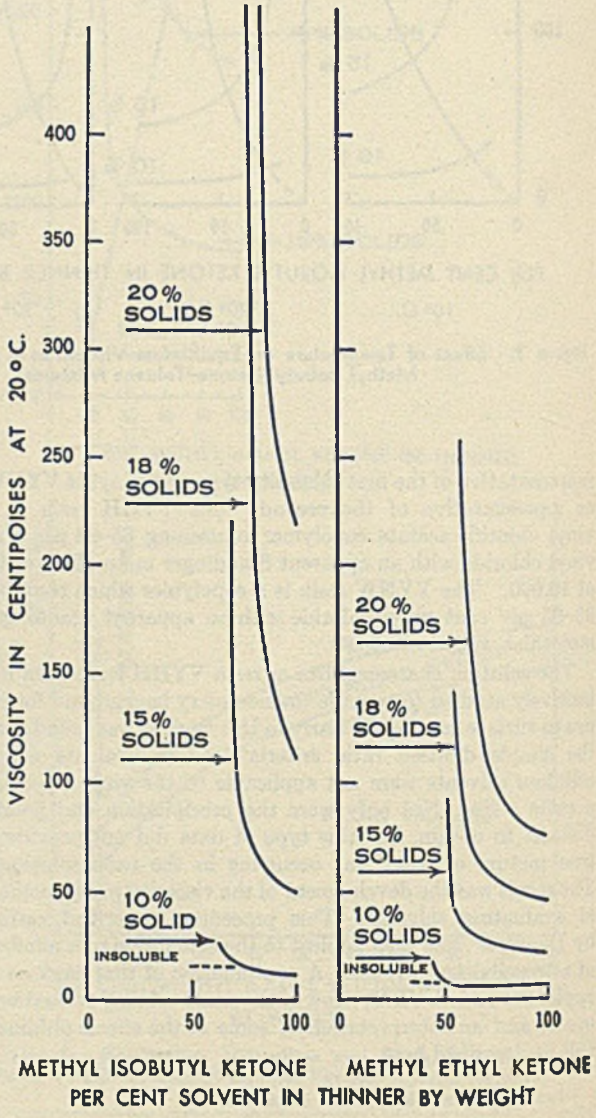

Figure 11. Equilibrium Viscosities of Resin VYHH in Ketone–Troluoil Diluent Mixtures

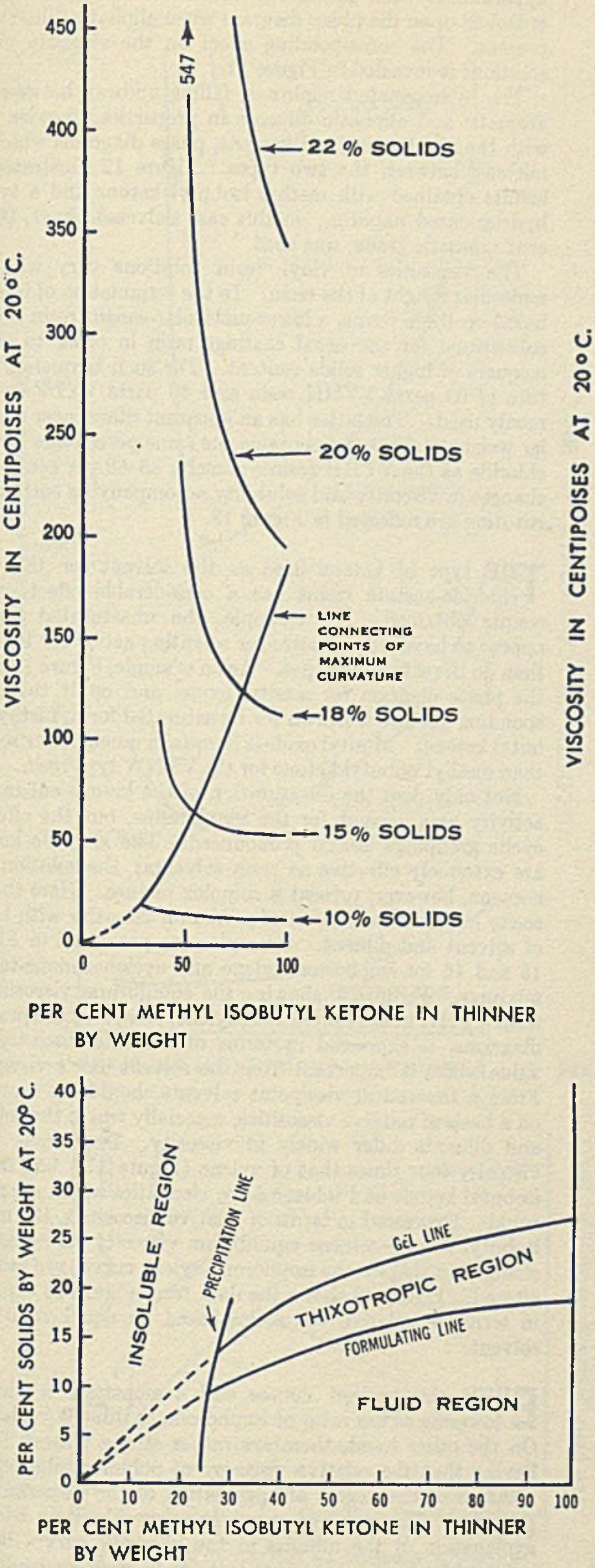

Figure 12. Equilibrium Viscosities and Phase Diagram of Resin VYHH in Methyl Isobutyl Ketone–Solvesso No. 1 Mixtures

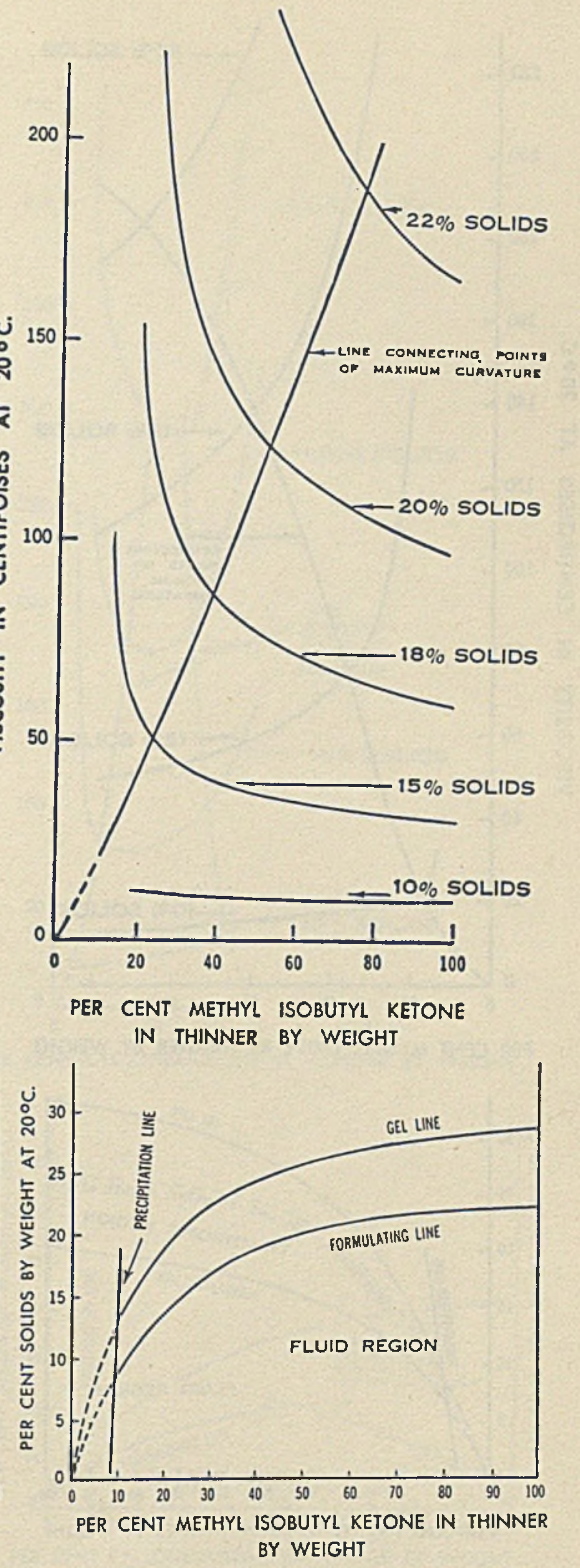

Figure 13. Equilibrium Viscosities and Phase Diagram of 3:2 Resin VYHH–VYLF Mixtures in Methyl Isobutyl Ketone–Toluene Thinners

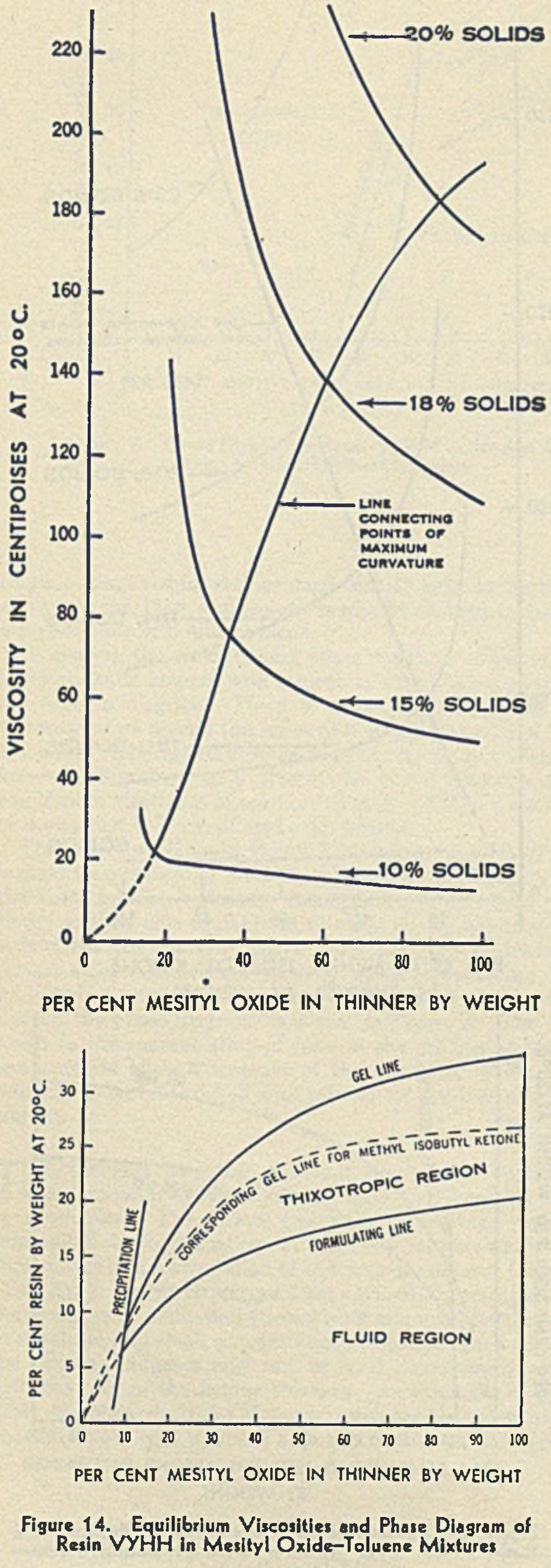

Figure 14. Equilibrium Viscosities and Phase Diagram of Resin VYHH in Mesityl Oxide–Toluene Mixtures

in Figures 9 and 10. By contrast with Figures 2 and 8, it is apparent to what an extent the insoluble region has encroached upon the phase diagram when aliphatic diluents are present. The corresponding effect on the viscosity of the solutions is revealed in Figure 11.

The hydrogenated naphthas, falling midway between the aromatic and aliphatic diluents in properties, likewise yield with the vinyl resins and ketones, phase diagrams which are midway between the two types. Figure 12 illustrates the results obtained with methyl isobutyl ketone and a typical hydrogenated naphtha; in this case Solvesso No. 1, 90 per cent aromatic grade, was used.

The viscosities of vinyl resin solutions vary with the molecular weight of the resin. In the formulation of lacquers based on these resins, a lower-molecular-weight resin is often substituted for the usual coatings resin in order to obtain lacquers of higher solids content. For such lacquers a mixture of 60 parts VYHH resin and 40 parts VYLF is commonly used. The latter has an apparent Staudinger molecular weight of 6000 and contains the same percentage of vinyl chloride as the VYHH resin—namely, 85–88 per cent. The changes in viscosity and solubility accompanying such a substitution are reflected in Figure 13.

THE type of ketone used as the solvent for the vinyl chloride-acetate resins has a considerable effect on the results obtained. For example, the unsaturated ketones appear to have a much stronger solvating action for the resin than do the saturated types. As an example, Figure 14 shows the phase diagram for mesityl oxide, and on it the corresponding gel line is drawn for its saturated form, methyl isobutyl ketone. Mesityl oxide is likewise a much better solvent than methyl isobutyl ketone for the VYNW type resin.

Not only does the unsaturation of the ketone enhance its activity as a solvent for the vinyl resins, but the effect of cyclic groupings is also pronounced. The alicyclic ketones are extremely effective as resin solvents; the solution phenomena, however, present a complex picture. Here the viscosity curves have a point of minimum viscosity with blends of solvent and diluent. Examples are presented in Figures 15 and 16 for isophorone-xylene and cyclohexanone-toluene mixtures. Figure 15, showing the equilibrium viscosities of resin VYHH in isophorone and xylene, as well as the previous diagrams, is expressed in terms of absolute viscosity, the value which is important from the solvent user's viewpoint. From a theoretical viewpoint solvents should be compared on a basis of relative viscosities, especially where the solvents and diluents differ widely in viscosity. Isophorone has a viscosity four times that of xylene (Figure 17), but methyl isobutyl ketone and toluene have viscosities which are nearly equal. Expressed in terms of relative viscosities, the methyl isobutyl ketone–toluene equilibrium viscosity curves are unchanged in shape; the isophorone-xylene curves are radically altered. Figure 18 shows the data from Figure 15 expressed in terms of relative viscosities based on equal volumes of solvent.

EVEN the revised curves still demonstrate a viscosity lowering as the ratio of isophorone to diluent is changed. On the other hand, there are rather strong reasons for believing that the relative viscosity of polymer solutions is a measure of the degree of aggregation of the dispersed resin particles. This point of view leaves us without an adequate explanation of the minima in the viscosity curves because we would expect a continual increase of resin aggregation as the ratio of solvent to diluent falls. These viscosity minima occur with a number of compounds, and they are not entirely characteristic of the alicyclic ketones or of the resin. For example, the same type of phenomenon was encountered with

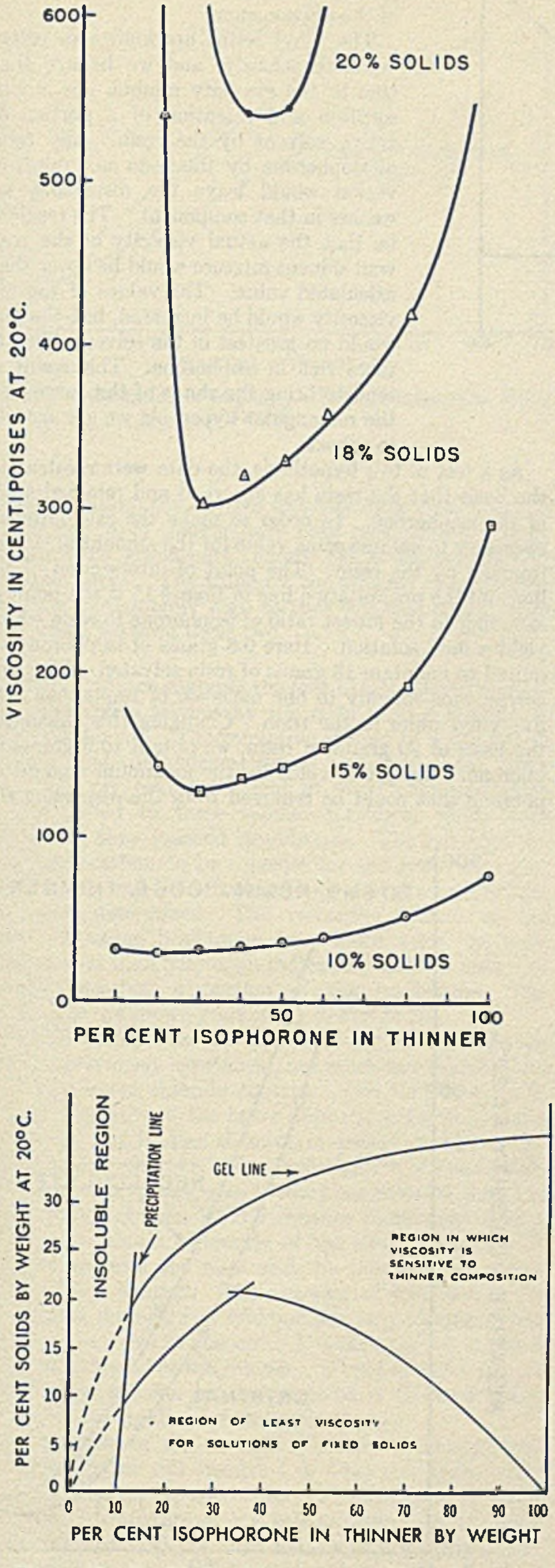

Figure 15. Equilibrium Viscosities and Phase Diagram of Resin VYHH in Isophorone-Xylene Mixtures

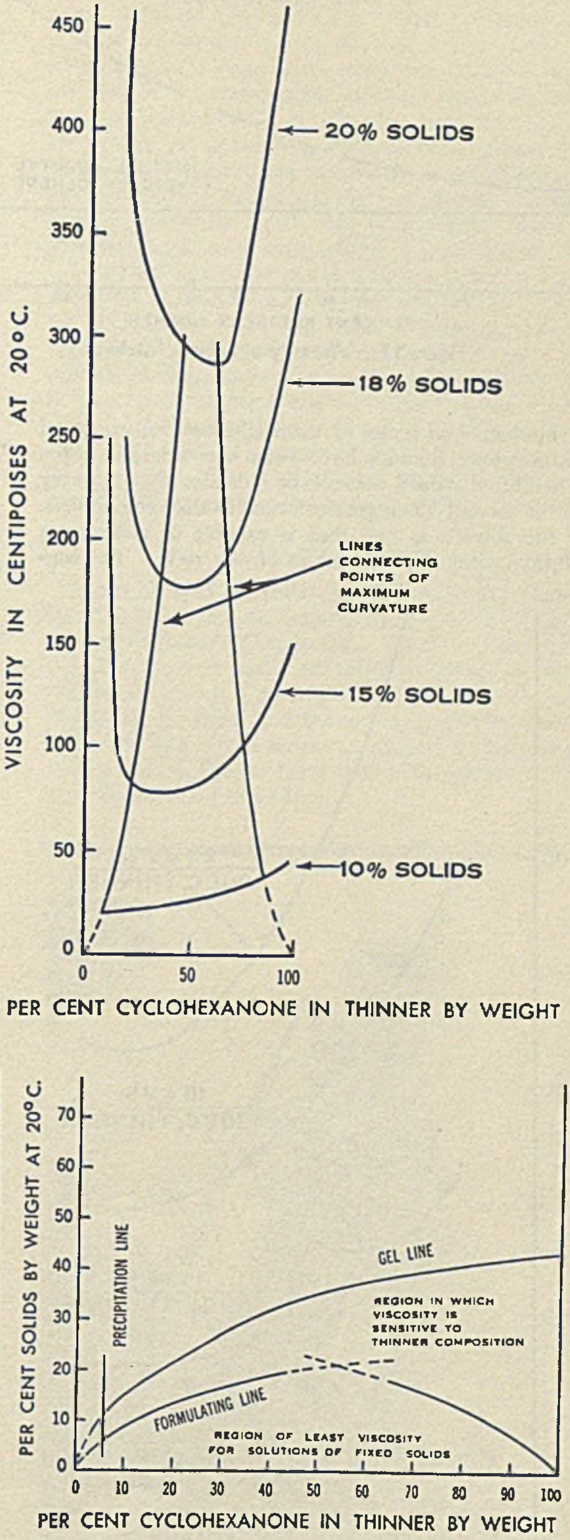

Figure 16. Equilibrium Viscosities and Phase Diagram of Resin VYHH in Cyclohexanone-Toluene Mixtures

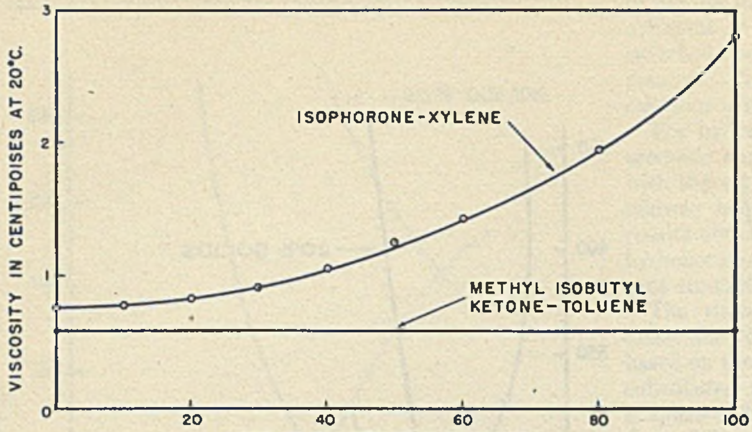

Figure 17. Viscosity of Solvent Mixtures

Cellosolve-toluene solutions of nitrocellulose[1]. A study of those cases where minima have been encountered as the solvent is diluted with a nonsolvent indicates that in every instance the solvent has a greater viscosity than the diluent. Usually the solvent is one that is capable of undergoing high dilution without precipitation of the resin. The suggestion has been made that the mini are due to association of the solvent. V would like to offer another and simpler pict of the phenomenon.

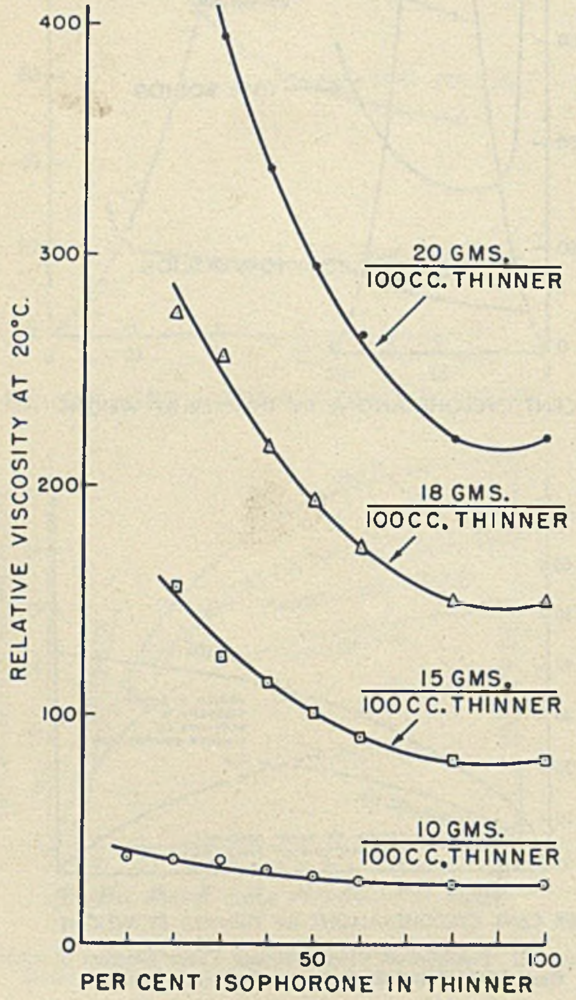

Figure 18. Relative Viscosities of Resin VYHH in Isophorone-Xylene Mixtures

The vinyl resins are known to retain s vents tenaciously, and we believe that t clue to the viscosity minima lies in this a sorption and retention of a portion of t active solvent by the resin. Any retenti of isophorone by the resin as a result of s vation would leave the dispersing solv weaker in that component. The result wou be that the actual viscosity of the true s vent-diluent mixture would be lower than t calculated value. The values of the relat viscosity would be increased, but the increa would be greatest in the solvent-diluent m tures rich in isophorone. This result wou tend to bring the shape of the curve closer the rectangular hyperbola we are accustom to expect.

As a test of this hypothesis, the data were recalculated the basis that the resin has absorbed and retained a porti of the isophorone. In order to make the calculations, it necessary to assume some value for the amount of isophoro retained by the resin. The point of intersection of the g line and the precipitation line in Figure 15 is the point cor sponding to the lowest ratio of isophorone to resin which w yield a fluid solution. Here 9.8 grams of isophorone are quired to maintain 18 grams of resin solvated. This amou corresponds roughly to one molecule of isophorone for ea five vinyl units in the resin. Changing this calculation the basis of 20 grams of resin, we obtain 10.9 grams of is phorone. Using this value for the maximum amount of is phorone that could be removed from the dispersing thinn

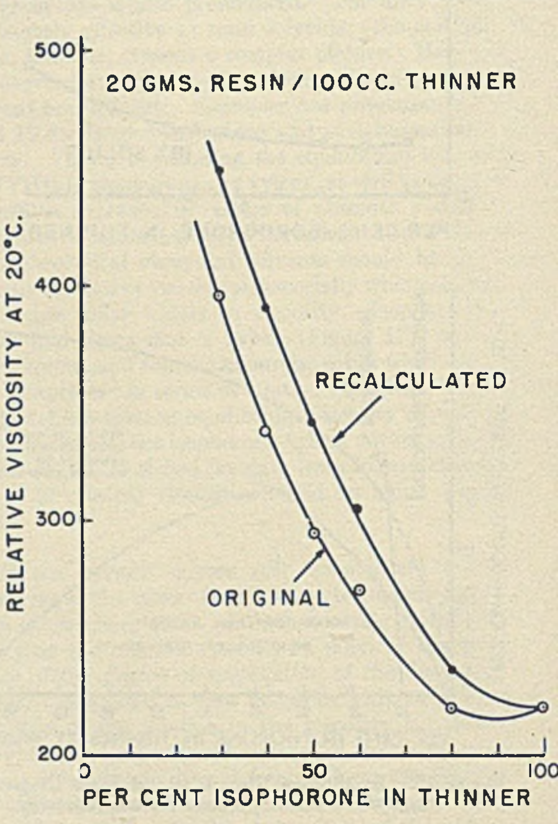

Figure 19. Equilibrium Viscosity of Resin VYHH in Isophorone-Xylene Mixtures at 20 Grams per 100 Cc. Thinner

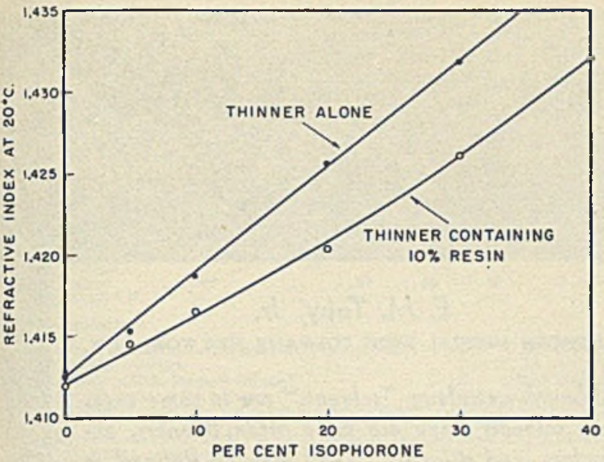

Figure 20. Absorption of Isophorone-Troluoil Thinners by Resin VYNW

owing to solvation, the relative viscosity data at 20 grams of resin per 100 cc. of thinner have been recalculated. These data are shown graphically (Figure 19) in comparison with the original curve. The value for the amount of isophorone adsorbed is undoubtedly high so that the true curve would lie somewhere between these two.

OTHER evidence supports the idea of selective adsorption of the active solvent by the resin from a mixture of solvent and diluent. The refractive indices of a number of isophorone–aliphatic hydrocarbon mixtures have been determined. Ten per cent by weight of vinyl chloride-acetate resin was added to these thinner mixtures, which were tumbled until they reached equilibrium. The mixtures too high in hydrocarbon to be solvents for the resin were permitted to settle and the refractive indices of the supernatant liquids were determined. The refractive indices of the thinners containing isophorone were lower after the resin had been added than before, an indication that the resin had selectively adsorbed a portion of the isophorone. The pertinent data are shown graphically in Figure 20.

The vinyl chloride-acetate resins of high vinyl chloride content, as previously mentioned, are much less soluble than the resins of lower chloride content. The VYNW resin is only slightly soluble in the lower aliphatic ketones at room temperatures, but it does dissolve in mesityl oxide, cyclohexanone, and isophorone. The investigation of the solubility characteristics of this resin is more complicated than the previous studies of resin VYHH because equilibrium results are difficult to obtain. Because of the slow attainment of equilibrium between the resin and the thinner, unexpected results are often secured. The viscosity of solutions of the resin in mixed thinners is a function not only of the thinner composition, but also of the order in which the resin is wet with the components of the thinner. Owing to these effects, stable solutions of resin can be prepared in thinners which would not ordinarily dissolve the resin directly.

As an example of the unusual phenomena encountered, methyl ethyl ketone will dissolve 1 to 2 per cent resin, while isophorone dissolves approximately 15 per cent at room temperature. A mixture of the two solvents in equal parts will form a viscous 10 per cent solution if the resin is dissolved directly in the mixed thinner. On the other hand, if we first wet the resin with methyl ethyl ketone and then add isophorone to the mixture, a gel is obtained. By reversing the process (wetting the resin first with isophorone and then adding the methyl ethyl ketone), a very fluid solution is obtained.

These phenomena are not transitory and further substantiate the hypothesis that at least a part of the solvent is tightly bound to the resin in solution. These solutions and gels of identical compositions have been stored for more than a year without any perceptible changes in state. Samples of the gels and the solutions have been heated to 100° C. for an hour in pressure bottles without erasing the differences between the two. The gels become softer and the solutions more fluid, but on returning to room temperature, they show no evidence of becoming identical. The fact is inescapable that the solvent with which the resin is first solvated is extremely tightly held; the rate of desolvation must be very slow compared to our expectations from the kinetic theory.

Here, perhaps, we have a clue that may lead to a new conception of the handling of macromolecular resins in solutions. As we are able to develop more powerful specific solvents capable of solvating these resins, we may find a practical method of dispersing many of the now essentially insoluble resins and of making available to the coatings industry the chemical inertness and toughness of resins which have hitherto defied attempts to incorporate them into soluble coatings. Already some of the ideas have yielded dividends in the handling of the more insoluble vinyl chloride-acetate resins.

ACKNOWLEDGMENT

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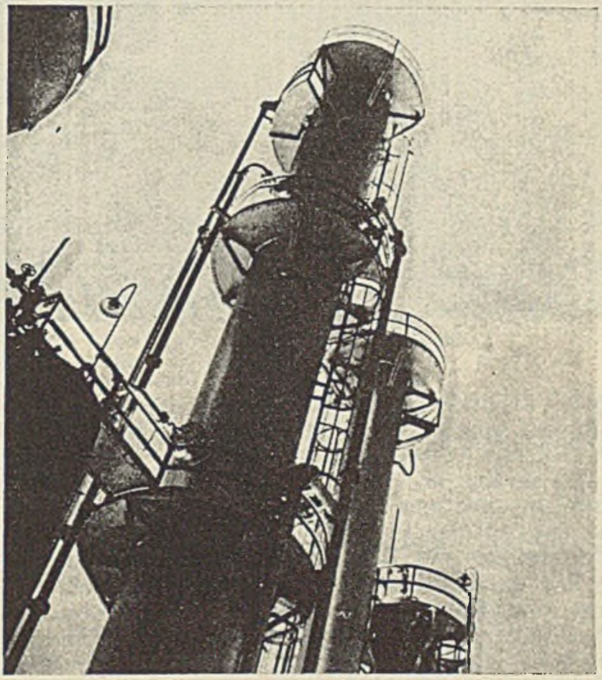


Fractionating Columns of the Phillips Petroleum Company
(See "Petroleum Solvents", page 1044)

PETROLEUM SOLVENT

E. M. Toby, Jr.

AMERICAN MINERAL SPIRITS COMPANY, NEW YORK, N. Y.

Although petroleum "solvents" are in some cases true solvents, they are more often thinners, extenders, and diluents. They may be defined as "a homogeneous mixture of paraffinic, naphthenic, and aromatic hydrocarbons of different boiling points". Limitless in number as are all mixtures, they are usually defined by their controlled evaporation rates. Three general classes of petroleum solvents are discussed: (1) straight-run solvents, predominantly paraffinic but sometimes cycloparaffinic in structure, (2) aromatic solvents, containing from 45 per cent aromatics to pure nitration grades, and (3) close-cut hydrocarbons, primarily hexane and heptane with 5° to 15° F. boiling ranges. (Photograph is reproduced through courtesy of Phillips Petroleum Company.)

SOLVENTS from petroleum is so broad a subject that its exact scope is difficult to define. Until recently, this was not true. Formerly a conventional petroleum refinery would distill crude petroleum, using first the old shell still, then later tube stills with modern fractionating equipment for manufacturing any number of hydrocarbon fractions. These fractions were first defined by their gravity and then by their distillation ranges. But as the petroleum industry grew from adolescence, the conventional refinery became a chemical plant and the petroleum technologist is now interested in the conversion of his raw material to finished products of many chemical structures.

With this change from refining to conversion, the petroleum solvent field has become complex. The conversion products will not be discussed in detail, but it is well to remember that they will play an ever increasing part in the development of the solvent consuming industries. This paper will be restricted to the nonconverted or natural hydrocarbon fractions, or petroleum naphthas, classified as follows: aliphatic and naphthenic, aromatic, and "close-cut" petroleum solvents.

ALIPHATIC AND NAPHTHENIC SOLVENTS

These products are manufactured by the distillation and fractionation of crude oil. Obviously, since no chemical transformation takes place in such a process, the finished solvents have the chemical characteristics of the crude oil from which they are derived. No two crude oils are exactly alike; therefore no two petroleum solvents derived from

Table I. Specifications for Standard Aliphatic and Naphthenic Solvents

Solvent No.[a]	1	2	3	4	5	6	7	8	9	10	11	12	13	14
A. P. I. gravity	70.5	70–73	64.0	62.0	62.0	55–61	55–60	45–53	47–54	41–43	46–51	50.0	43–48	43.0
Sp. gravity	0.7005	0.69–0.70	0.7238	0.7313	0.7313	0.73–0.75	0.74–0.76	0.77–0.80	0.76–0.79	0.81–0.82	0.77–0.79	0.7796	0.78–0.81	0.8109
Pounds/gal.	5.831	5.7–5.8	6.025	6.087	6.087	6.1–6.3	6.1–6.3	6.4–6.7	6.3–6.6	6.7–6.8	6.4–6.6	6.49	6.5–6.7	6.752
A. S. T. M. distillation, ° F.														
Initial B. P.	140	105	170	205	200	215–230	205–210	290	305	310	325	360	340–370	370
50% over	175	175–185	200	210	220	250	255–265	305	345	340	350	380	390–410	430
90% over	195	220	220	220	240	270	310–315	315–330	370	370	370	400	425–435	475
Dry point	205	245–260	235	232	260	295	365–370	325–345	395	395	395	405	455	505
End point	210	250–265	240	235	265	295–305	370–375	330–350	400	400	400	410	460	510
Kauri butanol[b]	33.5	34.0	37.5	38.0	38.0	35–39	35–39	36–47	31–40	42–46	34–36	31.0	29–37	32.0
Aniline point[c]	135	135	128	125	125	125–135	125–135	110–135	125–150	114–120	140	151	135–160	150
Nitrocellulose diln. ratio[d]	1.30	...	1.35	1.40	1.40	1.30	...	...	...	...	...	...	...	...
Flash point[e], ° F.	...	...	...	...	...	...	...	85	103	105	115	141	130–150	150

[a] Material key:

1 = light lacquer diluent, benzene replacement
2 = rubber solvent
3 = intermediate lacquer diluent
4 = special extraction solvent
5 = heavy lacquer diluent, toluene replacement
6 = V. M. & P. (close cut)
7 = V. M. & P. (long cut)
8 = xylene replacement
9 = mineral spirits
10 = naphthenic mineral spirits
11 = high-flash mineral spirits
12 = high-flash (140° F.) dry cleaning solvent and paint thinner
13 = flat-finish thinner
14 = slow-dry thinner

[b] Using Stewart Research Lab. standardized and certified Kauri butanol solution.

[c] Equal volume method, A. S. T. M. D611-41T.

[d] At 10% final concentration.

[e] Tag closed cup method, A. S. T. M. D56-36.

different crudes are alike. Crude oils are complex products containing paraffinic, naphthenic, and aromatic hydrocarbons from the lowest members of each group, well up into solids. A petroleum solvent is therefore a homogeneous mixture of these hydrocarbons; the percentages of the types present are dependent upon the crude base, and the molecular weights are dependent on the distillation limits of the fraction.

Inasmuch as the protective coating industry is the largest consumer of such solvents, most specifications have been written with the needs of this field in mind. For most industries the evaporation rate is the controlling usage specification. The average consumer of petroleum solvents specifies the desired evaporation rate by means of distillation specifications; however, experience has shown that the distillation test is not a true measure of evaporation, but merely a record of the boiling range of the solvent under arbitrarily set conditions. There is no standardized procedure, and each consumer and manufacturer has his own tests.

Industry is becoming increasingly solvency-minded. More and more it demands definite solvency values. These values are generally expressed in terms of Kauri butanol number, aniline point, nitrocellulose tolerance, characteristic factor, or aromaticity. The most widely accepted and used are aniline point and percentage of aromaticity, which are relatively simple and reproducible.

The aniline point is the critical solution temperature, and is indicative of the hydrocarbon groups present. Many important government specifications use this test as the basis of solvency evaluation.

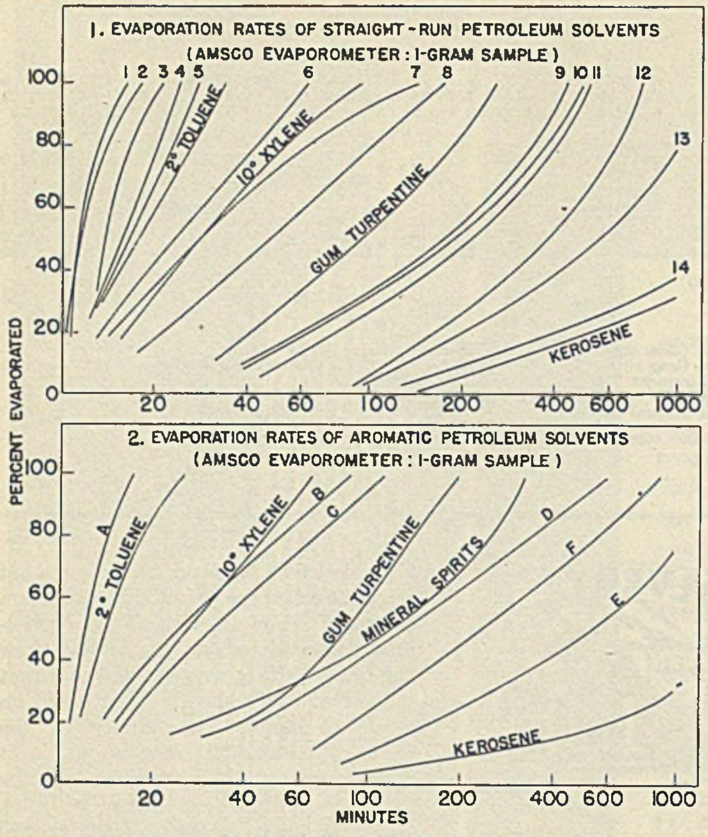
The percentage of aromaticity is best determined by the method developed by the Philadelphia Paint and Varnish Production Club. Their fuming sulfuric acid extraction method is inaccurate for low-aromaticity solvents, but silica gel gives reproducible results for these solvents. This method is being used more and more since its results are indicative of the solvency of the material under test. However, more extensive acceptance of this method will be slow because most small plants do not have Abbe refractometers.

Many other methods of solvency evaluation are under consideration, but none have been given national recognition. Many are based on the viscosities of the solvents with specific resins and give results pertinent to that resin used alone which are not applicable outside of the coating industry.

Table I lists the specifications of what might be called the "standard" petroleum solvents. They are indicative of available fractions today, but do not show the fractions that may be made to meet individual user's specifications based on usage demands. This ability on the part of petroleum refiners to meet wide demands is indicative of the extreme flexibility of these solvents. Table II indicates some of the general uses of these products. Figure 1 shows the relative evaporation rates of these products compared to other standard solvents. (The evaporation charts in this article were prepared from data secured with the Amsco Evaporometer. The temperature at which these tests were run is a controlled variable, based upon the volatility of the solvents under test, so that one chart cannot be compared with another.)

In addition to the general uses of the petroleum solvents in Table II, they are utilized in war industries in many ways. These cannot be divulged exactly but a general outline follows:

1 Protective coatings (paints, varnishes, lacquers, enamels)
    Zinc chromate primer for aircraft and other metal surfaces
    Camouflage
    Marine and army equipment
    Ordnance items such as bombs and shells
    Portable aeroplane landing mats
    Industrial plants making war equipment
    Installations such as barracks, arsenals, etc.
    Defense housing
    Gas masks, life rafts, life-saving vests
    Cases for ordnance, food, ammunition, etc.
    Cable insulation
2. Textile proofing
    Flame, rot, and waterproofing of canvas
    Mildew proofing of burlap and Osnaburg
    Camouflaging of all fabrics including leno cloth and shrimp nets
    Pigment printing and dyeing of uniforms and work clothes
    Rope, cordage, and fire hoses
    Raincoats and hospital sheeting
3. Manufacture of anticorrosive compounds, rust preventives, etc.
4. Extraction of fats and greases
5. Extraction of soybeans, castor beans, rosin, turpentine
6. Manufacture of mustard gas proofing compound
7. Washing of engines and metal parts, particularly aircraft engines
8. Manufacture of synthetic and natural rubber-coated fabrics, including barrage balloon fabric
9. Manufacture of tires, rubber tracks, etc.
10. Manufacture of surgical gloves, industrial, gloves, and similar rubber dipped goods



Figures 1 and 2

11. Adhesives, cements, tapes, identification tabs for aeroplane and tank assembly, weather-sealing equipment for domestic and overseas equipment
12. Military shoes and footwear

These give an idea as to the importance of petroleum solvents to the war effort. In some cases they cannot be used for the purpose without the incorporation of petroleum aromatic solvents.

The future of these aliphatic and naphthenic solvents is uncertain for the duration of the war. There are many competing uses, and the future availability of these products (particularly those with an end point of unde 300° F.) will be decided in the demands those competing war uses as balanced again our crude oil supply and available refinin capacity.

AROMATIC SOLVENTS

Aromatic petroleum solvents are, in a sens products of conversion. Their principal sourc today are (1) Edeleanu extracts of distillat of highly aromatic crude oils and (2) produc of catalytic cracking under certain condition General specifications on the available aromat petroleum solvents are listed in Table III, an their relative evaporation rates compared coal tar aromatic solvents are shown in Fi ure 2.

Today petroleum aromatic solvents are unde allocation by the War Production Board unde Order M-150. Those solvents with an aroma ticity over 30 per cent and with a 50 per cen distillation point below 330° F. fall under th order. The competing war demands for thes materials are for conversion into toluene an for incorporation into aviation gasoline. Princ pal allocated war uses are for extraction pharmaceuticals and vitamins (particularl the so-called sulfa drugs), the coating of textil (flame-proofing of canvas, hospital sheetin raincoats, etc.), barrage balloon coating, foo container linings, neoprene solutions, cab coatings, and protective coatings of many kind particularly aircraft.

One of the most widely used governmen specifications is AN-T-8b for "Thinner-Tolu ene Substitute" which, as amended January 27, 194 calls for:

Naphtha, petroleum[a]	
Aromatic type 1 Grade B	62%
Xylene	28
Alcohol	
n-Butyl	10

[a] Covered by Specification AN-VV-N-96. Material as listed und specification A meets this requirement.

Table II. General Uses of Aliphatic and Naphthenic Solvents

Solvent No.	Paints	Varnishes	Lacquers	Flat Finishes	Rubber Cements and Adhesives	Rubber Dip Goods	Rubber Tires and War Materials	Rosin Extn.	Castor Oil Extn.	Fat Extn.	Dry Cleaning	Rust Inhibitors	Textile, Flame, Rot, Water Proofing	Textile & Pigment Printing	Floor Coverings	Brake Linings	Artificial Leather	Rotogravure Inks	Adhesive Tapes	Leather Degreasing	Waxes	Shade Cloth	Metal & Machine Cleaning
1	..	..	X	..	X	..	X	..	X	X	..	..	X	X	..	X	X	X	X	X	..	..	..
2	X	..	X	..	X	..	X	..	X	X	..	..	..	..	..	X	..	X	X	X	..	..	..
3	..	..	X	..	X	..	X	..	X	X	..	..	X	..	..	..	X	X	X	X	..	..	..
4	..	..	..	..	..	..	..	X	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
5	..	..	X	..	X	..	X	X	X	X	..	..	X	X	..	..	X	X	X	X	..	..	..
6	X	X	X	..	X	X	X	X	X	X	X	..	X	..	X	X	X	X	X	X	X	X	X
7	X	X	..	..	X	X	..	..	X	X	..	..	X	..	X	X	..	..	..	X	X	X	X
8	X	X	X	..	X	X	..	..	..	X	X	X	X	X	X	..	..	X	..	X	X	X	X
9	X	X	..	X	..	..	..	..	..	..	..	X	X	X	X	X	..	X	..	X	X	..	X
10	X	X	..	X	..	..	..	..	..	..	..	X	X	X	X	X	..	X	..	..	..	..	X
11	X	X	..	X	..	..	..	..	..	..	X	X	X	X	X	X	..	..	..	..	..	..	X
12	X	X	..	X	..	..	..	..	..	..	..	X	X	X	..	..	..	..	..	..	X	..	X
13	X	X	..	X	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
14	X	X	..	X	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..

Another largely used government specification is: General Specification HOMB-ES-680A "Protective Coatings—Synthetic Type". The thinner prescribed with this coating is Class 637 thinner, which can be prepared by blending mineral spirits with 50–60 per cent of material C (Figure 2).

The government specifications in which the use of these materials is indicated are too numerous to mention. However, some Army-Navy aeronautical specifications which are widely used are:

Lacquer, cellulose nitrate
Primer, zinc chromate
Thinner, cellulose nitrate
Thinner, cellulose nitrate (blush-retarding)
Aluminum pigment paste—aircraft

Table III. Specifications for Aromatic Solvents

Solvent No.[a]	A	B	C	D	E	F
A. P. I. gravity	40.0–47.0	41.0	33.0–37.0	33.0	28.0	28.0–32.0
Sp. gravity	0.825–0.793	0.8203	0.860–0.840	0.8602	0.8871	0.887–0.865
Pounds/gal.	6.87–6.60	6.830	7.16–6.99	7.163	7.387	7.38–7.20
A. S. T. M. distillation, ° F.						
Initial B. P.	200–210	240	275–285	305	350	340–360
50% over	235–240	275	295–315	355	405	375–385
90% over	260–265	300	330–340	395	435	395–405
Dry point	270–275	330	350–360	410	460	405–410
End point	275–280	335	360–370	415	465	410–415
Kauri butanol[b]	63.0–80.0	74.0	75–90	75.0	75.0	75–85
Aniline point, ° F.	20–50	15	0–20	20	20	10–20
Mixed aniline point[c], ° F.	80–100	85	60–80	88	88	75–85
Nitrocellulose diln. ratio (10% final concn. with butyl acetate)	1.90–2.30	2.15	...	...	...	...
Per cent aromatics[d]	45.0–65	62.0	70–85	...	...	...

[a] Material key:

A = toluene replacement
B = light xylene replacement
C = heavy xylene replacement
D = Mineral spirits replacement
E = Medium boiling solvent
F = High boiling solvent

[b] Using Stewart Research Lab. standardized and certified Kauri butanol solution.

[c] Mixed aniline cloud point is run with 5.0 cc. of solvent, 5.0 cc. of mineral spirits of 140° F. aniline cloud point, and 10.0 cc. of freshly distilled c. p. aniline.

[d] Philadelphia Paint & Varnish Production Club method.

The availability of these products under M-150 will be scarce for the duration. The toluene replacement type is particularly unavailable today and is being allocated only to aircraft, barrage balloon cable coatings, and food container linings. Others who deserve allocation must use the heavier boiling products.

Many users of petroleum aromatic solvents must be satisfied with those materials outside of M-150. Such solvents as D, E, and F are available without allocation, provided the user can handle the higher boiling hydrocarbons present.

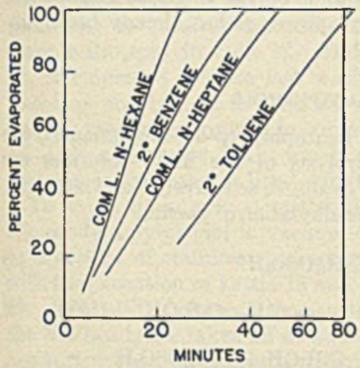


Figure 3. Evaporation Rates of Close-Cut Solvents (Amsco Evaporometer, 5-Gram Sample)

CLOSE-CUT SOLVENTS

A few years back, the user of petroleum solvents was fortunate to find materials with an over-all boiling range of 100° F. As refinery technique progressed, the boiling range of solvents dropped until certain specials were available with a boiling range of 40° F. The narrower the boiling range, the more even the evaporation curve and the better the evaporation control. This need was most apparent in extraction systems where the highest possible initial boiling point is necessary to keep plant losses down; at the same time the lowest end point is also necessary to ensure maximum solvent removal from the extracted product at the minimum temperature. Moreover, close-cut materials are also sought for use in rubber cements, adhesives, and special finishes where evaporation control is also important.

The close-cut solvents shown in Table IV and Figure 3 are prepared for such purposes, usually by the extremely close fractionation of natural gasoline. The equipment and towers used for such fractionation have heretofore been available in the laboratory alone. In ordinary refinery operations columns of about thirty plates are adequate, but in the manufacture of such products, columns of one hundred and fifty or more plates are used; a reflux ratio as high as 100 to 1 is sometimes employed. Such plants can separate, for example, butadiene and butylene from C_4 mixtures.

Some of these materials are used in large quantities. For example, commercial *n*-hexane is utilized in: soybean, cocoa bean, linseed oil foots, pharmaceutical, corn oil, peanut oil, and essential oil extractions; in cleaning precision mechanisms; in tire, rubber, rubber cement, and shoe manufacturing; in flame-proofing, artificial leather finishes, cellophane and marking tapes; and in crystallization operations. Commercial heptane is used for the extraction of castor oil, cocoa beans, peanut oil, corn oil, tankage, and grease; for intaglio inks and cellophane and marking tapes; and for tire and rubber manufacture.

Table IV. Specifications for Close-Cut Petroleum Solvents

Solvent No.[a]	1	2	3	4	5	6
Mol. wt.	86.10	...	100.20	...	70.13	84.16
Sp. gravity	0.668	0.668	0.691	0.724	0.739	0.748
Boiling range, ° F.	155.3–156.3	152–157	208.6–209.6	198–210	120.2–121.2	160.7–161.7
Vapor pressure at 100° F., lb./sq. in. abs.	...	4.9	...	...	...	...

[a] Material key:

1 = technical *n*-hexane
2 = commercial *n*-hexane
3 = technical *n*-heptane
4 = commercial heptane
5 = technical cyclopentane
6 = technical methylcyclopentane

CONCLUSIONS

The war uses of all three grades of solvents are most important. In some cases they are substitutes for other products, in others they are substitutes for substitutes for substitutes, and in still other cases they are prime products best designed and fitted for the job at hand. It is the duty of the petroleum industry to keep faith with the consuming industries by supplying them for the duration and for the postwar reconstruction. After the war the usage of the aromatic solvents will increase greatly due, in part, to their increased availability because of the conversion to solvent manufacture of plants built for other war purposes. We will also see new close-cut solvents and increased use of those already available as well as new types of deodorized naphthas and naphthas of specific chemical structures that tend to give increased body in protective coatings.

NONCHLORINATED COMPOUNDS Derived from Monochloropentanes

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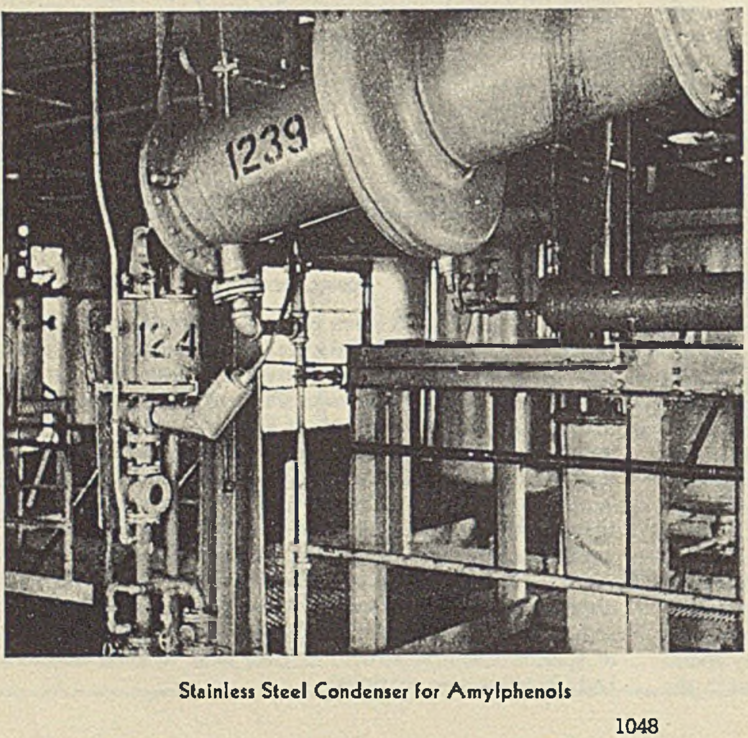
THE high-temperature vapor-phase chlorination of a mixture of pentane and isopentane for the production of monochloropentanes, the hydrolysis of the latter to amyl alcohols, amylenes, and amyl ether, and the acetylation of the amyl alcohols have been previously described (*1–6*). The acetates (Pent-Acetate) serve chiefly as a solvent and the alcohols (Pentasol) as a latent solvent for nitrocellulose lacquers. The alcohols also find application as a component of hydraulic fluids of the castor oil type, as an intermediate for amyl xanthates for use by the mining industry in the flotation of nonferrous ores, and as an intermediate for anesthetics.

Amyl ether is a solvent for many gums, resins, etc., and for the preparation of Grignard reagents.

The amylenes are composed of straight- and branched-chain isomers with 2-pentene and 2-methyl-2-butene predominating. 2-Pentene was formerly hydrated to *sec*-amyl alcoho with sulfuric acid but it is now utilized, alternatively wi amyl chlorides, for the alkylation of naphthalene. 2-Methy 2-butene is an intermediate for the manufacture of amy phenols. In addition to their hydrolysis to the amyl alcoho the amyl chlorides are processed to amylamines and am mercaptan.

In batch processes for the amylphenols, amylnaphthalene amylamines, and amyl mercaptan, all equipment is of ord nary steel construction unless otherwise noted. Bubble-ca columns, centrifugal pumps, steam heating, and water cooli are employed. A description of the building housing t amylamine and mercaptan processes has already been pu lished (*7*).



Stainless Steel Condenser for Amylphenols

AMYLPHENOLS

For the production of Pentaphen (*p-tert*-amylphenol), t amylenes from the hydrolysis of the amyl chlorides a treated with sulfuric acid to absorb selectively the isoamyle The acid also catalyzes the alkylation of phenol:

$$C_5H_{10} + H_2SO_4 \longrightarrow C_5H_{11}OSO_3H \qquad ($$

$$C_5H_{11}OSO_3H + C_6H_5OH \longrightarrow C_5H_{11}.C_6H_4OH + H_2SO_4 \qquad ($$

$$C_5H_{11}.C_6H_4OH + C_5H_{11}OSO_3H \longrightarrow (C_5H_{11})_2C_6H_3OH + H_2SO_4 \qquad ($$

Sulfuric acid of 62 per cent strength made up in mixing tank 1 (Figure 1) wi circulation through cooler 2. The acid pumped to a jacketed mixer, 3, to whi amylene recycled from the previous batch, is slowly fed with the temperature mai tained below 25° C. The temperature controlled to prevent the formation of amylenes. The mixture is pumped to ta 5 where it separates into two layers. T acid layer is dropped back to mixer 3, a the amylene is sent to crude 2-pente storage, 6. Fresh mixed amylenes, 7, a then fed to mixer 3. The mixture is aga pumped to separator tank 5; from there t acid is dropped back to mixer 3, the amyle being sent to the first amylene feed tan 4, for the next batch. Molten phenol, 8, dropped to mixer 3, and the mixture pumped to separator 5. Excess phenol employed to favor the formation of mon amylphenol. The acid layer is dropped acid mixing tank 1, and the other layer dropped to digester 9. There it is digest at 140° ± 5° C. for 4 hours and then wash three times with hot water from tanks 1

Nonchlorinated compounds derived from monochloropentanes are described and some of their uses are pointed out. Flow sheets and operating procedures for producing amylphenols, amylnaphthalenes, amylamines, and amyl mercaptan are given.

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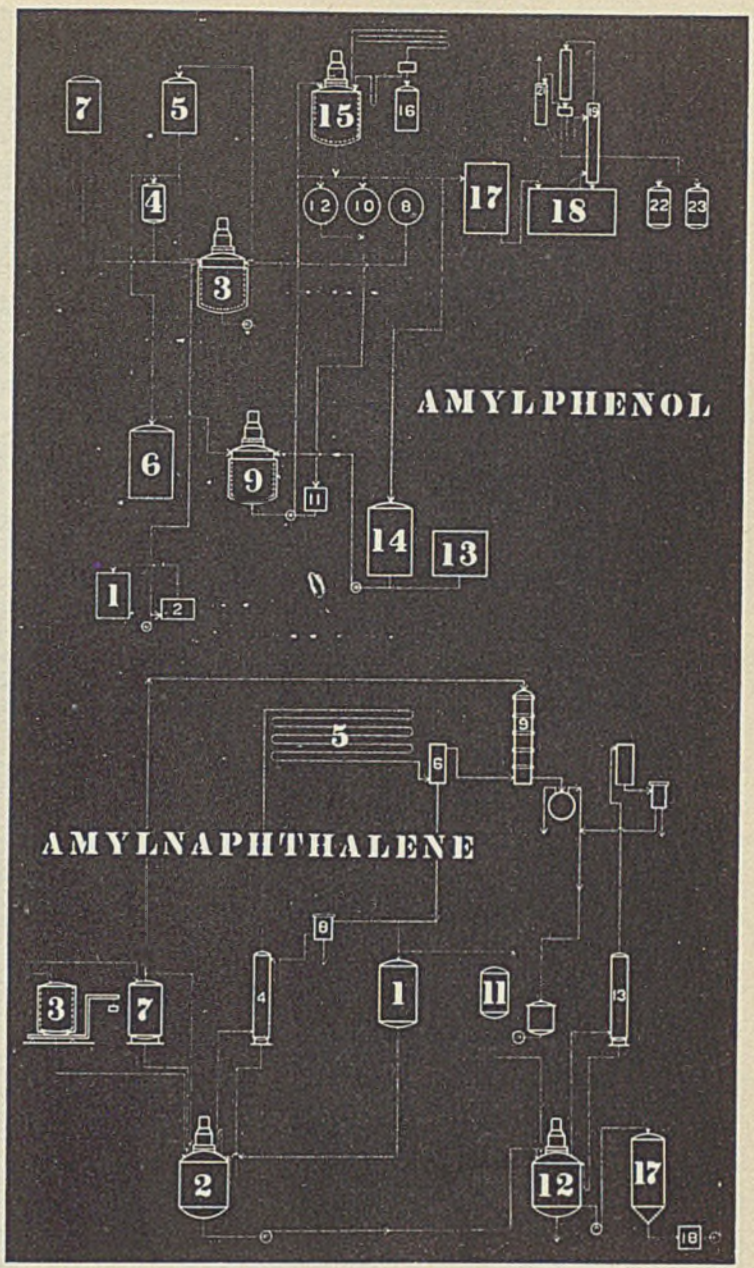


Figures 1 and 2. Flow Sheets of Amylphenol and Amylnaphthalene Processes

11, and 13. The first two washings are pumped to another tank, 12, while the third wash is pumped to the first of the above tanks, 10. Soda ash solution from tank 14 is pumped to a mixer and still, 15, and the water-washed reaction mass is then pumped on top of the soda ash solution. The mixture is refluxed with agitation, and amylene is taken off through a condenser to receiver 16. The aqueous layer is dropped to tank 12. Hot water, 13, is employed for the last wash. The washings are drained to soda ash tank 14 and the product is dropped to crude storage 17. All equipment with which sulfuric acid comes in contact is lined with lead.

To avoid discoloration of the distillate, the crude amylphenol is vacuum-distilled in a system of stainless steel construction with the exception of kettle 18 and column 19. This still is charged by vacuum, and the wet heads are taken off at atmospheric pressure. Vacuum is then applied at jet trap 21, and phenol is distilled into two of a battery of receivers, 22 and 23, followed by *o*-amylphenol, Pentaphen, and finally diamylphenol. The production of amylated phenols consists of about 0.5 per cent *o*-amylphenol, 9 per cent diamylphenol, and 90 per cent Pentaphen.

Pentaphen is a nearly white, crystalline solid sold in flake form. The standard grade melts at 84–91° C. and boils at 250–260° C. For killing certain types of bacteria it is about fifty times as powerful as phenol. The most outstanding property is the oil solubility of products manufactured from it. Thus, Pentaphen condenses with formaldehyde to form resins which are soluble in drying oils. Such resins produce varnishes with a high resistance to weathering.

o-Amylphenol is used as an antiskinning agent for paints, varnishes, and enamels. A few tenths per cent prevents skinning without an appreciable increase in drying time.

Diamylphenol is also useful as an antiskin in certain types of oleoresinous paints. Another use is as a repellent in soil fumigants.

AMYLNAPHTHALENES

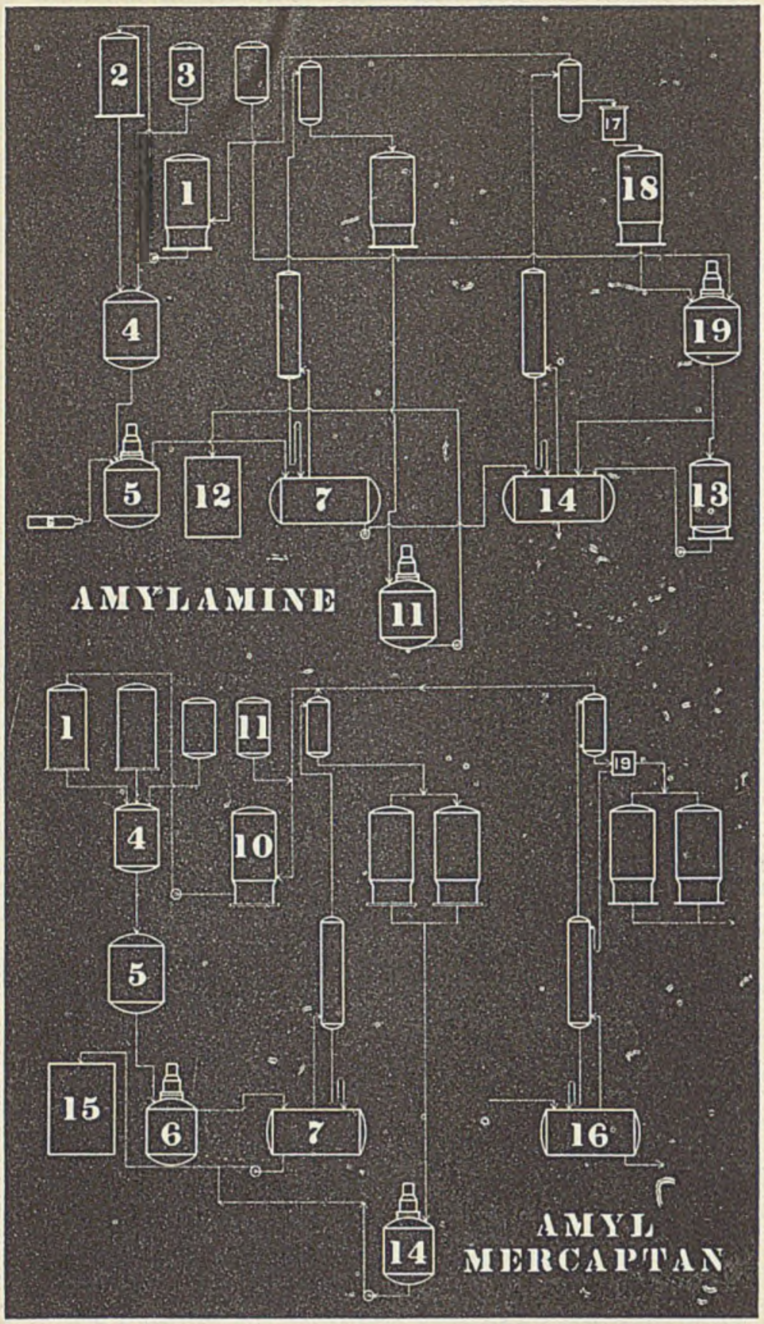
The amylnaphthalenes are manufactured by the alkylation of naphthalene with amyl chlorides or 2-pentene in the presence of aluminum chloride catalyst:

$$n\,C_5H_{11}Cl + C_{10}H_8 \xrightarrow{AlCl_3} (C_5H_{11})_nC_{10}H_{8-n} + n\,HCl \tag{4}$$

$$n\,C_5H_{10} + C_{10}H_8 \xrightarrow{AlCl_3} (C_5H_{11})_nC_{10}H_{8-n} \tag{5}$$

The 2-pentene is obtained from the amylphenol process and represents the amylene not extracted from mixed amylenes with 62 per cent sulfuric acid.

Mixed amyl chlorides, 1 (Figure 2), and molten naphthalene from weigh tank 3 are charged to reactor 2. The system comprising the reactor, column 4 packed with Raschig rings, condenser 5, and traps 6 and 8 is dehydrated by distilling half of the amyl chloride to receiver 1. Half of the anhydrous aluminum chloride catalyst is added to the reactor, and the temperature is increased to 120° C. When the rapid evolution



Figures 3 and 4. Flow Sheets of Amylamine and Amyl Mercaptan Processes

of hydrogen chloride ceases, the vapor line to wooden scrubber 9 is closed. 2-Pentene, 7, and the other half of the aluminum chloride are gradually added to the reactor to maintain the reaction temperature in the range of about 160–200° C. If the pressure rises above 45 pounds, the excess is vented to the scrubber. The reacted mixture is pumped to still 12 under the surface of very dilute caustic soda from tank 11. This decomposes the aluminum chloride complex, and the unreacted amyl chloride or 2-pentene is steam-distilled through a column, 13, packed with Raschig rings. The aqueous layer is then separated from the crude amylnaphthalenes, and the latter are pumped to aerator 17 for drying and finally through filter press 18. Crude is fractionated in a high-temperature vacuum d
tillation system to mono-, di-, and pol
amylnaphthalenes.

The ratio of di- to monoamylnaphth
lene is about 1.7 to 1, but it can be vari
to some extent. The configuration of t
amyl groups is predominantly seconda
with a small percentage of tertiary.

The amylnaphthalenes are oily, hig
boiling, stable liquids of interest as he
transfer media and coupling agen
Mono- and a mixture of mono- and
amylnaphthalene can be used in vehic
for inks and vitrifiable colors. Di- a
mixtures of mono- and diamylnaphth
lenes are sulfonated to produce wetti
agents for the textile industry. The s
fonates are also emulsifiers. Di- a
polyamylnaphthalenes are plasticize
the former being compatible with a wic
variety of resins.

AMYLAMINES

Amylamine and diamylamine are p
duced by the reaction of amyl chloric
with ammonia in the presence of alcol
as a mutual solvent:

$$C_5H_{11}Cl + NH_3 \longrightarrow C_5H_{11}NH_2.HCl$$

$$2C_5H_{11}Cl + 2NH_3 \longrightarrow (C_5H_{11})_2NH.HCl + NH_4Cl$$

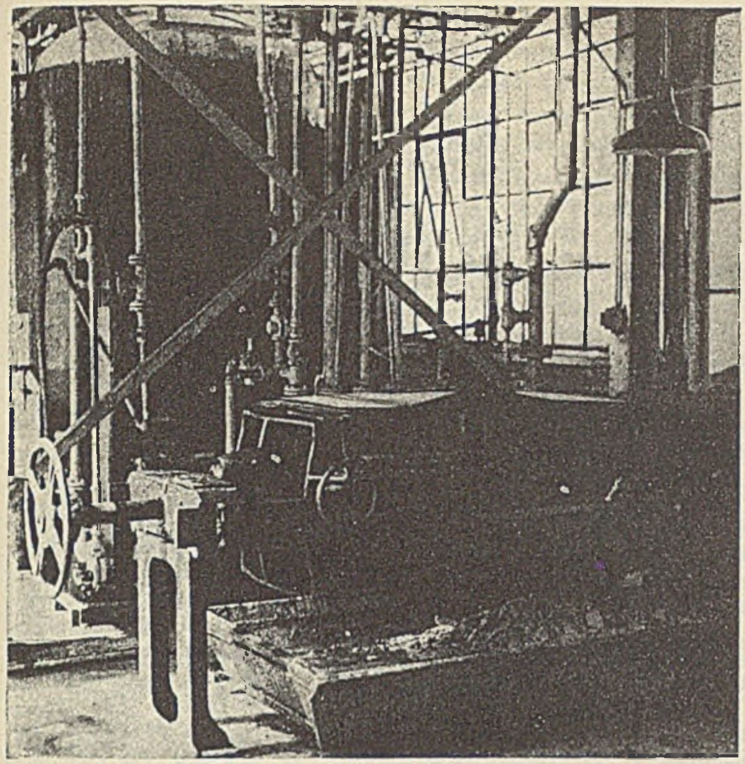
Relatively small amounts of triam
amine, amylene, and amyl alcohol
formed simultaneously:

$$3C_5H_{11}Cl + 3NH_3 \longrightarrow (C_5H_{11})_3N.HCl + 2NH_4Cl$$

$$C_5H_{11}Cl + NH_3 \longrightarrow C_5H_{10} + NH_4Cl$$

$$C_5H_{11}Cl + NH_3 + H_2O \longrightarrow C_5H_{11}OH + NH_4Cl$$ (

A solution of ammonia in ethanol
pumped from ammonia scrubber 1 (Fig
3) to charging tank 2. Mixed an
chlorides from measuring tank 3 a
the alcoholic ammonia are dropped
another tank, 4, and then to an au
clave, 5, where additional ammo
is charged from cylinders, 6. T
intermediate vessel, 4, permits another batch to be ma
ready while the previous one is being autoclaved. A re
tion temperature of 160–165° C. is maintained for 2 hou
and is then raised to complete the reaction, the pressure bei
held under 400 pounds for an additional 2 hours. The m
ture is discharged to still 7 at a pressure below 7 pounds
square inch. Ammonia is refluxed out through scrubbe
which actually consists of three scrubbers in series. T
alcohol in each scrubber is circulated through a coo
After the ammonia in the still is reduced to one per cent,
amylene, ethanol, unreacted amyl chlorides, amyl alcoh
and traces of amylamines from the dissociation of their hyd
chlorides are steam-distilled until the distillate consists o



Reactor, Kettle for Distillation of Unreacted Amyl Chlorides and 2-Pentene, and Filter Press in Amylnaphthalene Process

of water. The distillate is dropped to mixer 11 where water is added until an oily layer separates. The aqueous alcohol layer is pumped to storage 12, and the oil layer is fractionated into its components.

The residue in still 7 is transferred to another still, 14, and causticized to liberate the amines from their hydrochlorides. The remaining ammonia is driven to scrubber 1, and the wet amylamines are distilled. Water is separated in decanter 17. The amines are dropped from receiver 18 to mixer 19 for dehydration with concentrated caustic. The caustic layer is separated to tank 13 for later transfer to still 14 for causticization of a subsequent batch of amine hydrochlorides. The dehydrated amylamines are dropped to still 14 for fractionation.

Amylamine and diamylamine are formed in the ratio of about 3:2. The proportion of triamylamine formed is small, and for additional production diamylamine is reacted with amyl chloride in the presence of caustic:

$$(C_5H_{11})_2NH + C_5H_{11}Cl + NaOH \longrightarrow (C_5H_{11})_3N + NaCl + H_2O \quad (11)$$

Diamylamine, mixed amyl chlorides, and aqueous caustic soda of moderate strength are autoclaved for 4 hours at 205–210° C. Most of the unreacted amyl chlorides are removed with steam in still 7 (Figure 3). The residue is pumped to still 14 and steam-distilled. The crude distilled amines are separated from the water and fractionated by vacuum distillation.

The amylamines are liquids having an ammoniacal odor which becomes less pronounced as the number of amyl groups increases. Primary and secondary amyl radicals preponderate.

In the form of soaps such as the oleate, the amylamines are emulsifying agents for use in textile lubricants. Amylammonium oleate is a frother for the flotation of copper ore. Amylamine is an intermediate for dyestuffs. The phosphate of diamylamine is a corrosion inhibitor for use in hydraulic fluids of the castor oil type. Triamylamine has been employed as a pickling inhibitor, a color stabilizer for gasoline, and an insecticide.

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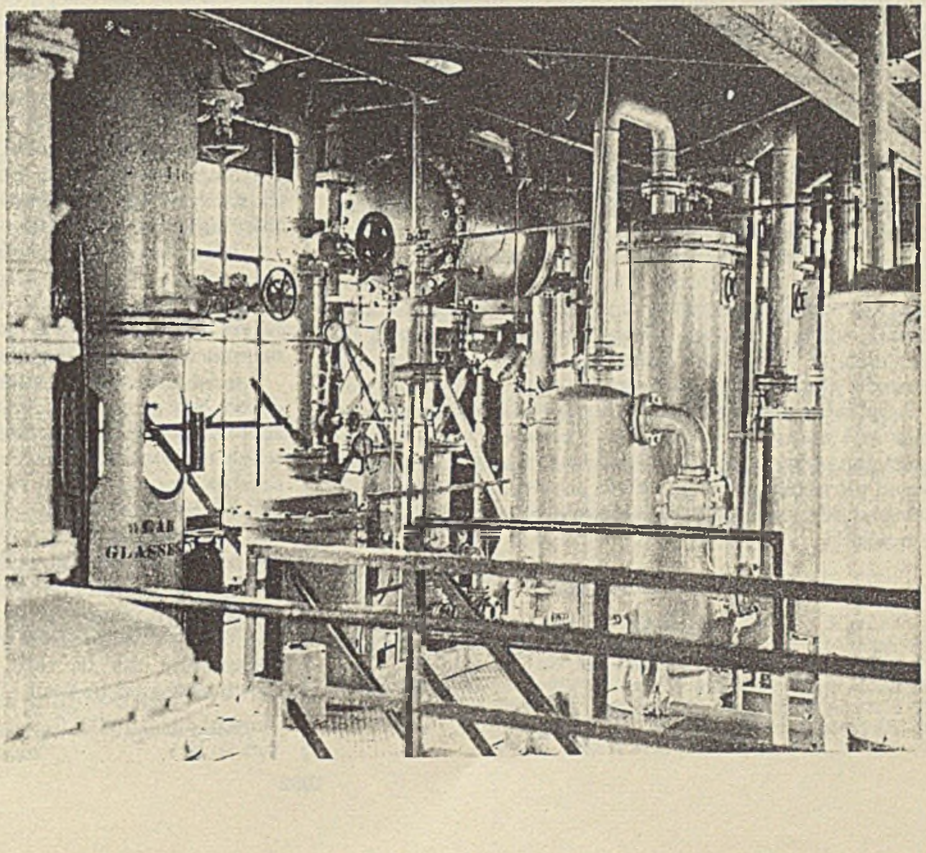

Columns, Condenser, and Scrubbers in Amyl Mercaptan Process

AMYL MERCAPTAN

Amyl chlorides are reacted with aqueous sodium hydrosulfide in the presence of ethanol as a solvent for the production of amyl mercaptan:

$$C_5H_{11}Cl + NaSH \longrightarrow C_5H_{11}SH + NaCl \qquad (12)$$

Other products recovered are amyl sulfides, amylene, amyl alcohol, and hydrogen sulfide:

$$2C_5H_{11}Cl + 2NaSH \longrightarrow (C_5H_{11})_2S + 2NaCl + H_2S \qquad (13)$$

$$C_5H_{11}Cl + NaSH \longrightarrow C_5H_{10} + NaCl + H_2S \qquad (14)$$

$$C_5H_{11}Cl + NaSH + H_2O \longrightarrow C_5H_{11}OH + NaCl + H_2S \qquad (15)$$

Mixed amyl chlorides, fairly concentrated aqueous sodium hydrosulfide, and ethanol are charged to measuring tank 4 (Figure 4) and dropped through tank 5 to autoclave 6 where the mixture is reacted for 5 hours at 140–150° C. The autoclave is discharged to still 7 at a maximum pressure of 6 pounds per square inch. Hydrogen sulfide is absorbed by scrubber 10 which is similar to the one mentioned in the amylamine process. It consists of three scrubbers in series; amyl sulfide is circulated in the first for the removal of entrained amylene. Caustic soda solution having an initial minimum concentration of 15 and 3 per cent, respectively, is circulated in the second and third scrubbers. When the strength of the caustic in the third scrubber falls to less than 1.75 per cent and that of the sodium hydrosulfide increases to above 21 per cent, the solution is pumped to hydrosulfide tank 1 for use in the process. The contents of the second scrubber are then transferred to the third, and 25 per cent caustic is charged from tank 11 to the second absorber. The last scrubber is vented through an activated carbon filter to prevent any possibility of hydrogen sulfide escaping to the atmosphere.

The mixture in still 7 is steam-distilled. The aqueous still residue is dropped to a sewer, and the residual amyl sulfide is pumped to storage tank 15. Chlorine is introduced at the sewer sump to oxidize obnoxious sulfur compounds. The distillate is dropped to mixer 14 for further dilution with water to throw out the alcohol-soluble products. The dilute alcohol layer and subsequent washings of the oil layer are pumped to storage, 15.

The washed product in mixer 14 is transferred to another still, 16. Any remaining hydrogen sulfide is refluxed out to scrubber 10. Amylene is then collected, and when the stream starts to separate in decanter 19, water is taken to a receiver and the other layer is returned to the still. After dehydration is complete, amyl mercaptan is separated by rectification from any remaining amylene, unreacted amyl chloride, amyl alcohol, and amyl sulfide. Vacuum is employed to finish the distillation. The steam from the jet is condensed and treated with chlorine to destroy malodorous sulfur compounds.

Amyl mercaptan is a liquid having a typical mercaptan odor. It is sold under the trade-mark "Pentalarm" as a warning agent for natural gas and odorless fuel gases. Less than a pound per million cubic feet of gas permits leaks to be readily detected long before an explosive concentration of gas in air is reached.

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VAPOR PRESSURE SLIDE RULE

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ONE of the most important propertie of a liquid is its vapo pressure. Knowledge o this property is needed i all calculations involvin evaporation, distillatio storage, and recovery o solvents. The boilin point is used as a criterio of purity and identity o liquids, and it is subject to correction for pressure change

Frequently vapor pressures are not known at the temperature desired. In the absence of data the change o vapor pressure with temperature must be estimated usin various theoretical and empirical rules. The laws of Clapeyron, Clausius, Dühring (*10*), Trouton (*31*), and Ramsay an Young (*28*) are best known. Many modifications of thes laws have been suggested (*4*, *18*, *27*, *34*). They are a somewhat awkward to use, and the final results are subjec to corrections which are often difficult to estimate.

Graphical methods are useful in this field since the ca culations are more rapid and usually sufficiently precis These methods make it possible to perform the calculation from either direction, which is not always easy with th equations. Two forms of vapor pressure plotting paper (9 are commercially available, and many special methods o graphing data have been published (*3*, *15*, *21*, *25*), of whic the Cox chart (*6*) is perhaps the most widely used. Some o these methods (*25*) require knowledge of the critical poin which is a disadvantage since this is not often known. Nomographs have been very successful in expressing vapor pressure data (*12*, *19*, *25*, *29*, *32*, *35*), especially the series b Davis (*8*). Crawford's nomograph (*7*) correlates vapo pressure and heat of vaporization data.

Special-purpose slide rules for these calculations have received less attention. Smith and Sharp (*30*) developed slide rule with parallel temperature and pressure scale which expresses hydrocarbon vapor pressures. A humidit slide rule for calculating vapor pressure of water, dew poin and relative humidity from wet- and dry-bulb temperature was published by Bilham (*1*). The simple construction an compactness of a nomograph is offset by the increased spee ease in reading, and precision of a slide rule.

The desired slide rule should have adjacent temperatur and pressure scales from which the vapor pressure at an temperature can be read. The critical point should b shown as the upper limit of the vapor pressure curve. Th

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The variation of vapor pressure with temperature is important in many fields. The laws and equations generally used to calculate the variations are awkward to apply and subject to inaccuracies. A slide rule has been developed which rapidly performs such calculations for all pure liquids with normal boiling points in range −38° to 400° C. The slide rule has two independently adjustable slides corresponding to the two variables—boiling point and entropy of vaporization (Trouton's constant). Any liquid is represented by a particular setting of the two slides; when this has been made, the entire vapor pressure curve can be read from adjacent pressure and temperature scales; the critical point and molal heat of vaporization at the boiling point are shown. Index points mark the settings for 87 known liquids. Settings for seven classes of liquids are shown by lines. Additional scales perform gas law calculations and conversions of temperature, pressure, and heat values to different units.

latent heat of vaporization, preferably at different temperatures, should be shown. Indices should mark the settings for important known liquids, and it should be possible to mark the setting for any new liquid. Provision should be made for rapid conversion of temperature, pressure, and heat units. In any estimation the slide rule should give the most probable value from the minimum of data, along with an estimate of the accuracy of this value. If more complete data are available, it should be possible to use them to make the calculation more accurate. The slide rule should permit the testing of data for consistency. The slide rule should not be limited in application to a single class of liquids (*30*) but should represent associated as well as nonassociated liquids. The scales should not be based on the vapor pressure of a single liquid (*6*); it is not desirable, however, to follow the laws derived from simple assumptions (*7*). By replacing these assumptions by empirical rules based on observed values for a large number of liquids, the scales can be laid out in such a way that positive and negative errors are equally probable.

DERIVATION OF EQUATIONS

The fundamental vapor pressure relation is the Clapeyron equation:

$$\frac{dp}{dT} = \frac{L}{T(V_g - V_l)} \tag{1}$$

where

p = vapor pressure
T = absolute temperature
L = molal heat of vaporization
V_g = molal volume of vapor
V_l = molal volume of liquid

This can be simplified by assuming that the volume of the liquid is negligible compared to the volume of the vapor, and that the vapor obeys the perfect gas laws:

$$V_g - V_l = V_g \tag{2}$$

$$pV_g = RT \quad \text{or} \quad V_g = \frac{RT}{p} \tag{3}$$

where R = gas constant, in appropriate units

Substitution in Equation 1 gives the simplified Clausius-Clapeyron equation:

$$\frac{dp}{dT} = \frac{Lp}{RT^2} \tag{4}$$

$$\frac{1}{p}\frac{dp}{dT} = \frac{d\ln_e p}{dT} = \frac{L}{RT^2} \tag{5}$$

This can be integrated, assuming that L does not vary with temperature:

$$\ln_e p = 2.303 \log_{10} p = -\frac{L}{RT} + 2.303\,A \tag{6}$$

where 2.303 A = integration constant

Dividing through by 2.303 to convert to common logarithms gives:

$$\log p = A - \frac{L}{2.303\,RT} = A - \frac{B}{T} \tag{7}$$

$$\text{where } B = \frac{L}{2.303\,R}$$

This is the usual two-constant equation for expressing vapor pressure data. When the logarithm of the pressure is plotted against the reciprocal of the absolute temperature, Equation 7 gives a straight line whose slope is proportional to the molal heat of vaporization.

Trouton's law (*31*) states that the molal entropy of vaporization at the normal boiling point is the same for all normal liquids, or that the heat of vaporization is proportional to the boiling point on the absolute scale.

$$\frac{L}{T_b} = \text{Trouton's constant} = 21 \text{ (for nonassociated liquids)} \tag{8}$$

where T_b = absolute temperature of normal boiling point

Dividing by 2.303 R gives

$$\frac{L}{2.303\,R\,T_b} = \frac{\text{Trouton's constant}}{4.575} = \frac{B}{T_b} = \phi \tag{9}$$

$$\text{where } \phi = \frac{1}{T_b}\left[\frac{d\log_{10} p}{d(-1/T)}\right] = \frac{1}{T_b}\left[\frac{T^2 d\log_{10} p}{dT}\right] \tag{10}$$

and has a value of 4.6 when Trouton's constant equals 21. Substituting $\phi\,T_b$ for B in Equation 7:

$$\log p = A - \phi\frac{T_b}{T} \tag{11}$$

If the pressure is expressed in atmospheres, the value of A is fixed:

$$\log P_{\text{atm.}} = \phi - \phi\frac{T_b}{T} = \phi\left[1 - \frac{T_b}{T}\right] \tag{12}$$

For two liquids F and G, at any pressure P', which is given by liquid F at T'_F and by liquid G at T'_G:

$$\log P' = \phi_F\left(1 - \frac{T_{bF}}{T'_F}\right) = \phi_G\left(1 - \frac{T_{bG}}{T'_G}\right)$$

If the liquids have the same Trouton constant, and $\phi_F = \phi_G$,

$$\frac{T_{bF}}{T'_F} = \frac{T_{bG}}{T'_G} \quad \text{or} \quad \frac{T_{bF}}{T_{bG}} = \frac{T'_F}{T'_G}$$

Similarly for another pressure, P'',

$$\frac{T_{bF}}{T_{bG}} = \frac{T''_F}{T''_G}$$

Combining,

$$\frac{T'_F}{T'_G} = \frac{T''_F}{T''_G} \quad \text{or} \quad \frac{T'_F}{T''_F} = \frac{T'_G}{T''_G} \tag{13}$$

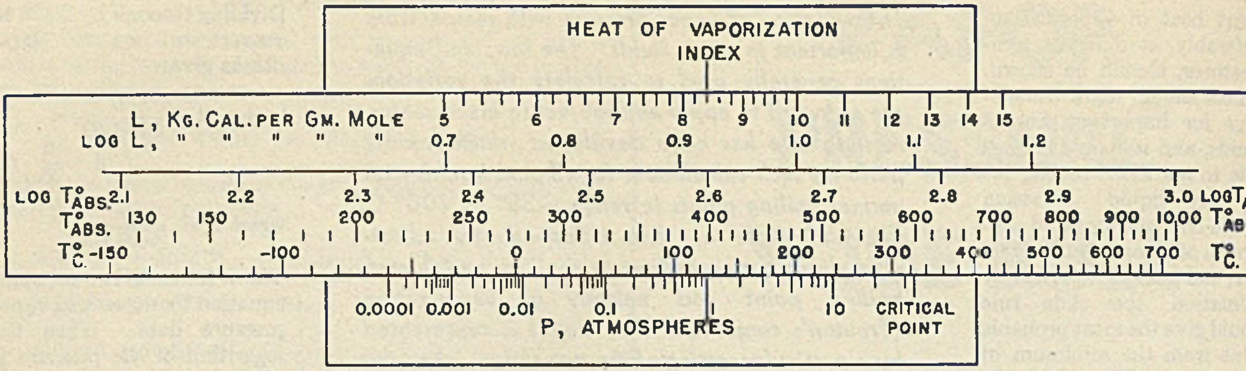


Figure 1. Simple Vapor Pressure Slide Rule Constructed for ϕ = 4.6 (Trouton's Constant = 21), Shown Set for a Liquid with a Nor Boiling Point of 125° C.

This is Dühring's rule (*10, 18*), with which the vapor pressure curve of a liquid can be calculated from one point, provided the curve for another similar liquid is known. The accuracy of Dühring's rule when applied to two liquids of the same chemical class is very good, better in fact than the assumptions used above to derive the rule, since the two liquids generally deviate from the assumptions in the same way. It is clumsy to use, however, especially if the table of data for the comparison liquid gives values at relatively large temperature intervals.

DERIVATION OF SCALES

From the proportionality of Dühring's rule in Equation 13 it appears that, to make a slide rule with parallel sliding pressure and temperature scales, the temperature scale should be laid out logarithmically,

$$x = \log T^\circ \text{ Abs.} \tag{14}$$

where x measures the horizontal distance along the rule from an arbitrary zero which may be beyond one end of the rule. The distance between P' and P'' on the scale will then be:

$$x' - x'' = \log T'_F - \log T''_F = \log T'_G - \log T''_G$$

The pressure scale to be used against this temperature scale can be derived from Equation 12:

$$\log P = \phi(1 - T_b/T) \tag{12}$$

$$T_b/T = 1 - \log P/\phi \tag{15}$$

$$\log (T_b/T) = \log (1 - \log P/\phi)$$

$$\log T - \log T_b = x = -\log (1 - \log P/\phi) \tag{16}$$

where x measures the distance from the point representing 1 atmosphere.

If a pressure scale is laid out by Equation 16 and used against the temperature scale of Equation 14, when the mark corresponding to 1 atmosphere is placed against the mark for the boiling point of any particular liquid, adjacent readings on the two scales will give values for the vapor pressure as calculated from Equation 12.

The upper limit of the vapor pressure curve is the critical point. The empirical rule of Guldberg and Geye states that on the absolute scale the boiling point of most compounds is two thirds of the critical temperature:

$$T_b = {}^2/_3 T_c \text{ or } \frac{T_c}{T_b} = 1.5 \tag{17}$$

$$\log T_c - \log T_b = x_c = 0.176$$

Therefore the pressure scale should not be continued bey x = 0.176, and this point should be marked as the crit point.

According to Equation 9 the molal heat of vaporizat is proportional to the absolute boiling point:

$$L = 2.303\,R\,\phi\,T_b$$

A logarithmic scale for this heat value, expressed in any un can be laid off on the slide above the temperature scale read against an index.

EMPIRICAL CORRECTIONS

A vapor pressure slide rule, constructed as described abo is shown in Figure 1. Calculations made with such a rule include errors because the assumptions which were made not agree exactly with the facts. To construct a rule wh will be as accurate as possible, each of these assumpti must be examined and replaced with an empirical rule agreement with the average of observed data. The s rule will then give the best estimate, and positive and ne tive errors will be equally probable.

Trouton's law is not exact; ϕ is not a constant but va in two ways: (*a*) Associated liquids have abnormally h values of ϕ. (*b*) For any one class of liquids, values c are close to one another but, in general, increase slo with increasing boiling point; this variation is expressed the laws of Nernst (*24*), Bingham (*2*), Forcrand (*11*), Hi brand (*14*), Kistiakowsky (*20*), and Mortimer (*22*).

Assuming one value of ϕ for all liquids in the range to covered, as in Equation 16 and Figure 1, would introd errors so large as to impair seriously the accuracy of the s rule. [These errors occur when Dühring's rule (Equation 1 used with water as a comparison liquid in calculations fo nonassociated liquid.] The slide rule is therefore arrange that the slide carrying the temperature and heat scales car moved vertically over a card carrying the pressure scale the heat index (Figures 4, 5, 6). A number of pressure sc are laid out on the card, one above the other. The m for each pressure becomes a curve through the x values culated using different values for ϕ. All liquids boiling tween −38° and 400° C. have Trouton constants betw 19.5 and 30.9 (ϕ = 4.26 to 6.75, log ϕ = 0.63 to 0.83), this range is therefore sufficient.

The vertical ϕ scale is laid out as

$$y = \log \phi$$

Table I. Two- and Three-Constant Vapor Pressure Equations

Author	Equation: $\log P =$	Heat of Vaporization: $L = (2.303RT^2)\dfrac{d \log_{10} P}{dT} =$	For Pressure Scale of Slide Rule: $x = \log T - \log T_b =$
....	$A - \dfrac{B}{T} = \phi\left(1 - \dfrac{T_b}{T}\right)$	Constant, $L_b = 2.3R\phi T_b$	$-\log\left(1 - \dfrac{\log P}{\phi}\right)$
Antoine	$A - \dfrac{B}{T - C} = \gamma\left[1 - \dfrac{T_b - C}{T - C}\right]$ where $\gamma = \left[\dfrac{T_b - C}{T_b}\right]\phi$	$2.3R\gamma(T_b - C)\left(\dfrac{T}{T - C}\right)^2 =$ $L_b\left[\dfrac{T(T_b - C)}{T_b(T - C)}\right]^2$	$-\log\left(1 - \dfrac{\log P}{\gamma}\right)$ used with $x = \log(T - C)$
Kirchoff	$A - \dfrac{B}{T} - C \log T$	$L_b - CR(T - T_b)$	$-\log\left[1 - \dfrac{\log P}{\phi + \dfrac{C}{2.3}} + \dfrac{C}{\phi + \dfrac{C}{2.3}} \log \dfrac{T_b}{T}\right]$
Chipman	$A - \dfrac{B}{T} - \dfrac{C}{T^2}$	$L_b + 2(2.3RC)\left[\dfrac{1}{T} - \dfrac{1}{T_b}\right]$	$-\log\left[1 - \dfrac{\log P}{\phi} - \dfrac{C}{\phi}\left(\dfrac{1}{T_b} - \dfrac{1}{T}\right)^2\right]$
Henglein	$A - \dfrac{B}{T^C} = \dfrac{\phi}{1 + D}\left[1 - \left(\dfrac{T_b}{T}\right)^{1+D}\right]$	$L_b\left(\dfrac{T_b}{T}\right)^D$	$-\dfrac{1}{1 + D}\log\left[1 - \dfrac{(1 + D)\log P}{\phi}\right]$

where y represents a vertical distance on the card. The heat of vaporization index becomes a straight line with a 1:1 slope since

$$L = 2.303\ R\phi T_b \tag{9A}$$

$$\log L = \log(2.303\ R) + \log \phi + \log T_b \tag{9B}$$

CORRECTION FOR CURVATURE

It was assumed (Equation 6) that the latent heat of vaporization is constant for any given liquid. Actually L is not constant but decreases with increasing temperature; therefore when $\log p$ is plotted against the reciprocal temperature, the line shows a slight curvature. A straight line does not represent the vapor pressure accurately over a long range but shows incorrectly high pressures at both high and low temperatures. International Critical Tables (*16*) give curves showing the variation of ϕ with temperature; in this paper, however, ϕ is considered to be a constant for any one liquid, and its value is calculated by Equation 10 at the normal boiling point.

To represent vapor pressure data with the correct curvature, various three-constant equations are used; some of them are shown in Table I. Most of these equations are not applicable to the construction of pressure scales on the slide rule. If the Antoine equation is used, the construction of the temperature scale is altered by the inclusion of an arbitrary constant. This gives good pressure *vs.* temperature readings but makes the construction of the heat of vaporization scale impossible. With the Kirchoff and Chipman equations this difficulty is avoided, but the calculations for the pressure scale layout are very difficult because the equations for x are nonimplicit and must be solved by successive approximations.

The Henglein equation (*13*) is based on the assumption that the logarithm of the latent heat decreases linearly with the logarithm of the temperature:

$$\log L = \log L_b - D(\log T - \log T_b) = \log[2.303\ R\ \phi\ T_b] - D[\log T - \log T_b] \tag{20}$$

$$L = 2.303\ R\ \phi\ T_b\left(\frac{T_b}{T}\right)^D \tag{21}$$

This expression is substituted in the simplified Clausius-Clapeyron Equation 5 which is then integrated to give the vapor pressure equation:

$$\log P = \frac{\phi}{1+D} - \frac{\phi}{1+D}\left(\frac{T_b}{T}\right)^{1+D} = \frac{\phi}{1+D}\left[1 - \left(\frac{T_b}{T}\right)^{1+D}\right] \tag{22}$$

This may be rearranged to give the formula for laying out the pressure scales:

$$x = \log T - \log T_b = -\frac{1}{1+D}\log\left(1 - \frac{(1+D)\log P}{\phi}\right) \tag{23}$$

This equation does not have the disadvantage of the Kirchoff and Chipman equations, but allows direct calculations of x values.

To test the four three-constant equations of Table I, constants were evaluated for each which gave the correct vapor pressure of water at 0°, 100°, and 250° C. The maximum deviation of the calculated pressures from the known values (*16*) gave a measure of the closeness of fit. Only the Chipman equation (*5*) was superior to the Henglein, which showed a maximum deviation of 0.7 per cent in this range.

It remained to find the best value of D to use in laying out the pressure scales. For this purpose constants for Equation 22 were calculated to fit twenty-five liquids for which vapor pressure data were available of sufficient accuracy to give a measure of the curvature of the $\log p$ *vs.* $1/T$ lines. Smoothed data from International Critical Tables (*16*) were used. The boiling point and two other points differing as widely as possible were selected as reference points. The calculation of D from such data involves the use of successive approximations, but the remaining calculations are straightforward.

The values found for D are plotted against $\log \phi$ in Figure 2. A point on the base line would correspond to a straight line for $\log p$ *vs.* $1/T$, since Equation 22 reduces to 12 when $D = 0$. All of the liquids show a curvature in the same direction; D is positive in all cases, varying from 0.054 for valeric acid to 0.556 for propyl alcohol. If necessary, a different value of D could be used in laying out the pressure scale for each value of ϕ. In an attempt to determine the

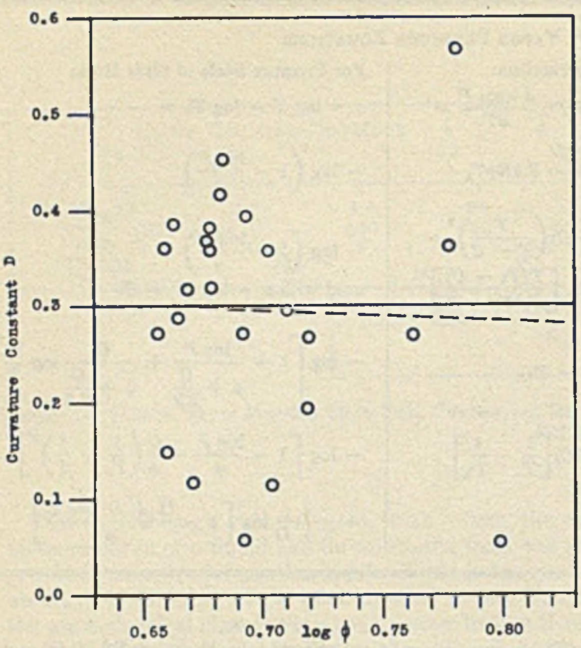


Figure 2. Curvature of Vapor Pressure Lines, Values of D in the Equation

$$\log P = \frac{\phi}{1+D}\left[1 - \left(\frac{T_b}{T}\right)^{1+D}\right]$$

variation of D with ϕ, the method of least squares was used to determine the best line for

$$D = a + b \log \phi$$

This line, shown broken in Figure 2, is practically horizontal; its slope is negligible in comparison with the deviations of the points. Since no dependence of D upon ϕ is apparent, one value, $D = 0.3$, is used with all values of ϕ. This is close to the average, 0.295, and the median.

The pressure scales are therefore constructed using the equation:

$$x = -\frac{1}{1.3}\log\left(1 - \frac{1.3 \log P}{\phi}\right) \qquad (24)$$

This corresponds to the vapor pressure equation:

$$\log P = \frac{\phi}{1.3}\left[1 - \left(\frac{T_b}{T}\right)^{1.3}\right] = A - \frac{B}{T^{1.3}} \qquad (25)$$

The curve given by this equation for any liquid is tangent at the boiling point to the straight line given by the simpler Equation 12, but at higher and lower temperatures it deviates from the straight line with a curvature corresponding to observed vapor pressure curves. The molal heats of vaporization calculated from the two equations are equal at the boiling point. Because Equation 25 gives a better fit than the simpler form, it is suggested that it be generally used instead of 7 to express vapor pressure data, even when the data are not complete or precise enough to justify the use of a three-constant equation.

CRITICAL POINT

The empirical rule that the boiling point is two thirds of the critical temperature on the absolute scale is only approximate. A more accurate relation was published by Watson (*33*). For use in the slide rule it is important to determine whether the quotient, T_c/T_b, varies with ϕ. Values for seventy-nine organic liquids boiling in the range of the slide rule were calculated from data in International Critical Tables (*16*). It appeared that the quotient varies only slightly with ϕ but is dependent to a greater degree on the boiling point. The following empirical relation was found using the method of least squares:

$$\log T_c - \log T_b = 0.655 - 0.030 \log \phi - 0.177 \log T_b \qquad (26)$$

The average deviation from this relation is 15° C. Three broken lines whose positions were calculated by Equation 26 for liquids with normal boiling points of 0°, 100°, and 200° C., respectively, are placed on the card. Only a few critical data are available for liquids boiling above 200° C. Interpolations can be made between these lines to give the best estimate of the critical temperature. Some liquids are specially marked on the card. Mercury is exceptional with a critical point over 1550° C.

INDEX POINTS AND LINES

The vapor pressure curve of any liquid can be expressed by an expression (Equation 25) in which the constants are T_b and ϕ, and for each liquid there is a setting of the slide rule corresponding to these values. This setting can be marked by an index point on the upper half of the card for use against a liquid index on the slide. The coordinates of each index point are $\log T_b$ (increasing from right to left) and $\log \phi$. These coordinates were evaluated for all liquids for which sufficient data are given in International Critical Tables (*16*), and the settings for eighty-seven of the more important liquids are marked on the card and numbered according to the key to liquids (page 1058) on the back of the card.

Various empirical and theoretically derived laws have been published which express the relation between entropy of vaporization and boiling point (*2*, *11*, *14*, *20*, *22*, *24*). For use on the slide rule it is sufficient to find for each class of liquids a purely empirical relation of the form:

$$\log \phi = a + b \log T_b \qquad (27)$$

Plots of $\log \phi$ *vs.* $\log T_b$ were therefore made for each class of liquids, and the constants in Equation 27 were

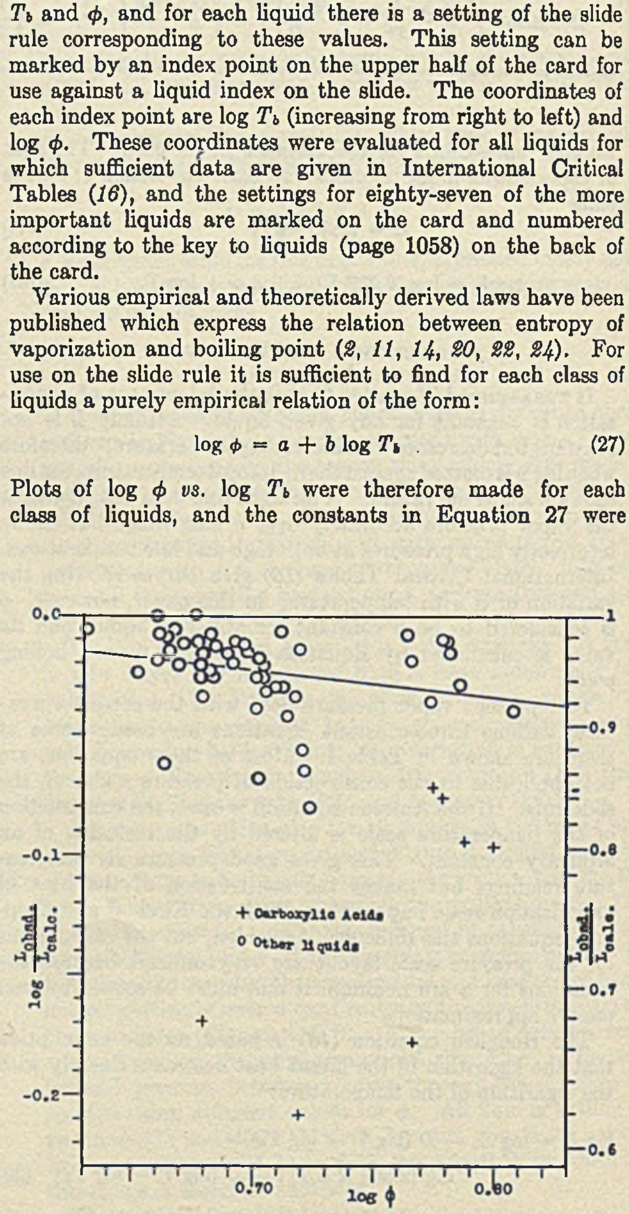


Figure 3. Deviations of Heat of Vaporization from the Clausius-Clapeyron Equation

evaluated by the method of least squares. The constants for each class are shown in Table II. The corresponding line was placed on the card to show the settings for that particular class.

Lines I, II, and III are typical of "normal" liquids, but suggest increasing association in the order of the classes. The line for amines is exceptional in that it has a negative slope. Replacing the hydrogen atoms of ammonia with alkyl radicals raises the molecular weight and hence the boiling point but also lowers association by reducing the probability of hydrogen bond formation. Lines V and VI are typical of associated liquids. Formic and acetic acids do not fall in line with the higher members of this class. Inorganic hydrides and halides show a larger deviation from the average line than do the organic compounds.

LATENT HEAT OF VAPORIZATION

Values for the molal heat of vaporization at the boiling point calculated by the simplified Clausius-Clapeyron, Equation 4 or 5, or by 9B are not exact because the assumptions that the volume of the liquid is negligible compared to that of the

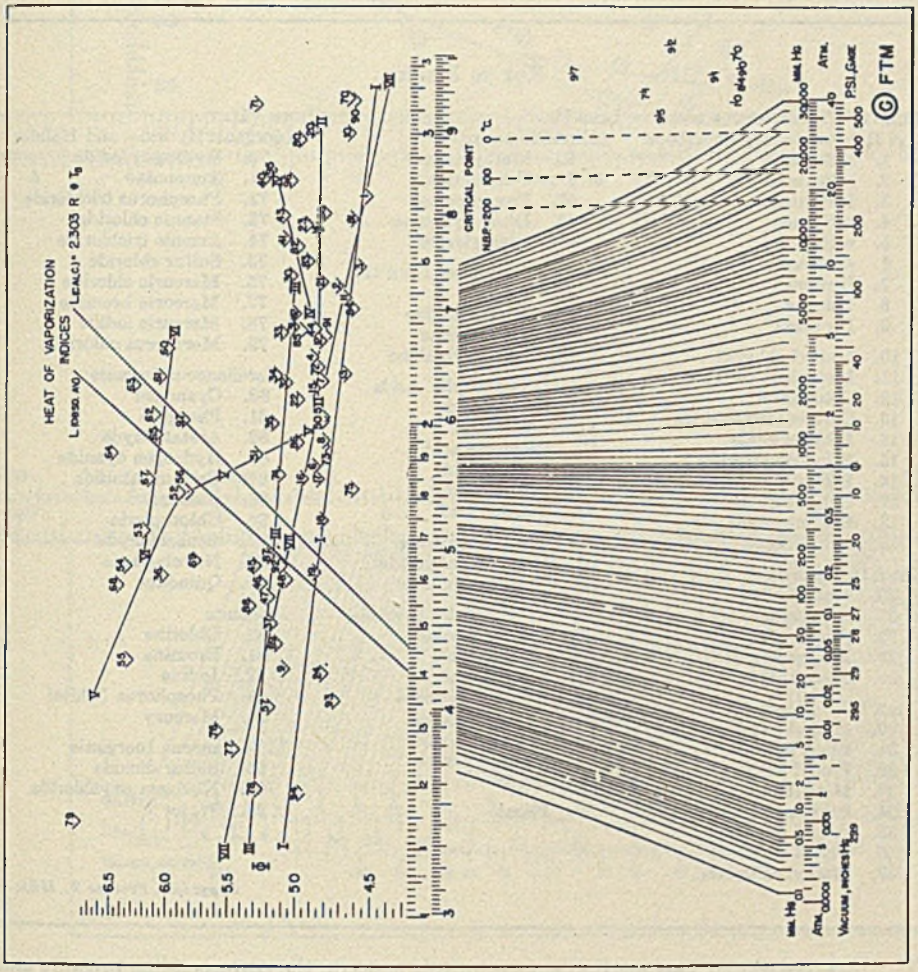
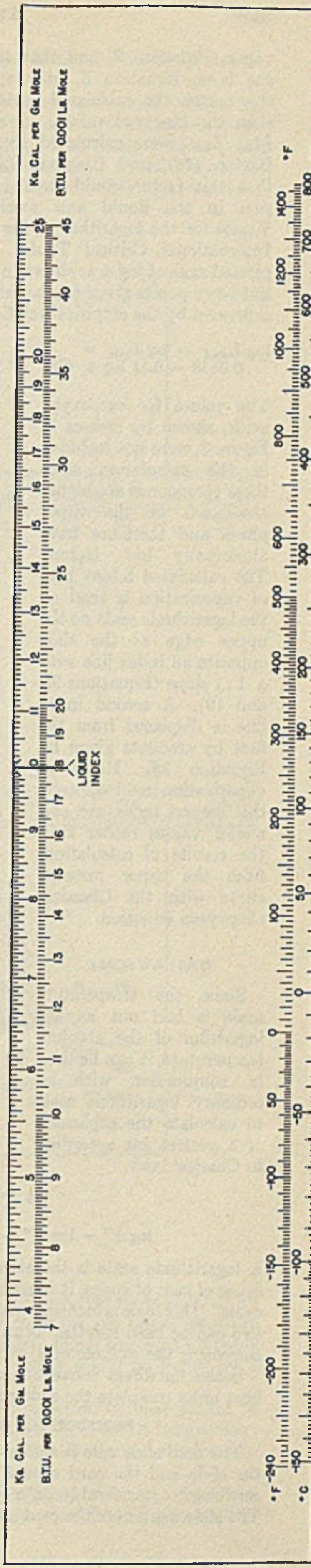


Figure 4. Vapor Pressure Slide Rule

Line No.	Class	Liquids Used, No.	a	b
I	Hydrocarbons and halogenated hydrocarbons	56	+0.370	+0.120
II	Ethers	8	+0.662	+0.009
III	Esters	20	+0.504	+0.078
IV	Aliphatic amines	6	+1.296	−0.241
V	Carboxylic acids (not including formic and acetic)	7	−0.316	+0.416
VI	Aliphatic alcohols	5	+0.431	+0.136
VII	Inorganic hydrides and halides	24	+0.137	+0.214

Table II. Constants in the Equation, $\log \phi = a + b \log T_b$, for Classes of Liquids



vapor, Equation 2, and that the vapor obeys the perfect gas laws, Equation 3, only approximate the facts. For this reason the calculated heats of vaporization are higher than the observed values. Average values for the factor, $L_{\text{obsd.}}/L_{\text{calc.}}$, were calculated by Mortimer (*22*), Parks and Barton (*26*), and Chipman (*4*). It would be expected that this factor would depend on the degree of association in the liquid and would therefore vary with ϕ. Values for the logarithm of the factor, based on data from International Critical Tables (*17*), were calculated and plotted against log ϕ as shown in Figure 3. The line through sixty-two points given by the method of least squares can be expressed by the empirical relation:

$$\log L_{\text{obsd.}} - \log L_{\text{calc.}} = 0.0543 - 0.11 \log \phi \quad (28)$$

The values for carboxylic acids, shown by crosses in Figure 3, were not included in the calculation since these compounds are highly associated in the vapor phase and therefore have abnormally low factors. The calculated latent heat of vaporization is read on the logarithmic scale on the upper edge of the slide opposite an index line with a 1 : 1 slope (Equations 9B and 19). A second index line is displaced from the first by amounts given by Equation 28. Heats of vaporization read opposite this second index are corrected values rather than the results of calculations from the vapor pressure curve with the Clausius-Clapeyron equation.

GAS LAW SCALE

Since the temperature scale is laid out as the logarithm of the absolute temperature, it can be used in conjunction with an ordinary logarithmic scale to calculate the expansion of a perfect gas according to Charles' law:

$$\frac{V'}{V''} = \frac{T'}{T''} \quad (29)$$

$$\log V' - \log V'' = \log T' - \log T'' \quad (30)$$

A logarithmic scale is therefore located on the card. Because of lack of space, it must be split to provide a complete cycle. This scale is identical with the latent heat scale, and the two can be used together as an ordinary slide rule—e. g., for correcting the volume of a perfect gas for pressure changes.

Scales for direct conversion of temperature, pressure, and heat units complete the slide rule.

PROCEDURE FOR USING SLIDE RULE

The final slide rule is shown in Figure 4. The two parts, the slide and the card should be cut out and mounted on cardboard or preferably on a stiff transparent plastic sheet. The slide lies across the card and readings are made from the edge of the slide down onto the card. A frame, made of cardboard, plastic, or light sheet metal, should be made to hold the two parts so that the slide can be moved horizontally and the card vertically, and so that the edges of the two parts are held parallel.

Use of the slide rule involves two steps, setting and reading. The method of setting depends on the data available. If the liquid is given in the list on the back of the card, the point of the liquid index in the middle of the heat of vaporization scale is set to coincide with the index point on the upper part of the card marked with number given in the key to liquids. If the liquid is not given in the key, but vapor pressures at two temperatures are known, the slide is moved until one of the temperatures is opposite the corresponding pressure and then the card is raised or lowered until both points are correctly shown on the temperature and pressure scales. If the vapor pressure at only one temperature is known and the liquid falls into one of the seven classes given in the key, the known vapor pressure and temperature are kept together and the card is moved until the liquid index is on the line for the appropriate class. If only one pressure-temperature value is known and the liquid is of a class not represented by a line, a liquid of the same class is selected from the miscellaneous list for use as a comparison liquid, and the rule is set so that the known pressure-temperature value is correctly shown and the upper edge of the slide lies on the index point for the comparison liquid. If a suitable comparison liquid is not found in the key, it will be necessary to find the setting point for the comparison liquid from other data and

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KEY TO LIQUIDS

Line I. Hydrocarbons and Halogenated Hydrocarbons
1. *n*-Butane
2. *n*-Pentane
3. Isopentane
4. *n*-Hexane
5. *n*-Heptane
6. *n*-Octane
7. Benzene
8. Toluene
9. Diphenyl

10. Methyl chloride
11. Methylene chloride
12. Chloroform
13. Carbon tetrachloride
14. Ethyl chloride
15. Ethylene chloride
16. Ethylene bromide
17. Chlorobenzene
18. Bromobenzene
19. Iodobenzene

Line II. Ethers
20. Methyl ether
21. Ethyl ether
22. Propyl ether
23. Ethylene oxide
24. Phenyl ether

Line III. Esters
30. Methyl formate
31. Ethyl formate
32. Propyl formate
33. Methyl acetate
34. Ethyl acetate
35. Propyl acetate
36. Glycol diacetate
37. Methyl salicylate

Line IV.
Aliphatic Amines
40. Methylamine
41. Ethylamine
42. Propylamine
43. Dimethylamine
44. Diethylamine

Aromatic Amines (Line III)
45. Aniline
46. Methylaniline
47. Ethylaniline
48. Dimethylaniline

Line V. Carboxylic Acids
50. Formic acid
51. Acetic acid
52. Propionic acid
53. Butyric acid
54. Valeric acid
55. Benzoic acid

56. Acetic anhydride
57. Phthalic anhydride
58. Carbon suboxide

Line VI. Aliphatic Alcohols
60. Methyl alcohol
61. Ethyl alcohol
62. Propyl alcohol
63. Isopropyl alcohol
64. *n*-Butyl alcohol
65. Isobutyl alcohol
67. Isoamyl alcohol
68. Glycol

69. Phenol

Line VII.
Inorganic Hydrides and Halides
70. Hydrogen iodide
71. Ammonia
72. Phosphorus trichloride
73. Stannic chloride
74. Arsenic trichloride
75. Sulfur chloride
76. Mercuric chloride
77. Mercuric bromide
78. Mercuric iodide
79. Mercurous chloride

Miscellaneous Organic
80. Cyanogen
81. Phosgene
82. Acetaldehyde
83. Hydrogen cyanide
84. Carbon disulfide
85. Acetone
86. Chloropicrin
87. Benzaldehyde
88. Nitrobenzene
89. Quinoline

Elements
90. Chlorine
91. Bromine
92. Iodine
93. Phosphorus (white)
94. Mercury

Miscellaneous Inorganic
95. Sulfur dioxide
96. Nitrogen oxychloride
97. Water

to proceed as above. This procedure is equivalent to using Dühring's law.

The vapor pressure data may be available as an equation of the form,

$$\log p_{\text{mm.}} = A - \frac{B}{T} \quad (7)$$

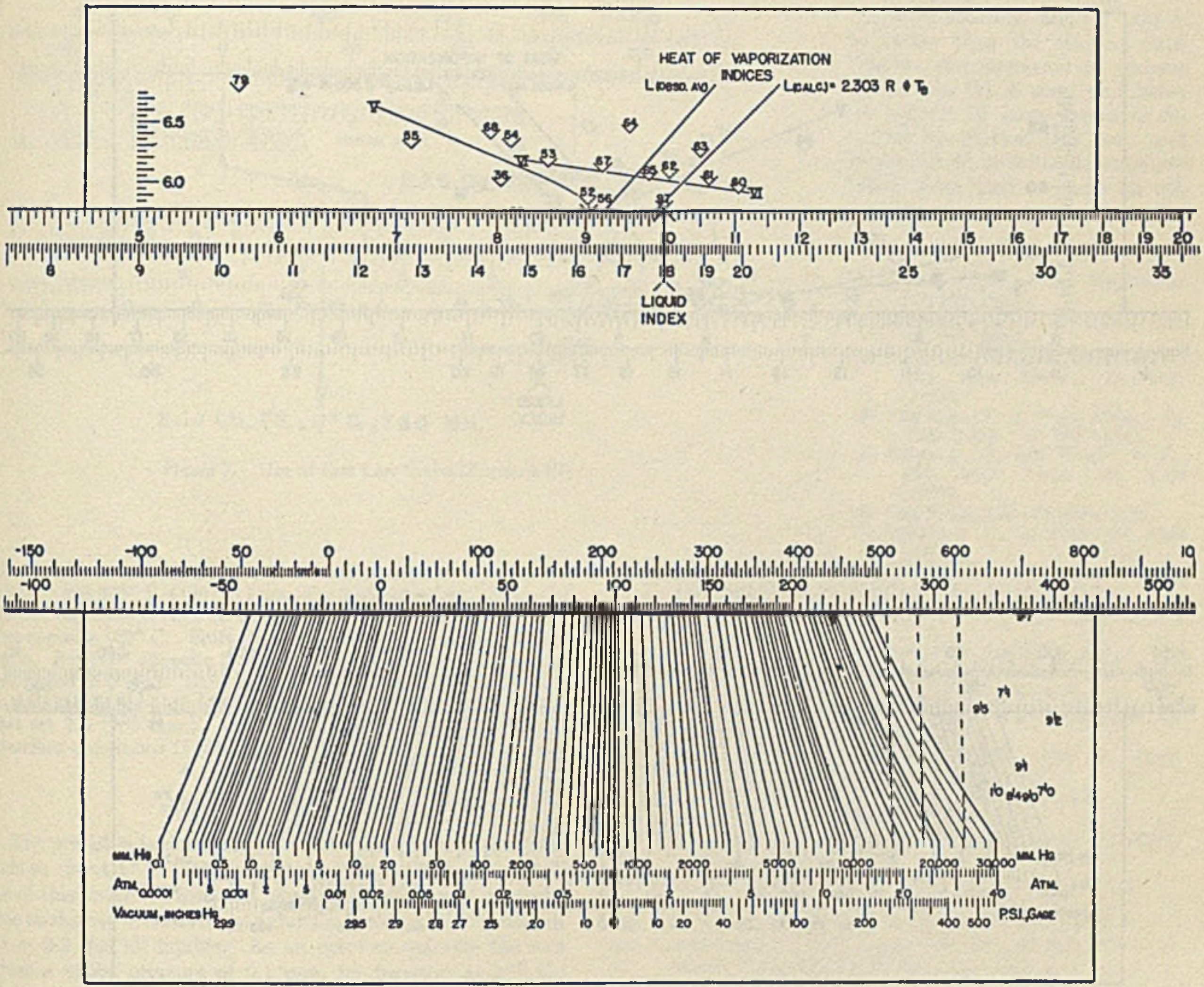

Figure 5. Setting for Water, No. 97 (Example I)

In this case values for the boiling point and for ϕ are calculated as follows:

$$\phi = A - 2.8808 \quad (31)$$

$$t_b \text{ °C.} = T_b - 273.1 = \frac{B}{A - 2.8808} - 273.1 = \frac{B}{\phi} - 273.1 \quad (32)$$

The rule is then set so that the boiling point lies on the one atmosphere line and the upper edge of the slide lies on the correct value on the vertical ϕ scale.

Once the setting for a liquid has been found, the point on the card under the liquid index point may be marked or the values of the boiling point and ϕ may be recorded for reference.

The vapor pressure at any temperature is read by following the curved pressure line from the desired temperature down to the mm. Hg scale. The latent heat at the boiling point is read from the heat of vaporization scale where it is cut by one of the heat of vaporization indices. The right-hand index, L (calc.), gives the value which would be calculated by the Clausius-Clapeyron equation from the vapor pressure curve, while the L (obsd. av.) index shows the most probable value of the true latent heat, which would be found by a calorimetric measurement.

To convert the temperature, pressure, or heat values to the other units shown by the additional scales, it is important that the new reading be made directly above or below the previously determined value.

To estimate the critical temperature of an organic liquid, it is first necessary to read the normal boiling point. The critical point is then read, using the three broken lines at the right-hand end of the pressure scales. By interpolation the critical temperature may be estimated to about 20° C. The critical point index for the higher boiling liquids is displaced to the left. The critical temperatures of nine liquids having abnormally high values are marked to the right of the pressure scales using the index numbers given in the key.

vertically down through 18.5 atmospheres to 255 pounds pe square inch gage pressure (true value 262 pounds per squar inch).

Example II. Methyl isobutyrate boils at 0° C. under 12 mm pressure. Find the normal boiling point, latent heat of vaporization at the boiling point, boiling point under 2 atmospheres pressure, and critical point (Figure 6). Methyl isobutyrate is not i the key of liquids, but esters as a class are represented by lin III. Keeping the 0° C. mark on the 12 mm. curve, move th card until the point of the liquid index falls on line III.

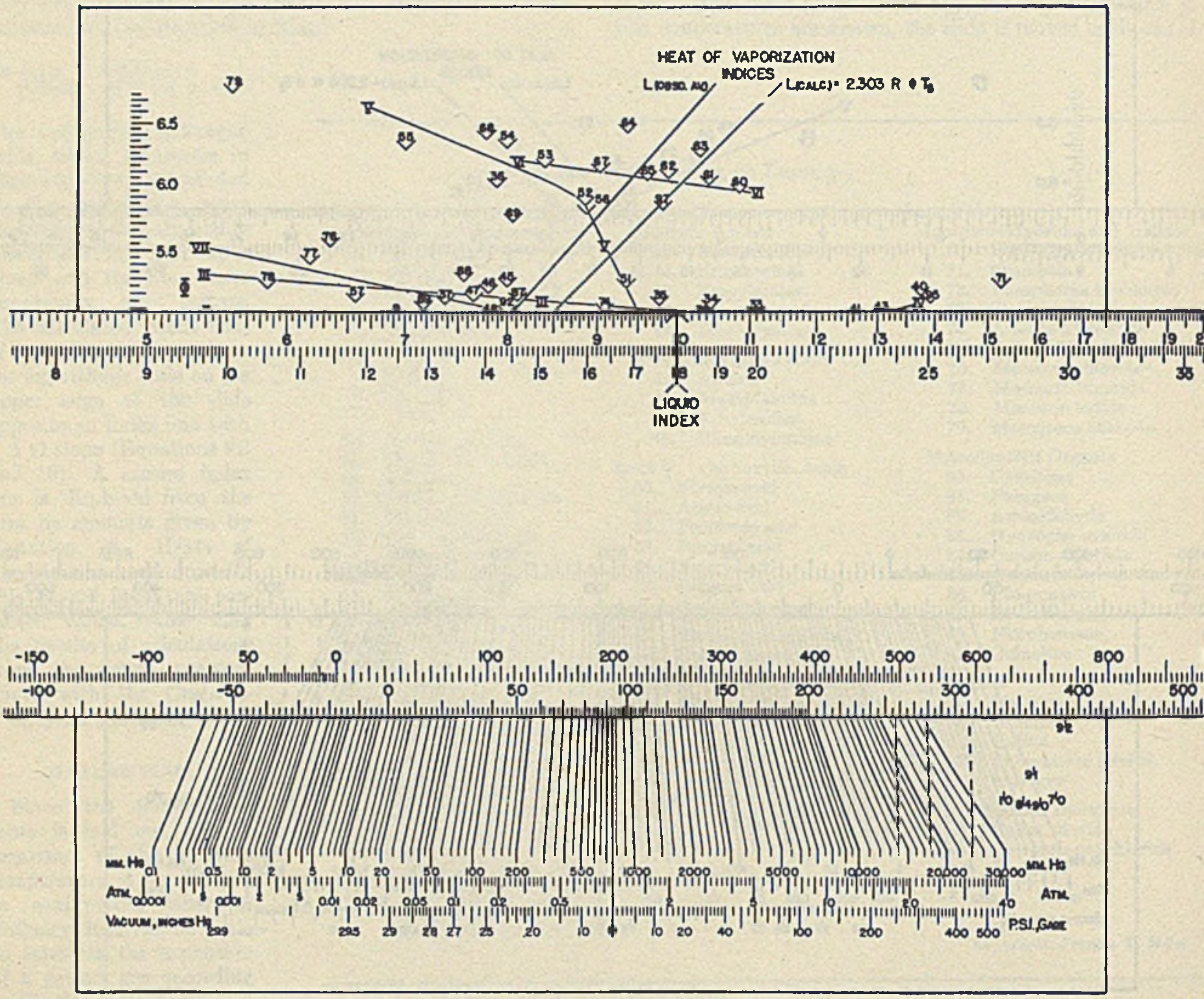

Figure 6. Setting for Methyl Isobutyrate (Example II)

To estimate the limits of error of a calculation from a single pressure-temperature value, the procedure given above is repeated, setting the ϕ values 0.2 higher and lower than the value first used.

Example I. Find the critical temperature of water and the gage steam pressure at 410° F. (Figure 5). In the key to liquids find water, No. 97; set the point of the liquid index on the point of the V marked 97.

Since water has an abnormally high critical point, it is specially marked. Above this mark, 97, read the critical temperature, 374° C. (705° F.). From 410° F. read vertically down to 210° C.; follow the curved pressure line down to 14,000 mm. and then

Opposite the 1 atmosphere line read the normal boiling poi 93° C. (true value 92.3°). Opposite the heat of vaporizatic indices read 8.5_1 and 8.0_7 kg.-cal. per gram mole, the calculate and corrected values, respectively, for the molar heat of vapor zation (true value 7.98). From the 2 atmosphere mark rea directly up to 15_{20} mm. (interpolated) and follow the curve u to 117° C., the boiling point under 2 atmospheres pressure (tr value 116.8° C.). To find the critical temperature, interpolatic between the two right-hand broken lines on the card giv 282° C. (true value 267.6).

Example III. To make gas law calculations the split log rithmic scale in the middle of the card is used with the temper ture and latent heat scales just as with an ordinary slide ru For example, to correct a volume of 3.58 cubic feet at 320° and 720 mm. to standard conditions: Move the card down un

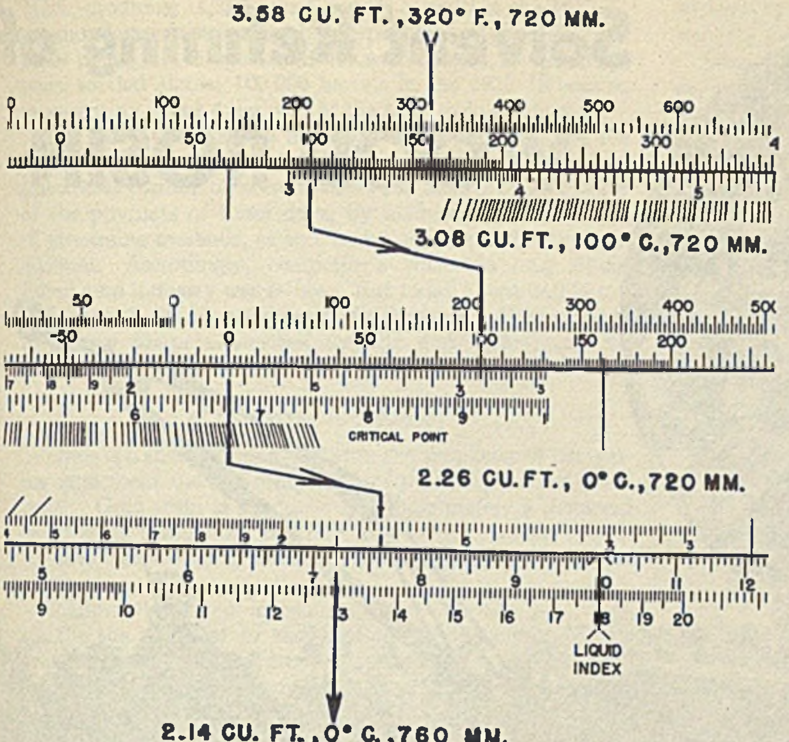

Figure 7. Use of Gas Law Scales (Example III)

the temperature scale lies on the lower of the two logarithmic scales. Set 320° F. (160° C.) opposite 3.58 cubic feet. Since the desired calculation runs off the end of the scale, read 3.08 cubic feet opposite 100° C. Shift the card to use the upper logarithmic scale. Set 100° opposite 3.08; opposite 0° read 2.26 cubic feet (corrected to 0° C.). Shift the card so that the logarithmic scale is next to the heat of vaporization scale. Opposite 2.26 cubic feet set 7.6 (760 mm.). Opposite 7.2 read 2.14 cubic feet at standard conditions (Figure 7).

PRECISION AND ACCURACY

The precision is limited by the size and construction of the rule to about 1° C. For most calculations the accuracy will be of this order. There is a small inherent lack of accuracy due to the use of an average value for the curvature constant, $D = 0.3$, for all liquids. As an extreme example the rule gives a vapor pressure of 0.1 mm. for mercury at 93° C.; the true values are 0.1 mm. at 82° or 0.19 mm. at 93°. This error, 11° or 90 per cent of the pressure, represents the maximum inaccuracy caused by this approximation, since the calculation covers the widest possible range and mercury has an abnormally low curvature, $D = 0.056$. The limits of error caused by improper setting because of lack of data are found by resetting at a higher and lower ϕ value. The percentage accuracy of the corrected heat of vaporization values can be judged from Figure 3. The estimate of the critical point is the least accurate calculation, the average error for organic liquids is about 15° C.

LIMITATIONS

Vapor pressures should not be calculated for solids below the melting point unless the slope is corrected for the latent heat of fusion. For example, iodine (No. 92) melts at 114° C. at which it has a vapor pressure of 90 mm. The molal heat of vaporization, L (calc.) is 10.6; the heat of fusion is 2.97 kg.-cal. per gram mole. If the slide rule is reset so that 90 mm. is opposite 114° C. and the calculated heat of vaporization reads 13.5_7 (= 10.6 + 2.97), the vapor pressures for solid iodine down to 0.1 mm. can be accurately read.

The estimations are, of course, no better than the starting data. Pressure measurements in vacuum distillations at 5 mm. and below are subject to large errors as described by Morton (*23*), and such values should be critically examined before being used as bases for calculations.

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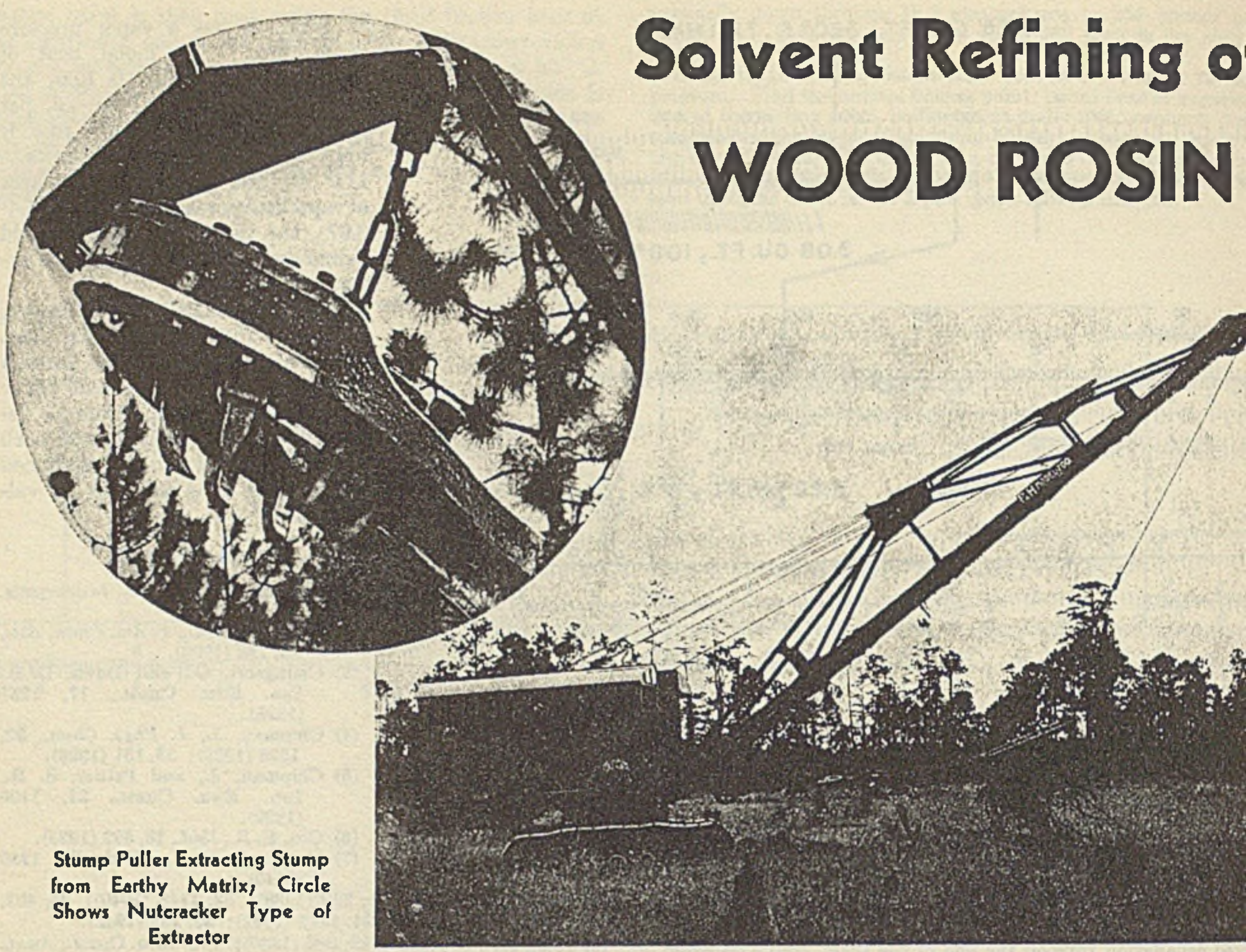
Solvent Refining o
WOOD ROSIN



Stump Puller Extracting Stump from Earthy Matrix; Circle Shows Nutcracker Type of Extractor

I. W. Humphrey
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ESSENTIALLY all of the rosin given by the pine tree is classified either as gum or wood rosin; the former flows from the living tree, the latter is extracted from its dead stump. The oleoresinous products of the pine can boast an ancient lineage extending back to those days when the Phoenician sailors of the first great commercial nation caulked their rude ships with the pitch of the pine. Devotees of the pine tree assert that Noah "pitched his ark within and without" by means of pine pitch, but it must be admitted that this ancient mariner may have used a natural asphalt. A report submitted to Sir Walter Raleigh over three and a half centuries ago stressed the value of the great pine forests of the Carolinas (*58*). Our first commercial shipment of industrial products carried naval stores comprising tar, pitch, rosin, and turpentine from the Virginia shores in 1608.

The name "naval stores", however, arose from the highly valued use of pine tar and pitch for caulking leaky ships and preserving their rigging. Today this use has almost vanished, yet the primary oleoresinous products of the pine tree—rosin and turpentine—are still called "naval stores"; the term usually includes some of its other products such as pine oil, pine tar, and pitch, or more loosely covers the multitude of resinous and terpene derivatives procured by tapping or extracting the pine tree.

That modern sector of the industry known as wood na stores was born at the turn of this century, without ben of much engineering or chemical technology. Today wo naval stores contribute more than one third of this countr rosin and turpentine by processing stumps from the south pine belt. In addition, all of our pine oil is supplied by wood naval stores industry, given by Mother Nature to m as a bonus for his ingenuity in applying chemurgy to the c over pine lands.

During the first decade of this century, the experts prop sied that the gum naval stores industry would wither a shrivel because of the gradual depletion of the virgin p forests. But this calamity was averted by the self-seed of the rapidly growing slash pine in the cut-over pine lan as well as by improved methods for procuring gum oleoresi

In the meantime, adventurous spirits hastened to fores the threatened shortage by processing some of the milli of pine stumps in the southland. Ventures that were a only to steam the milled wood for turpentine and pine proved economically unsound. Subsequent solvent traction of the wood to recover its approximately 20 per c rosin content was also necessary.

The first successful commercial operation (*66*, *68*), know the steam and solvent process, was pioneered by Homer Yaryan at Cadillac, Mich., in 1909. His plant at Gulfp

Miss., produced 14,300 round barrels of rosin in the 1910–11 season, along with considerable turpentine and pine oil. Another plant, still in operation, was soon opened, so that wood rosin totaled almost 100,000 barrels in the 1912–13 season, representing about 4 per cent of the total rosin production.

The wood naval stores industry throughout much of the decade and a half following its inception was placed in a precarious position on account of certain defects in the quality of the products of those days, by inadequate development of processing methods, as well as by occasional drastic price declines. Accordingly, competition with the long established gum industry was feeble. But today about half of our rosin is produced by wood naval stores plants. Refined wood rosin now competes successfully with gum rosin in a wide range of applications.

GUM ROSIN PROCESSING

There is a sharp contrast between the simplicity of harvesting gum rosin and the complexity of procuring refined wood rosin. Gum rosin is produced at approximately a thousand small stills throughout the pine belt which extends over a thousand miles along the south Atlantic and Gulf Coastal plains.

Shallow, V-shaped incisions are cut on the pine tree, usually the long leaf or slash species. Additional hackings are made during several gum-flowing seasons. The oleoresin or gum which oozes down the face of the tree is collected, then heated in a small copper still to drive off spirits of turpentine. The molten rosin is filtered and barreled, its color depending largely on the period over which the tree has been bled, as well as on the care exercised in collecting and processing its oleoresin. The small-scale gum rosin producer has been handicapped by lack of technical control. Modern technology, however, is now coming to his aid, chiefly in the form of large, central, modern processing units, fostered by federal agencies.

WOOD ROSIN PROCESSING

The wood rosin producer carries on after the gum rosin farmer and lumberman have passed by, leaving their legacy of countless pine stumps. But wood oleoresin will not gush forth from the old pine stump merely by hacking its weather-beaten face. Drastic and intricate operations are necessary to separate and refine its rosin. The cost of a large, modern, wood naval stores plant runs into millions of dollars, as compared to thousands for the usual small gum rosin plant. There are about twelve wood naval stores plants in this country. Production of wood naval stores is a science, in contrast to the colorful art practised by the gum naval stores industry since colonial days.

The gum rosin from the oleoresin of the living pine tree formerly was the only source of rosin. In recent years 40–50 per cent of our total rosin production has been obtained by extracting wood rosin from the stumps of the cut-over pine lands of the southern states. The refining of crude wood rosin sufficiently to render it competitive to gum rosin proved a difficult problem. Its commercial solution was first achieved by treatment with furfural using a dual, immiscible solvent procedure. Furfural selectively extracts the dark resin fraction, leaving the refined rosin in the petroleum naphtha layer. Other types of solvents for rosin color bodies are discussed as well as the selective solvent refining of the rosin derivatives.

After the stump has remained in the ground ten years or so, its bark and sapwood have sloughed off, leaving the rosin concentrated in the rich heartwood. The pine stump analyzes approximately 18 per cent water, 5 per cent terpene oils, 22 per cent rosin, and about 4 per cent of a gasoline-insoluble resin, leaving about 51 per cent of cellulosic- and ligneous-type materials (*18*).

Methods of extracting the stump from its earthy matrix vary with the terrain. Dynamite is often used, as well as various forms of tractors and stump pullers (*62*). One type has a nutcracker which, dropping on the stump, firmly grips and pulls it from its footing along with its anchoring tap root, simulating a gigantic dental operation. After some splitting and trimming, the stump-wood, along with roots and any other rich resinous wood which happens to be available, is loaded on gondolas. It has been estimated that the wood naval stores industry is responsible for annually clearing approximately 200,000 acres of cut-over pine lands, releasing them for agricultural use.

When the harvested wood arrives at the naval stores plant, it is either stored in the stock pile or conveyed directly to the mill rooms. There it is devoured by a mechanical hog provided with a rotary disk chipper, then shredded by hammer mills to splinter-type chips suitable for extraction.

The extraction procedure has long been known as the steam and solvent process since both are employed in removing the volatile oils and rosin. The milled wood is placed in a series of vertical towers about 24 feet high, each holding about 13 tons of chips. After steaming for turpentine and part of the pine oil, the wood is countercurrently solvent-extracted by flooding with a petroleum naphtha cut. In a recent modification of the process, the steaming step is omitted, the turpentine, pine oil, and rosin being extracted from the wood by a suitable volatile solvent. Solvent, turpentine, intermediate terpene cuts (chiefly dipentene, terpinene, and terpinolene), and finally pine oil are fractionally separated, leaving as residue crude wood rosin. Around 12 gallons of volatile oils are obtained per ton of wood.

WOOD ROSIN REFINING

When wood rosin was first produced about thirty-five years ago, it enjoyed only a limited market. The manufacturer could boast both of its uniformity and cleanliness as compared to the variable quality of the gum rosin produced by hundreds of farmers; but the single grade of wood rosin of that era had several defects when measured by the accepted standards for gum rosin.

Wood rosin possessed a little lower melting point and also a poorer solubility in petroleum hydrocarbons than gum rosin. The wood rosin plant was frequently infested by an unknown species of "gremlin" which delighted in mysteriously transforming the otherwise clear and uniform unrefined wood rosin into a sugarlike, semicrystalline mass, unacceptable to any consumer. Fortunately "*Chemlin Abieticus*" fell under the spell of chemical technology and accordingly ceased crystallizing wood rosin.

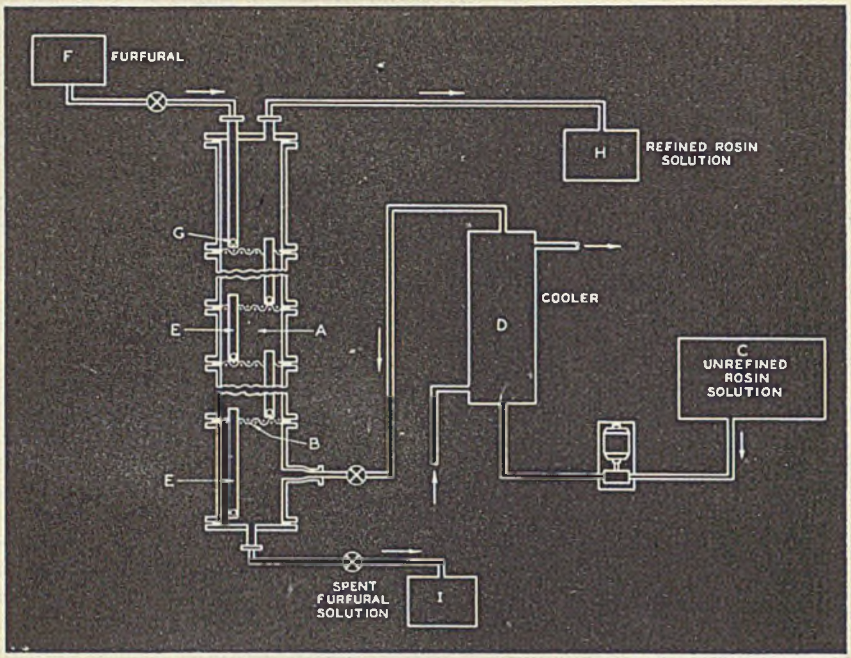


Figure 1. Lister Rosin Refining Tower

The unforgivable sin of unrefined wood rosin, however, was its characteristic, dark red color, differing notably from the conventional yellow to brown color grades of orthodox gum rosin. Furthermore, color differences between gum rosin and the unpurified wood rosin of that day were magnified on contacting them with air and alkali. The wood rosin soap rapidly acquired an objectionable, deep brown color with exterior discoloration zones forming in the soap bar. Relatively little change occurred in gum rosin soap, and therefore wood rosin was effectively barred from entering the soap, ester gum, and varnish fields as well as from much of the paper sizing business. Until properly bleached, it was doomed to remain in the lower-priced rosin market, with outlets chiefly in linoleum, core oils, and the darker sized grades of papers.

Many were the attempts to refine it to a paler grade before a process was finally developed which could be commercialized. Yaryan found that treatment with sulfuric acid (*67*) improved its color greatly, but the process could not be economically developed. Other chemical reagents, including amphoteric metallic chlorides (*31*, *52*), boric acid (*3*), hexamethylenetetramine or formaldehyde (*32*), alkali (*40*), etc., effected considerable improvement, especially if followed by distillation under reduced pressure. Yet the performance of none of these early refined types of wood rosin on testing in soaps and varnishes was such as to warrant plant-scale production.

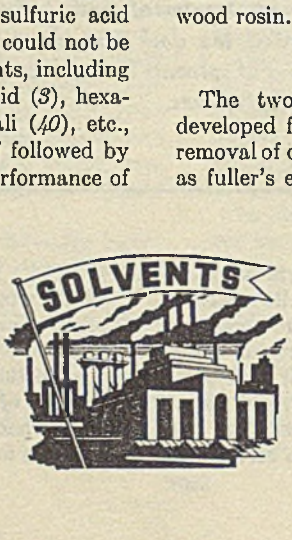
The reactive nature of the rosin acids is not auspicious to the removal of a substantial proportion of assorted color bodies from wood rosin on a technical scale. The two unsaturated linkages and tertiary carboxyl group of the abietic and pimaric type rosin acids afford an entering wedge for the attack of drastic chemical reagents. Accordingly, a physical rather than a chemical treatment was indicated.

Prior to the era of chemical treatments directed toward the decolorizing of wood rosin, it was found (*19*) that distillation of the darker grades of gum rosin under reduced pressure improved their color. Investigation showed that reduced pressure distillation of wood rosin by modified procedures (*16*, *47*) also yielded pale grades; but some of its latent or potential color bodies of a phenolic type were carried over, producing deep yellow to brown colors when the distillate was contacted with alkali. Fractional distillation (*29*) or condensation (*41*, *46*) were helpful but the last traces of these soap-discoloring components stubbornly resisted eviction from distilled wood rosin. Wood rosin still remained an outcast, lacking eye appeal, and unwelcomed by the soap, varnish, and much of the paper sizing industries. But today the improved and desirable characteristics of refined wood rosin are recognized throughout the rosin consuming industries.

By virtue of the insolubility of many of the wood rosin color bodies in petroleum fractions, they could be almost eliminated on refrigeration of the rosin in butane solution (*28*). However, the small fraction which remained proved sufficient to prohibit industrial usage of this type of refined wood rosin.

FURFURAL REFINING

The two commercially successful processes eventually developed for refining wood rosin depend upon the physical removal of color bodies either by an adsorbent (*57*, *59*, *64*) such as fuller's earth or by the selective solvent furfural. Commercial production of furfural-refined wood rosin was achieved fifteen years ago, based upon the invention of Kaiser and Hancock (*45*). The refined wood rosin thus produced possesses properties which make it suitable for fields formerly closed to wood rosin.



In the selective solvent refining procedure, wood rosin is fractionated by intimately contacting it with two substantially immiscible liquids, one of which preferentially dissolves its color-bearing components and leaves the purified rosin in the other liquid phase.

In some detail a solution of wood rosin in a petroleum naphtha cut is agitated with a relatively small proportion of furfural and then allowed to separate into two layers. The higher-specific-gravity furfural layer contains substantially all of the colored components of the rosin along with a small proportion of its rosin acids. Evaporation of the furfural for recycling leaves a resin of dark color. From the gasoline phase is recovered the refined rosin, its improvement in color depending, with certain limitations, upon the refining conditions imposed (*23*, *48*).

TABLE I. CHARACTERISTICS OF COMMERCIAL WOOD ROSINS AND EXTRACTED RESINS

Grade	Approx. Lovibond Color[a]	Acid No.	Saponification No.	Unsaponifiable, %	Methoxyl, %	Gasoline-Insol., %	Softening Point, ° C. Hercules drop	Softening Point, ° C. Ring & ball	Refractive Index (20° C.)	Density (20° C.)
				Wood Rosins						
Crude	80A + 190R	150	170	8.5	1.7	25	86	74	1.56	1.10
Refined										
H	40A + 8R	162	169	7.5	..	0.05	81	72–5	1.5470	1.069
I	40A + 4.5R	163	171	7.5	0.50	Trace	82	72–5	....	1.069
K	40A + 2.5R	164	171	7.0	0.45	Trace	82	72–5	1.5453	1.069
M	40A + 0.75R	165	171	7.0	0.35	Trace	82	72–5	....	1.067
N	39A	165	172	6.0	0.30	Trace	83	73–8	....	1.067
WG	27A	166	172	6.0	0.20	Trace	83	73–8	1.5453	1.067
X[b]	12A	171	174	7.0	..	Nil	82	73–8	1.5450	1.065
				Extracted Resins						
Primary	Too dark	90	160	8.0	5.5	95	114	102	1.58	1.21
Secondary	Too dark	119	150	12.0	3.5	64	83	73	1.58	1.15

[a] A = amber, R = red (7/8-inch standard cube).

[b] By reduced pressure distillation of I grade.

The essential step of effectively contacting rosin with furfural may be performed by one of several methods. Thus, unrefined rosin, petroleum naphtha, and furfural may be heated sufficiently to form a single phase, separation into two layers occurring on cooling to room temperature. Also, rosin-naphtha solution at room temperature may be washed once batchwise or countercurrently by several small portions of furfural. Refrigeration may be included to separate refined rosin more completely from its color bodies.

Wood rosin is purified commercially on a continuous scale by washing with furfural in the Lister rosin refining tower (*50*), shown in Figure 1. This tower may be approximately 30 feet high and 6 inches in diameter, but in present plant practice is about 40 feet high and 3 feet in diameter. It is divided into chambers *A*, perhaps 8 inches high, by means of plates *B* formed of fine mesh screening. Approximately 15 per cent crude rosin in petroleum naphtha solution, *C*, which may pass through a cooler, *D*, moves up the tower through the screens as it is washed by the descending furfural, *F*, collected in pools. The latter are retained on the screens and overflow into the tops of the downpipes, *E*, provided with side outlets *G* near the bottom. Refined rosin solution *H* is drawn off from the top of the tower and spent furfural solution *I* from the bottom.

Prior to the foregoing treatment, the rosin solution is generally given a preliminary wash with a small amount of furfural, with separation of a primary extract. It is then washed with an increased proportion of furfural, somewhat as described above, to yield a secondary furfural extract and the petroleum naphtha solution of refined rosin. Approximately two thirds of the crude rosin is converted into refined rosin.

The petroleum naphtha is distilled off from the refined rosin by passage through a series of three evaporators. Most of the solvent is flashed off in the first, a horizontal-tube Yaryan evaporator, operating under partial vacuum and at about 50 pounds steam pressure. Low-pressure evaporators, provided with tubes of special aluminum alloy, remove the remaining solvent and volatile oils by heating and sparging with around 140 pounds of steam. Details of various plant operations have been described elsewhere (*18*).

The primary incentive for the selective solvent refining of crude rosin is to procure a major rosin fraction of improved color, acceptable to the ultimate consumer. Yet the partitioning of the crude rosin into fractions of pale and dark color is only a fortuitous effect, depending upon the differential solubility of the crude rosin components by virtue of physical characteristics less conspicuous than that of color.

Some degree of analogy exists between the furfural refining of the polycyclic components of wood rosin and the separation of lubricating stocks into two fractions by means of furfural. For simplicity, the latter system may be considered to include three major components: furfural, cyclic hydrocarbons paraffinic in character from bearing long chains, and polycyclics having a few relatively short chains (*21*). The latter tend to dissolve preferentially in the furfural as the extract phase.

On the other hand, the crude wood rosin system comprises four major components: furfural, petroleum naphtha, hydroaromatic or unsaturated rosin acids, and the less acidic, more complex, naphtha-insoluble and furfural-soluble resin fraction which is more aromatic and more highly oxygenated than the rosin acids. The naphtha-soluble rosin acids generally carry an isopropyl group and two methyl side chains. It should be noted, however, that the rosin acids are also furfural soluble.

TABLE II. METAL CONTENT OF COMMERCIAL WOOD ROSINS AND EXTRACTED RESINS

Grade	Metal Content, P. P. M. Fe	Al	Cu	Mn
		Refined Rosins		
H	1	2	<1	<0.1
I	1	2	<1	<0.1
K	1	2	<1	<0.1
M	1	2	<1	<0.1
N	1	2	<1	<0.1
WG	1	2	<1	<0.1
X	<1	<2	<1	<0.1
		Extracted Resins		
Primary	100	..	50	..
Secondary	15	5	2	<0.5

The furfural refining process is flexible; it yields seven commercial grades of refined wood rosin ranging from G to WG by the arbitrary, time-honored rosin color scale. The paler grades, such as WG, are obtained by sacrificing some yield to the dark resin fraction. Furfural-refined rosins in most instances can be used equivalently to corresponding grades of gum rosin. They have the added advantages of superior uniformity, the presence of only a trace of gasoline-insoluble material, and heat bleaching to about one grade when processing above 250° C. in varnish or ester gum formulation.

The effect of furfural refining upon the chemical and physical characteristics of wood rosin is shown in Tables I and II. Wood rosin exhibiting these properties has competed successfully with gum rosin for over a decade in the paint and varnish, soap, paper size, and other industries. The major difference between the various grades of furfural-refined rosin is that of color. Yet, as color decreases, there is a slight but gradual tendency for increase in acidity and melting point, with trend toward decreases in unsaponifiable content and density.

The pale rosin recovered from the petroleum naphtha phase comprises approximately 90 per cent rosin acids, chiefly $C_{19}H_{29}COOH$. In comparison, the dark, relatively complex resin dissolved in the primary furfural extract phase exhibits the greater density, refractive index, melting point, viscosity, molar weight, methoxyl and noncarboxylic hydroxyl values, oxygen content, carbon-hydrogen ratio, and resistance of air oxidation, but the lower acidity and solubility in hydrocarbons generally.

The furfural-soluble fractions of the crude rosin are dark in color and relatively high melting, and exhibit considerable differences in acid number and saponification number as the result of the presence of oxidized rosin acids, phenolic type components, etc. The 5.6 per cent methoxyl content of the resin from the primary extract points to its aromatic character. Special uses have been developed for these resins, depending upon their reactivity with formaldehyde, stabilizing action on soil, core-binding properties, value in certain types of plastics, ability to emulsify asphalt, and valuable properties imparted to cement (*54*).

The wood rosin industry is a tank car consumer of furfural. Since the latter costs around 10 cents per pound as compared to about 4 cents for currently-selling refined wood rosin, furfural losses must be held at the minimum (*63*). This loss represents around 1 per cent by weight of the refined rosin (*43*).

After furfural refining, various secondary types of refining can sometimes be applied to advantage, as distillation under reduced pressure (*22*), crystallization (*37*), iodine treatment (*49*), or furfural refining a noncrystalline fraction (*14*).

The usual solvent for the refined rosin phase is a light petroleum fraction, such as a cut of gasoline or naphtha. With pentane or butane (*60*) the distribution ratio favors higher yields of refined rosin than gasoline. Petroleum hydrocarbons of high aniline point, showing small content of olefinic and aromatic hydrocarbons, are preferable to the usual run of petroleum hydrocarbons (*53*). Pinene, as well as other terpenes, are inferior to paraffin hydrocarbons as rosin solvents.

OTHER SELECTIVE REFINING SOLVENTS

There are a considerable number of selective solvents for rosin color bodies in addition to furfural. To varying degrees these fulfill the requirements essential for refining wood rosin by the selective immiscible solvent procedure:

1. Good solvent action on its colored components.
2. Substantial immiscibility, or capability of being rendered immiscible with the refined rosin phase, separating as a liquid phase.
3. Volatility such as to be readily separable by distillation from both refined rosin solvent and the resins.
4. Absence or low degree of reactivity with the rosin and its refining equipment.
5. Commercial availability at a sufficiently low price to compensate for any refining loss.

Laboratory studies have shown that certain correlations exist between the molecular structure of an organic compound and its capacity for refining wood rosin by the differential solvent method (*24*). Predictions are sometimes fallible but the following generalizations are indicated:

I. Molecular simplicity is favorable, the lower members of a homologous series being superior to the higher. Methanol (*34*) is superior to ethanol; ordinary phenol (*27*) to the cresols aniline (*25*) to methylaniline; furfural to methylfurfural (*38*) methyl acetate to ethyl acetate; etc.

II. Cyclic structure promotes refining. Alcohols, esters ethers, and aldehydes having a cyclic group normally are better than simple aliphatics carrying the same group. Thus, furfura is greatly superior to acetaldehyde.

The simple furan derivatives are usually more effective than their more or less analogous benzene counterparts. Furfura exerts more refining action than benzaldehyde; likewise, furfury ethers (*65*) and furoic acid esters (*33*), such as methyl furoate than the corresponding benzene derivatives.

III. Unsaturation in the molecule may be helpful. Ordinary phenol is far superior to cyclohexanol, and furfuryl alcohol (*44* to tetrahydrofurfuryl alcohol.

IV. Various substituents are essential, both for promotion o immiscibility of the two phases, as well as for specific solven action on the components of the extract phase. These specific groups include OH (*27*, *34*), NH_2 (*25*), CHO (*45*), SCN (*7*), NO (*65*), COOR (*33*), etc.

V. Two or more similar specific refining groups are generally inferior to one. Polyhydric phenols such as resorcinol (*56*) are less effective than carbolic acid, but various means (*1*, *5*) have been employed to enhance the refining action of the former Ethylene and diethylene glycols (*30*) are preferred to glycerol.

Two dissimilar specific groups are usually superior to two which are alike. Thus, ethylene chlorohydrin (*26*) or ethylene glyco monoacetate are more potent than ethylene glycol. Ortho-substituted compounds, such as guaiacol, salicyclic acid, or *o*-anisidine, are superior to catechol but not to resorcinol.

Substituted ethers (*35*) and substituted esters (*33*) exert much more refining action than the simple ethers and esters. Dichloroethyl ether is effective, but ethyl ether fails to refine.

Certain substances normally crystalline, such as furoic acid o *p*-chloroaniline, are effective solvents but only when they can be induced to separate from the rosin solution in liquid phase. The latter state sometimes is attained on liquefying with a small proportion of water or an organic solvent, also at times by dissolving in a suitable liquid such as alcohol (*6*) or ethylene glycol (*38*) The selective solvency of poorly immiscible liquids such as aceti acid or acetonitrile may also be enhanced by the latter procedure

Inorganic reagents such as liquid sulfur dioxide (*55*), sulfu dioxide dissolved in an organic liquid such as acetone (*10*), and certain inorganic salts dissolved in organic liquids (*4*) refine rosin by the selective immiscible solvent procedure.

REFINING OF ROSIN DERIVATIVES

Rosin derivatives have also been refined by the selective immiscible solvent procedure, which distributes their components into two or more fractions in a ratio different from that occurring in the whole product. Various modification of the procedure improve the color of rosin esters (*8*). Rosi and also its esters (*12*) which have been subjected to rearrangement (*51*) can be thus fractionated.

Table III. Average Annual Approximate Production o Rosin in the United States

Period	Round Barrels[a] (Annual Av.)			Wood, % of Total
	Gum	Wood	Total	
1910–17	2,078,000	64,000	2,142,000	2.8
1917–27	1,629,000	180,000	1,809,000	9.9
1927–37	1,788,000	471,000	2,259,000	20.9
1937–42	1,410,000	927,000	2,337,000	39.8

[a] 500 pounds gross each.

Polymerized rosin and polymerized rosin esters may b selectively solvent-refined (*13*) and also simultaneousl polymerized and refined (*9*).

Hydrogenated rosin and its esters are amenable to differential solvent refining (*11*), separating into fractions exhibiting varying degrees of saturation.

Alcohols of chemically modified rosins, including those which have been polymerized, hydrogenated, or rearranged, are fractionated when subjected to the selective solvent refining process (*15*).

ROSIN PRODUCTION

When wood rosin was first produced commercially a little over thirty years ago, it represented less than 1 per cent of our total rosin production. In the 1941–42 season, its production (1,146,000 round barrels) in this country for the first time surpassed that of gum rosin (990,000 barrels); there was a heavy carry-over of gum from the previous season.

The steady increase in the average annual wood rosin production both as to tonnage and percentage of total rosin production in this country is shown in Table III. Average annual production is condensed into arbitrary periods for brevity. A great spurt in wood rosin production began in 1927 with the advent of refined wood rosin. Incidentally, in recent normal years about 40 per cent of the world production of gum rosin was harvested abroad, but foreign production of wood rosin was relatively small.

The diverse but united efforts of many were required to produce and market the first barrel of I wood rosin procured by the furfural refining process. Its appearance was preceded by years of prolonged and expensive laboratory research and pilot plant development along various lines of rosin refining. The labors of those who shared in this development are but partly reflected in the appended references. So great became the increasing demand for this new type of wood rosin that one producer now refines his entire production of crude rosin. The unrefined FF grade which comprised his entire output prior to 1927 is now no longer made.

It has often been pointed out that rosin constitutes the cheapest source of a high molecular weight, monobasic organic acid. Rosin contains about 90 per cent of rosin acids, mostly of the abietic and pimaric types. The individual acids are difficult to isolate in high purity in considerable yield (*20*). Accordingly, it is fortunate that commercial usage of rosin could be built upon the properties of the admixture of rosin acids as they happen to occur in rosin, plus the important modifying effects of its neutral fraction. But as the inquiring eye of research pries into one of the oldest of the chemical industries, commercial uses will develop for some of its pure individual components. The first step in this direction was the furfural refining of crude wood rosin, a process which concentrates the rosin acids by transferring to the furfural extract its oxidized rosin acids, as well as its components which are more definitely aromatic than the rosin acids themselves.

With the manufacture of purified wood rosin of uniform quality, the way was opened for production of new rosin derivatives. Hydrogenated rosin, as well as hydrogenated methyl abietate (*17*, *36*), both noted for superior resistance to air oxidation and lack of color, are now made commercially. Hydrogenated rosin alcohols (*39*) are a commercial probability. Pale polymerized rosin (*61*), softening and flowing at temperatures above those required for wood or gum rosins, is another important technical development. The only ester of rosin long available to the industrial consumer was its glycerol ester, the well known ester gum. Today a softer derivative, the methyl ester (*42*), as well as the high-melting esters derived from pentaerythritol (*2*), have developed from laboratory curiosities into products of increasing technical importance.

During colonial times the outstanding naval stores product was the pine tar obtained by the destructive distillation of the pine tree. Later, gum turpentine became of prime importance. But since the turn of this century, chemical technology has caused the billion or so pounds of rosin annually procured in this country from the pine to become the most valued naval stores product.

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CONDENSATION OF VAPORS

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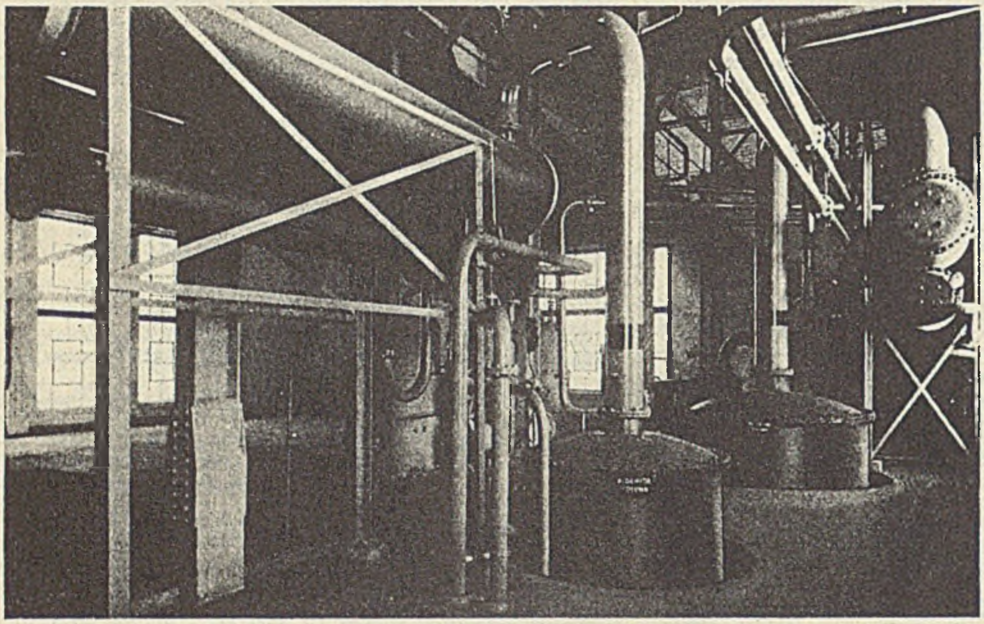
Film Coefficients for Alcohols, Esters, and Ketones



Courtesy, Vulcan Copper and Supply Company

Condenser Level Showing Vapor and Vent Condensers for Distillation Unit for Pure Alcohol (190° Proof)

A PREVIOUS paper (*7*) described a simple, compact apparatus giving highly consistent data for the rates of condensation of lower alcohols. This allows the determination of heat transfer coefficients using a small amount of material, requiring a short time, and measuring all quantities precisely. In this apparatus the same temperature drop was maintained throughout the entire length of the heating surface since the heat transfer surface was maintained substantially isothermal by the passage of eight streams of liquid through channels drilled longitudinally in a solid bar, 1.94 inches in diameter and 20.15 inches in effective length; adjacent streams were flowing in opposite directions to equalize the temperature of the mass of the bar and of the heat transfer surface. Variations in temperature normally encountered around the circumference of a tube were not investigated but were probably minimized, owing to the large metal mass of the bar as compared to a tube.

Furthermore, vapor velocity was reduced by installing the condensing surface directly in the vapor space of the boiler itself as done in earlier research (*4*). This gives the lowest possible vapor velocities and coefficients (safest from design standpoint); it also eliminates the corrections usually necessary for different velocities and pressures of vapors surrounding a tube where the vapors enter one end of an annular space around the tube, and are condensing and losing volume and velocity from inlet to outlet.

The purpose of the study was to determine data for the design of commercial heat transfer equipment. Only two factors were to be considered as affecting the rate of condensation of organic vapors at their normal boiling points, which are the usual condensing temperatures in practice: (*a*) the nature of the compound itself—i. e., its chemical formula; and (*b*) the temperature drop from the vapors to the condensing surface.

In the previous work the data for iso, secondary, and tertiary alcohols did not correlate well with coefficients for straight-chain alcohols. These runs were repeated, starting with the lowest temperature drop obtainable (highest cooling water temperature) and progressively increasing the temperature drop. After the maximum temperature drop was reached, the procedure was repeated with successively lower temperature drops. The coefficients for this second series were lower than those obtained during the ascending series of temperature drops.

Thus, it appeared that noncondensable gases were accumulating during the time of the run and lowering the coefficients obtained after the apparatus had been run for a few hours. Noncondensable gases might be formed by decomposition of the alcohols boiling in contact with the copper heating coils; for it is known that copper acts as a catalyst for the production of hydrogen and aldehydes, particularly from the branched-chain alcohols. This decomposition has never, however, been reported at such low temperatures.

DECOMPOSITION OF ALCOHOLS

A special gas manometer was previously devised to determine the amount of air in steam (*5*) by measuring the partial pressure of air or other noncondensable gas present. A

The film coefficients of heat transfer for the condensation of a total of some eighteen alcohols, esters, and ketones have been determined at their normal boiling points over a wide range of temperature differences, by the method previously described. Vapor velocity and temperature difference along the tube were both held constant, which reduces the variables to: (a) the material itself—i. e., the chemical configuration of the vapor molecules; (b) the temperature difference from vapor to tube surface. The method was modified to allow for possible decomposition of alcohols, which gives amounts of noncondensable gases large enough to reduce the coefficients seriously. The data agree among themselves within the relatively low experimental error; they were correlated with the physical properties controlling condensation and were well within the accuracy of the physical data available.

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similar device to determine the decomposition of alcohols boiling in contact with a copper immersion heater is shown in Figure 1, using a special 22-liter glass flask and fittings.

When the system was filled for operation, the bulb contained air at about 450 mm. partial pressure. Alcohol filled both sides of the manometer above the mercury, filled the funnel, and partially filled the bulb as shown. At thermal equilibrium, the partial pressure of the alcohol in the bulb equaled that in the flask and canceled it on the manometer. When the vapor space of the flask was free of noncondensable gases, the manometer read directly the pressure of the air in the bulb. This was the highest reading on the manometer. As noncondensable gas formed in the flask, it caused a decrease in the manometer reading; and this decrease equaled the partial pressure of noncondensable gases formed.

At the beginning of a run, 2.5 gallons of the alcohol were charged; then approximately 1 gallon was boiled off to sweep out all air from the vapor space. The system was closed off at a pressure somewhat above atmospheric; and the manometer was read to give the partial pressure of air in the bulb. The total pressure in the flask was also read and maintained constant by the pressure-regulating system described previously (6). Runs were made with the surface of the copper heater dull or oxidized and also bright (after an acid wash). In every case a silver mirror test showed the presence of aldehydes in a sample of the alcohol taken after the run, whereas no test was obtained with a sample of the alcohol at the start. A summary of the data obtained in 5-hour runs follows:

Alcohol	Condition of Heater	Mm. Hg in Gas Manometer		Pressures, Mm. Hg			% Noncondensables
		Initial	Final	Δp	Partial	Total	
Isobutanol	Oxidized	463	451	12	11.28	998	1.13
Isobutanol	Bright	496	476	20	18.80	828	2.27
tert-Butanol	Oxidized	448	434	14	13.19	941	1.40
tert-Butanol	Bright	451	425	26	24.41	920	2.66
Ethanol	Bright	458	449.5	8.5	8.01	915	0.88

This study shows that alcohols partially decompose on boiling in contact with a copper heating coil to give a noncondensable gas (probably hydrogen). The larger decomposition obtained with the branched-chain alcohols explains the low values previously reported (7) in the plot of the film coefficient against temperature drop for these alcohols; and the different slope was probably due to a gradual increment of noncondensables as the runs progressed. The vapor film coefficient indicates very small amounts of gaseous impurities; as little as 0.5 per cent noncondensable gas lowers the coefficient by 50 per cent (4).

Figure 2 shows the general arrangement of the apparatus. A detailed description was given in the earlier paper (7).

CONTINUOUS VENTING. Figure 2 illustrates the method adopted to remove traces of noncondensable gas formed by allowing the system to vent continuously. Exhausting vapors traveled through the inner $^1/_4$-inch line to glass condenser L, and the noncondensables swept out with the vapor were vented while the hot condensate returned to the boiler through an annular space, G, and a 12-inch seal with drain cock, N. Only a small percentage of the vapors formed in the flask passed to the condenser; this small amount had no appreciable effect on the velocity of approach of the vapors to the main condensing surface. To maintain a positive pressure (to ensure that no air leaked into the system), the condenser end of the $^1/_4$-inch vapor exhaust line was slightly constricted to throttle the vapors.

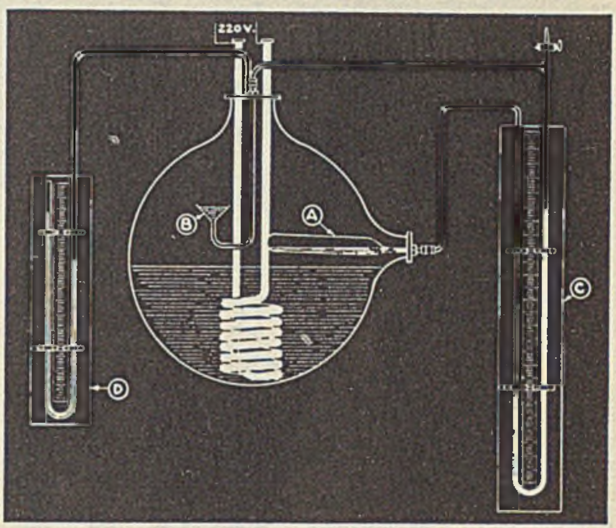


Figure 1. Gas Manometer Arrangement for Determining Noncondensable Gas in Vapors

A. Bulb with same liquid as that boiling in flask, and with predetermined amount of air in supernatant vapors
B. Funnel to ensure liquid filling low-pressure side of manometer
C. Manometer to indicate difference of pressure of noncondensable gas between bulb (known) and flask
D. Manometer to measure total pressure in flask

COOLING WATER SYSTEM. With higher boiling liquids, cooling water at a higher temperature than that from the tap was used to obtain a smaller temperature drop. The heated primary cooling water emerging from the condensing system was recirculated through a cooler made of $^1/_2$-inch copper tubing inside 1-inch copper tubing. Fresh tap water (secondary cooling water) from a constant level tank passed through the annular space. Thus it was possible to adjust the temperature of the entering cooling water of the primary system from that of fresh tap water up to within a few degrees of the boiling point of the liquid (if it boiled below 100° C.). The boiler body was insulated with a $^1/_2$-inch layer of magnesia, in which a window was left for observation.

OPERATION

CLEANING AND CHARGING. Liquid from a prior run was siphoned out through a rubber hose inserted through F (Figure 2). A gallon of new material was charged and the manometer connection replaced. The new material was boiled for about 30 minutes; the boiler was drained again, and air was drawn through to dry the system thoroughly. The condensate return line was drained, and the external condenser was rinsed with fresh liquid and dried. About 2 gallons of new material were then charged.

REMOVAL OF AIR. The electrical heating circuit was closed and the liquid boiled. With the external condenser in the reflux position (as in Figure 2) the recycling pump on the cooling water system was started, and the cooling water rates were adjusted. The cooling water was recycled to be heated to the maximum temperature obtainable in the apparatus. (To hasten the process, hot water was usually charged to the sump tank.)

Table I. Data on Normal Alcohols

Vapor Temp., ° C.	Tube Temp., ° C.	ΔT, ° C.	ΔT, ° F.	Water Temp. Rise, ° C.		Water Rates, Lb./Hr.		Q, P. C. U./Hr.	h
				L	R	L	R		
Methanol									
64.40	62.90	1.50	2.70	1.44	1.27	542	565	1500	1180
64.40	62.46	1.94	3.50	1.72	1.71	539	564	1890	1150
64.40	61.96	2.44	4.40	1.82	1.85	540	560	2022	980
64.40	61.50	2.90	5.22	2.07	1.95	543	570	2255	918
64.30	61.02	3.28	5.90	2.06	2.42	541	562	2475	891
64.30	59.85	4.45	8.00	2.58	2.88	545	559	3017	800
64.20	58.87	5.33	9.60	3.04	3.11	545	556	3384	750
64.15	58.53	5.62	10.11	3.16	3.24	545	557	3522	740
64.14	57.66	6.48	11.67	3.16	3.32	592	605	3880	707
64.13	55.70	8.43	15.17	3.57	3.76	621	630	4585	642
64.10	53.72	10.38	18.70	4.05	4.35	625	631	5280	601
64.08	50.69	13.39	24.10	4.85	5.10	620	629	6215	549
Ethanol									
78.40	72.57	5.83	10.50	2.58	2.37	502	500	2480	503
78.40	71.35	7.05	12.70	2.87	2.68	510	501	2800	470
78.40	69.96	8.44	15.20	3.32	2.99	508	507	3200	448
78.30	69.74	8.66	15.60	3.32	3.06	514	511	3265	446
78.30	68.91	9.39	16.90	3.36	3.19	522	514	3396	428
78.30	67.30	11.00	19.80	3.84	3.60	517	510	3820	410
78.30	65.00	13.30	24.00	4.25	4.03	515	514	4260	379
78.30	62.90	15.40	27.70	4.71	4.50	516	514	4740	363
78.20	61.50	16.70	30.10	4.98	4.70	519	512	4990	353
78.10	59.70	18.40	33.10	5.23	4.97	522	511	5300	340
78.10	56.00	22.10	39.80	5.80	5.61	525	520	5960	318
Propanol									
98.7	90.32	8.38	15.1	2.62	2.55	540	530	2765	390
98.7	89.54	9.16	16.5	2.84	2.69	535	529	2943	380
98.7	87.70	11.00	19.8	3.22	3.06	532	528	3326	357
98.6	85.40	13.20	23.8	3.62	3.49	529	524	3744	335
98.5	82.50	16.00	28.8	3.67	3.51	532	527	3802	318
98.3	79.90	18.40	33.1	4.51	4.34	530	526	4670	300
98.1	77.00	21.10	38.0	4.92	4.75	536	529	5150	288
98.0	75.00	23.00	41.4	5.15	4.94	540	533	5410	278
Butanol									
117.4	105.1	12.30	22.1	3.49	3.08	520	515	3404	327
117.4	104.6	12.80	23.0	3.40	3.18	525	527	3460	319
117.2	103.7	13.50	24.3	3.50	3.19	541	536	3606	315
117.3	103.3	14.00	25.2	3.46	3.12	552	560	3655	308
117.2	102.1	15.10	27.2	3.56	3.25	560	570	3850	301
117.1	100.7	16.40	29.5	3.77	3.43	568	580	4130	297
117.1	99.0	18.10	32.6	3.94	3.48	571	595	4320	282
116.9	96.5	20.40	36.7	4.17	3.77	585	605	4720	273
116.9	95.2	21.70	39.1	4.51	3.94	582	606	5010	272
116.9	93.7	23.20	42.7	4.53	3.98	585	605	5060	258

When the cooling water temperature approached within about 20° C. of the boiling point of the liquid (or 90° C., whichever was lower), the recycling pump was stopped; the orifice outlets were plugged with corks to keep the hot water in the orifice cans and cooling system. The external condenser was turned down by rotation around the vapor inlet, and about 3 to 4 quarts of liquid were condensed and drawn off. This removed the last traces of air. If the temperature of the cooling water in the sump tank dropped too low, additional hot water was added. The orifices were unstoppered, the recycling pump started, and the external condenser was turned to the reflux position. The heater rheostat was set to maintain an amount of boiling such that there was a liquid level in the external condenser just sufficient to cover the 1/4-inch vapor line to the condenser (a few millimeters of mercury positive pressure); and slight irregularities in heat flow were absorbed in variation of the amount of vapors passed to the external condenser.

Sequence of Runs. The primary cooling water was recycled until it came to a constant temperature. No secondary cooling water was passed through the cooler; and the highest possible cooling water temperature (lowest temperature drop) resulted as a balance between the heat absorbed by the cooling water in passing through the condensing system and the heat losses to the surroundings through the orifice cans, sump tank, and recycling lines.

After temperatures became constant, the unit was allowed to run undisturbed for 20 to 25 minutes to ensure steady state conditions. Readings were then taken in the following order: vapor thermocouple, tube thermocouples, thermocouples for measuring temperature rise in cooling water streams, and orifice manometer readings. The system was allowed to run unchanged for an additional 10 minutes, and a check set of readings was obtained. If a third set of readings in agreement with the previous two sets was obtained after 5 more minutes, the value of the coefficient at the given temperature drop was considered to be established.

The next run was made by increasing the electrical heat input and removing heat from the primary cooling water by passing a small amount of secondary cooling water through the cooler. To hasten the attainment of a thermal steady state, it was found desirable not to vary the rates of flow of the primary cooling water, as indicated by the two orifice flowmeters. Successive runs at increasing temperature drops were obtained through successively decreasing the inlet temperature of the primary cooling water by adjusting the flow rate of the secondary cooling water. Data were thus obtained over as wide a range of temperature drops as possible.

DISCUSSION OF RESULTS

The data accumulated in checking the previous work are omitted because of the uncertain effect of the noncondensable gases presumed to be present. All the data presented here were obtained with the boiler continuously venting. Only one set of check data for each run is recorded, although at least one other set was always taken. The tube temperature given is the average value of the four thermocouple readings. (One thermocouple was damaged in the installation and was removed.) The maximum variation between the four tube thermocouple readings was never more than 1° C.

The film coefficient was calculated from the total heat absorbed by the two streams of primary cooling water in pound-centigrade units per hour (P. C. U./hour). This is the product of flow rate in pounds per hour and corresponding temperature rise in degrees centigrade. The temperature drop is the difference between the vapor temperature and the average surface temperature. The condensing surface area was 0.847 square foot.

Data were taken on series of normal alcohols, branched-chain alcohols, acetates, and methyl ketones, all boiling below 150° C. The purest materials commercially available were used, as received. Some additional purification might have been experienced since approximately half of the charge was boiled out in the removal of air. No attempt at purification was made, as it was desired to obtain results on technical materials which would be representative of those in commercial use.

A positive pressure of 5 to 10 mm. of mercury was always maintained to prevent possible infiltration of air through unknown leaks. As the barometer was usually slightly below 760 mm., the values may be regarded as being substantially at the normal barometric pressure.

The data are summarized in Tables I to IV, and are plotted as film coefficient h against the temperature drop across the condensate film in Figures 3 to 6.

Physical values (*1*, *2*, *8*) were taken at average temperatures and used in the Nusselt equation (*3*) which for this unit reduces to

$$h = 163.56\ (L\rho^2K^3/\mu\Delta T)^{1/4}$$

Comparison of experimental coefficients with previous work (*7*) and with coefficients predicted by Nusselt's equation are given in Figures 7 to 9. The substantially lower coefficients previously reported (*7*) for the branched-chain alcohols can probably be attributed to the presence of noncondensable gases produced by decomposition of the alcohols into aldehydes and hydrogen.

Figure 2. Arrangement of Apparatus

A.	Boiler
B.	Electric immersion heater
C.	Condensing surface
D.	Tube thermocouple junction
E.	Vapor thermocouple junction
F.	Charging inlet (plugged)
G.	Continuous venting system
H.	Ice bath for cold junctions
I.	Selective switchboard
J.	Potentiometer
K.	Galvanometer
L.	External condenser
M.	Heater control panel
N.	Petcock for draining venting system, return line
O.	Rubber connecting tubes (not shown)
P.	Primary cooling water feed headers
Q, Q′.	Secondary cooling water inlet and outlet
R.	Orifice meters (4)
S.	Primary cooling water recycling pump
T.	Primary cooling water feed tubes
U.	Cooling water outlets
V, V′.	Cooling water temperature difference thermocouples (hot junctions)
W, W′.	Cooling water temperature difference thermocouples (cold junctions)
Y.	Secondary cooling, double pipe exchanger
Z.	Outside pipe

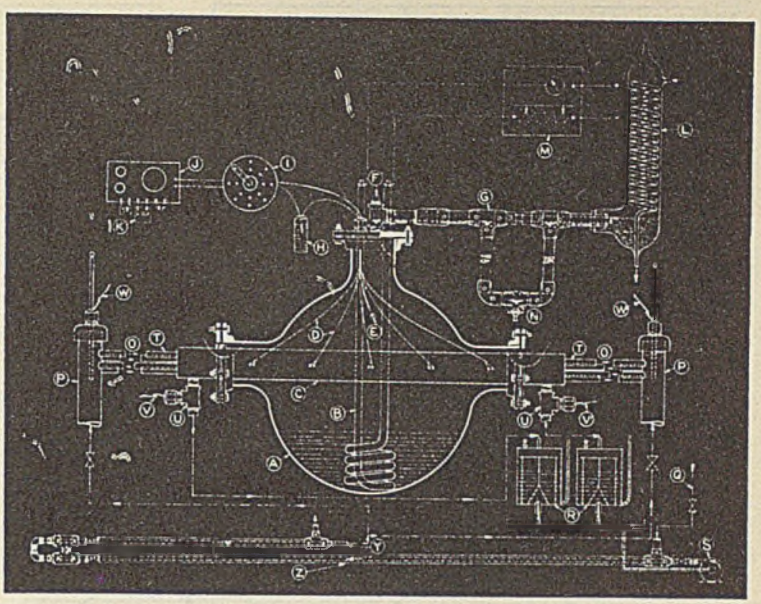


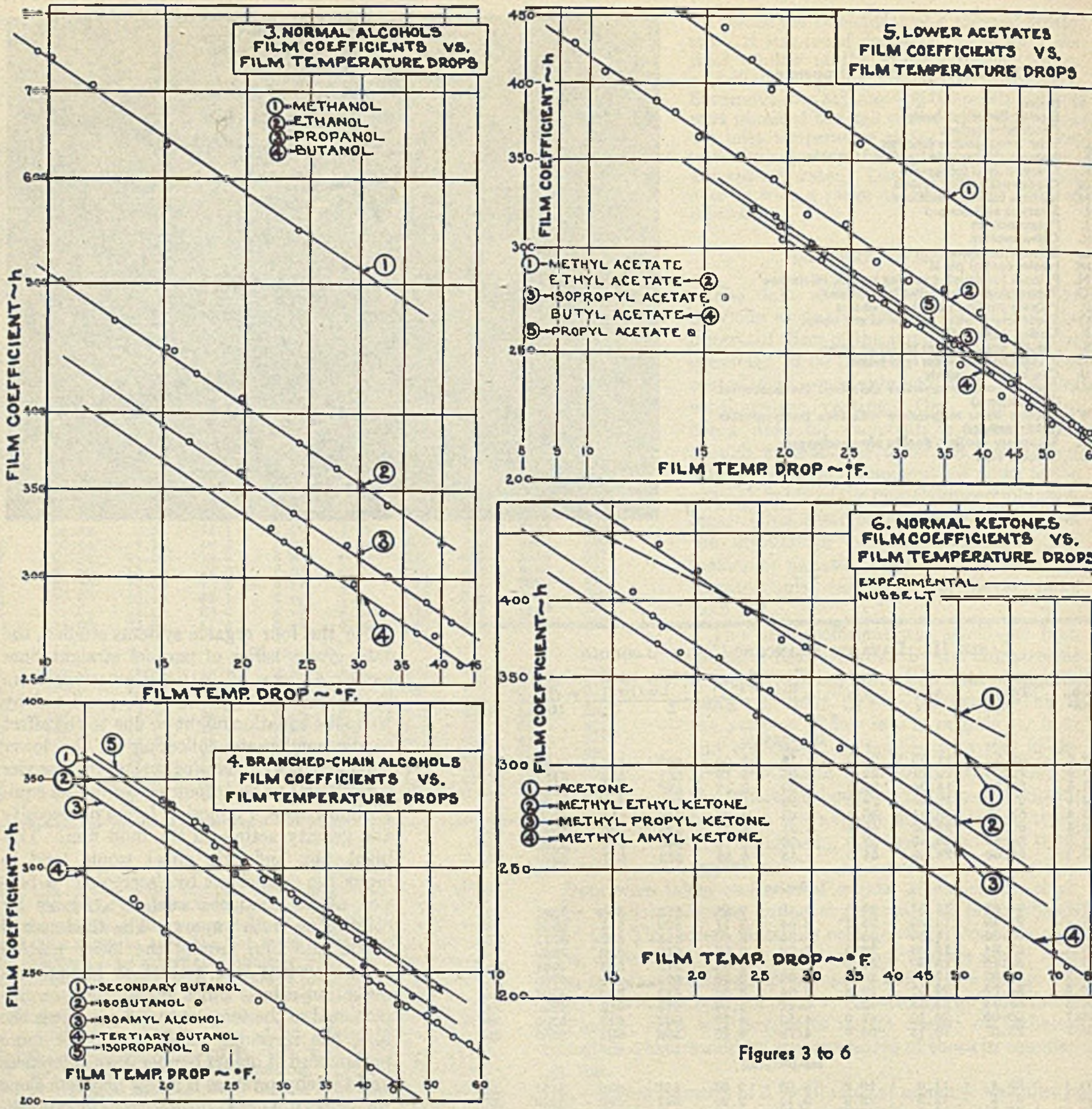
Table II. Data on Branched-Chain Alcohols

Vapor Temp., ° C.	Tube Temp., ° C.	ΔT, ° C.	ΔT, ° F.	Water Temp. Rise, ° C. L	Water Temp. Rise, ° C. R	Water Rates, Lb./Hr. L	Water Rates, Lb./Hr. R	Q, P.C.U./Hr.	h
				Isopropanol					
83.6	62.32	11.28	20.3	3.16	2.99	523	518	3199	335
83.6	70.89	12.71	22.9	3.38	3.18	531	523	3459	321
83.5	69.50	14.00	25.2	3.60	3.47	530	520	3714	313
83.4	67.00	16.40	29.5	3.99	3.79	529	525	4100	295
83.4	63.19	20.21	36.4	4.62	4.45	522	515	4700	274
83.4	60.60	22.80	41.1	4.91	4.75	528	526	5090	263
83.3	56.90	26.40	47.5	5.28	5.15	540	532	5590	250
83.2	54.60	28.60	51.5	5.55	5.36	543	537	5890	243
				Isobutanol					
107.7	94.63	13.07	23.5	3.42	2.88	528	540	3361	304
107.4	93.40	14.00	25.2	3.54	3.11	522	641	3532	298
107.5	93.00	14.50	26.1	3.34	2.60	624	633	3721	303
107.3	91.24	16.06	28.9	3.28	2.96	612	620	3849	283
107.0	88.10	18.90	34.0	3.87	3.48	579	583	4264	267
107.2	87.80	19.40	34.9	3.52	3.28	624	636	4280	260
106.8	84.73	22.07	39.8	3.94	3.66	618	620	4704	251
106.8	83.34	23.46	42.2	4.21	3.79	615	618	4930	248
106.7	80.60	26.10	47.0	4.50	4.23	602	612	5300	240
106.7	78.57	28.13	50.6	4.75	4.46	598	608	5550	233
				sec-Butanol					
99.4	88.4	11.0	19.8	3.03	2.85	532	540	3151	338
99.3	87.1	12.2	22.0	3.11	2.90	547	560	3339	323
99.1	85.5	13.6	23.5	3.37	3.18	542	557	3598	312
99.0	83.5	15.5	27.9	3.41	3.08	584	601	3842	293
98.8	81.7	17.1	30.8	3.44	3.21	621	629	4160	287
98.7	81.3	17.4	31.3	3.49	3.25	615	623	4165	283
98.7	79.2	19.5	35.1	3.80	3.55	620	629	4590	278
98.7	78.1	20.6	37.1	3.93	3.63	619	629	4710	270
98.8	77.2	21.6	38.9	3.99	3.70	621	630	4810	263
98.7	75.5	23.2	41.7	4.21	3.93	620	631	5090	259
				tert-Butanol					
82.4	72.5	9.9	17.8	2.20	1.76	605	592	2373	283
82.4	72.4	10.0	18.0	1.97	1.61	658	665	2363	280
82.4	71.4	11.0	19.8	2.04	1.78	649	660	2497	268
82.3	70.2	12.1	21.8	2.14	1.93	650	660	2662	260
82.3	69.0	13.3	24.0	2.33	2.07	638	650	2830	251
82.2	67.0	15.2	27.4	2.46	2.19	646	659	3032	238
82.2	65.6	16.6	29.9	2.69	2.44	642	653	3320	236
82.1	62.8	19.3	34.7	2.90	2.67	650	658	3642	223
82.0	59.2	22.8	41.0	3.21	2.98	649	657	4039	209
82.0	57.6	24.4	44.0	3.32	3.05	648	655	4151	201
				Isoamyl Alcohol					
129.3	106.9	22.4	40.3	3.88	3.57	625	628	4650	247
129.2	105.8	23.4	42.2	3.99	3.68	626	630	4820	243
129.1	104.2	24.9	44.9	4.19	3.82	621	624	4980	236
129.1	103.5	25.6	46.1	4.27	3.85	625	631	5100	235
129.1	101.7	27.4	49.3	4.47	4.11	624	630	5380	232
129.1	100.6	28.5	51.4	4.51	4.20	628	635	5500	228
129.1	99.0	30.1	54.2	4.67	4.33	625	632	5660	222
129.0	97.2	31.8	57.3	4.84	4.54	628	637	5930	220

For the four organic systems studied, the data give a series of parallel straight lines having a slope of $-1/3$. Deviations from the theoretical slope of $-1/4$ predicted by Nusselt's equation might be due to the effect of the condensate collecting on the lower portion of the condensing surface in a heavier layer than can be accounted for by the equilibrium between opposing forces of viscosity and gravity acting on the fluid film. This blanketing and drip effect would tend to lower the coefficients by "screening" a portion of the condenser surface available for condensing fresh vapors. The thickness of condensate film around the lower portion of the surface was greater at higher condensation rates. Since these rates are proportional to the temperature drop across the film, the screening effect should be more pronounced at higher temperature differences and thereby produce a larger negative slope than that predicted theoretically by Nusselt. The absolute values of all coefficients obtained agree with corresponding values calculated by Nusselt's equation, although the slopes of lines are different. The Nusselt lines intersect the experimental lines at progressively lower values of temperature drop as an homologous series is ascended.

Figure 10 is a log-log plot of the data for water compiled in Table V, over the small range of temperature drops obtainable with the experimental unit. The data checks extrapolated values of Othmer (4) within 10 per cent. Values calculated by the Nusselt equation are also indicated.

The spread of the families of parallel lines indicates that, at any given temperature drop, the coefficient is an inverse function of the length of the carbon chain in the alkyl group. A cross plot was made (Figures 11, 12, and 13) of the loga-



Figures 3 to 6

rithm of the coefficient against the reciprocal of the number of carbon atoms, N, in the homologous alkyl group for the normal alcohols, acetates, and methyl ketones. Within the experimental accuracy, each of the organic series gives a set of parallel straight lines.

The slope of the set of lines for the normal alcohols shown in Figure 11 is one third (0.333) as previously reported (7). For the acetates in Figure 12, the slope is 0.133 and for the ketones in Figure 13, the slope is 0.114. The smaller slopes obtained for the acetates and ketones are attributable to the fact that the various physical properties affecting the film thickness for successive homologs do not differ so much as in the case of the normal alcohols. This is to be expected; since adding a CH_2 group to the relatively heavy acetate and methyl ketone functional groups should not have as much effect in changing the physical properties as a similar addition on the OH group.

EMPIRICAL EQUATION

From the series of parallel straight lines obtained in Figur 3 to 6, the general equation of the film coefficient as a functi of temperature drop across the condensate film may written:

$$\log h = a \log \Delta T + b$$

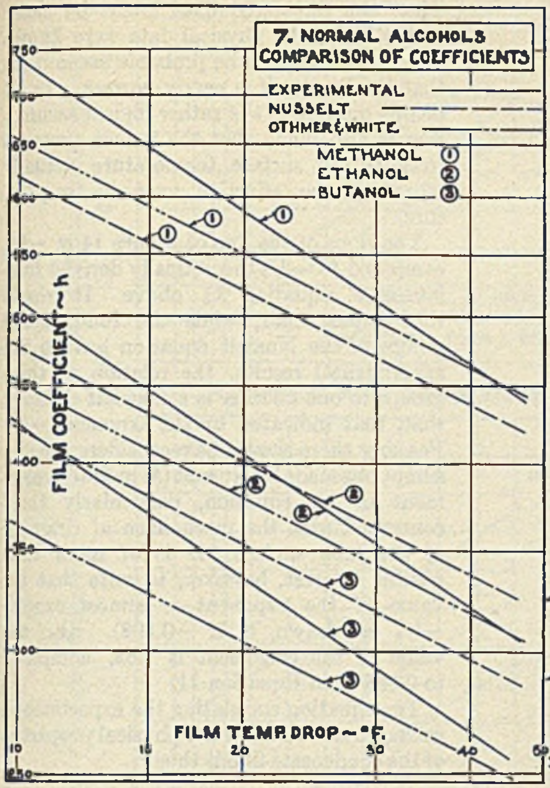
Similarly from Figures 11 to 13, for any member of homologous series at a given temperature drop:

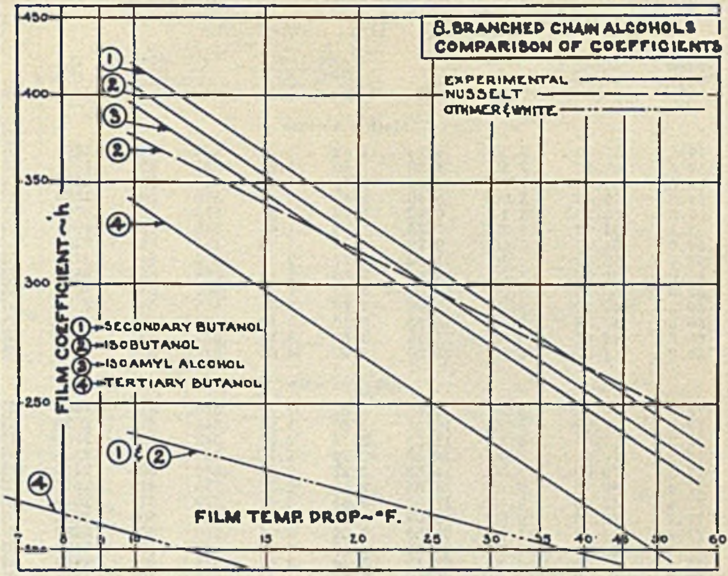
$$\log h = m/N + C$$

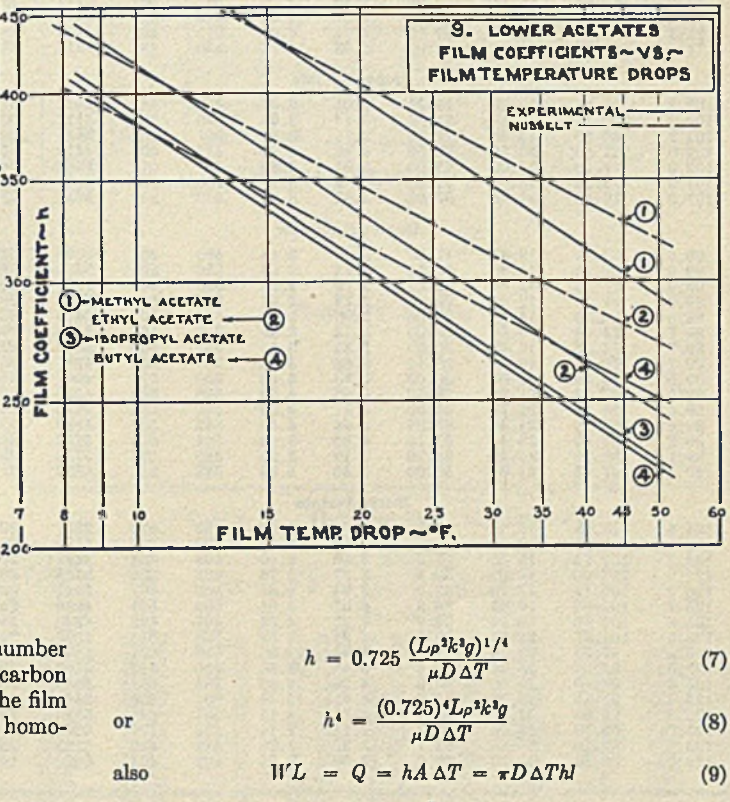
These two equations may be combined and the constan evaluated readily to give, within the experimental accurac

For normal alcohols:

$$\log h = \frac{0.333}{N} - {}^1/_3 \log \Delta T + 2.87$$







Figures 7, 8, and 9

For acetates:

$$\log h = \frac{0.133}{N} - {}^1/_3 \log \Delta T + 2.9 \qquad (4)$$

For methyl ketones:

$$\log h = \frac{0.144}{N} - {}^1/_3 \log \Delta T + 2.944 \qquad (5)$$

More generally for a homologous series, if N_a is the number of carbon atoms in homolog A and N_b is the number of carbon atoms in homolog B; and if at any given ΔT, h_a is the film coefficient of homolog A and h_b is the film coefficient of homolog B:

$$\log h_a = \log h_b + m\left(\frac{1}{N_a} - \frac{1}{N_b}\right) \qquad (6)$$

Equation 6 permits the ready calculation of the film coefficient at any film temperature drop for one member of a homologous series from the coefficient at the same temperature drop of any other member of the series. It should be possible to use this equation for other series of compounds where the data were known or could be calculated for two compounds of the series.

CORRELATION

The Nusselt equation (*3*) for condensation on a horizontal tube is presented in Equation 7.

$$h = 0.725\,\frac{(L\rho^2k^3g)^{1/4}}{\mu D\Delta T} \qquad (7)$$

or

$$h^4 = \frac{(0.725)^4 L\rho^2k^3g}{\mu D\Delta T} \qquad (8)$$

also

$$WL = Q = hA\Delta T = \pi D\Delta Thl \qquad (9)$$

$$h = \frac{wL}{\pi D\Delta T} \qquad (10)$$

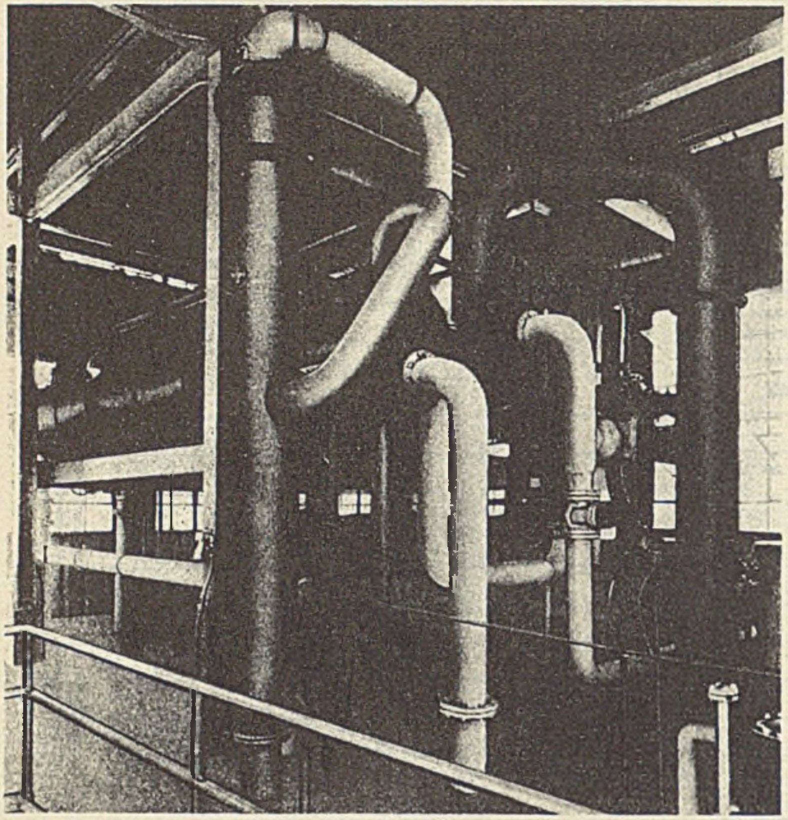
Dividing Equation 8 by Equation 10:

$$h^3 = \pi(0.725)^4\left(\frac{\rho^2k^3g}{w\mu}\right) = \pi(0.725)^4\,\frac{(\rho^2k^3g)(\mu)}{(\mu^2)(w)}$$

Rearranging, simplifying, and substituting:

$$\frac{h}{k}\left(\frac{\mu}{\rho}\right)^{2/3}\frac{1}{g^{1/3}} = 0.955\left(\frac{w}{\mu}\right)^{-1/3} \qquad (11)$$

Both sides of Equation 11 are dimensionless; and it is possible to check the coefficient, exponent, and constant of the right-hand group by a plot of these groups against each other.



Preheater and Final Condenser Assembly for Condensing Organic Vapors

Photos Courtesy, Vulcan Copper and Supply Company

lines. For each other compound the corresponding intermediate pivot points were also found. Since the location of the point with reference to the film coefficient and the film temperature drop scales is dependent upon the slope of the line from the original data plots, and since all of these slopes were the same and equal to $-1/3$, the loci of all of these pivot points will be equidistant from the film coefficient scale, and thus all of these points for the individual components fall on a parallel line. Furthermore, since the slopes are all $-1/3$, the ratio of the distances from the intermediate line to the film coefficient line and from the intermediate line to the film temperature drop line is 1 to 3.

Table V. Data for Water

Vapor Temp., ° C.	Tube Temp., ° C.	ΔT, ° C.	ΔT, ° F.	Water Temp. Rise, ° C.		Water Rates, Lb./Hr.		Q, P.C.U./Hr.	h
				L	R	L	R		
100.3	99.50	0.80	1.44	3.92	3.47	478	487	3562	5260
100.2	99.23	0.97	1.75	4.19	3.51	490	498	3800	4630
100.2	99.12	1.08	1.95	4.48	3.75	498	510	4140	4520
100.1	98.78	1.32	2.37	4.95	4.21	504	515	4660	4170

It is also obvious that the distances between the points of the several members of any homologous series on this line will also follow a definite relation, as indicated by the relation between the logarithm of the coefficient and the reciprocal of the number of carbon atoms expressed in Figures 11, 12, and 13.

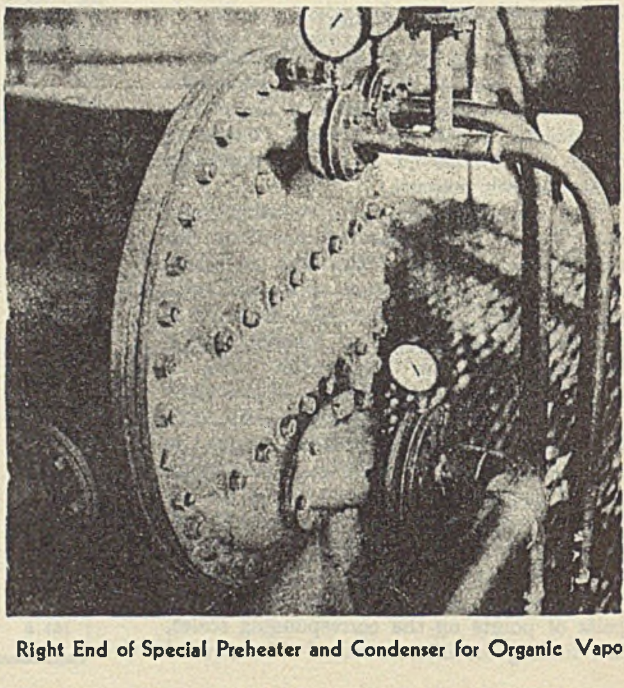
Figure 15 is used by drawing a straight line between the desired film temperature drop and the point representing the individual compound on the intermediate scale, to give the value of the coefficient on the left-hand scale. This represents a convenience in design calculations for condensers at atmospheric pressure utilizing any of the seventeen compounds investigated in this work. Presumably, pivot points for other compounds could also be spotted on the intermediate scale if data were available.

ACKNOWLEDGMENT

Appreciation is expressed for the cooperation of the following companies in supplying materials for this research: Carbide & Carbon Chemicals Corporation, Commercial Solvents Corporation, E. I. du Pont de Nemours & Company, Inc., Sharples Solvents Corporation, Stanco, Inc., and U. S. Industrial Chemicals, Inc.

NOMENCLATURE

A = condensing surface area (0.847 sq. ft.) for exptl. apparatus
D = diameter of condensing tube (0.1616 ft.) for exptl. apparatus
g = gravity constant = 4.18×10^8 ft./(hr.)(hr.)
h = film coefficient, B. t. u./hr./sq. ft./° F.
K = thermal conductivity
L = latent heat
l = tube length (1.68 ft.) for exptl. apparatus
N = No. carbon atoms in alkyl group
Q = total heat transferred through condensate film
ΔT = film temp. drop, ° F.
W = condensate, lb./hr.
w = W/l = lb./hr. condensate/ft. length of tube



Right End of Special Preheater and Condenser for Organic Vapor

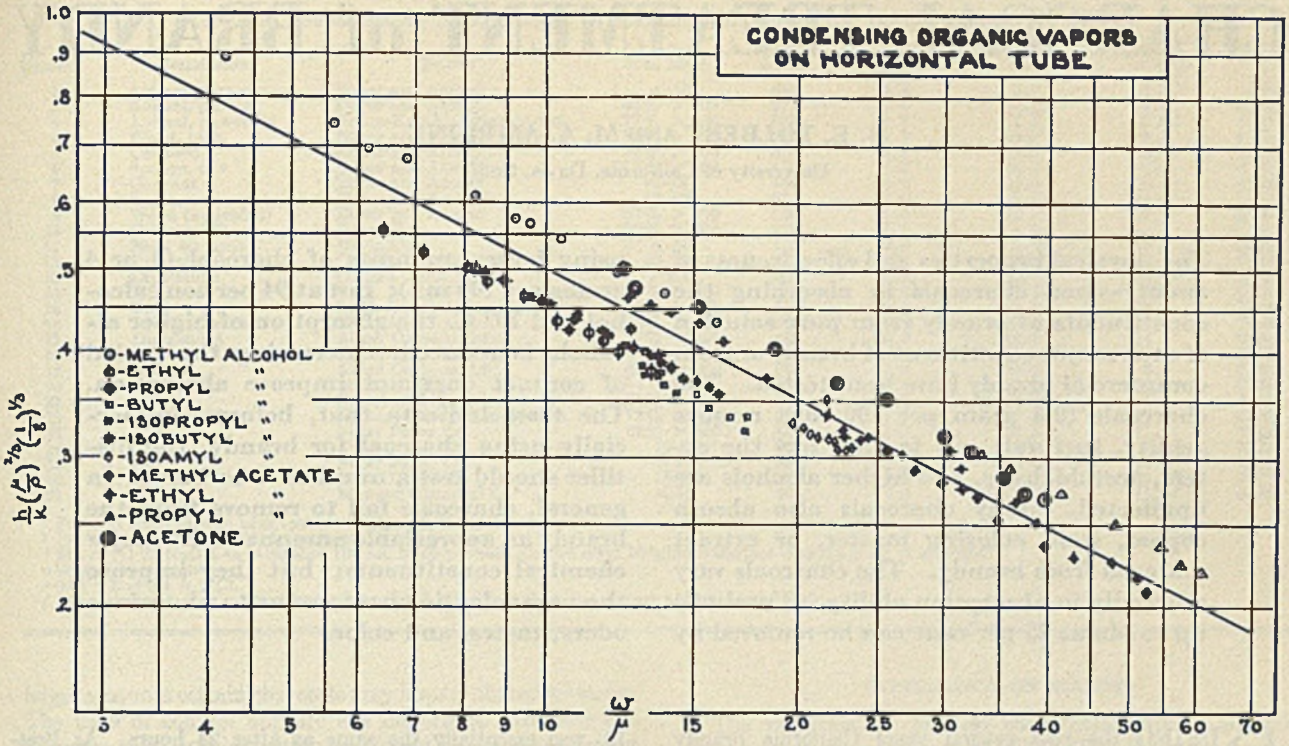
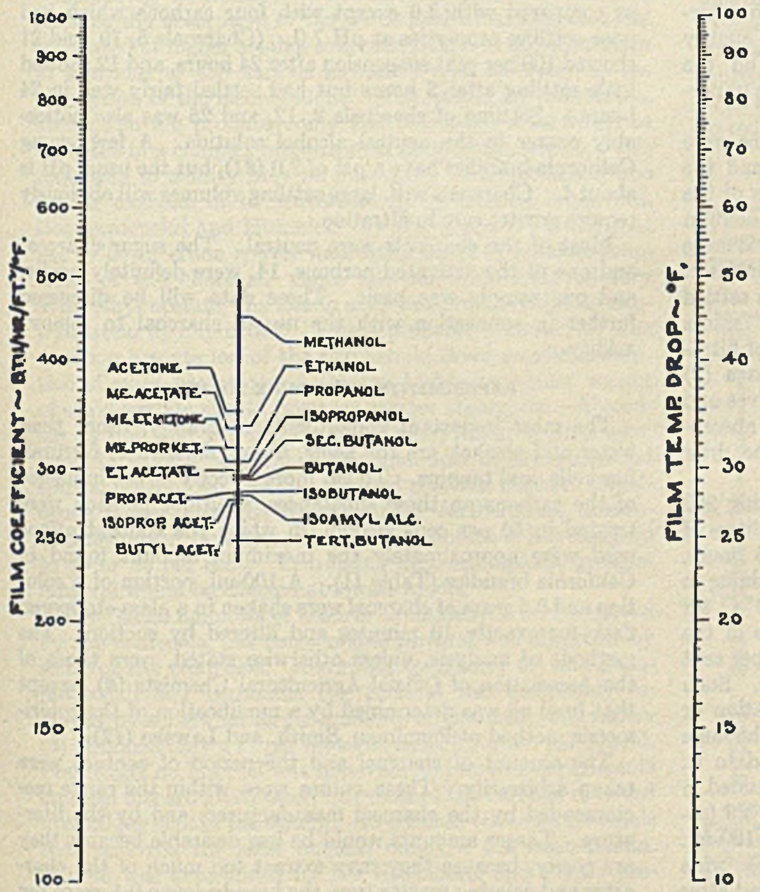


Figure 14. Correlation of Data for Condensing Organic Vapors by Plotting Dimensionless Functions of Controlling Physical Variables



a, b, m, c = constants for any one homologous series
μ = viscosity
ρ = density
Subscripts a, b = homolog a and homolog b, respectively

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Figure 15. Nomograph for Film Coefficients of Condensing Organic Vapors at Atmospheric Pressure

[END OF SYMPOSIUM]

CHARCOAL TREATMENT of BRANDY

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The physical properties and effectiveness of twenty-seven charcoals in absorbing the constituents of brandy from pure solution of each major constituent of brandy or from commercial brandy have been tested. The charcoals (0.5 gram per 100 ml.) remove acidity, furfural, and tannin, but the esters, acetaldehyde, and higher alcohols are unaffected. Many charcoals also absorb copper, iron, coloring matter, or extract material from brandy. The charcoals vary markedly in absorption ability. Fusel oils up to about 25 per cent can be removed by using larger amounts of charcoal (3 or 4 grams per 100 ml.); but at 94 per cent alcohol and 70° C. the absorption of higher alcohols is reduced. Increasing the period of contact does not improve absorption. The tests indicate that, before commercially using charcoal for brandy, the distiller should test a number of carbons. In general, charcoals fail to remove from the brandy an appreciable amount of the major chemical constituents; but they improve the organoleptic character as to obnoxious odors, tastes, and color.

DURING the past several years California brandy distillers have become interested in charcoal for correcting abnormalities in high-proof and beverage brandies. Hassler (*11*) recommended activated charcoal for removing objectionable impurities of color, taste, or odor from all types of spirits. This study was planned to determine how various charcoals affect the composition and quality of commercial brandy. Data are also reported on the effect of charcoals on alcoholic solutions of the more important constituents of brandy.

Table I describes the charcoals used. Tyler screens were used for measuring the predominant particle size, and the density, per cent moisture, and suspension properties of the charcoals were determined by methods suggested by Laughlin (*14*). According to Sharf (*20*) the volume of charcoal is more important than the weight in the contact-type carbon filter. The charcoal must also have weight enough to remain settled in the unit during flow. On the other hand, other factors are important—size of particles, packing, and speed of filtration (*8*). For gas absorption Bardan and Scarlatescu (*3*) found that charcoals differ in activity from themselves and one another at 20 per cent moisture compared to the absorption when nearly dry. Where equally effective, the drier charcoals should be preferred.

The suspension property was determined by placing 200 mg. of a carbon in a jar, thoroughly shaking with 10 liters of water, and allowing the suspension to stand for 15 hours. Nine liters were then siphoned off; the carbon remaining in the jar was filtered onto a Gooch crucible, dried at 140° C. for 4 hours, cooled in a desiccator, and weighed. Nine of the carbons possessed good settling properties, over 97.5 per cent of the carbon settling into one tenth of the volume. Such charcoals were obviously preferable for ease of filtration or decantation. The settling volume is not necessarily the same as the per cent suspension, though probably related to it. To determine the settling volume, 3 grams were suspended in 100 ml. of a 50 per cent alcohol solution at a pH of 3.6 (secured by adding 0.0555 mole of acetic acid) in a 100-ml. graduated cyclinder. The sedimentation volumes were determined after 2 and 24 hours, but the results secured after 2 hours are omitted because the volume, except for charcoal 19, was essentially the same as after 24 hours. As Bretschneider (*5*) showed that electrolytes markedly influence the sedimentation volume of activated charcoals, the experiment was repeated with a neutral 50 per cent alcohol. No great difference was found in the settling volume at pH 7.0 as compared with 3.6 except with four carbons which had poor settling properties at pH 7.0. (Charcoals 5, 19, and 21 showed 100 per cent suspension after 24 hours, and 12 showed little settling after 2 hours but had settled fairly well in 24 hours.) Settling of charcoals 2, 12, and 25 was also noticeably poorer in the neutral alcohol solution. A few young California brandies have a pH of 7.0 (*21*), but the usual pH is about 4. Charcoals with large settling volumes will obviously require greater care in filtration.

Most of the charcoals were neutral. The sugar charcoal and one of the activated carbons, 14, were definitely acidic, and one sample was basic. These data will be discussed further in connection with the use of charcoal to remove acidity.

EXPERIMENTS WITH PURE SOLUTIONS

The most important constituents of brandy, other than water and alcohol, are the acids, esters, aldehydes, furfural, fusel oils, and tannins. To get more directly at the influence of the carbons on these substances, solutions of each were treated in 50 per cent alcohol, in which the concentrations used were approximately the maximum amount found in California brandies (Table II). A 100-ml. portion of a solution and 0.5 gram of charcoal were shaken in a glass-stoppered flask for exactly 10 minutes and filtered by suction. The methods of analysis, unless otherwise stated, were those of the Association of Official Agricultural Chemists (*2*), except that fusel oil was determined by a modification of the colorimetric method of Penniman, Smith, and Lawshe (*17*).

The amount of charcoal and the period of contact were taken arbitrarily. These values were within the range recommended by the charcoal manufacturers and by the literature. Larger amounts would be less desirable because they are costly, because they may extract too much of the character and coloring matter from the brandy (even 0.5 gram per 100 ml. of some of the charcoals is excessive), and because in

TABLE I. DESCRIPTION, SOURCE, AND PHYSICAL AND CHEMICAL PROPERTIES OF CHARCOALS USED

Number	Description	Source	Particle Size, Mesh	Density, G./L.	Moisture, %	Suspension[a], %	Settling Vol.[b], %	Acidity[c], Ml.
1	Animal, granular	Eimer and Amend	< 10	667	2.8	0.0	7.5[d]	0.00
2	Animal, purified	Eimer and Amend	43% > 200	571	29.1	6.8	10.0	0.15
3	Animal, powdered	Braun-Knecht-Heimann Co.	77% > 200	833	3.2	1.2	5.5[d]	0.00
4	Blood, tech.	Eimer and Amend	69% > 200	714	1.9	16.2	9.5	0.00
5	Calcined	Eimer and Amend	93% > 200	625	3.9	11.2	9.0	0.00
6	Sponge, C. P.	Eimer and Amend	77% > 200	476	7.8	14.0	14.0	0.00
7	Coconut	Eimer and Amend	10–18	454	0.2	0.0	8.5[d]	Trace
8	Sugar, C. P.	Eimer and Amend	18–200	370	7.8	0.0	14.0[d]	1.01
9	Wood (activated)	Eimer and Amend	87% > 200	286	11.0	28.4	21.0	0.00
10	Carbon, S51	Darco Corp.	82% > 200	476	1.1	4.6	12.3	0.00
11	20 × 40 mesh	Darco Corp.	< 60	384	2.8	0.0	11.1	0.13
12	Crystalline	Carlisle Lumber Co.	40–200	476	3.8	1.8	11.0	Trace
13	Crystalline	Carlisle Lumber Co.	> 200	500	6.9	0.0	8.0[d]	0.00
14	KB Darco	L. H. Butcher Co.	65% > 200	357	21.2	7.5	17.0	0.91
15	G60	L. H. Butcher Co.	73% > 200	408	18.1	6.0	16.8	Trace
16	Magnechar P120	E. S. Browning Co.	80% > 200	364	8.4	18.3	16.3	Trace
17	Diamond A	Allied Carbons, Ltd.	97% > 200	416	15.4	12.1	14.3	0.00
18	Diamond D	Allied Carbons, Ltd.	70% > 200	730	5.1	11.3	100.0	0.00
19	No. 3A	Allied Carbons, Ltd.	64% > 200	769	5.4	17.7	8.0	0.00
20	No. 3N	Marshall Dill	> 200	714	10.5	15.1	14.6	0.08
21	No. 1N	Marshall Dill	71% > 200	645	5.5	21.5	8.0	0.00
22	Nuchar WW	Braun-Knecht-Heimann Co.	78% > 200	270	8.7	12.4	22.5	0.00
23	C16	Filter Paper Co.	69% > 200	337	10.3	12.5	17.2	Trace
24	C1	Filter Paper Co.	10–60	769	1.1	0.1	5.2[d]	0.00
25	C4	Filter Paper Co.	> 200	384	11.2	29.4	13.6	Basic
26	C17	Filter Paper Co.	18–60	256	5.0	3.3	20.0[f]	0.06
27	No. 5A	Mefford Chemical Co'	< 10	408	4.6	2.4	11.0[f]	0.00

[a] Per cent suspended in nine tenths of volume after 15 hours.
[b] Per cent volume occupied by carbon after 24 hours.
[c] Ml. of 0.1 *N* NaOH to neutralize 100 ml. of 50 per cent alcohol after 10-minute contact with 0.5 gram of charcoal.
[d] Settled immediately.
[e] 0.60 ml. of 0.1 *N* HCl.
[f] Most of the charcoal settled immediately, but some floated on the surface after repeated shaking.

larger amounts certain charcoals may impart obnoxious tastes. The time of contact appears less important. Kolback and Schwabe (*12*), working with beers, found 1 minute as effective as 10. The long period of contact observed by Dudley (*8*) and Feret (*9*) was probably due to the nonactivated charcoals used.

According to Amiot (*1*), in mixtures of acetic acid and alcohols the absorption of the acetic acid by animal charcoal is reduced at higher alcohol concentration, and the absorption in solutions of the various alcohols varies inversely as the absorption of the alcohol alone. The figures for the relative absorption are probably only approximately what would be expected in a complex mixture such as beverage brandy. The reduction in acidity may be due either to direct absorption by the charcoal or to neutralization by alkaline impurities. Bogojawlenskij and Humnicki (*4*) and Caspe (*7*) found that the acids in crude spirits were neutralized by alkaline properties of the charcoal. Since the charcoals removed very little ethyl acetate, the loss in acid was probably due to neutralization by impurities. This is probable because: (*a*) The common acetate ion of the two should favor greater absorption of ethyl acetate; and (*b*) the higher molecular weight of ethyl acetate should favor its greater absorption. According to Reif and von der Heide (*18*) and Zaharia, Angelescu, and Motoc (*23*) acetic acid, the chief acid in newly distilled spirits, is absorbed less by activated charcoal than are homologous higher-molecular-weight acids; furthermore, absorption decreased rapidly as the alcohol content is increased up to 40 or 50 per cent. In treating high-acid spirits, greatest removal would be effected at lowest proofs.

Only small amounts of ester or acetaldehyde were removed by the charcoals, but considerable furfural was absorbed by some of the charcoals. According to Dudley (*8*) and Bogojawlenskij and Humnicki (*4*), furfural was completely removed by somewhat larger amounts of charcoal; but Cafere (*6*) obtained only a 27 per cent loss using 0.5 gram per 100 ml. Practically no fusel oil was removed, and further experiments on fusel oils are given later. Several of the carbons removed over 50 per cent of the tannin. In general, the same charcoals that removed the least furfural removed the least tannin. Tannin was determined by the Rosenblatt and Peluso procedure (*19*).

EXPERIMENTS ON BRANDY

The removals of chemical constituents from California beverage brandy are shown in Table III. Since the brandy contained only about half as much total acid as the prepared solutions, there was, in most cases, a much larger percentage removal; and in fifteen cases the actual grams of acid removed from the brandy was as great or greater. Absorption of acid is not a simple process depending solely on the concentration of acid. Brandy 2, which contained only one fourth as much fusel oil, lost slightly larger amounts of acid in all but four cases, although Amiot (*1*) found higher alcohols to reduce the absorption of acid. The high removal of non-

TABLE II. PER CENT LOSS OF ACID, ESTER, ALDEHYDE, FURFURAL, HIGHER ALCOHOLS, AND TANNIN FROM 50 PER CENT ALCOHOL SOLUTIONS TREATED WITH CHARCOALS[a]

Charcoal No.	Acetic Acid	Ethyl Acetate	Acetaldehyde	Furfural	Higher Alcohols	Tannin
1	2.18	0.10	0.13	0.98	1.45	1.2
2	1.05	0.10	2.60	21.82	1.97	39.3
3	22.03	+0.29	1.17	16.50	+1.64	30.3
4	3.52	1.16	0.52	8.82	1.45	15.8
5	16.33	+2.12	0.58	2.94	1.45	3.4
6	33.64	1.36	1.75	27.45	+1.12	29.2
7	1.14	1.26	1.95	2.94	1.45	5.0
8	+7.03	2.92	0.59	0.00	+1.12	2.0
9	3.61	3.23	3.38	55.38	+1.12	67.3
10	2.18	0.00	2.28	52.20	2.43	56.4
11	8.93	0.31	1.82	20.50	1.45	15.9
12	6.08	0.78	2.86	45.86	4.73	53.5
13	2.28	0.10	1.30	29.88	0.92	10.4
14	+4.37	2.24	0.39	7.60	+1.77	74.5
15	1.99	0.19	1.75	36.00	+0.59	75.8
16	1.99	0.83	1.82	34.80	1.45	49.2
17	5.70	+0.19	5.13	38.22	1.97	83.7
18	2.38	0.63	0.26	0.00	0.92	0.6
19	9.68	0.73	0.00	0.00	+1.12	6.4
20	0.95	0.97	4.10	39.00	1.45	75.9
21	9.22	1.15	3.44	8.33	+2.16	3.1
22	3.04	+0.10	4.61	39.44	1.45	67.6
23	1.05	2.72	1.75	61.00	4.73	25.8
24	1.05	0.63	0.00	0.00	0.46	0.6
25	20.70	7.28	2.74	13.48	2.43	22.7
26	2.09	2.29	4.10	3.19	+1.12	8.8

[a] Filtered, untreated samples contained 105.2 mg. acetic acid, 103 mg. ethyl acetate, 15.4 mg. acetaldehyde, 4.08 mg. furfural, 152.2 mg. higher alcohols (made from 4 parts of isoamyl alcohol and 1 part of isobutyl alcohol), or 65.6 mg. tannin (all per 100 ml.); 0.5 gram of each charcoal was used per 100 ml. with 10-minute contact time.

TABLE III. EFFECT OF CHARCOAL TREATMENT ON COMPOSITION AND QUALITY OF CALIFORNIA BRANDY[a]

Charcoal No.	Total Acid[b], %		Non-volatile Acid, %,	Esters, %,	Alde-hydes, %,	Furfural, %,	Higher Alcohols, %,	Tannin, %,	Color, %		Copper, %		Extract, %		Taste Score	
	Brandy 1	Brandy 2	Brandy 2	Brandy 1	Brandy 1	Brandy 1	Brandy 1	Brandy 1	Brandy 1	Brandy 2	Brandy 1	Brandy 2	Brandy 1	Brandy 2	Brandy 1	Brandy 2
1	3.5	5.2	0	4.06	+0.66	2.4	3.0	+1.0	+6	+12	0	0	3.8	+[c]	73[d]	78[d]
2	4.3	5.8	78	2.27	1.24	43.5	3.5	48.8	48	[e]	72	[e]	14.4	12.8	66	[e]
3	38.2	42.0	90	1.12	1.57	12.8	1.5	29.7	37	[e]	80	[e]	3.0	7.5	68	[e]
4	7.1	9.9	73	1.83	2.23	3.4	1.5	24.4	31	50	62	57	3.7	2.8	74	75
5	24.7	19.1	75	1.83	+0.17	29.7	+1.5	4.3	+6	5	23	55	+	+	74	70
6	50.8	38.9	73	2.27	1.65	61.5	2.0	54.5	68	77	62	89	+	1.5	73	74
7	2.0	3.0	71	4.65	0.99	10.0	3.5	1.4	+4	+11	0	6	+	+	74	76
8	+15.7	+16.1	73	1.71	0.33	6.9	1.0	+2.4	5	6	0	18	1.2	+	73	79
9	17.7	19.5	90	6.38	5.60	58.5	0.5	68.5	77	84	62	94	21.7	19.3	72	75
10	12.0	14.1	64	0.06	1.90	55.5	3.0	62.2	86	89	0	0	19.9	19.6	74	75
11	15.3	14.1	46	0.06	4.28	36.1	6.6	49.3	31	44	15	39	1.8	2.6	73	77
12	19.4	28.4	88	6.38	3.38	29.4	1.0	68.5	64	63	62	78	17.9	15.9	72	75
13	4.7	6.0	82	6.30	3.55	27.3	7.6	12.4	3	10	0	25	1.5	4.6	73	78
14	+0.6	+2.8	46	3.03	1.65	45.4	2.0	66.5	90	91	54	68	20.3	21.6	71	74
15	13.3	14.9	55	2.27	1.81	30.2	6.1	82.8	89	90	49	75	28.4	29.0	72	74
16	12.8	13.7	85	2.27	0.83	52.0	+2.0	57.0	76	88	23	45	22.0	21.6	73	75
17	19.0	19.9	83	3.92	1.65	33.9	3.5	81.3	93	92	69	89	11.3	15.9	72	77
18	4.3	3.5	38	3.27	0.17	29.4	5.1	+1.4	+8	+22	0	15	+	+	73	76
19	4.9	5.8	27	1.71	0.17	45.5	6.6	7.2	27	+ 3	10	23	..	0.3	73	75
20	9.6	13.1	59	2.30	5.94	31.5	2.5	84.6	93	94	80	79	27.3	22.2	73	74
21	16.9	16.9	50	0.53	1.98	36.1	+1.0	3.4	7	+ 4	23	52	+	+	74	75
22	14.1	17.3	64	3.92	1.57	51.3	2.0	68.0	83	83	80	94	27.2	25.1	73	72
23	9.6	11.3	82	4.65	2.47	58.7	2.0	62.2	67	80	62	43	21.8	21.9	73	75
24	0.0	2.2	0	0.18	4.45	11.8	5.1	+0.5	17	7	0	9	+	1.7	73	77
25	24.7	44.1	79	4.65	5.19	42.2	+2.0	24.9	10	+31	80	89	+	+	73	76
26	1.4	3.0	66	2.36	4.86	26.5	3.5	1.4	+3	[e]	0	[e]	+	+	69	[e]
27	1.4	1.8	27	1.42	0.70	20.9	6.0	24.8	5	6	15	29	..	+	73	75

[a] Brandy 1 (90° proof) before treatment contained 51.0 mg. acid as acetic, 33.98 mg. esters as ethyl acetate, 12.12 mg. aldehyde as acetaldehyde, 0.593 mg. furfural, 198 mg. higher alcohol, 20.9 mg. tannin, 128.3 mg. extract, and 0.065 mg. copper (all per 100 ml.). Brandy 2 (100° proof) contained 49.6 mg. acid as acetic, 9.2 mg. nonvolatile acid as acetic, 0.235 mg. copper, and 65.4 mg. extract (all per 100 ml.).

[b] Per cent loss in each case except for taste scores.

[c] Extract losses are only approximate, since it was difficult to remove all of the charcoal by filtration. Determinations marked + indicate that sufficient charcoal came through the filter to increase the extract content.

[d] The taste score on untreated brandy 1 was 73, and on brandy 2, 75.

[e] Brandy 1 treated with charcoals 2, 3, and 26 had a bad off-taste, and these charcoals were not used in brandy 2.

volatile acids from brandy 2 indicates that acids of higher molecular weight than acetic are apparently selectively absorbed. Since the acid contents of these brandies are normal, charcoals that remove the least acid should be used.

As in the alcoholic solutions, only small amounts of esters and aldehydes were removed from the brandy. Cafere (*6*) obtained an absorption of 10 per cent of the aldehyde and 26 per cent of the esters, using the same concentration of charcoal. Since the ester and aldehyde contents of the brandy are normal, their removal would be undesirable.

Little fusel oil was removed. The excessive higher alcohol content of brandy 1 was its primary defect, and unless this fusel oil concentration could be lowered by charcoal treatment, the brandy will not be materially improved. These results agree with those of Cafere (*6*) who used the same amounts of charcoal, but Bogojawlenskij and Humnicki (*4*) reported a decrease in fusel oil when raw spirits were filtered through charcoals.

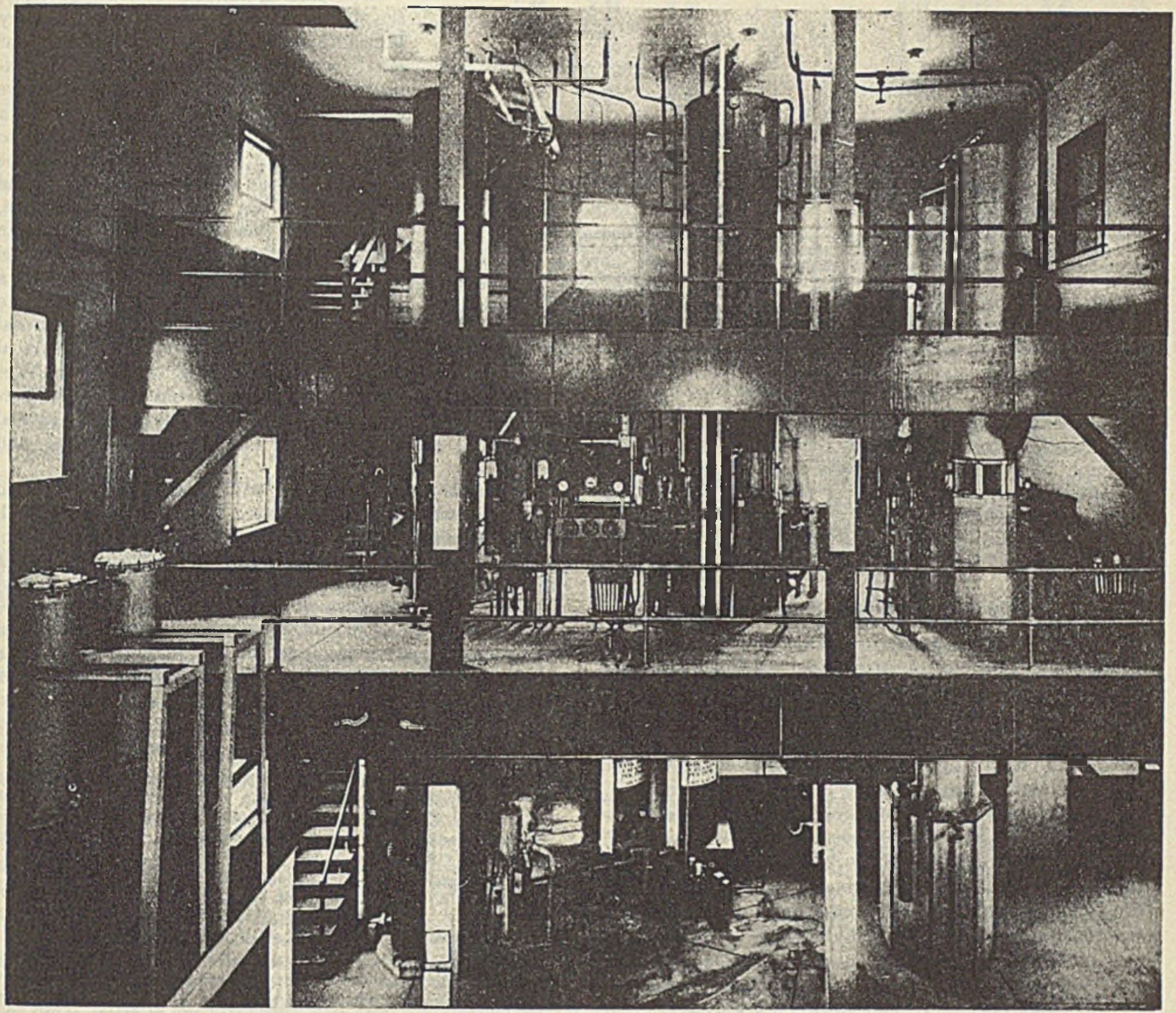
Furfural and tannin removal from brandy 1 is unnecessary, since the amounts present are not excessive. However, certain charcoals will remove large amounts of these two constituents. The per cent removals from the brandy were similar to that from the pure alcohol solutions.

The decolorizing power of different charcoals varies greatly. This property may be tested on caramel or on methylene blue solutions (*13*). Vines (*22*), however, considers such methods as artificial and as sometimes yielding anomalous results. In these tests the decolorizing power was determined by matching the color of the untreated and treated brandies against a standard color. Eastman A. B. C. dyes were separately dissolved in water (0.25 gram in 50 ml.); aliquots (1.1 ml. of the red, 1.0 ml. of the yellow, and 0.2 ml. of the blue for brandy 1, and 0.8, 1.0, and 0.3 ml., respectively, for brandy 2) were mixed and diluted to 100 ml. volume. An apparent increase in color was obtained in a few cases because very fine particles of the carbon were suspended in the treated brandy after filter-paper filtration. The percentage of color removed was similar for the two brandies, but the figures do not necessarily reveal the relative merits of the carbons in removing foreign colors. Brandy 2 had a slight greenish coloration, and in some cases its color was improved. Such off-colorations can be corrected only by experimenting with various charcoals.

The extract content (roughly the soluble solids) was determined before and after charcoal treatment for both brandies. The removal from either of the two brandies was small and of the same order of magnitude. In some cases it was impossible to secure accurate extract-removal data because of the difficulty in removing the finer charcoal particles by filtration.

The two brandies had 0.65 and 2.35 mg. per liter of copper. Tolbert (*21*) found in twenty-eight commercial California brandies from 0.20 to 7.0 mg. per liter (average 1.54); and in thirty 4-year-old brandies, whose preparation and aging were controlled by this laboratory so that there had been no known copper contamination, 0.20 to 0.50 mg. per liter. The Marsh procedure (*15*) was used for determining copper. The charcoal treatment markedly reduced the copper content of the two brandies except in a few cases. More copper was removed from brandy 2, as the low concentration of copper in brandy 1 was apparently a limiting factor in its removal by certain of the charcoals. Some of the undesirable metallic taste and dark green color of brandy 2 was probably due partially to its high copper content and also to a high iron content. Addition of iron sulfate in amounts of 2.5 to 5 mg. per liter markedly increased the greenish-black color. Per cent removal of iron from brandy 2 was approximately similar to the removal of copper.

The most sought-for improvement of charcoal treatment is in the palatability of the brandies. Mathieu (*16*) in reviewing the literature reports that the charcoal treatment removed many off-odors and off-tastes. Blind organoleptic examination of the treated and untreated samples were made, using a simple scoring system that did not take into account changes in color. The tasting was done several days after treatment to allow the brandy to recover partially from the severe oxidized or aerated taste that results from charcoal treatment. Brandy 1 was an ordinary unaged California brandy, particularly high in fusel oil. None of its treated samples were found to be improved on account of this predominative organoleptic effect. Charcoal 2 imparted a moldy smell, and charcoals 3 and 26 a kerosene or resin smell



Courtesy, Padre Vineyard Company

Modern Control Room in a California Brandy Distillery

TABLE IV. PERCENTAGE LOSS IN HIGHER ALCOHOL CONTENT OF PURE SOLUTIONS AND BRANDY WHEN LARGER AMOUNTS OF CHARCOAL ARE USED[a]

Charcoal No.	Amount Used, G./100 Ml.	% Loss in Higher Alcohol Content[b] At 0° C.	At 22° C.	At 70° C.	In 94% at 22° C.	2 hr. at 22° C.	Hexyl alcohol[c]	Brandy 1
1	6.0	1.8	7.1	1.5	7.0	3.0	3.8	18.5
5	4.0	3.5	5.8	+1.5	3.0	3.3	3.0	7.5
7	3.0	5.0	16.0[d]	12.3	4.5	17.8	23.8	23.0[d]
8	3.0	..	5.6	..	...	..	..	10.8
13	3.0	14.0	16.7	8.5	6.0	16.5	37.2	26.0
15	3.0	17.0	17.0	10.3	4.5	16.8	38.8	28.1
18	4.0	0.5	1.2	+5.3	4.5	2.3	2.7	10.8
19	4.0	3.0	2.3	2.8	4.5	6.8	7.2	9.3
20	4.0	18.9	16.9	14.3	5.5	17.5	42.7	28.1
21	4.0	0.3	7.1	0.3	4.0	8.3	7.0	17.2
22	3.0	7.3	10.1	4.5	4.5	12.3	26.2	17.5
23	3.0	16.3	13.1	4.5	4.5	15.0	33.5	22.9
24	4.0	0.5	0.5	0.0	3.5	6.5	2.7	5.5
25	4.0	5.8	4.8	+0.3	2.5	5.8	15.0	13.1
27	6.0	1.0	4.7	+0.3	5.0	4.3	2.3	..

[a] Contact period, 10 minutes unless otherwise noted.

[b] Standard made of 4 parts isoamyl and 1 part isobutyl alcohol; total 200 mg. per 100 ml. in 50 per cent ethyl alcohol unless otherwise noted.

[c] 200 mg. per 100 ml.

[d] Using 4 grams per 100 ml.

[e] This charcoal was recovered from the filter paper and re-used on a new sample, but without drying the charcoal. The process was repeated three times. The rate of absorption of the fusel oil decreased 75 per cent for the first re-use in the 0° C. test, and 50 per cent for the first re-use in the 22° C., 2-hour, and hexyl alcohol tests. The charcoal was nearly ineffective for the second and third re-uses. For the 70° C. and 94 per cent alcohol tests it was nearly ineffective on the first re-use. The maximum absorption capacity of 3 grams of this charcoal of the isoamyl-isobutyl standards is about 23 per cent.

to the brandy. Brandy 2 was a sound California brandy of moderate acid, ester, and aldehyde content and low fusel oil. The odor, however, was burny and woody, and the taste was rather sharp and astringent ("metallic"). Treatment with certain charcoals was effective in improving the organoleptic quality of this brandy. The hot and woody aroma was often reduced, and the taste was less astringent.

REMOVAL OF HIGHER ALCOHOLS

The generally unsatisfactory results of removing fusel oils with 0.5 gram per 100 ml. of charcoal led to further tests using larger amounts of charcoal, different temperatures, and other methods of treatment (Tables II and IV). Increasing the amount of charcoal from 0.5 to 3.0 or 4.0 grams per 100 ml. increased the percentage absorption in most cases, but still the fusel-oil removal was not great enough to be profitable.

Zaharia, Angelescu, and Motoc (*23*) obtained better absorption of fusel oil at lower concentrations of ethyl alcohol; and Amiot (*1*) reported that ethyl alcohol only slightly influenced the absorption of the alcohols by animal charcoal. In this study, increasing the percentage of ethyl alcohol in which the fusel oil was dissolved from 50 to 94 per cent reduced the fusel oil absorption except with four charcoals, where the absorption was small. Little difference in absorption was noted between 0° and 22° C., but raising the temperature to 70° C. reduced the absorption in all cases, except one. Running the hot distillate directly through charcoal filters will therefore probably be less effective in removing higher alcohols than cooling and cutting with water before filtering. Increasing the period of contact to 2 hours, with continuous mechanical shaking, did not materially change the percentage absorption of fusel oils except with charcoal 24.

The tests with larger amounts of charcoal were repeated on the high fusel oil brandy 1 (Tables III and IV). Some increases in the absorption were obtained in all but one case, and the taste scores were also improved. Charcoals 5, 13, 21, and 25 used in these large amounts communicated pronounced off-tastes of unknown source to the brandy.

Considerably more fusel oil was removed from the brandy than from the isoamyl-isobutyl alcohol standards. A much larger percentage of higher alcohol was removed from a hexyl alcohol standard than from an isoamyl-isobutyl standard. Fusel oil removal from brandy by charcoals, therefore, appears subject to variation, depending on the type of higher alcohols present.

COMMERCIAL APPLICATION

In purchasing charcoal for treating brandy, the distiller should be guided by preliminary tests with several charcoals on the particular lot of brandy to be treated. A more expensive charcoal may be the least expensive if its efficiency is greater. Treatment of a spirit for fusel oil removal alone is likely to be impractical, as better results can be obtained more economically by careful separation of the tails during distillation. The same is true of color where one can carefully control the addition of caramel sirup. If, however, the brandy picks up a green or dark coloration, perhaps owing to contamination with metals, then charcoal treatment has a definite value. Charcoal may also improve harsh or rough brandies by removing some of the tannin and furfural. The removal of these constituents from normal brandy is undesirable, since they impart character and body.

In general these results agree with Dietrich (*10*) who found that the quantities of acids, esters, higher alcohols, furfural, and aldehydes should be controlled by proper distillation. However, the charcoal treatments are valuable in improving the organoleptic character of brandies that have woody, metallic, or other obnoxious tastes. Charcoal should always be used in the smallest possible amounts, particularly on aged brandies. Excessive amounts of charcoal either remove too much flavor or produce oxidized or off-tastes.

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Kinetics of Oxidation of CELLULOSE with PERIODIC ACID

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Hercules Powder linters and regenerated cellulose from copper oxide–ammonia solution were oxidized with sodium periodate. It was found that the rate of this oxidation can be explained by assuming that the sample consists of more easily and more difficultly accessible areas. The amount of the easily accessible (amorphous) material can be estimated by extrapolation. The oxidation of the individual glucose units is a two-step reaction, which can be followed with fair approximation by a simple kinetic scheme (Equations 6 and 8).

MOST high polymers in the solid state seem to consist of two phases. One is geometrically highly organized and usually referred to as the crystallized, ordered, or micellar state; the other, in which a high degree of randomness prevails, is called the amorphous or disordered state (*1, 2, 5, 6, 9, 10, 13, 15, 21, 23*). X-ray investigation (*13, 19*) gave the first qualitative indication for the coexistence of these states in cellulose and other high polymers. It has recently been used by several investigators to study the situation more thoroughly (*2, 6, 18, 23*). Any quantitative statement as to the relative proportion of the two phases, however, is based on intensity discussions of the scattered radiation, which is not easy to measure and difficult to interpret. It is therefore desirable to have independent experimental methods for the investigation of the two- (or poly-) phase nature of solid high polymers.

The kinetic study of mild chemical reactions seems to provide such an opportunity, at least in the case of cellulose. Nickerson (*21*), Purves (*7, 14*), and others (*8, 22*) have shown that the progress of such reactions with time suggests the existence of more easily and of more difficultly accessible regions in the samples, which seem to correspond to the amorphous and crystalline areas as conceived by x-ray investigation. This paper presents some experimental contributions to the problem.

OXIDATION METHOD AND PROCEDURE

The reaction chosen was the oxidation of cellulose with periodic acid. This oxidation, discovered by Hudson and Jackson (*11*), occurs under mild conditions (room temperature, diluted aqueous solution, slow progress of reaction) and has been more closely studied by Davidson (*4*), Harris and co-workers (*17, 22*), and Purves and collaborators (*7, 14*). In order that the periodate ions (IO_4^-) can oxidize the two adjacent hydroxyl groups (in the 2 and 3 positions) of any glucose residue to aldehyde groups, they have first to reach this individual glucose residue by diffusion. This process of diffusion, which is very slow in the crystalline areas and comparatively faster in the amorphous regions, determines the rate of the total reaction; for the oxidation itself has been found to be much faster, once the periodate ion is in the immediate neighborhood of an individual pair of 2,3-hydroxyl groups. The order of magnitude of the three rate constants involved is approximately given by:

$$k_o \simeq 100\, k_a \simeq 20\, k_c \qquad (1)$$

where k_o = rate of oxidation
k_c = diffusion in crystallized phase
k_a = diffusion in amorphous phase

Following the total amount of oxygen consumed as a function of time, curves are obtained as shown in Figure 1. They can be interpreted as superposition of a fast and a slow process, as represented in Figure 2. The saturation value for the fast reaction (*AB*) corresponds to the total amount of the easily accessible (amorphous) areas. It can be obtained from the graphs by extrapolating the linear part of the observed curve (*CD* in Figure 2) to the ordinate. In the case of Figure 2 it amounts to 10 per cent by weight of the total material. The residue of 90 per cent is much more difficultly accessible and seems, therefore, to correspond to the crystalline phase.

The experimental procedure to obtain curves as shown in Figure 1, using various samples of cellulose, was as follows (compare also citations *3, 20, 26*):

Oxidation was carried out in aqueous solutions of potassium metaperiodate at a pH of less than 1 (sulfuric acid). Two grams of purified Hercules Powder cotton linters were treated, with frequent shaking, with 100 ml. of oxidant in a constant temperature bath for the desired length of time. Each run was accompanied by a blank determination to account for any decomposition of oxidant which might have occurred.

After the desired length of time, the cellulose was filtered off with suction, and aliquot portions of the oxidant were removed for analysis. The cellulose was washed free of acid.

The analyses were carried out on a semimicro scale. The aliquot portions (1 ml.) of oxidant were diluted with 10 ml. of distilled water. The system was then neutralized with sodium hydroxide, and 10 ml. of a boric acid–sodium tetraborate buffer (50 grams boric acid–50 grams borax per liter solution) were added. The use of this buffer was originated by Willard and Boyle (*25*) and yielded a solution of pH about 8. Three milliliters of a saturated potassium iodide solution were added, and the iodine liberated by the remaining periodate was titrated with standard thiosulfate solution. The total oxygen consumed was calculated by the difference between periodate present in the blank and periodate present in the solution after oxidation.

The aldehyde content of the oxycellulose was measured by means of the iodine method of Martin, Smith, Whistler, and Harris (*17*). However, the borax–boric acid buffer mentioned above was used instead of sodium carbonate-bicarbonate according to Harris and co-workers. One hundred milliliters of buffer, chilled to 0° C., were added to 2 grams of oxycellulose. To this were added 50 ml. of 0.05 *N* iodine in potassium iodide solution which had also been previously chilled to 0°. The reactants were allowed to stand for 3 hours at 0° (a higher temperature will cause some unoxidized cellulose to be oxidized by the iodine) and then the remaining iodine was titrated with standard thiosulfate solution. Care was taken in the titration to make sure that all the iodine, adsorbed on the oxycellulose, was liberated and accounted

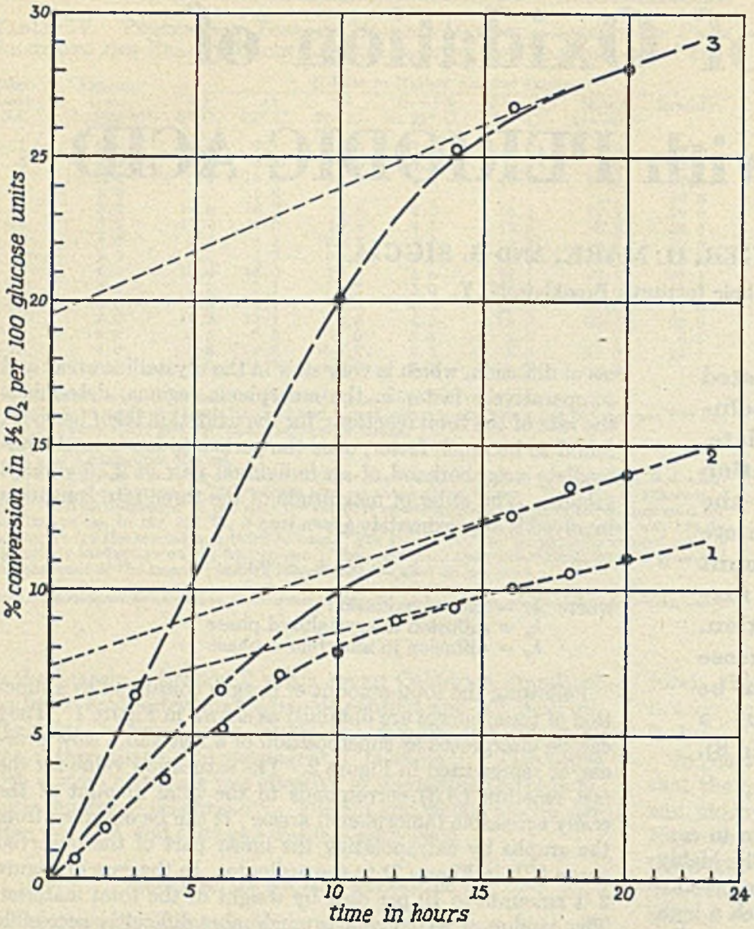


Figure 1. Total Oxygen Consumption of Various Cellulose Samples

for in the titration. This was done by vigorous shaking when very close to the end point.

A blank was run with each determination, and since the measurement of aldehyde depends on only a small change in iodine concentration, a buret which could be read to 0.002 ml. was used to reduce the error incurred in titration. The aldehyde was calculated by the difference in iodine present in the blank and that present in the sample after the aldehyde groups had been oxidized.

The carboxyl content of the oxycellulose was determined by the method of Kenyon (*12*). To 2 grams of oxycellulose were added 100 ml. of 1.0 *N* calcium acetate, and the reactants were allowed to stand for 2 hours. At the end of the 2 hours the acetic acid, liberated by the reaction of the carboxyl groups with the calcium acetate, was titrated with standard sodium hydroxide (phenolphthalein as indicator).

Since we have a buffer system set up—namely, acetic acid-calcium acetate—the end point of the titration is not an instantaneous color change. However, by using blank determinations, titrated to a definite color change, results can be obtained within 0.03 ml. when using 0.1 *N* sodium hydroxide.

The regenerated cellulose was prepared by dissolving cotton linters in cuprammonium solution and precipitating with hydrochloric acid. The precipitated cellulose was washed free of acid with distilled water. Half of the washed material was dried at 70° C. in a vacuum oven, and the rest of the precipitated cellulose was allowed to soak in acetone to replace the water. Then the acetone was replaced with benzene and the sample dried from benzene (70° C. in a vacuum oven).

The water-dried sample was a hard, rather dense material; the benzene-dried cellulose, however, was soft and fluffy.

OXYGEN CONSUMPTION

Figure 1 shows the total oxygen consumption of various cellulose samples plotted against time; the values for the amount of easily accessible material according to Figure 2 are listed in Table I. The value of 6 per cent for cotton linters agrees reasonably with the figures obtained by Nickerson (*21A*) with the hydrochloric acid–ferric chloride method and also with earlier estimations on the basis of x-ray patterns and gas adsorption (*16*). Mercerizing or regenerating cellulose from solution increases this readily attainable (amorphous or disordered) phase, which is to be expected according to previous observations of Nickerson (*21*) and others (*15*, *16*). Finally, drying from a homopolar liquid (benzene) renders still larger areas of the sample favorable for penetration. This is also concordant with previous observations and may be explained by the fact that the hydroxyl groups, distributed along the cellulose chains in the swollen system, have less chance to interact with one another when comparatively large homopolar molecules are removed by isothermal evaporation.

It seems, therefore, that the evaluation of the experimental curves of Figure 1 according to the scheme of Figure 2 provides for a comparatively simple way to estimate the relative amount of the crystalline and amorphous material in the investigated sample.

As pointed out in the experimental part, however, it is possible not only to determine the total amount of oxygen consumed but also the amount of aldehyde and carboxyl groups at any instant. Previous investigators (*11*, *17*) had already noticed that the oxidation proceeds stepwise, and Harris and collaborators (*17*, *22*, *24*) recently studied the relative stability of the aldehyde and carboxyl stage. The following data contribute further to these findings.

Figure 3 represents as functions of time the values obtained for aldehyde groups present, carboxyl groups present, and total oxygen consumed if Hercules Powder cotton linters are oxidized. The aldehyde curve first follows the total oxidation, reaches a distinct maximum after about 16 hours, and

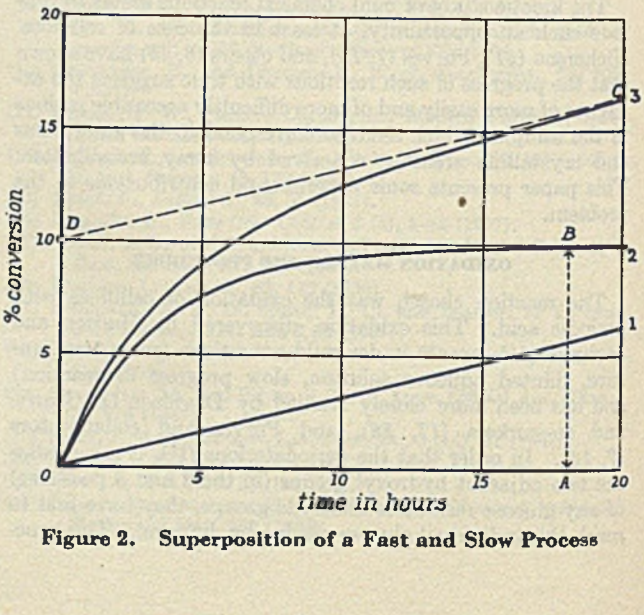


Figure 2. Superposition of a Fast and Slow Process

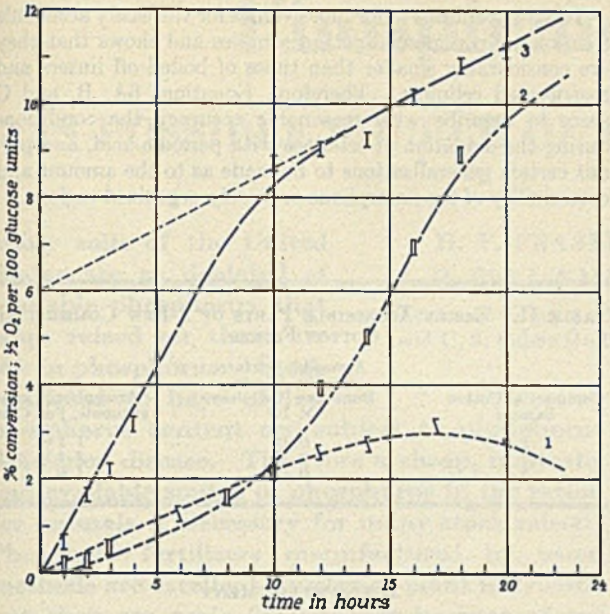
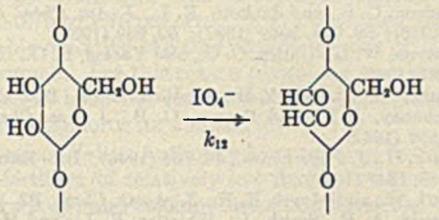


Figure 3. Aldehyde Groups Present (1), Carboxyl Groups Present (2), and Total Oxygen Consumed (3), as Functions of Time

declines later so that almost no aldehyde groups can be found experimentally after 24 hours. On the other hand, the carboxyl curve starts rising slowly, reaches its steepest part where the aldehyde concentration is highest, and follows closely the total oxygen consumption as soon as all the easily accessible material is used up.

MECHANISM FOR TOTAL REACTION

This suggests the following step mechanism for the total reaction: Upon immersion in the oxidizing solution, the loosely arranged (amorphous) portions of the fiber are penetrated by the liquid and the 2,3-hydroxyl configurations in the chains are oxidized by the periodate ions according to a rate constant, k_{12}, which incorporates a certain collision factor A_{12} and activation energy E_{12}. This step provides for the conversion of normal glucose rings into dialdehyde groups:



Denoting the total number of glucose units in the easily accessible parts at the beginning of the experiment by N_0, the number present at each instant by N_1, the number of aldehyde groups present at each instant by N_2, and the activity of the periodate ions by a, the rate of disappearance of glucose units in the amorphous regions becomes:

$$-\frac{dN_1}{dt} = k_{12}aN_1 \tag{2}$$

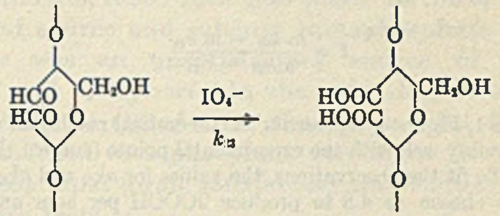
TABLE I. "ACCESSIBLE SURFACE" OF CELLULOSE SAMPLES

Sample	Accessible Surface, Sq. Cm./Gram Bone-Dry Cellulose, × 10⁴	Amorphous Constituents, Per Cent
Hercules cotton linters	1.0	6.0
Cellulose regenerated from cuprammonium solution		
Dried from water	1.23	7.4
Dried from benzene	3.20	19.5

At the same time this is the rate at which pairs of aldehyde groups are produced. Hence the rate of appearance of aldehyde groups in the system will be:

$$+\frac{dN_2}{dt} = 2k_{12}aN_1 \tag{3}$$

These aldehyde groups, however, are consumed by the next step,



according to the equation,

$$-\frac{dN_2}{dt} = k_{23}aN_2 \tag{4}$$

and carboxyl groups N_3 are produced at the same rate,

$$+\frac{dN_3}{dt} = k_{23}aN_3 \tag{5}$$

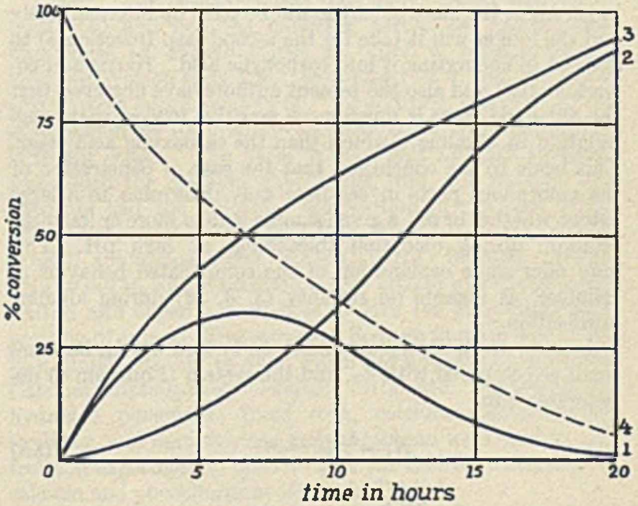


Figure 4. Graphical Representation of Equations 6A, B, and C

Periodate is always present in large excess, and its activity, a, can therefore be considered not to change throughout the experiment. Treating it as a constant, we obtain for the number of glucose units, aldehyde groups, and carboxyl groups present at each instant, t, the following expressions:

$$N_1 = N_0e^{-k_{12}at} \tag{6A}$$

$$N_2 = 2N_0 \frac{k_{12}}{k_{23} - k_{12}} [e^{-k_{12}at} - e^{-k_{23}at}] \qquad (6B)$$

$$N_3 = 2N_0 \left[1 - \frac{1}{k_{23} - k_{12}} (k_{23} e^{-k_{12}at} - k_{12} e^{-k_{23}at}) \right] \qquad (6C)$$

Equation 6A describes (Figure 4) how the glucose units in the amorphous parts of the sample are used up; it is a smoothly declining exponential function, which can be obtained from the total amount of oxygen consumed after subtracting the contribution of the slow oxidation of the crystallized portions according to Figure 2. Curve 4, Figure 4, represents the general shape of this function, which is in fair agreement with the actually observed curves.

Equation 6B shows (curve 1, Figure 4) how aldehyde is first piled up according to reaction 3 and later consumed by reaction 4; it reaches a maximum at

$$t = \frac{\ln k_{23} - \ln k_{12}}{a(k_{23} - k_{12})} \qquad (7)$$

Curve 1, Figure 4, represents the theoretical result and agrees reasonably well with the experimental points (curve 1, Figure 3). To fit the observations, the values for ak_{12} and ak_{23} have to be chosen as 4.8 to produce 2COOH per hour and 100 glucose units, and 18.6 to produce 2COOH per hour and 100 glucose units, respectively.

Finally, Equation 6C represents the accumulation of the end product of oxidation in the amorphous areas; it is illustrated in curves 2 and 3, Figure 4, together with the observed values (curves 2 and 3, Figure 3).

It seems that Equations 6A, B, and C represent with reasonable accuracy the stepwise oxidation of cellulose in the easily accessible areas, when k_{12} and k_{23} are comparable in magnitude.

The looser the structure of the amorphous parts, the larger will be the rate constant k_{12} of the first step. Furthermore, the larger k_{12} is, the more aldehyde will be piled up intermediately and the longer will it take for the second step (reaction 4) to succeed in converting it into carboxylic acid. Harris and coworkers (*22*) and also the present authors have observed that the aldehyde stage is much more sensitive toward chain degradation in alkaline medium than the carboxylic acid stage. This leads to the conclusion that the ease of penetration of the amorphous parts in cellulose may determine to a large extent whether or not a given sample suffers more or less degradation during oxidation (bleaching) at high pH. This may offer some explanation of the complicated behavior of cellulose, as regards its stability (*4*, *8*, *12*) during alkaline purification.

As soon as all amorphous material is used up, k_{12} becomes small as compared with k_{23}, and the system (Equation 6) degenerates into

$$N_1 = N_0 e^{-k_{12}at} \qquad (8A)$$

$$N_2 = \frac{2N_0 k_{12}}{k_{23}} [e^{-k_{12}at} - e^{-k_{23}at}] \qquad (8B)$$

$$N_3 = 2N_0[1 - e^{-k_{12}at}] \qquad (8C)$$

According to 8B, the aldehyde concentration is now very small ($k_{23} > k_{12}$); actual observations confirmed this. Equations 8A and C show that the consumption of glucose in the crystallized areas is reflected directly in the production of carboxylic acid. This agrees with the experimental findings in curves 2 and 3, Figure 3, at all times larger than 24 hours.

Table II contains a few more values for the easily accessible fractions of commercial cotton samples and shows that they are considerably smaller than those of boiled off linters and regenerated cellulose. Therefore, Equations 6A, B, and C seem to describe with reasonable accuracy the conditions during the oxidation of cellulose with periodic acid, and permit certain generalizations to be made as to the amount and accessibility of the amorphous or loosely organized regions.

TABLE II. EASILY ACCESSIBLE PARTS OF A FEW COMMERCIAL COTTON FIBERS

Commercial Cotton Sample	Accessible Surface, Sq. Cm./Gram Bone-Dry Cellulose, × 10⁴	Amorphous Constituents, Per Cent
1	0.18	1.1
2	0.35	2.1
3	0.17	1.0

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Phosphate Fertilizers

AS POSSIBLE SOURCE OF PHOSPHORUS FOR ANIMALS

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Many soils of the United States are so depleted of available phosphorus that crops raised on them are low in phosphorus. Stock restricted to hays of low phosphorus content are subject to phosphorus deficiency disease. Therefore a cheap, nontoxic, and available source of phosphorus in the ration for animals is necessary for many stock raisers. Phosphate fertilizers manufactured by usual methods are excellent sources of plant nutrients, but they are toxic for animals because of too high a fluorine content. Fused rock phosphate fertilizer and calcium metaphosphate fertilizer have a relatively low fluorine content, and were therefore tested for the availability of their calcium and phosphorus in rat nutrition. As compared to controls under the conditions of these experiments, fused rock phosphate fertilizer was a good source and calcium metaphosphate fertilizer was an unsatisfactory source of calcium and phosphorus in the nutrition of rats. It should be stated that the commercial feeding of fused rock phosphate fertilizers to farm animals must await satisfactory nutritional and toxicity tests.

REPEATED investigations of the soils of the United States have shown many to be so depleted of available phosphorus that crops raised on them are low in content of this element (*15*). Stock restricted to hays grown on soils of low phosphorus content are in imminent danger of phosphorus deficiency disease (*13*). Animals thus afflicted have been observed in many sections of the country, and the disease has been designated by such names as stiffs and sweeny (*2*). As a result of these observations, the need in certain stock-raising areas for a cheap, nontoxic, and available source of phosphorus in the ration for animals is now generally recognized.

Phosphate rock deposits which have been extensively converted to phosphate or superphosphate fertilizers for addition to the soil as plant nutrients are abundant in phosphorus and calcium. The fluorine content of phosphate rock is approximately 3.5 per cent, and that of superphosphate fertilizer ranges from 0.75 to 1.75 per cent (*10, 11*), or a toxic amount if an appreciable quantity of either phosphate rock or the fertilizer is consumed. For this reason phosphate rock and phosphate fertilizers have not been used as a dietary source of calcium and phosphorus for animals (*6*).

The Tennessee Valley Authority has produced two types of phosphate fertilizer of relatively low fluorine content—fused phosphate rock (*5*) and calcium metaphosphate (*3*). Should the phosphorus and calcium of these fertilizers be available and nontoxic for rats, there would be evidence to presume that similar findings would result in the case of domesticated animals.

FEEDING TESTS

The general principle of approach was to ascertain the amount of storage of calcium and phosphorus in young, rapidly growing rats fed selected phosphate fertilizers, as compared with the amount of storage of these elements in litter mates given calcium and phosphorus salts of known availability. Feeding tests were conducted on four hundred rats, and the determination was made of the calcium and phosphorus content of the animals at the conclusion of a 30-day test period. Selected representative experiments on two hundred animals are presented.

RATS. 25-day-old weanling male and female rats were used. They were raised on a diet of Purina Dog Chow supplemented with cabbage 5 days a week. In the course of comparative experiments, litter mates of the same sex and approximately the same size were used.

DIETS. The basal diet was that of Schneider and Steenbock (*16*) and had the following percentage composition: Egg white 18, cooked starch 20, Vitab 4, phosphorus-free modified Wesson salts 1.267, cottonseed oil 4, cod liver oil 2, and cerelose approximately 50. In addition, 526 micrograms of riboflavin per 100 grams of diet were added by incorporating it in the Vitab. The basal Wesson salt mixture to which was added the calcium, phosphorus, iron, and fluorine constituents had the following composition in per cent of the entire diet: $NaCl$ 0.42, KCl 0.48, $MgSO_4$ anhydrous 0.36, $MnSO_4$ anhydrous 0.005, $KAl_2SO_4.24H_2O$ 0.00036, $CuSO_4.5H_2O$ 0.00156, and KI 0.0002. Iron citrate was added to the control and experimental diets to give the percentage composition of iron in Wesson salts. Sodium fluoride was added in a similar manner to diets which did not contain fertilizer. Calcium diphosphate, calcium carbonate, potassium dihydrogen phosphate, fused rock, calcium metaphosphate fertilizer, and pure calcium metaphosphate were used in control and experimental diets to give the desired percentage of calcium and phosphorus as shown in Table I.

In some series of experiments a basal salt mixture patterned after that of Hubbell, Mendel, and Wakeman (*9*) was employed and contained constituents in the following percentages: $NaCl$ 0.185, KCl 0.301, $MgSO_4$ anhydrous 0.043, $MgCO_3$ 0.0672, $MnSO_4$ anhydrous 0.00094, $CuSO_4.5H_2O$ 0.0024, and KI 0.00022. The desired percentage of calcium, phosphorus, iron, and fluorine was then obtained as in the case of Wesson salts. Both basal salt mixtures have been demonstrated to be equally efficacious in tests on availability of calcium and phosphorus using Schneider and Steenbock's basal diet. Diets 525, 535, and several check experiments,

Table I. Total Percentage and Source of Calcium and Phosphorus in Experimental Diets

Dietary Source of Ca and P	Expt. I, Diet 535		Expt. II, Diet 552		Expt III, Dict 525		Expt. IV						Expt. V				Expt. VI					
							Diet 536		Diet 537		Diet 538		Diet 539		Diet 540		Diet 541		Diet 542		Diet 542a	
	Ca	P	Ca	P	Ca	P	Ca	P	Ca	P	Ca	P	Ca	P	Ca	P	Ca	P	Ca	P	Ca	P
Basal diet	0.01	0.04	0.01	0.04	0.01	0.04	0.01	0.04	0.01	0.04	0.01	0.04	0.01	0.04	0.01	0.04	0.01	0.04	0.01	0.04	0.01	0.04
$CaHPO_4$	..	..	..	..	...	..	0.155	0.12	...	..	0.05	0.04	...	..	...	..	0.246	0.19	...	..	...	..
$CaCO_3$	..	..	0.19	..	0.191	..	0.035	...	...	..	0.10	..	0.002	..	0.119	..	0.214	..	0.331	..	0.331	..
KH_2PO_4	..	..	..	..	...	..	...	...	...	0.04	..	..	...	0.04	...	..	...	..	...	..	...	0.08
$NaH_2PO_4.H_2O$	..	0.19	..	..	...	0.04	...	...	...	..	..	..	...	..	...	..	...	..	...	..	...	..
$Ca(PO_3)_2$, c. p.	..	..	..	..	...	..	...	...	...	..	..	..	...	..	0.081	0.12	...	..	0.129	0.19	0.129	0.19
$Ca(PO_3)_2$ fertilizer	..	..	..	..	...	..	...	...	...	..	0.05	0.08	...	..	...	..	...	..	...	..	...	..
Fused rock, 0.05% F	..	..	..	..	...	..	...	...	0.201	0.08	..	..	...	..	...	..	...	..	...	..	...	..
Fused rock, 0.22% F	..	..	..	..	...	..	...	...	...	..	..	..	0.198	0.08	...	..	...	..	...	..	...	..
Total	0.01	0.23	0.20	0.04	0.201	0.08	0.200	0.16	0.211	0.16	0.21	0.16	0.210	0.16	0.210	0.16	0.470	0.23	0.470	0.23	0.470	0.31

not reported in detail, used the basal salt mixture of Hubbell, Mendel, and Wakeman; diets 536 through 542, 542a, and 552 used Wesson salts as a base.

Repeated analyses of the individual ingredients of the basal diet showed that the complete diet with no added calcium or phosphate salts contained 0.04 per cent phosphorus and 0.01 per cent calcium.

The amount and source of calcium and phosphorus in each diet are shown in Table I. Diets 525, 535, 541, 542, 542a, and 552 were fed ad lib. Diets 536, 537, and 538 were fed in a triplicate feeding experiment with the amount of food intake of any group of three litter-mate rats controlled by the animal in the group which ate the least. Diets 536, 539, and 540 were also fed in triplicate. Food was weighed to the nearest 0.1 gram and fed daily.

Composition. The phosphate fertilizer and pure calcium metaphosphate compositions are shown in Table II.

Utilization. The method of ascertaining efficiency of utilization of calcium and phosphorus in fertilizers and c. p. calcium metaphosphate follows the principle of Williams, MacLeod, and Morrell (*17*). The chief modifications in their procedure were as follows: Experiments reported here employed 25-day-old instead of 30-day-old rats. In accordance with Fincke (*7*), the calcium and phosphorus content of the rats at the beginning of the experiment was either interpolated directly from that ascertained in a litter mate of the same sex and age or interpolated from the mean of a series of twenty-four male and fourteen female 25-day-old rats analyzed in this laboratory. The mean calcium percentage of 25-day-old rats was 0.869 ± 0.015 for males and 0.908 ± 0.019 for females. The mean phosphorus percentage of 25-day-old rats was 0.616 ± 0.008 for males and 0.630 ± 0.006 for females. The standard error of the mean (*8*) is listed for each group. In experiments III, IV, and V the calcium and phosphorus content of animals was interpolated from that of an ashed litter mate. In experiments I, II, and VI the calcium and phosphorus content of the animals at the beginning of the experiment was interpolated from that of the means, as listed above. In each experiment the results obtained on each animal which started the experiment are included except in the case of five sets of three animals in which the ash was disposed of by mistake. In determining the calcium and phosphorus content of rats, the whole animal was analyzed, including the intestinal tract and its contents. At the conclusion of feeding experiments, the food intake was reduced slightly on the day before killing to avoid an excessive amount of food in the intestinal tract at the time of death.

Table II. Composition of Phosphate Fertilizers and c. p. Calcium Metaphosphate

Compound Tested	Total P, %	Citrate-Insol. P, %	Ca, %	Fe_2O_3, %	F, %	SiO_2, %	Sieve Size[a]	% through Sieve
Fused phosphate rock I (3.4% Al_2O_3)	12.7	1.0	31.9	2.9	0.05	20.1	170	88
Fused phosphate rock II	13.1	1.5	32.4	3.5	0.22	19.4	40	90
Ca metaphosphate fertilizer (2.1% Al_2O_3)	27.7	0.9	17.2	2.8	0.57	6.4	70	89
$Ca(PO_3)_2$, c. p.	31.1	4.4	21.1	...	..	..	140	92

[a] U. S. standard.

Calcium and Phosphorus Content of Fertilizers, Foods, and Animals. In the case of fertilizers and foods, the analytical determinations were made according to standardized procedures of the Association of Official Agricultural Chemists (*1*). The entire rat was ashed in accordance with procedure 10 in Chapter XXXIV except that a temperature of 550° C. was employed. The ash was treated as in procedure 8*a* in Chapter II (*1*) made up to 200 ml., and filtered. A 10-ml. aliquot was taken for each calcium and phosphorus determination. Phosphorus was determined according to procedure 9 of Chapter II, and calcium according to procedure 10 of Chapter XII (*1*), except that the precipitated calcium was determined gravimetrically as CaO.

CALCIUM AND PHOSPHORUS RETENTION

The results of all experiments are summarized in Table III and Figure 1.

Experiment I. Although the amount of calcium in the basal diet was determined chemically, this point was checked by rat assay for its available calcium content. When phosphorus, but no calcium, was added to the basal diet, an average of only 1 mg. of calcium was stored by each rat during the 30-day period.

Experiment II. The amount of phosphorus available in the basal diet for the rat was ascertained in this experiment. When calcium, but no phosphorus, was added to the basal diet, an average of only 7 mg. of phosphorus was stored by each rat during the 30-day test. In addition, on a low-phosphorus diet these rats showed a significant net loss of body calcium. This is in accordance with experiments of Day and McCollum (*4*). Their explanation is that young rats on a low phosphorus intake require phosphorus for growth of soft tissue; an insufficient amount is available from the diet and so it is mobilized from the bone. The associated bone calcium can no longer be utilized in the bone and is not required in the soft tissues; therefore it is excreted in the urine.

Experiment III. Each experiment used to test the availability of the phosphorus in the fertilizers investigated contained phosphorus from three sources as follows: 0.04 per cent in the basal diet, 0.04 per cent in a salt of known good availability, and 0.08 per cent from the fertilizer under test. It was considered desirable to investigate the amount of

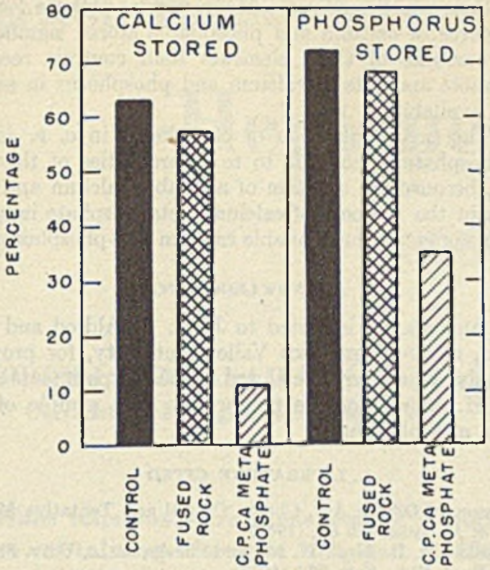

Figure 1. Percentage of Calcium and Phosphorus Stored by Control Rats and by Rats Given Fused Rock Phosphate Fertilizer or C. P. Calcium Metaphosphate. (Data Derived from Experiment V by Combining Results on Males and Females)

phosphorus which would be stored if the animals received phosphorus from two of these sources—namely, 0.04 per cent from the basal diet and 0.04 per cent from added salts of good availability. This procedure was followed with diet 525, which afforded only 53.6 per cent of the storage of phosphorus which resulted when the phosphorus was present at a level of 0.16 per cent as in diet 536.

In subsequent tests of fertilizers in experiments IV and V, the storage abilities of the animals for calcium may be compared with those in experiment I, and the storage abilities of the animals for phosphorus may be compared with those in experiment III.

Experiment IV. This shows that, in regard to storage of calcium and phosphorus, fused rock phosphate containing 0.05 per cent fluorine compares favorably with the salts of known availability in diet 536. This point was confirmed with seventy rats in two other analogous mineral balance experiments using the Hubbell, Mendel, and Wakeman basal salt mixture. In addition, experiment IV demonstrates that controls stored significantly larger amounts of phosphorus than comparable animals which received calcium metaphosphate fertilizer as a source of phosphorus.

Experiment V. Fused rock phosphate containing 0.22 per cent fluorine was shown to be a good source of calcium and phosphorus for the rat when the tests were made during a period of 30 days. It should be noted that in experiments IV and V the calcium content of the fertilizer diets was about 5 per cent higher than that of control diet 536. A preliminary experiment indicated that this difference should be introduced so that the available calcium in the fused rock phosphate fertilizer would approximate that of control diet 536. When calcium metaphosphate fertilizer was tested, only 0.8 mg. of phosphorus per gram of food was stored, in comparison with 1.09 mg. per gram of food of controls; consequently, it was considered possible that the calcium metaphosphate fertilizer might contain some impurities which are toxic for rats. To check this hypothesis, pure $Ca(PO_3)_2$ was prepared by the fusion of $Ca(H_2PO_4)_2.H_2O$ at approximately 1000° C., and the purity of the resulting $Ca(PO_3)_2$ was confirmed by chemical analysis. This calcium metaphosphate was used in experiment V; as shown in Table III, c. p. $Ca(PO_3)_2$ is not a satisfactory source of phosphorus for rats. The results of experiment V are expressed graphically in Figure 1.

Experiment VI. Although diet 540, containing c. p. $Ca(PO_3)_2$, has 0.119 per cent available calcium, only a slight amount of the element was stored by the animals. This would indicate that in this experiment the phosphorus of calcium metaphosphate was only slightly available to the rats. To test this hypothesis, experiment VI was set up using diets

Table III. Calcium and Phosphorus Retention on Control Diets as Compared with Fused Rock and Calcium Metaphosphate Fertilizers and Pure Calcium Metaphosphate

Expt. No.	Diet		Sex and No. of Animals		Av. Food Intake, G.	Av. Wt. Gain, G.	Ca Stored		P Stored		
	No.	Type					Mg.	%[a]	Mg.	%[a]	Mg./g. of food
I	535	Control basal diet; 0.19% P added, no Ca added	M	4	271	52	1	0.1	108	17.5	0.40
			F	2	244	45	1	0.1	101	18.0	0.41
II	552	Control basal diet; 0.19% Ca added, no P added	M	8	146	26	−51	0.0	7	12.2 ± 5.0	0.05
III	525	Control basal diet; 0.19% Ca and 0.04% P added	M	10	276	63	104	17.6 ± 1.7	165	74.2 ± 2.1	0.59
			F	7	262	56	132	23.9 ± 1.4	160	75.9 ± 1.1	0.61
IV	536	Control	M	14	256	81	294	54.6 ± 1.5	285	69.6 ± 0.9	1.11
			F	5	233	58	291	59.7 ± 2.5	248	66.7 ± 1.6	1.07
	537	Fused rock (0.05% F)	M	14	256	80	289	50.8 ± 2.0	280	68.0 ± 1.8	1.09
			F	5	233	60	279	54.4 ± 3.2	240	64.5 ± 3.2	1.03
	538	Ca metaphosphate fertilizer	M	14	256	77	134	23.6 ± 3.0	201	49.4 ± 1.9	0.79
			F	5	233	55	164	32.3 ± 3.2	186	50.2 ± 1.9	0.80
V	536	Control	M	12	227	65	292	61.4 ± 2.4	261	71.9 ± 3.1	1.15
			F	8	207	53	284	65.0 ± 2.4	241	72.9 ± 1.3	1.16
	539	Fused rock (0.22% F)	M	12	227	61	291	58.4 ± 1.7	256	70.5 ± 1.9	1.13
			F	8	207	50	260	56.6 ± 1.7	221	67.0 ± 1.9	1.07
	540	Ca metaphosphate c. p.	M	12	227	54	44	9.0 ± 2.8	125	34.6 ± 3.1	0.55
			F	8	207	47	62	12.6 ± 5.4	119	35.1 ± 3.7	0.56
VI	541	Control	M	2	254	85	637	47.5	361	69.9	1.61
			F	2	262	67	600	45.1	326	63.1	1.45
	542	Sol. Ca as $Ca(PO_3)_2$	M	2	180	37	75	8.1	92	22.9	0.53
			F	2	175	22	53	8.9	84	21.6	0.50
	542a	Sol. Ca as $Ca(PO_3)_2$; sol. P	M	2	274	88	420	34.4	307	40.9	1.27
			F	2	272	63	463	37.6	305	42.2	1.31

[a] ± Standard error of the mean (8).

541, 542, and 542a. In diet 542 pure $Ca(PO_3)_2$ was relied upon as the source of phosphorus, but an additional 0.331 per cent of calcium was provided from $CaCO_3$. Diet 542 shows a restricted utilization of both calcium and phosphorus. The addition of 0.08 per cent phosphorus in the form of KH_2PO_4 as in diet 542a, however, produced an excellent storage of both calcium and phosphorus, an indication that the $Ca(PO_3)_2$ was not inherently toxic, but rather that the phosphorus of c. p. $Ca(PO_3)_2$ was largely unavailable for the nutrition of the rat. Since experiment VI contained only four rats in each group, it was repeated with a similar number of rats; entirely comparable results were observed.

NUTRITIONAL AND TOXICITY ASPECTS

The net gain in weight of the rats on the various diets is shown in Table III. Experiments IV and V were designed to test the availability of the calcium and phosphorus in various phosphate fertilizers. Therefore the food intake of littermate rats was kept the same and extreme differences in growth are not demonstrable. Unrestricted feeding experiments with and without fertilizers would be necessary to test this point. Likewise, since the experiments lasted only for 30 days, no statement can be made concerning the toxicity of these fertilizers for rats. Independent experiments have been set up to test the rate of growth and toxicity of these fertilizers over a feeding period of three generations.

The ratio of fluorine to phosphorus concentration is intimately tied up with the toxicity of defluorinated phosphate rock fertilizers. In a summary of the fluorine problem in livestock feeding, the National Research Council's Committee on Animal Nutrition states that, from a critical study of published data of a quantitative nature, a concentration of 0.01 per cent fluorine in the total dry feed appears to be the approximate border line between safe and unsafe levels for swine, sheep, and cattle (*14*). As a conservative figure "the committee recommends that the permissible levels of fluorine in the total dry feed of an animal be considered tentatively as 0.003 per cent for cattle, sheep, and swine".

Assuming no distortion of the calcium and phosphorus ratio and a considerable proportion of the dietary phosphorus present in an available form, the minimum daily requirements of growing rats for phosphorus would be satisfied by 0.2 per cent phosphorus in the entire ration on a dry weight basis (*17*). If fused phosphate rock containing 0.22 per cent fluorine were used in compounding a ration for rats, half the daily minimum requirements of phosphorus could be provided, and only 0.0017 per cent fluoride would be added to the ration. Nevertheless, the extension of these observations to the feeding of farm animals must await satisfactory nutritional and toxicity tests of these fertilizers on such animals.

A survey of the literature has revealed no pertinent references to fused or defluorinated rock phosphate fertilizer or calcium metaphosphate fertilizer as a source of phosphorus or calcium for animals.

MacLeod and Utley (*12*) have presented evidence showing that the phosphorus of calcium metaphosphate fertilizer was not stored as well as phosphorus fed as the orthophosphate to control rats.

SUMMARY

1. Under the conditions of these experiments, fused rock phosphate fertilizers containing 0.05 and 0.22 per cent fluorine have demonstrated that a high proportion of the calcium and phosphorus in these compounds is available for the nutrition of the rat. (These experiments were not designed to test the toxicity of these fertilizers for rats.)

2. Rats which received calcium metaphosphate fertilizer as a source of calcium and phosphorus stored significantly lower amounts of these elements than controls receiving comparable amounts of calcium and phosphorus in salts of known availability.

3. The small utilization of phosphorus in c. p. calcium metaphosphate is not due to toxic properties of this compound, because the addition of available calcium and phosphorus in the presence of calcium metaphosphate induced a normal storage of the available calcium and phosphorus.

ACKNOWLEDGMENT

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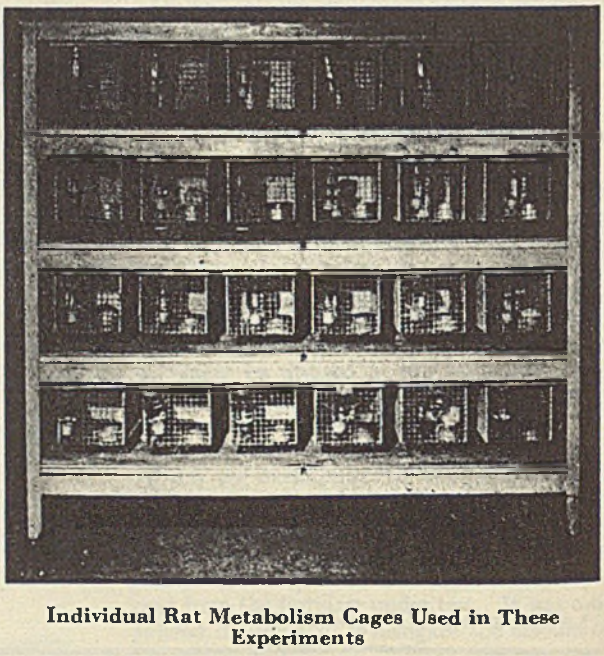

Individual Rat Metabolism Cages Used in These Experiments

SURFACE TENSION OF
n-Heptane and *n*-Butane
CONTAINING DISSOLVED NITROGEN

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Surface tensions were measured of *n*-heptane containing dissolved nitrogen at 200, 500, and 1000 pounds per square inch at 77°, 131°, and 185° F., and of *n*-butane containing nitrogen at these pressures at 77° F. The data were used to compute a parachor for nitrogen dissolved in *n*-heptane of 41. When dissolved in *n*-butane, the parachor for nitrogen is 60 which is in agreement with the value obtained for pure nitrogen.

NITROGEN dissolves in liquid hydrocarbons, as reported by Johnson and Boomer (*2*) for nitrogen in *n*-heptane and by Frolich and co-workers (*1*) for nitrogen in several hydrocarbons, including *n*-butane. The dissolved nitrogen may be expected to reduce the surface tension of the liquid in a manner similar to the effect shown for methane dissolved in propane (*7*). Surface tension data on hydrocarbons containing nitrogen provide the necessary information for computing the parachor for nitrogen. This parachor provides a method for evaluating the effects of nitrogen on the surface tension of hydrocarbon mixtures.

Surface tension measurements were made in the apparatus developed by Weinaug (*7*). The capillary tube contained in a glass-windowed pressure cell was calibrated in place with benzene, giving an apparent radius of 0.02168 cm. as compared with the 0.02177 previously measured (*7*).

n-Heptane was obtained from the California Chemical Company (d_4^{20} 0.68385), and C. P. *n*-butane was furnished by the Phillips Petroleum Company. Commercial water-pumped nitrogen under pressure was used.

The measurements of capillary rise were made with a cathetometer which could be read to 0.001 cm. with a vernier. From two to four readings were taken at each condition with individual readings varying up to 0.005 cm. from the reported value. The capillary rise for *n*-butane and for *n*-heptane in the presence of nitrogen at one atmosphere was obtained prior to injecting nitrogen into the cell. Nitrogen was admitted successively to give an equilibrium pressure of 200, 500, and 1000 pounds per square inch. Three isotherms were measured for *n*-heptane corresponding to the temperatures used by Johnson and Boomer, 77°, 131°, and 185° F. The measurements on nitrogen-butane solutions were taken only at 77° F., since solubility data at other temperatures were not available. The capillary rise data at measured temperatures and pressures are given in Table I.

The calculation of surface tension requires the density of the liquid and vapor phases. The densities in Table I were computed using the methods previously described (*4*, *5*). The apparent density of nitrogen dissolved in *n*-heptane was computed to be 0.49 gram per cc. from Johnson and Boomer's data at 1482 pounds per square inch (*2*). The compositions of the liquid phases were calculated for the *n*-heptane series by assuming a straight-line solubility from atmospheric pressure to 1482 pounds per square inch. The solubility data (*1*) were used to obtain liquid composition for nitrogen in *n*-butane. The vapor phase compositions were computed using ideal equilibrium constants. These compositions provided sufficient information for the density computations.

The surface tensions of the equilibrium liquids (Table I) were computed from the capillary rise, the difference in density between the liquid and vapor, the apparent radius of the capillary, and the usual constant. The data are plotted in Figure 1. The atmospheric pressure value for *n*-heptane at 77° F. was obtained by adjusting the 72° F. value in accord with the known surface tension change with temperature (*3*). The 131° and 185° F. values for *n*-heptane at atmospheric pressure were computed from the parachor (*6*, *7*) for *n*-heptane of 311 calculated from the measurement at 72° F.

TABLE I. SURFACE TENSION DATA

Temp.° F.	Pressure, Lb./Sq. In. Abs.	Capillary Rise, Cm.	Calcd. Mole Fraction N_2 in Liquid	Calcd. Density, Gram/Cc. Liquid, d_L	Vapor d_V	$d_L - d_V$	Surface Tension, Dynes/Cm.
			n-Heptane–Nitrogen				
77	214	2.663	0.0193	0.6785	0.0172	0.6613	18.71
	514	2.535	0.0455	0.6789	0.0416	0.6373	17.16
	1016	2.351	0.0856	0.6785	0.0820	0.5965	14.90
131	214	2.282	0.0211	0.6533	0.0162	0.6371	16.12
	514	2.208	0.0494	0.6535	0.0379	0.6156	14.44
	1016	2.018	0.0930	0.6529	0.0741	0.5788	12.41
185	214	2.054	0.0229	0.6262	0.0161	0.6101	13.31
	513	1.921	0.0532	0.6262	0.0360	0.5902	12.04
	1001	1.787	0.1002	0.6252	0.0693	0.5559	10.55
			n-Butane–Nitrogen				
77	216	1.897	0.0312	0.5750	0.0207	0.5543	11.12
	514	1.760	0.0725	0.5765	0.0448	0.5317	9.95
	1015	1.485	0.1342	0.5850	0.0855	0.4995	7.89
			n-Heptane				
72.4	14.3	2.775	...	0.682	...	0.682	20.11
			n-Butane				
77	35	2.043	...	0.5824	0.0000	0.5764	12.58

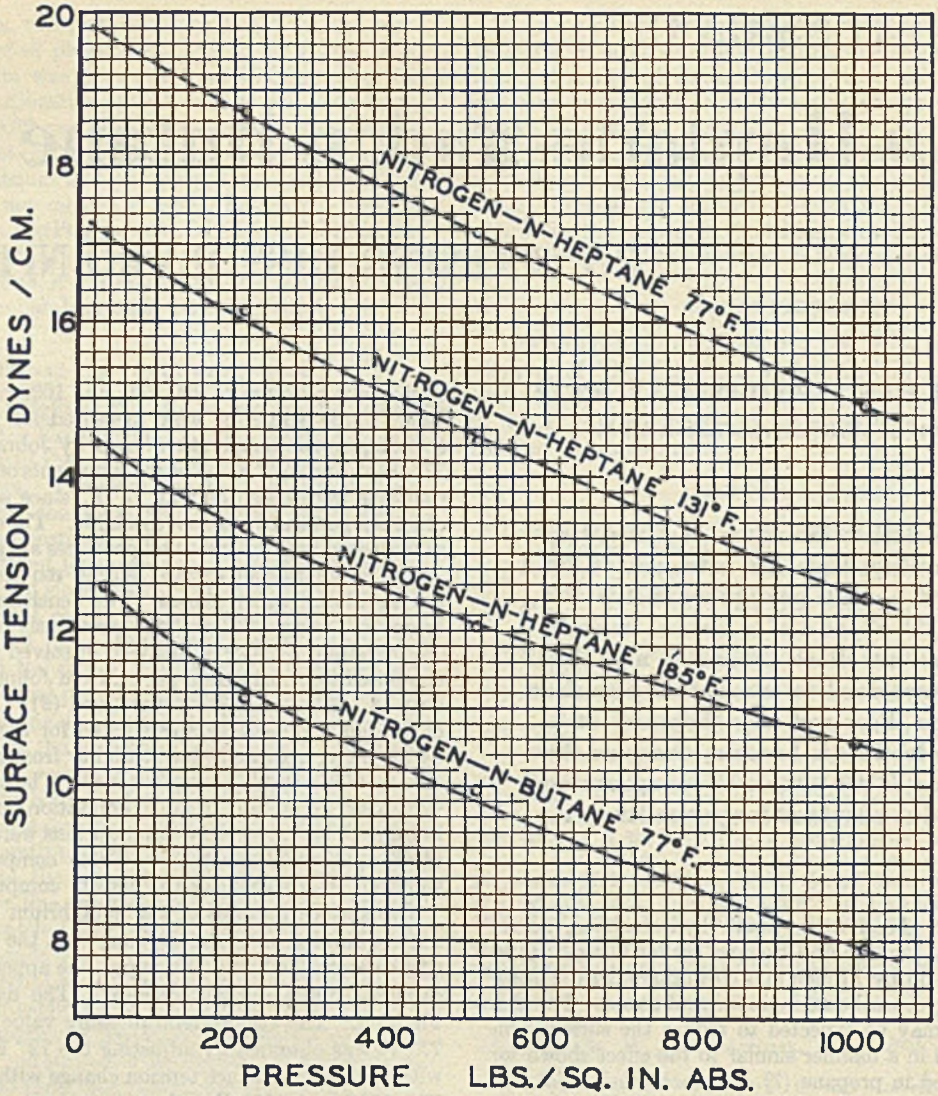

Figure 1. Effect of Dissolved Nitrogen on Surface Tension of *n*-Heptane and *n*-Butane

The reductions in surface tension due to the dissolved nitrogen at 1000 pounds per square inch vary from 20 to 29 per cent of the surface tension without nitrogen for concentrations of 8.5 to 13.4 mole per cent (2.5 to 6.9 weight per cent) nitrogen.

PARACHOR FOR NITROGEN DISSOLVED IN HYDROCARBONS

Parachors provide the necessary characterization of a substance to permit computation of the surface tension of a mixture from its composition by the following equation (*7*):

$$\gamma^{\frac{1}{4}} = P_1\left[x_1\frac{d_L}{M_L} - y_1\frac{d_V}{M_V}\right] + P_2\left[x_2\frac{d_L}{M_L} - y_2\frac{d_V}{M_V}\right] \qquad (1)$$

where γ = surface tension, dynes/cm.
P = parachor for component
x = mole fraction of component in liquid phase
y = mole fraction of component in vapor phase
d_L = density of liquid phase, grams/cc.
d_V = density of vapor phase, grams/cc.
M_L = molecular weight of liquid phase
M_V = molecular weight of vapor phase
Subscripts 1, 2 = constituents 1 and 2

For a pure hydrocarbon at atmospheric pressure, the parachor may be computed from a surface tension measurement, the density of the liquid, and the molecular weight. These parachors may then be used for the constituent when it is a component in a hydrocarbon mixture (*7*).

The parachor for nitrogen was computed from its surface tension at its boiling point (8.85 dynes), density difference of liquid and vapor (0.804 gram per cc.), and molecular weight as 60. However, this value may not hold for nitrogen dissolved in hydrocarbons at the temperature conditions of this study.

The above equation may be used to compute the parachor for nitrogen from the surface tension of the solutions and the compositions of the phases. Also, the surface tension of the mixtures may be computed for various parachors for nitrogen. The latter was done in Table II, using parachor values of 41 and 60. The parachor of 41 was selected as giving the least average deviation between the computed surface tension and the smoothed values. The results of using 60 as the parachor in the heptane-nitrogen mixtures demonstrates that the 1000-pound points are more significant for evaluating the correct parachor than the low pressure values.

TABLE II. CALCULATION OF SURFACE TENSION FROM NITROGEN PARACHORS

Temp., ° F.	Pressure, Lb./Sq. In. Abs.	Surface Tension, Dynes/Cm.		A*	B**	A + B	Surface Tension, Dynes/Cm.			
							N Parachor = 41		N Parachor = 60	
		Exptl.	Smoothed				Calculated	Smoothed minus calcd.	Calculated	Smoothed minus calcd.
n-Heptane–Nitrogen[a]										
77	214	18.71	18.7	2.094	−0.019	2.075	18.54	+0.16	18.25	+0.45
	514	17.16	17.15	2.078	−0.047	2.031	17.02	+0.13	16.32	+0.83
	1016	14.90	14.9	2.050	−0.094	1.956	14.64	+0.26	13.39	+1.51
131	214	16.12	16.0	2.013	−0.016	1.997	15.90	+0.10	15.65	+0.35
	514	14.44	14.5	1.998	−0.040	1.958	14.70	−0.20	14.16	+0.34
	1016	12.41	12.45	1.963	−0.079	1.884	12.60	−0.15	11.64	+0.81
185	214	13.31	13.3	1.938	−0.013	1.925	13.73	−0.43	13.53	−0.23
	513	12.04	12.1	1.901	−0.033	1.868	12.18	−0.08	11.76	+0.34
	1001	10.55	10.55	1.870	−0.067	1.803	10.57	−0.02	9.83	+0.72
n-Butane–Nitrogen[b]										
77	216	11.12	11.25	1.838	−0.006	1.832	11.26	−0.01	11.19	+0.06
	514	9.95	9.8	1.796	−0.022	1.774	9.90	−0.10	9.68	+0.12
	1015	7.89	7.9	1.747	−0.049	1.698	8.31	−0.41	7.80	+0.01

* $A = P_1\left[x_1\frac{d_L}{M_L} - y_1\frac{d_V}{M_V}\right]$ for hydrocarbon.

** $B = P_2\left[x_2\frac{d_L}{M_L} - y_2\frac{d_V}{M_V}\right]$ for nitrogen.

$A + B$ = fourth root of surface tension.

[a] P for *n*-heptane = 311.2.

[b] P for *n*-butane = 190.1

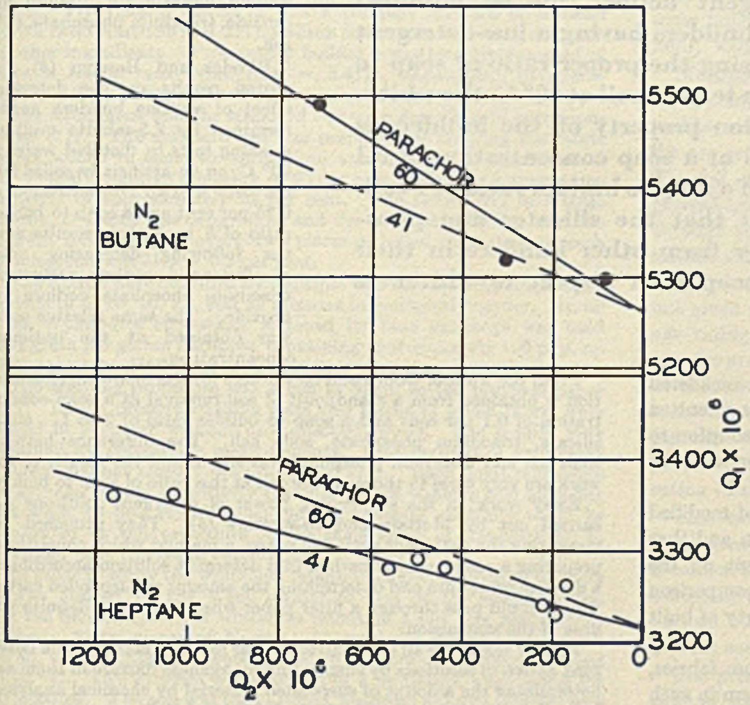

Figure 2. Plot of Data Using Equation 2

To demonstrate the agreement between the experimental data and Equation 1, the equation is rewritten as follows:

$$Q_1 = \frac{P_2}{P_1}Q_2 + \frac{1}{P_1} \tag{2}$$

where $Q_1 = \dfrac{\left(x_1\dfrac{d_L}{M_L} - y_1\dfrac{d_V}{M_V}\right)}{\gamma^{\frac{1}{4}}}$ $\quad Q_2 = \dfrac{\left(x_2\dfrac{d_L}{M_L} - y_2\dfrac{d_V}{M_V}\right)}{\gamma^{\frac{1}{4}}}$

P_1 = parachor for hydrocarbon (311.2 *n*-heptane, 190.1 *n*-butane)
P_2 = parachor for nitrogen (60 and 41)

Constant parachors for the two constituents permit plotting Q_1 (for hydrocarbon) as a straight-line function of Q_2 (for nitrogen) for each measurement with the ratio of the parachors as the slope and the reciprocal of the parachors as the intercepts. Figure 2 gives the lines for both 60 and 41 as the nitrogen parachor. Although the value of 60 computed from pure nitrogen satisfies the point of high nitrogen concentration in butane, this value does not satisfactorily represent the nitrogen–*n*-heptane surface tension data. The parachor of 41 computed as showing a minimum difference between experimental and calculated surface tensions gives a line through the values for the nitrogen-heptane mixtures. The scattering of the points around the latter line indicates no trend in the parachor with changes in nitrogen concentration due to the increase of pressure or temperature.

These computations involve calculated compositions and densities of the two phases. Nitrogen–*n*-heptane solutions at 1482 pounds at each temperature were the basis for the liquid density calculations, and they should be more reliable for the heptane solutions than for the butane solutions. It should be noted that these phase densities were used in computing the experimental surface tensions as well as in the parachor comparison.

Parachors of hydrocarbons remain constant for the pure substances and for varying concentrations in mixtures. The results on nitrogen dissolved in *n*-heptane show that the parachor remains constant at 41 while the results on nitrogen dissolved in *n*-butane indicate that the parachor of 60 computed from pure nitrogen is satisfactory. Although the computation of the parachor for nitrogen from surface tension data is sensitive to small errors in measurement, the data indicate that the parachor for nitrogen dissolved in all paraffin hydrocarbons may not be a constant.

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Properties of Detergent Solutions

COMPARISON OF DETERGENT ACTION AND WHITENESS RETENTION OF LAUNDRY SOAP BUILDERS

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In washing tests made at 60° C. with artificially soiled muslin the effect of 0.05 per cent of various alkaline builders on the detergency of 0.1 per cent soap solutions is investigated. The results of a previous paper (*11*) are studied, and it is shown that high detergent action can be obtained with some builders having a low detergent rating by using the proper ratio of soap to builder. In tests of soil at 60° C. the whiteness retention property of the builders is investigated at a soap concentration of 0.1 per cent and a soap to builder ratio of 1 to 1. It is shown that the silicates and phosphates differ from other builders in their action on soap with respect to whiteness retention.

THE term "detergency" as applied to the laundry field has in its broadest sense often been used to imply the permanent removal of soiling matter from fabrics. It has sometimes been confused with the terms "suspending power" and "whiteness retention", and the three factors have often been considered equivalent. Although it seems logical to regard detergency, suspending power, and whiteness retention as interdependent, a definite line of demarcation may be drawn.

In this series of papers (*1*, *11*) the removal of soiling matter from fabrics is considered as detergency, whether such removal be permanent or temporary. The power of a detergent solution to hold soil in suspension and thus prevent settling is considered as the suspending power of that solution. Whiteness retention is considered a measure of the ability of a detergent solution to prevent the deposition of soil on fabrics from a suspension of the soil in solution.

The second paper (*11*) showed that the addition of modified soda to soap solutions increases their detergent action and that the increase in detergent action is largely dependent on the modified soda concentration. The present study is a comparison of the detergent action and whiteness retention property of built soap solutions.

Not only must a detergent solution remove soil from fabrics, but it must also change the characteristics of the system in such a way as to minimize redeposition. Some builders are very effective with respect to soil removal but not with respect to whiteness retention. On the other hand, some builders possess both properties. The comparison of laundry soap builders presented in this paper is based entirely on soil removal and whiteness retention studies, and should not be taken as a guide to over-all efficiency, since other properties such as rinsibility, water softening action, etc., are of considerable importance.

Previous work by Snell (*10*) on detergency gave a comparison of various builders as determined by 10-minute multiple washing tests in distilled water at 40° C. with artificially soiled fabrics at a soap concentration of 0.1 per cent and a soap to builder ratio of 1 to 1. Based on several factors, he obtained the following classification in order of decreasing efficiency: sodium orthosilicate, sodium metasilicate, sodium metasilicate–soda ash blend, caustic soda, modified soda, soda ash.

Morgan (*6*) also presented laboratory work on the relative detergent efficiency of various laundry builders shown by multiple 10-minute washing tests in distilled water at 50° C. with artificially soiled fabrics. He presented results which show the following decreasing order of efficiency at a soap concentration of 0.1 per cent and a soap to builder ratio of 2 to 1: sodium metasilicate, soda ash, trisodium phosphate, sodium hydroxide. At a soap to builder ratio of 2 to 1, only a slight difference was found between soda ash and trisodium phosphate. The relative efficiency, however, at the optimum builder concentration was considerably different; in decreasing order of efficiency it was: sodium metasilicate, sodium hydroxide, trisodium phosphate, soda ash.

Rhodes and Bascom (*8*) presented results on the detergent effect of various builders as determined by 7.5-minute multiple washing tests in distilled water at 40° C. on an artificially soiled fabric. At a soap concentration of 0.25 per cent and a soap to builder ratio of 5 to 1 their results gave the following decreasing order of efficiency: sodium carbonate, trisodium phosphate, sodium hydroxide. The same relative order was obtained at the optimum concentration.

From the work of Cobbs and co-workers (*3*) the following classification is obtained from a standpoint of soil removal at a soap concentration of 0.1 per cent and a soap to builder ratio of 2 to 1: metasilicate, trisodium phosphate, soda ash. The difference between soda ash and trisodium phosphate was small, and the results of this work are very close to those of Morgan at this ratio of soap to builder.

Early work on the suspending power of detergent solutions was carried out by McBain and co-workers (*5*). They proposed, for measuring the detergent action of soaps, a method which consisted of preparing a suspension of carbon in a detergent solution according to a definite procedure and determining the amount of suspended carbon which would pass through a filter paper when filtering a definite volume of the suspension.

In later work by Fall (*4*) an attempt was made to measure the detergent action of solutions by suspending manganese dioxide in them and determining the amount of suspended material by chemical analyses.

Snell (*9*) carried out work similar to that of Fall, using a soil composed of umber, mineral oil, a saponifiable oil, and oleic acid. He showed that silicates and phosphates were more effective than sodium hydroxide, sodium carbonate, and modified soda in holding materials in suspension.

Carter (*2*) carried out studies of this type by preparing suspensions of various soils in detergent solutions and agitating pieces of white cloth in the suspension using the Launder-Ometer. Carter showed that the silicates and phosphates prevented deposition to a larger extent than did sodium carbonate, sodium hydroxide, and modified soda. Sodium metasilicate was less effective than other silicates, and the silicates as a whole were not so effective against a carbonaceous soil as against other types of soil.

More recent work was carried out by Powney and Noad (*7*) on ilmenite as a soil. Their work was conducted on various unbuilt sodium salts of fatty acids, alkaline builders, and a few built soaps. In general, the silicates were found to be more effective than sodium carbonate and sodium hydroxide.

WASH TESTS

The commercial laundry soap used in this investigation has already been described (*1*). The various builders were of commercial grade with the exception of sodium hydroxide, which was C. P. grade. The modified soda was the same as that described previously (*1*). The following builders were studied: sodium hydroxide, sodium meta-

TABLE I. SOIL REMOVAL FOR BUILT SOAP SOLUTIONS

Total Washing Time, Min.	None	$NaHCO_3$	Modified soda	Na_3PO_4.-12H_2O	Na_2CO_3	Na_2SiO_3.-5H_2O	P. B. No. 1	P. B. No. 2	NaOH	P. B. No. 3
	Per Cent Change in Reflectivity with Following Builders[a]:									
5	5.5	5.0	5.5	6.4	6.0	6.8	6.6	6.8	6.6	6.1
15	6.4	7.3	8.8	9.1	10.0	10.9	10.6	11.1	10.5	11.6
30	8.8	9.2	11.3	13.0	13.1	13.2	13.2	14.9	13.6	15.3
50	10.4	10.9	14.5	15.6	17.1	17.3	18.2	18.4	21.1	19.1
75	14.9	13.5	18.2	19.6	19.9	18.4	21.2	20.2	22.2	21.4
Av. % change in reflectivity during 75 min. of washing	9.3	10.0	12.24	13.55	14.08	14.22	15.08	15.35	15.78	15.78
Rate compared to soap as 1	1	1.08	1.32	1.46	1.51	1.53	1.62	1.65	1.70	1.70

[a] All solutions contain 0.1 per cent soap and 0.05 per cent builder.

silicate, sodium carbonate, trisodium phosphate, modified soda, sodium bicarbonate, proprietary builder 1, proprietary builder 2, and proprietary builder 3 (abbreviated as P. B. No. 1, P. B. No. 2, and P. B. No. 3 in the graphical representations).

Proprietary builder 1 was composed of silicates (molal ratio $Na_2O:SiO_2$ = 2.6:1), sodium carbonate, and tetrasodium pyrophosphate. Proprietary builder 2 was a complex mixture of silicates (molal ratio $Na_2O:SiO_2$ = 2:1), sodium carbonate, and small amounts of other ingredients. Proprietary builder 3 was largely composed of silicates (molal ratio $Na_2O:SiO_2$ = 3.4:1), tetrasodium pyrophosphate, and moderate amounts of organic materials.

The equipment and the standard soil were described in a previous paper (*11*). The standard soil was prepared by allowing the fabric before soiling to come to equilibrium at a dry bulb temperature of 76° F. and a relative humidity of 30 per cent, and had an average reflectivity of approximately 22 per cent. The reflectivity of a large number of pieces was determined and the samples paired so that the average reflectivity of every two pieces of soiled cloth used in each washing test was 21.9 ± 0.1 per cent.

The results were obtained by multiple wash tests, using single wash periods of 5, 10, 15, 20, and 25 minutes in consecutive order. In all cases Wyandotte city water softened by base exchange was used (0-1 grain per gallon hardness, containing approximately 100 p. p. m. of bicarbonate, HCO_3^-).

The washing procedure was given in detail in the previous paper (*11*). In the present washing tests two pieces of soiled fabric were placed in each jar without any unsoiled fabric. The results were obtained by reflectivity measurements. The method of expressing soil removal has already been described (*11*). Each point represents an average of four reflectivity readings before washing and after the last wash on one set of soiled cloths. Results generally could be duplicated by this procedure on the same batch of standard soil to ±0.5 per cent change in reflectivity.

In order to study the whiteness retention characteristics of builders it was desired to use a soil similar to that on the soiled fabrics. For the determination of whiteness retention a soil was prepared as follows: Sixty grams of Norit C, 60 grams of melted Crisco, and 30 ml. of lubricating oil were placed in 2 liters of Stoddard solvent at 27° C. This mixture was agitated in a miniature wash wheel for 10 minutes. The soil was then filtered, air-dried at room temperature on an absorbent blotter for 48 hours, and placed in a suitable container.

In determining the whiteness retention property of various built soap solutions, 50 mg. of the prepared soil were placed in each of five Launder-Ometer jars containing ten rubber balls, $^3/_8$ inch (9.5 mm.) in diameter and eight steel balls $^1/_4$ inch (6.35 mm.) in diameter. Into each of these jars 100 ml. of the desired detergent solution were poured at a temperature of 140° F. (60° C.). The jars were placed in the Launder-Ometer which was run for 30 minutes at 140° F. At the end of the 30-minute period two pieces, each $2^1/_2$ × $3^1/_4$ inches (8.3 × 6.4 cm.), of Indian Head muslin (desized with Degomma 80 A) were placed in each jar, and the jars were again agitated in the Launder-Ometer. At the end of 5, 10, 15, 20, and 25-minute periods one jar was removed, samples of cloth were rinsed under running Wyandotte water and ironed, and the reflectivity of the cloth was determined with the Hunter reflectometer, using the green filter and a background with a reflectivity of 53.8 per cent. Four reflectivity readings were made on each set of cloths and averaged. The reflectivity of the original white cloth was 75 per cent, and the whiteness retention was calculated by dividing the reflectivity after soil deposition by 75 and multiplying by 100. Results generally could be duplicated by this procedure to ±0.6 per cent whiteness retention.

DETERGENCY RESULTS

In laundry practice the soap to builder ratio varies with the type of alkali as well as with the soil classification, and in general no attempt is made to use optimum soap to builder ratios. In this study a fixed soap to builder ratio of 2 to 1 and a soap concentration of 0.1 per cent was selected as representative of general laundry practice. With some builders such as modified soda this ratio may be somewhat high; with other builders such as sodium hydroxide it may be low.

Multiple wash tests were conducted at 140° F. on all the builders studied, using a soap concentration of 0.1 per cent and a builder concentration of 0.05 per cent. The results in reflectivity are reported in Table I; the data were treated as follows: The soil removal expressed as per cent change in reflectivity was plotted against total washing time, and the best curve was drawn through the experimental points. The curves so obtained were similar and, in some cases, very close together. Since the difference between some builders was small, the various builders were not given a comparative rating at any washing time. An average rating was obtained, however, by measuring with a planimeter the area under the curves of soil removal, as per cent change in reflectivity against time. From this area the average soil removal as per cent change in reflectivity during the entire washing time (75 minutes) was obtained by dividing the area in proper units by the washing time. This gave a comparative rating (Table I and Figure 1) for all builders.

This comparative rating is independent of time and gives much greater weight to all of the experimental points than could a comparative rating at any time period. The graphical representation of Figure 1 shows the comparative detergency of the various built soap solutions as well as their improvement over unbuilt soap.

The present study indicates a comparative order different from that of some previous investigations. These results, however, are not directly comparable to previous work due to modifications in the testing procedure—e. g., soap concentration, builder concentration, standard soil, temperature, etc. Previous standard soils have been prepared by immersing fabrics in soiling sus-

TABLE II. WHITENESS RETENTION OF 0.1 PER CENT SOAP SOLUTIONS BUILT WITH 0.1 PER CENT OF VARIOUS BUILDERS

Total Washing Time, Min.	No Builder	P. B. No. 2	P. B. No. 1	Modified Soda	$NaHCO_3$	Na_3PO_4.-12H_2O	Na_2SiO_3.-5H_2O	P. B. No. 3	Na_2CO_3	NaOH
0	100	100	100	100	100	100	100	100	100	100
5	91	87.2	86.0	86.0	85.0	83.4	82.0	83.0	85.5	82.5
10	86	81.7	80.2	80.8	81.3	78.0	81.0	76.5	81.0	78.8
15	82	79.8	77.4	76.9	76.5	74.6	75.0	73.8	78.0	73.3
20	79	78.7	77.0	74.4	73.5	74.6	73.0	72.1	73.4	70.6
25	78.3	76.0	76.0	71.5	73.0	71.6	70.3	69.6	70.4	69.0
			Whiteness Retention as Read from Graphs							
10	86	82.3	80.4	80.5	80.6	78.0	77.5	76.5	80.6	77.5
25	78.3	76.5	75.6	72.3	72	71.6	71.5	71.0	70.7	69.0
Av. whiteness retention	86.6	83.3	81.6	80.7	80.7	79.2	79.3	78.2	80.7	78.0

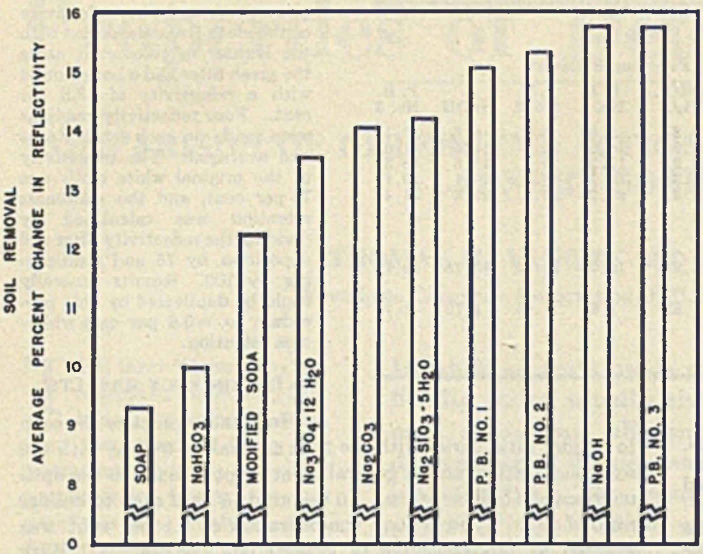

Figure 1. Comparative Soil Removal Capacity of Various Built Soap Solutions

pensions, drying the soil, and then aging it before conducting washing tests. This made it possible to remove a large amount of soil in the first wash in comparison to that removed in later washes. Snell (*10*) showed this clearly when he obtained a brightness regain of over 10 units with distilled water in the first wash. Succeeding washes with distilled water, however, removed very little soil.

The method of preparing the standard soil used in this work included a wash-back so that the amount of soil which could be removed by distilled water was approximately the same in all washes and was very small in all cases. This makes it possible to obtain a much smaller soil concentration in the first wash in comparison to succeeding washes than could be done with previous standard soils. In addition, the washing time of each wash was increased, each one starting with a 5-minute period for the first wash. This procedure made it possible to carry approximately the same soil concentration in the bath during all of the washes. As a result, the effect of redeposition has been minimized in the present study and the results represent actual soil removal to a much greater extent.

Although the techniques, type of water, etc., of this work are not the same as those of previous investigators, some comparison may be made. Both Morgan (*6*) and Cobbs and co-workers (*3*) found metasilicate superior to soda ash and trisodium phosphate at a soap concentration of 0.1 per cent and a soap to builder ratio of 2 to 1. In the present work the same conclusion was arrived at. Under the same conditions Morgan obtained about the same detergent efficiency for soda ash as for trisodium phosphate, while Cobbs and co-workers obtained a slightly higher detergent action with trisodium phosphate than with soda ash. The present work shows soda ash to be slightly better than trisodium phosphate. The agreement between the three papers on these three builders is quite good in view of the varying techniques and type of water.

Both Snell (*10*) and Morgan (*6*) showed caustic to be less effective than metasilicate. Of the builders studied, this material has the highest redeposition tendency and therefore would be expected to show up better under the conditions of the present work. The work of Rhodes and Bascom (*8*) was conducted at a soap concentration of 0.25 per cent and probably should not be compared with other work conducted at a much lower soap concentration.

If the value of the average per cent change in reflectivity during 75 minutes of washing time (Table I) is considered directly proportional to the quantity of soil removed during the five multiple washes, then division of the values for the built soap solutions by the value for soap should give the rate of soil removal compared to soap as one. This treatment yields a value of 1.32 for modified soda. In a previous paper (*11*) the rate of soil removal for soap and soap built with modified soda was presented in terms of a specific soil removal rate, constant K. The ratio of K for the built soap (soap to builder ratio of 2 to 1) and soap alone gives a value of 1.35. This agreement is quite good considering the different methods of approach.

These ratios or comparative rates of soil removal have been calculated for the detergent solutions studied and are given in Table I. By multiplying these values by 100, the detergent efficiency of a built soap solution may be obtained in per cent compared to soap at 100. For example, soap built with proprietary builder 3 (0.1 per cent soap, 0.05 per cent builder) has a detergent efficiency of 170 per cent.

This treatment assumes that the reflectivity *vs.* removable soil content of the cloth is linear over the working range of this study. This would be over the reflectivity range of 22 to 33.2 per cent. A study of Figure 12 of a previous paper (*11*) indicates that, over the greater portion of this range, the relation may be considered approximately linear. This treatment of the data also assumes that the removable soil content of the cloth after five washes with soap and with built soap is not large. The error due to the shape of the curve relating reflectivity to removable soil content, however, becomes progressively larger as one proceeds from the least to the most effective builder.

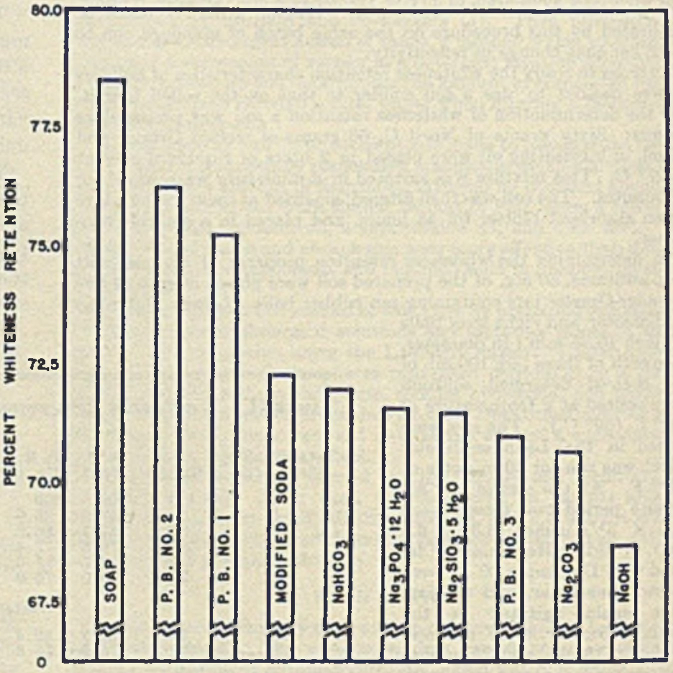

Figure 2. Comparative Whiteness Retention of Various Built Soap Solutions

It is interesting to compare previous results (*11*) (Figures 5 and 6) in which the specific soil removal rate was obtained over a wide range of modified soda concentration. With modified soda at a concentration of 0.2 per cent and a soap concentration of 0.1 per cent, an efficiency of 212 per cent was obtained. From Figure 6 of the previous paper (*11*) the soap to builder ratio necessary with modified soda to get the same detergent efficiency obtained with proprietary builder 3 or sodium hydroxide (the builders rating highest from a detergent point of view) was determined as approximately 1 to 1.2. It thus becomes evident that the same detergency can be obtained with some builders having either a high or low detergency rating (at constant soap concentration) by adjusting the soap to builder ratio.

WHITENESS RETENTION

The experiments were conducted at a soap concentration of 0.1 per cent, since it was desired to study only the effect of the addition of a builder to a commercial soap on whiteness retention. Preliminary experiments showed that unbuilt soap gave the best whiteness retention and that the lowering of whiteness retention by the addition of builder increased with an increase in the builder concentration. In view of this fact, a builder concentration of 0.1 rather than 0.05 per cent was used in the experiments to be presented. Preliminary experiments also indicated that approximately the same relative order among various builders would be obtained at a builder concentration of 0.1 per cent as at a builder concentration of 0.05 per cent.

The fact that unbuilt soap shows a higher whiteness retention than does built soap with respect to carbon soil was also brought out by Carter (*2*). Figure 10 of his paper indicates the effect of various builders on sodium oleate with respect to the deposition of carbon black. This work is not directly comparable with the present work, since a constant built soap concentration was used instead of a constant soap concentration. The drop in whiteness retention obtained by Carter in going from a straight soap to a very lightly built soap, however, is large.

Carter's Figure 10 also indicates that approximately the same order would be obtained with various builders as the builder concentration is increased. Although there is considerable crossing of broken line graphs in Figure 10 as the composition of the built soap is changed, those builders which show a lower rating at one end of the composition axis also show a low rating at the other end.

The results of this study are given in Table II. The data were treated as follows: The whiteness retention data were plotted as a function of time for each builder, and the best curve was drawn through the experimental points. From these curves the whiteness retention at 10 and 25 minutes was read; these readings are also given in Table II. The whiteness retention at the end of the 25-minute period is graphically represented in Figure 2, which shows the effect of various builders.

In addition, the data of Table II were treated as follows: Broken line graphs of whiteness retention against time were prepared for each builder, and the area under each graph was determined with a planimeter. From this area the average whiteness retention was obtained (Table II). This treatment changed the order only slightly and the probable reason for this change will become apparent. Examination of the whiteness retention–time curves for built soaps obtained from Table II indicates two types of curves. This is shown more effectively in Figure 3, where the whiteness retention at the end of a 10-minute period is plotted against that at the end of a 25-minute period.

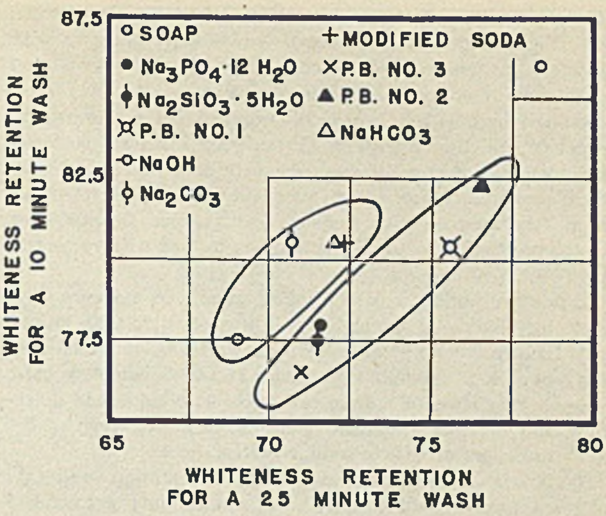

Figure 3. Whiteness Retention of Built Soap Solutions after 10-Minute Wash *vs.* Retention after 25-Minute Wash

Two curves are drawn around the experimental points dividing the builders into two sets, with trisodium phosphate, sodium metasilicate, proprietary builder 1, proprietary builder 2, and proprietary builder 3 in one set, and modified soda, sodium bicarbonate, sodium carbonate, and sodium hydroxide in the other. This treatment shows a difference between those builders high in silicates and phosphates and those high in carbonates and caustic. It indicates that, at early time periods during the initially high deposition of soil from suspension in solutions of soap built with silicates or phosphates, a change takes place in the characteristics of the fabric-soil-detergent-water system so as to diminish further deposition. This change does not occur with the carbonates and sodium hydroxide. This difference is one of degree rather than type and probably depends largely on the composition of the builder.

As the soil concentration is decreased to that common in laundry practice, the amount of deposition per unit time and the deposition during the early time periods are both decreased. In order to show that builders high in silicates have the same action with respect to whiteness retention at lower soil concentrations as they do at high soil concentrations, a set of experiments was run with a soil concentration of 10 mg. per 100 ml. of detergent solution. The results are given in Table III.

Table III. Whiteness Retention Measurements at a Lower Soil Concentration

Total Washing Time, Min.	Whiteness Retention[a]	
	P. B. No. 2	Na_2CO_3
5	93.0	94.2
10	91.5	91.3
15	89.8	89.0
20	89.6	87.4
25	89.5	84.8

[a] All solutions contained 0.1 per cent soap and 0.05 per cent builder.

Table III indicates that at a lower soil concentration the degree of deposition is lower. These data also show the same characteristics as did the data of Table II in that at the early time periods the rate of deposition with proprietary builder 2 is larger than that with sodium carbonate, but with increasing time the rate of deposition with sodium carbonate is larger than with proprietary builder 2.

The silicates and phosphates show an action with respect to whiteness retention not characteristic of other builders but, due to the high deposition at the early washing periods with silicates and phosphates, other types of builders may be as effective in over-all performance. A study of Figure 2 shows that, although modified soda and sodium bicarbonate do not possess the same characteristics as do silicates and phosphates, they are quite effective with respect to whiteness retention. If, however, the washing time had been extended beyond 25 minutes, their effectiveness with respect to whiteness retention would probably have dropped considerably.

Comparison of whiteness retention with detergency results shows that builders which may be exceedingly effective with respect to soil removal are not necessarily effective with respect to whiteness retention. For example, caustic soda, which rates exceedingly high with respect to soil removal, is the poorest with respect to whiteness retention. Proprietary builder 3 possesses a detergent action equal to that of caustic soda and at the same time is measurably superior with respect to whiteness retention. Proprietary builder 2 is very effective with respect to detergency and the most effective of all the builders studied with respect to whiteness retention.

Proprietary builder 1, which differs greatly in make-up from proprietary builder 2, is only slightly less effective than proprietary builder 2 with respect to both whiteness retention and detergent action. Sodium metasilicate and trisodium phosphate, although very close to sodium carbonate with respect to detergency and over-all whiteness retention, exhibit a type of behavior not characteristic of sodium carbonate.

The fact that soil removal and whiteness retention studies do not give the same results indicates that equilibrium is not reached between clean fabrics, soil, and soiled fabrics either under laboratory or commercial laundry conditions. It also indicates that for a series of builders the relative order with respect to their rate of soil removal is different from their relative order with respect to rate of soil deposition.

SUMMARY

From the point of view of detergency, at a soap concentration of 0.1 per cent and a soap to builder ratio of 2 to 1, the soap builders studied may be classified in descending order of effectiveness as follows: Proprietary builder 3, sodium hydroxide, proprietary builder 2, proprietary builder 1, sodium metasilicate, sodium carbonate, trisodium phosphate, modified soda, sodium bicarbonate. Equivalent detergent action may be obtained with builders both high and low in detergent action by adjusting the ratio of soap to builder.

From the point of view of whiteness retention at a soap concentration of 0.1 per cent and a soap to builder ratio of 1 to 1, the soap builders studied may be classified in decreasing order of effectiveness as follows: proprietary builder 2, proprietary builder 1, modified soda, sodium bicarbonate, trisodium phosphate, sodium metasilicate, proprietary builder 3, sodium carbonate, sodium hydroxide. In each of these classifications some of the builders studied are quite close together. In the formulation of proprietary builders, not only should soil removal be considered but also soil deposition, and a proper balance should be obtained.

Beside soil removal and whiteness retention, other properties such as water softening action and rinsibility must be considered when comparing the over-all efficiency of laundry builders.

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IRON ALLOY SCALING

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IN CHOOSING a steel for service at elevated temperature, one must take into consideration not only its resistance to applied stress at the temperature contemplated but also its resistance to scaling, both of which decrease rapidly with increasing temperature above about 1100° F. Because of this situation and of a dearth of reliable information on the progress of scaling of iron alloys over a protracted period, the work reported here was undertaken. A secondary purpose was to learn, from comparable measurements of scaling of a series of related iron alloys at a number of temperature levels, how far it is possible to predict scaling behavior from composition. Accordingly, scaling tests lasting 1000 hours were carried out on duplicate specimens of thirty-six alloys of iron at five temperature levels, 1100°, 1300°, 1400°, 1500°, and 1700° F., though all alloys were not examined at each temperature.

The experimental procedure was a modification of that of Heindlhofer and Larsen (*1*)—namely, to maintain the specimen at constant temperature in an appropriate electric furnace and to weigh it at suitable intervals without withdrawing it from the furnace. To test a single specimen at a time, as they did, when the scaling behavior of a large number of steels at several temperature levels, each over a period of hundreds of hours, is to be compared, requires either an inordinate amount of equipment or an impracticably long time. To surmount this disadvantage, the measurements were made in a furnace, large enough to accommodate thirty-nine specimens simultaneously, so designed that the gain in weight of any specimen could be followed without removing it from the uniform temperature zone of the furnace. A check was made to ensure that no scale dropped off the specimen during the test, both by use of duplicate specimens and by the regularity of the curve of weight against time. At the end of the run one of each pair of specimens was allowed to cool, the scale was removed by pickling in an inhibited acid bath, and the specimen was reweighed as a measure of the amount of metal lost; this served also as a check on the general reliability of the measurements but does not compare in precision with the measured gain in weight of the specimens while still in the furnace. This loss of weight is included as a measure of the thickness of the metal removed by oxidation in 1000 hours at a given temperature so that comparisons in terms of loss of thickness may also be available.

The results are presented (Table II and Figure 2) as the gain in weight by air oxidation per unit of surface in 1 day, 1 week, or 6 weeks at a given temperature. The alloys are arranged in decreasing order of resistance to air oxidation in the range 1100–1300° F.; the significance of the data, like that of any rate of reaction in a heterogeneous system, is relative only. They cannot be readily summarized because each alloy behaves in this respect more or less as an individual; it forms its own oxide layer, whose composition and imperviousness are specific to the alloy, the temperature, and the length of sojourn at the temperature. Consequently, even apparently slight differences in composition of the alloy or in the atmosphere—for instance, the presence of some sulfur compound or even of steam—may exert a substantial influence upon the type of scale and hence upon the progress of scaling. Moreover, the elements in an alloy may differ greatly in tendency to oxidize; therefore at the scale-metal interface the proportion of the more readily oxidizable element (for instance, chromium) may be considerably less than in the alloy as a whole. In view of these possible differences, it is difficult to make many general statements; at present only two are presented:

1. It is not safe to predict the resistance to scaling over a long period from observations extending over only 24 hours or even a week, nor at one temperature from observations at another.
2. The element contributing most to scaling resistance, especially at the highest temperatures, is chromium when present in appreciable concentration, a greater concentration being necessary the higher the temperature; at equal concentration the most effective is probably silicon, but the gain from its use is in practice limited by its deleterious effect upon the working and mechanical properties of iron alloys.

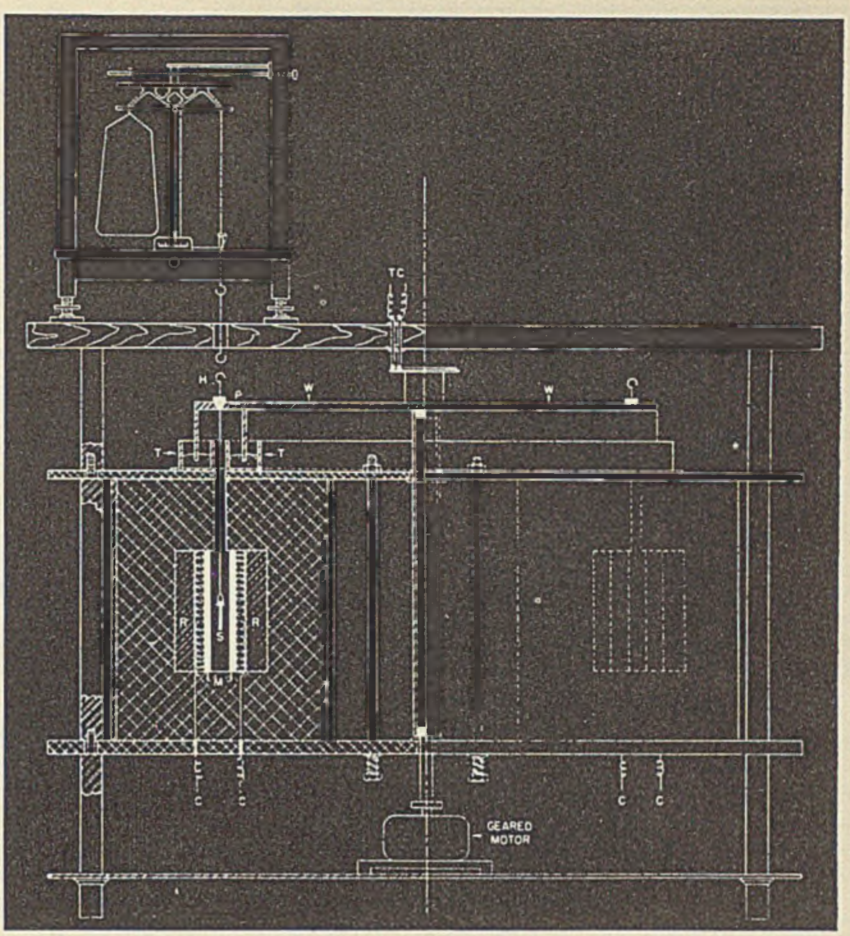

Figure 1. Annular Furnace with a Capacity of Thirty-Nine Specimens Simultaneously

It is to be emphasized that the data have only relative but no absolute significance; that they refer strictly only to oxidation by air at constant temperature; and that even a minor impurity in the air may alter the relative resistance to scaling of the alloys, particularly at the higher temperatures. Moreover, it is not unlikely that differences in prior treatment—resulting, for instance, in differences in microstructure or in the type of initial film formed on the surface—also would affect the relative oxidation resistance of some of the alloys at least.

An apparatus suitable for continual weight gain measurements of the scaling by air oxidation of a large number of specimens simultaneously is described; the results of 1000-hour tests on thirty-six alloys of iron at temperatures ranging from 1100° to 1700° F. are presented. The results show principally that it is not safe to predict long-time scaling resistance from tests of only short duration and that the effect of alloying elements is not generally additive. Of the added elements studied, chromium contributes most to scaling resistance when present in appreciable concentration; for smaller concentrations silicon is the more effective.

FURNACE CONSTRUCTION

The furnace consists of an annular muffle, *M* (Figure 1), 12 inches deep and 2 inches wide; it was made by bending two $^{1}/_{4}$-inch plates of 27-chromium steel and welding the free ends to form two rings, one 34, the other 38 inches diameter, which were then set concentrically. The primary purpose of this muffle is to aid in equalizing the temperature over the annular space in which the specimens move, but it also serves to protect the current windings, *CC*. There are four current windings, each made by shaping a helix, $^{1}/_{2}$ inch in diameter, of No. 18 Nichrome wire, and distributing it over one half of a side of the muffle; the current in each winding is controlled separately by an appropriate transformer. The total resistance of all four windings in parallel is about 8.1 ohms. The maximum temperature for which the furnace was designed is 2000° F. but it has not been used above 1700°.

The windings are backed by refractory brick *RR*, 2 inches thick, and this in turn by insulating block, except for the annular slot above the muffle. A similar slot below the muffle was provided with dampers, but this slot was not used because it produced a chimney effect which caused marked inequalities of temperature, and because experience showed that there is never any lack of oxygen in the atmosphere in contact with the specimens. The base and top of the whole furnace are of asbestos board, 1 and 0.5 inch thick, respectively, held in place by steel bolts; the vertical sides are steel rings, and the whole is supported on an appropriate frame. Surmounting the annular slot are two annular troughs *TT*, of sheet metal, half filled with

Table I. Identification and Composition[a] of Alloys

Number	Composition, % Cr	Mo	Si	Mn	C	Miscellaneous
1	27	(Nominal—not analyzed)				
2	18.1	...	0.32	1.51	0.07	11.1 Ni; 0.82 Cb
3	17.5	...	0.39	0.52	0.05	10.9 Ni; 0.44 Ti
4	18.4	...	0.43	0.28	0.06	9.9 Ni
5	17	(Nominal—not analyzed)				
6	5.21	0.48	1.55	0.26	0.12	...
7	11.9	0.47	0.36	0.38	0.06	...
8	12	(Nominal—not analyzed)				
9	5.46	0.54	1.05	0.42	0.08	0.50 Cb
10	4.86	0.54	1.04	0.40	0.06	0.40 Ti
11	9.47	1.04	0.43	0.43	0.12	...
12	5.45	0.92	0.36	0.54	0.15	...
13	5.18	0.58	0.41	0.36	0.06	0.46 Ti
14	4.09	0.56	0.36	0.40	0.09	0.59 Cb
15	5.16	4.03	0.28	0.27	0.27	...
16	3.19	0.55	1.59	0.46	0.11	...
17	4.50	2.03	0.25	0.40	0.38	...
18	...	5.15	0.27	0.37	0.32	...
19	3.61	...	0.26	0.48	0.37	...
20	0.52	5.02	0.30	0.45	0.34	...
21	1.88	5.08	0.25	0.39	0.41	...
22	0.56	0.56	0.30	0.45	0.32	...
23	4.48	0.59	0.29	0.45	0.37	...
23	5.41	0.52	0.44	0.38	0.12	...
24	1.89	2.04	0.28	0.51	0.36	...
25	2.02	0.52	0.27	0.44	0.35	...
25	2.09	0.46	0.19	0.46	0.12	...
26	...	1.36	0.09	0.36	0.21	...
27	0.51	2.01	0.30	0.45	0.33	...
28	1.78	0.75	0.57	0.52	0.17	...
29	...	0.96	0.17	0.42	0.17	...
30	2.22	1.01	0.14	0.34	0.10	...
31	...	2.11	0.20	0.41	0.33	...
31	...	1.89	0.03	0.32	0.14	...
32	1.97	...	0.28	0.45	0.32	...
33	0.56	...	0.24	0.38	0.37	...
34	1.31	0.48	0.82	0.44	0.13	...
35	...	0.55	0.20	0.42	0.39	...
35	...	0.55	0.15	0.81	0.21	...
35	...	0.53	0.04	0.49	0.14	...
36	...	...	0.23	0.39	0.36	...
36	...	...	0.16	0.50	0.18	...

[a] In all cases phosphorus and sulfur were negligible, being below (usually much below) 0.02%.

sand to serve as a seal in which the rotating member *W* that supports the specimens moves. This member, driven slowly (about 1 r. p. m.) by a geared motor as shown, is essentially a wheel whose rim is an inverted trough, in the upper surface of which are forty small holes equally spaced around the rim. Each of these holes is fitted with a small, loose, keyed plug *P*, to which is attached a Nichrome ribbon. The lower end of the ribbon is provided with a stirrup to support specimen *S* in position in the slot; this plug is keyed to ensure that the specimen remains with its width in the circumference of the muffle and therefore does not lose any scale by coming in contact with the muffle. When the specimen is to be weighed, the rotating member is stopped at the proper place (with the aid of an auxiliary switch in the motor circuit); care is taken that the support moves freely through the hole, and hook *H* is hung on the hook on the wire extending downward from the arm of the analytical balance. The balance is supported on a board 1.5 inches thick which protects it from the heat of the furnace.

Uniformity of Temperature. The temperature at one point in the muffle is controlled by a fixed thermocouple (not shown in Figure 1) in combination with a commercial controller and recorder. The degree of temperature uniformity around the muffle was observed by always having a chromel-alumel thermocouple in a place which otherwise would have been occupied by a specimen; this thermocouple was connected through a simple commutator on the axis of rotation through lead wires *TC* to the measuring circuit; uniformity was attained by appropriate adjustment of current through the four separate semicircular heating elements. In the work later recorded, the variation in temperature of the specimens, as indicated by the rotating thermocouple, was not more than ±10° F. which is good enough in view of the fact that each specimen passes through the whole cycle about once each minute. The thermocouples were recalibrated at appropriate intervals.

The purpose of the sand seal is to aid in attaining a uniform temperature; without it, stray drafts in the room may set up irregular differences of 100° F. or more in the muffle. Care must be taken that none of the sand from the seal works out of its trough and onto any specimen; in that event, a thin adherent scale of ferrous silicate is formed over a relatively large area of the surface of the specimen, so that the change of weight is no longer a significant index of the progress of oxidation of the specimen.

MEASUREMENT OF SCALING

Specimens. The specimens were forged from the material available (usually 1-inch rounds) to a convenient thickness for machining a flat specimen, $2^3/_8 \times 1 \times {}^1/_8$ inch. The forged specimens were all furnace-cooled from 1650° F. Corners and edges were rounded, and the specimen was finished by polishing with 00 emery, as the most convenient means of securing a reasonably reproducible surface; this point is discussed later. Through one end of the specimen was drilled a ${}^1/_8$-inch hole into which was fitted a small porcelain insulator tube to keep the supporting Nichrome stirrup from touching the specimen. The initial weight of the specimen, as well as that of the assembly (specimen + supporting wire + plug) was recorded. The area of the surface was calculated with all the accuracy required for the purpose from the dimensions of the specimen; it is taken as 5.25 square inches (33.9 sq. cm.).

Procedure. When a stationary condition at the desired temperature level had been established in the annular muffle by appropriate adjustment of the controller and of the current through the separate windings, the several specimen assemblies (previously weighed, as noted above) were placed in position, and the rotating member was set in motion. At appropriate intervals it was stopped, each specimen assembly was weighed, and the gain in weight recorded. In general, few weighings were made until after at least 48-hour exposure, since the later steadier rate of scaling, not the initial rate, was desired. The total period of exposure was 1000 hours (6 weeks) except when some obvious irregularity showed up in the curve of weight against elapsed time—for example, when a specimen had lost some scale or had become completely oxidized. As a further safeguard, duplicate specimens were always tested, and each group of specimens included one of the highly resistant 27-chromium alloy as a check on the accuracy of the weighing procedure. The results from each pair of duplicate specimens were, with few exceptions, in satisfactory agreement; consequently, only the mean result, taken from the curves of weight against time at a given temperature, is tabulated. The accuracy of the result is more than ample for all practical purposes.

Materials. Altogether thirty-six different compositions were included in the program; in five instances (23, 25, 31, 35, 36) two separate batches were tested—one a laboratory product, the other a commercial material of the same nominal composition. The composition of these steels is listed in Table I, in decreasing order of the observed resistance to scaling in the range 1100-1300° F. over a period of 1000 hours. They range from stainless steels through steels with decreasing proportions of chromium and other alloying elements to plain carbon steels; there are subgroups which differ only in the proportion of a single element (e. g., chromium, molybdenum). In addition, six carbon steels were used in a number of preliminary runs; their composition follows:

Steel	Carbon	Manganese	Silicon
A	0.03	0.06	0.01
B	0.20	0.41	0.07
C	0.28	0.55	0.26
D	0.45	0.47	0.21
E	0.71	0.62	0.06
F	1.00	0.44	0.23

This series of relatively nonresistant steels was used to test the apparatus, procedure, and reproducibility of results, and to learn in how far the observed progress of scaling is likely to be influenced by the mode of finishing the specimen and by its carbon content. Accordingly the gain in weight of quadruplicate specimens, all finished alike by milling, of steels A to F, at 1100° F. in air was observed for a total period of 1000 hours with the results as shown in the following table:

Steel	Carbon, %	Total Gain in Weight (Grams) in Air at 1100° F. after: 500 hours 1	2	3	4	1000 hours 1	2	3	4
A	0.03	0.590	0.594	0.577	0.580	0.805	0.837	0.805	0.807
B	0.20	0.647	0.614	0.624	0.623	0.898	0.871	0.886	0.867
C	0.28	0.799	0.760	0.660	0.730	1.250	1.172	1.059	1.124
D	0.45	0.781	0.754	0.730	0.717	1.246	1.194	1.151	1.148
E	0.71	0.875	0.821	0.838	0.969	1.330	1.258	1.288	1.461
F	1.00	0.678	0.828	0.674	0.870	1.080	1.204	1.011	1.173

These results indicate that the specimens with lowest carbon are more reproducible; that while the steels with higher carbon show a greater gain of weight, there may well have been some loss of carbon which complicates the interpretation of the results. The conclusion is reached that scaling progresses somewhat faster, the higher the carbon (other things being equal); but this influence of carbon is in itself not great enough to affect appreciably the comparisons between the thirty-six steels in the main series (Table I), except in so far as the carbon impoverishes the matrix in chromium or other elements which form stable carbides, resistant to oxidation.

Likewise, triplicate samples of steel B were finished by (*a*) polishing with 00 emery paper, (*b*) pickling in acid, (*c*) milling, or (*d*) milling and dipping in a dichromate solution; the gain in weight was observed with the following results:

Treatment of Steel B	Total Gain in Wt. (Grams) in Air at 1100° F. after: 500 hours 1	500 hours 2	500 hours 3	1000 hours 1	1000 hours 2	1000 hours 3
a. Polished	0.508	0.508	0.496	0.764	0.754	0.760
b. Pickled	0.565	0.529	0.561	0.824	0.762	0.816
c. Milled	0.614	0.624	0.623	0.871	0.886	0.867
d. Milled and dipped	0.566	0.540	0.523	0.867	0.829	0.829

Consequently the method of polishing was selected as yielding the most reproducible result. The somewhat greater, and less regular, gain of weight of specimens finished by the other three methods is doubtless to be attributed to a somewhat greater, and less uniform, effective area of the surface at the beginning of the test. In line with this, the gain in weight during the second 500 hours, when presumably the influence of the initial surface condition has disappeared, ranges only from 0.256 to 0.264 gram for seven of the nine specimens in classes *a*, *b*, and *c*.

PROGRESS OF OXIDATION

The curve of gain in weight against time is smooth, with a few exceptions at the higher temperatures where some specimens showed occasional relatively rapid changes in rate for which there is no obvious explanation; it is in general parabolic in shape, in accord with previous general experience (*2*). In general the gain in weight of each pair of duplicate specimens agreed well. The difference was usually less than 5 per cent except at the highest temperature; consequently only the mean value is given. This mean gain in weight, expressed in milligrams per unit (sq. cm.) surface area of the specimen is listed (Table II) for an exposure of 1 day, 1 week (168 hours), and 6 weeks (1000 hours) at each temperature level at which the steel was tested. These three intervals were chosen as the most significant way of presenting the data within a reasonable compass; they enable anyone to draw the curves for himself.

There are two series of results by different observers. Several nominally identical steels (one experimental, the other commercial) are present in both series. The agreement is good for pairs 31 and 35, but not so good for 23 and 25; this may be attributed to differences in composition, for the second (commercial) of pair 23 contains nearly 1 per cent more chromium and 0.15 per cent more silicon, both of which increase oxidation resistance; and the first of pair 25 contains slightly more silicon. These illustrate the differences in oxidation resistance which are likely to be found between different batches of steel made to meet the same composition specifications.

To facilitate comparison, the graphical presentation in Figure 2 was chosen as the clearest of those tried. The data of Table II, for each temperature level are represented by a series of bars so shaded as to represent the gain in weight after 24 hours, 1 week, and 6 weeks; the percentage of each of the most significant elements is indicated by a series of narrow bars at the left. The upper portion refers to alloys 1 to 11 at 1400°, 1500°, and 1700° F.; the lower, to alloys 6, 9, 10, and 12–36 at 1100°, 1300°, 1400°, and 1500° F., all on the same scale. All of the alloys numbered 12 or higher which were tested at 1700° F. scaled so rapidly that they were completely oxidized in less than 1000 hours; these results are omitted from the chart.

The progress of oxidation at constant temperature of a pure metal, on which the scale is continuous (free from cracks) and coherent, commonly follows a simple parabolic law; namely, the thickness of the scale (or roughly the gain in weight) is proportional to the square root of the elapsed time. However, the presence of one or more alloying elements complicates the situation, especially if the free energy of formation of the oxide of the alloying element differs greatly from that of the oxide of the base metal, as is the case with chromium or silicon or aluminum in comparison with iron. Consequently, although the observed curves are parabolic in form, they do not always fan out regularly from the origin but some of them cross. For example, at 1500° F. steel 31 (0 Cr–2 Mo) is more resistant than 32 (2 Cr–0 Mo) for a day or a week, but at 6 weeks the latter is considerably better. Again at 1100° F. the gain in weight of many of the alloys, although nearly the same after 24 hours and even after a week, differs appreciably after 1000 hours. Therefore it is unsafe to predict long-time behavior from short-time tests, however much one may wish to do so.

That this should be true is to be expected. In a chromium-iron alloy, for instance, the chromium has a greater tendency to oxidize than the iron, and does oxidize more rapidly until the process is in effect stopped by the barrier set up by the oxide film formed; correspondingly, the ratio of chromium to iron in this oxide film is much higher than in the original metal, in which the ratio is higher than in the surface layer of the metal after oxidation has begun. Consequently the initial rate of oxidation of iron containing some chromium is often greater than that of iron alone; but the continued rate of further progress depends upon the effectiveness of the oxide film as a barrier impervious to diffusing particles, and in this respect chromium (or its oxide) is quite effective. Moreover this selective oxidation immediately alters the chromium content (*1*) of the metal surface (unless conditions are such that it is replenished by diffusion) and to that extent alters the situation. In other words, the continued progress of oxidation depends upon the precise composition and properties of the oxide film or layer formed upon the surface of the metal under the specific conditions of exposure, especially upon its resistance to passage of diffusing atoms and upon its adherence; the latter, in turn, is influenced by the degree of similarity of the lattice spacing of the oxide and the adjacent metal. In view of this and of the further fact that we are dealing with multicomponent systems of elements differing greatly in tendency to oxidation and in the protective characteristics of the several oxides and oxide mixtures, it is not surprising that each alloy should behave more or less as an individual, that the effect of an element is not additive, and consequently that few generalizations can be made.

The effect of temperature is pronounced, as Figure 2 shows. Since the progress of formation of a continuous scale by oxidation is largely a matter of diffusion rate and since diffusivity increases exponentially with temperature, scaling rate may be expected likewise to increase exponentially (*1*). The data are in rough accord with this expectation, but again the complexities of the oxidation process in iron alloys preclude exact (in some cases even approximate) agreement. A striking example of this irregularity is steel 15 (5 Cr–5 Mo) which after 1000 hours showed a gain of 5 mg. per sq. cm. at 1100°, 0 at 1300°, and 210 at 1500° F.; apparently in this case the several conditions which retard scaling fit together, so to speak, at 1300°, but less perfectly both at higher and lower temperature. Other less obvious irregularities may be seen in Figure 2.

EFFECT OF INDIVIDUAL ELEMENTS

In the range of compositions included in this investigation, the alloying element with the most pronounced influence upon oxi-

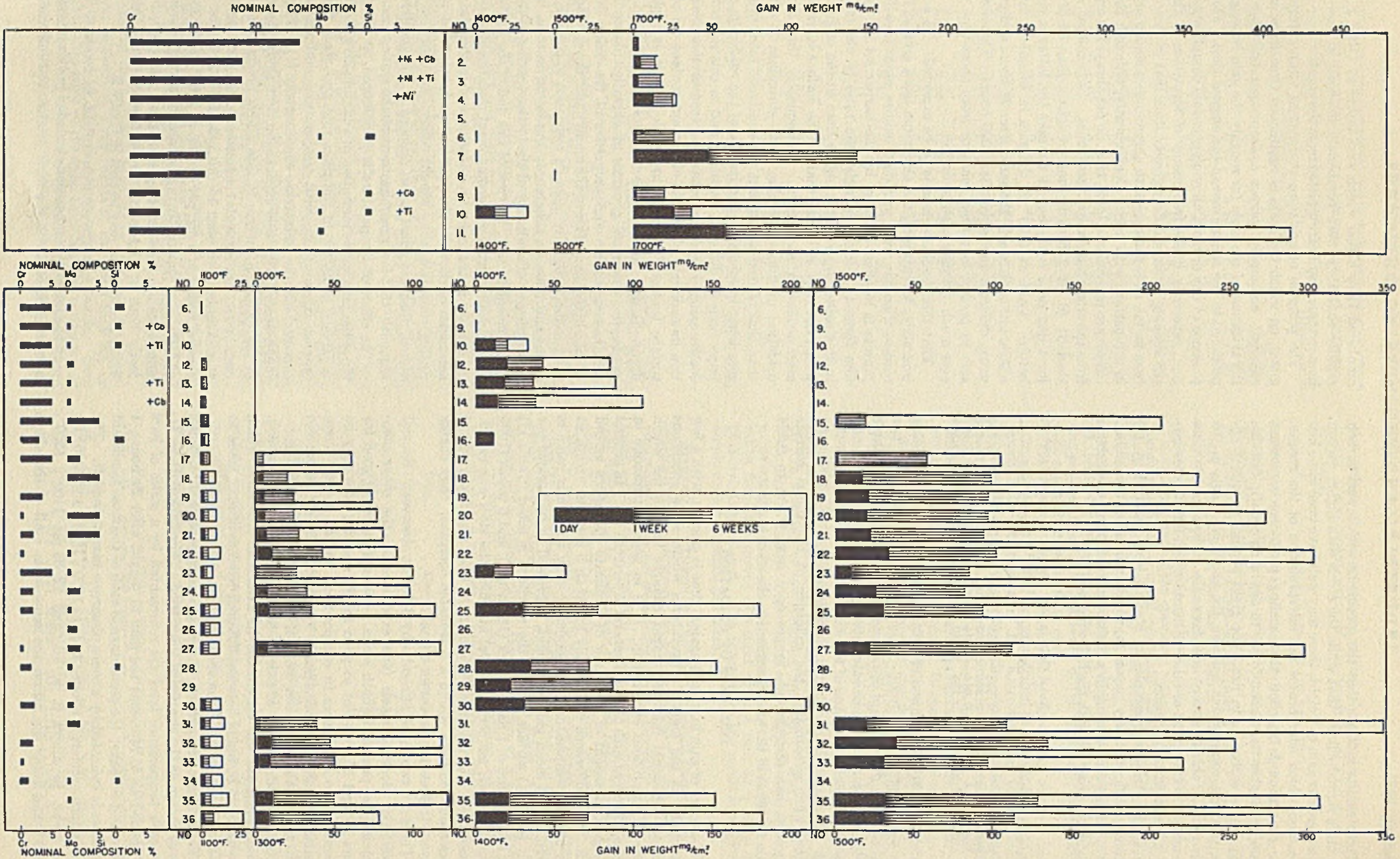

Figure 2. Relative Resistance to Oxidation of Various Steels in Air at Five Temperatures

Table II. Relative Resistance to Oxidation of Various Steels in Air at Five Temperatures

Gain in Weight[a], Milligrams per Square Centimeter of Surface

Steel	1100° F.				1300° F.				1400° F.				1500° F.				1700° F.			
	a	b	c	d	a	b	c	d	a	b	c	d	a	b	c	d	a	b	c	
1. 27 Cr	0	0	0	0	0	0	0	0	0.03	0.06	0.12	...	0.12	0.4	1.0	1.8	0.1	1.9	2.1	...
2. 18 Cr, 8 Ni + Cb	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	4.4	13.5	...	...
3. 18 Cr, 8 Ni + Ti	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	2.9	17.3	...	...
4. 18 Cr, 8 Ni	...	...	...	...	...	...	...	...	0.09	0.15	0.18	0.5	...	...	...	...	12.7	24.8	27.0	...
5. 17 Cr	0	0	0	0	0	0	0	0	...	...	...	...	0.06	0.3	1.0	1.2	...	...	...	...
6. 5 Cr, 0.5 Mo, 1.5 Si	0	0	0	0	...	...	...	...	0.18	0.23	0.35	0.5	...	...	...	...	0.5	25.7	117	...
7. 12 Cr, 0.5 Mo	...	...	...	...	...	...	...	...	0.12	0.18	0.35	0.9	...	...	...	...	48.0	142	307	...
8. 12 Cr	0	0	0	0	0	0	0	0	...	...	...	...	0.03	0.2	0.9	1.6	...	...	...	...
9. 5 Cr, 0.5 Mo, 1 Si + Cb	...	...	...	...	...	...	...	...	0.55	0.67	0.73	1.1	...	...	...	...	0.44	19.6	350	...
10. 5 Cr, 0.5 Mo, 1 Si + Ti	...	...	...	...	...	...	...	...	12.0	20.0	33.0	84	...	...	...	...	26.0	37.1	153	...
11. 9 Cr, 1 Mo	...	...	...	...	...	...	...	...	0.20	0.26	0.41	0.8	...	...	...	...	58.5	166	417	...
12. 5 Cr, 1 Mo	1.2	2.3	3.1	8.1	...	...	...	...	19.8	42.5	85	340	...	...	...	...	...	...	...	...
13. 5 Cr, 0.5 Mo + Ti	1.2	2.3	3.8	9.3	...	...	...	...	18.0	36.5	89	230	...	...	...	...	...	...	...	...
14. 5 Cr, 0.5 Mo + Cb	1.2	2.3	2.9	7.7	...	...	...	...	14.0	38.0	106	293	...	...	...	...	...	...	...	...
15. 5 Cr, 5 Mo	2.4	3.9	4.6	11	0	0	0	0	...	...	...	...	0.06	19	207	485	...	...	...	...
16. 3 Cr, 0.5 Mo, 1.5 Si	1.8	2.7	4.9	15	...	...	...	...	9.3	10.2	10.5	28	...	...	...	...	...	...	...	...
17. 5 Cr, 2 Mo	2.0	4.0	5.5	13	0.3	5.0	61	154	...	...	...	...	0.6	58	105	285	...	...	...	...
18. 5 Mo	2.0	4.7	9.2	28	4.8	20.2	55	155	...	...	...	...	17	99	230	620	...	...	...	...
19. 3.5 Cr	2.0	4.4	9.9	27	5.4	24.1	74	207	...	...	...	...	21	97	255	720	...	...	...	...
20. 0.5 Cr, 5 Mo	2.0	4.6	10.0	27	5.7	24.3	77	204	...	...	...	...	20	97	273	760	...	...	...	...
21. 2 Cr, 5 Mo	2.3	4.8	10.0	28	7.0	27.9	81	213	...	...	...	...	21	94	206	595	...	...	...	...
22. 0.5 Cr, 0.5 Mo	1.7	4.9	12.6	41	10.5	42.7	90	255	...	..	...	...	34	102	304	900	...	...	...	...
23. 5 Cr, 0.5 Mo	2.0	4.8	9.7	24	2.5	26.3	100	245	...	...	...	...	10	85	189	545	...	...	...	...
23. 5 Cr, 0.5 Mo	1.8	2.7	4.9	13	...	...	...	...	11.7	23.4	57	156	...	...	...	...	...	...	...	...
24. 2 Cr, 2 Mo	1.9	4.5	9.2	24	7.6	32.0	98	249	...	...	...	...	26	82	202	535	...	...	...	...
25. 2 Cr, 0.5 Mo	1.9	4.7	10.2	25	8.8	35.2	114	306	...	...	...	...	31	94	190	585	...	...	...	...
25. 2 Cr, 0.5 Mo	2.3	5.9	13.9	36	...	...	...	...	29.2	77.5	180	500	...	...	...	...	...	...	...	...
26. 1.4 Mo	2.3	5.9	11.9	32	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
27. 0.5 Cr, 2 Mo	1.8	4.7	11.3	29	7.6	5.1	117	300	...	...	...	...	22	112	298	760	...	...	...	...
28. 1.8 Cr, 0.7 Mo, 0.6 Si	...	...	...	...	...	...	...	...	35.0	72.0	153	450	...	...	...	...	...	...	...	...
29. 1 Mo	...	...	...	...	...	...	...	...	22.2	87.0	189	520	...	...	...	...	...	...	...	...
30. 2.2 Cr, 1 Mo	3.0	6.6	12.6	32	...	...	...	...	31.0	100	210	670	...	...	...	...	...	...	...	...
31. 2 Mo	2.4	5.6	16.2	44	2.6	38.9	115	293	...	...	...	...	20	109	343	930	...	...	...	...
31. 2 Mo	2.5	6.6	14.1	39	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
32. 2 Cr	2.1	5.5	13.5	36	10.0	47.6	118	326	...	...	...	...	39	135	254	760	...	...	...	...
33. 0.5 Cb	1.9	5.3	13.7	37	9.4	50.6	118	367	...	...	...	...	31	97	221	640	...	...	...	...
34. 1.3 Cr, 0.5 Mo, 0.8 Si	2.5	6.6	13.9	36	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
35. 0.5 Mo	2.2	5.9	17.6	49	11.4	50.0	122	349	...	...	...	...	32	129	308	935	...	...	...	...
35. 0.5 M	2.2	6.1	17.7	45	...	...	...	...	21.6	71	152	432	...	...	...	...	...	...	...	...
35. 0.5 Mo	2.5	6.6	16.2	44	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
36. Carbon	2.1	7.8	26.6	67	8.8	47.8	78	252	...	...	...	...	31	114	278	835	...	...	...	...
36. Carbon	...	...	...	...	...	...	...	...	20.5	71	182	510	...	...	...	...	...	...	...	...

[a] After (a) 1 day; (b) 1 week; (c) 6 weeks, interpolated from the mean curve representing duplicate observations on 36 steels; (d) observed weight loss after pickling one of each pair of specimens after 6-week exposure.

dation resistance is chromium; for small percentages chromium is less effective than silicon which, however, cannot be used in large percentages (even if it were then effective) because of its adverse effect upon mechanical properties.

Chromium, alone or in combination with molybdenum or silicon, contributes to increased resistance at 1100° F., but at 1300° amounts less than 3–4 per cent appear to lessen the resistance although larger percentages are again beneficial; at 1500° it is beneficial, yet the alloy with 0.5 per cent chromium was better than that with 2 or with 3.5 per cent. Large amounts of chromium are very effective, the 27-chromium alloy scaling only slightly in 6 weeks even at 1700° F.

The results from the alloys containing both chromium and molybdenum show no obvious regularity with variation in composition. Molybdenum, alone or with chromium, contributes to scaling resistance at 1100°; but at both 1300° and 1500° F. amounts less than 3–4 per cent seem to exert an adverse effect although 5 per cent is again beneficial.

Silicon was present (apart from the usual residual percentage) in only a few of the alloys and only up to 1.5 per cent in amount. It has a beneficial effect at temperatures up to 1400° F. as shown by comparison of steels 6, 9, 10 with 12, 13, 14 at 1400°. The resistance of steels 6 and 9 deteriorated, however, when kept at 1700° F.; evidently at this temperature the beneficial effect of silicon is not permanent, presumably because of some change in composition of the oxide layer as oxidation of these steels continued to progress selectively.

The influence of a small amount of titanium or columbium in the alloys tested is apparently not consistent. Thus in steels 9 (Cb) and 10 (Ti), the former was better at 1400°, the latter at 1700° F. The resistance of 18–8 steel is improved by either titanium or columbium and to about the same extent; this improvement is presumably due to the formation of the carbide, thereby releasing to the matrix the chromium which otherwise would have been tied up with carbon.

Nickel was present in appreciable amount in only three of the alloys, and at nearly the same percentage in all three; the data are therefore insufficient to justify a statement as to its influence on rate of oxidation in air at high temperature.

LITERATURE CITED

(1) Heindlhofer and Larsen, *Trans. Am. Soc. Steel Treating*, 21, 865–95 (1933).
(2) "Review of Oxidation and Scaling of Heated Solid Metals", London, H. M. Stationery Office, 1935.

STABILITY OF FURNACE OIL

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The fouling of domestic oil burner systems by unstable furnace oils is discussed. A stability test is described, and data are presented relating this test to results obtained by circulating oils through the essential parts of a gravity-feed burner system; the latter results have been found to correlate with practice. Data on both refined and unrefined oils are included. The stability test is based on the reaction of oils to two metal pairs, iron-copper and iron-lead, under controlled conditions. The test was originally designed for straight-run oils, and its limitations in regard to cracked oils are pointed out.

THE extensive use of furnace oil for domestic heating has placed new demands on quality. The criteria of performance are a clean burning flame and uninterrupted automatic operation. To obtain the latter condition, the oil must be free of solid material and must be stable in storage in the consumer's burner system where it is in contact with metals known to promote sludge formation. Burners that are particularly sensitive to small amounts of solids in the oil are the gravity feed type rather widely used in some sections of the eastern United States.

Much of the previous work on the stability of fuel oils has been concerned with the heavier grades. Batchelder (*1*) developed a method of predicting the heater-coating tendencies of these oils; Voskuil and Robu (*5*) and Batchelder and Wellman (*2*) pointed out the factors involved in blending cracked tars and straight-run oils in order to prevent the precipitation of asphaltenes. Trusty (*4*), in discussing the problem of producing stable furnace oils, outlined several test methods reported in use. Hawes and Miller (*3*) presented a test for determining potential sludge formation in light oils. However, neither of the last two references offers any evidence to indicate that the methods described will predict what happens to the oils in practice.

The test presented in this paper was developed primarily for light distillate furnace oils and has been in use by this company for approximately three years with excellent results. It is designed for straight-run oils and is not entirely indicative of the performance of cracked oils. However, no cracked oils have been encountered which are stable in practice yet fail to meet the requirements of the test.

FOULING OF BURNER SYSTEMS

The use of unstable oils in domestic burner systems results in sludge formation and the corrosion of parts, particularly brass, leading to clogged strainers and valves. In many systems the flow of oil depends on gravity, and since the effective "head" may be as small as one foot, only small amounts of sediment are required to retard this flow. Both straight-run and cracked oils may show this type of instability.

The appearance of sludges removed from fouled burner systems varies from dark viscous materials to light colored substances of a flocculent or gelatinous nature. Analysis of these sludges showed the presence of metallic constituents, all of which were identified as parts of the burner system (Table I). Zinc is usually found in the sediments where the oil may have been in contact with brass parts. Lead, cadmium, and nickel result from the corrosion of solder, cadmium-plated parts, and Monel metal. Copper is seldom found in the sludges, although many furnace oils discolor and oxidize when allowed to stand in contact with metallic copper. During periods when fuel oils lie stagnant in burner systems, it is probable that copper accelerates their deterioration.

Solubility analyses of material removed from cotton strainers placed in the feed lines of domestic installations are shown in Table II. The alcohol-soluble portion of these sludges was identified as consisting largely of soaps formed by the reaction of oil constituents with metals. The sludges containing large percentages of alcohol-soluble material in general were the most gelatinous.

TABLE I. METALLIC CONSTITUENTS IN SLUDGES REMOVED FROM CLOGGED BURNER SYSTEMS

Metallic Constituent	Sediment Removed from: Oil storage tank	Strainer	Float bowl
Iron	Present	Present	Present
Zinc	Present	Present	Present
Lead	Present	None	Present
Cadmium	None	Present	None
Copper	None	None	Trace
Nickel	None	Present	Present

TABLE II. TYPICAL SOLUBILITY ANALYSES OF GELATINOUS SLUDGE FOUND IN STRAINERS OF FOULED GRAVITY-FEED BURNER SYSTEMS

Solvent	% of Material Soluble[a] No. 1	No. 2	No. 3	No. 4
88° naphtha	75.5	92.6	93.7	89.6
D-30 alcohol	22.7	6.8	4.3	1.7
Acetone-benzene, 50-50	0.3	0.6	0.5	5.7
Water	1.5	0.0	1.5	3.0

[a] In order of extraction.

STABILITY TEST

From the above sludge analyses, which disclosed the presence of metals, and the soapy gelatinous nature of the sludge, it was considered likely that an indication of fouling of burner parts of furnace oil could be found in a study of the action of these oils in the presence of metals. Such a study was undertaken along with an investigation of the sludging of various oils in a circulating system consisting of the essential parts of a typical domestic gravity-feed burner system. As a result of this work a stability test was developed for furnace oil based on the stability of the oil in the presence of two metal pairs—namely, iron-copper and iron-lead. A description of the test follows:

APPARATUS. Metal test strips were selected of standard materials. The lead was $^1/_2 \times 4 \times {}^1/_{64}$ inch commercial sheet. The copper strips, $^3/_8 \times 4 \times {}^3/_{32}$ inch in size, were cleaned by pickling in a sulfuric-nitric acid solution for 30 seconds, washing, and drying. The pickling bath contained 22 per cent of sulfuric and 12 per cent nitric acid by weight. If a strip was not entirely bright after this treatment, the procedure was repeated.

The iron strips consisted of $^3/_8 \times 4 \times ^3/_{16}$ inch cold-finished steel (cold drawn, S. A. E. X1020). They were cleaned by pickling in a 40–50 per cent (by weight) solution of sulfuric acid until the surface scale was removed. All surfaces of the strip were scrubbed with a brush, washed free of acid with water, and immediately dried with acetone.

New standard 4-ounce oil sample bottles were used. They were supplied with a neoprene stopper secured by about 8 inches of No. 18 gage copper wire. Corks impregnated with a material to close the pores may be substituted for the neoprene stoppers.

Oxygen was supplied from a cylinder equipped with reducing valve. The oxygen delivery tube was glass, 5–6 mm. inside diameter with outlet reduced to 1 mm. i. d. The oxygen gas was bled into the sample through a glass tube about 5 or 6 mm. in diameter with the outlet reduced to 1 mm. diameter.

Other equipment used were an oven thermostatically regulated within ±2° F., an analytical balance sensitive to 0.1 mg., several Coors No. 4 Gooch crucibles, a desiccator, and crucible tongs.

PROCEDURE. The method consisted of determining the amount of sludge formed by the oil in the presence of (*a*) iron and copper and of (*b*) iron and lead under test conditions. Duplicate tests were run for each of the two metal combinations.

Fifty milliliters of the furnace oil are introduced into each of two 4-ounce bottles, after filtering through a No. 42 Whatman filter paper. To one bottle is added a piece of iron and of copper and to the other a piece of iron and of lead. Oxygen is bubbled through the oil at the rate of 300 cc. per minute for 5 minutes. Each bottle is stoppered immediately on withdrawal of the oxygen delivery tubes so that no oxygen above the oil is lost, and the stopper is securely wired in. The samples are placed in an oven maintained at 210° F. ± 2° for 4 days, after which they are removed and cooled. The metal strips are withdrawn. Any sludge adhering to the strips is returned to the oil in the bottle with the aid of a rubber policeman. The oil is filtered through an asbestos mat in a weighed Gooch crucible. Sludge adhering to the glass bottle after draining the oil is removed with a rubber policeman and 88° naphtha. A total of 10 to 15 ml. of 88° naphtha is used to wash the sludge from the bottle and to wash the oil from the sludge in the crucible. The crucible is then dried at 210° F. for 1 hour, cooled, and weighed. Tests are always run in duplicate.

The results obtained on check analyses showed the reproducibility to be ±1 mg. in the iron-copper test and ±2.5 mg. in the iron-lead test (Table III).

CORRELATION OF STABILITY DATA WITH RESULTS IN CIRCULATING SYSTEMS

A correlation between the stability test and the performance of the oils in the circulating systems was established from data obtained by circulating oils through the essential parts of a typical gravity-feed burner system and determining the extent of corrosion of the parts and the amount of sludge deposited (Figure 1).

This laboratory circulating system consisted of an elevated charge container, 1, from which oil flowed into 15 feet of copper tubing, 6, then into a float bowl assembly, 3, 4, and from there to a receiver, 9, from which the oil could be periodically forced by low-pressure air into the charge container. Two weighed brass test pieces were placed in each float bowl for corrosion determination. The copper tubing (feed line) and float bowl assembly were painted black and heated by an infrared lamp, 2, so adjusted as to produce an oil temperature of 140° F. measured at the float bowl outlet, 5.

TABLE III. TYPICAL STABILITY TESTS SHOWING REPRODUCIBILITY

Description	Mg. Sludge/50 Cc. Oil Iron-copper	 Iron-lead
Refined medium furnace oils		
A	8	10
	6	10
B	3	20
	6	21
C	7	16
	7	16
D	11	8
	12	10
Raw straight-run medium furnace oils		
E	49	38
	49	41
F	14	68
	15	63
G	9	63
	10	70
Cracked medium furnace oil (refined)		
H	13	27
	9	28

A test run in this system was made as follows: 10 gallons of oil to be tested were filtered through a funnel containing a wad of absorbent cotton, charged to the system, and circulated for 5 days at 140° F. and then for 2 days at room temperature. This cycle was repeated on the same batch of oil. At the end of the second week the charge was drained from the system without disturbing the oil in the float bowl and a fresh 10-gallon batch of the test oil was charged. This second 10 gallons of oil was circulated through the system for two cycles, the operation being identical with that used on the first 10-gallon portion. The total time required to make a test was 28 days. The rate of oil flow through the system was maintained at 12–15 cc. per minute; 10 cc. of water were added to the system weekly. The oil in the receiver was forced back into the charge container once each day, and the whole charge agitated by hand stirring for about 5 minutes. The rate of oil flow through the system was checked twice daily and a record kept of any noticeable tendency for the valves to become clogged.

At the end of the 28-day operating period, the following information was used to evaluate the oil: (*a*) the appearance and amount of sediment deposited in the float bowl assembly, (*b*) the extent of corrosion of parts and the loss in weight of the added brass pieces, and (*c*) the clogging of valves and strainer retarding the rate of oil flow through the system.

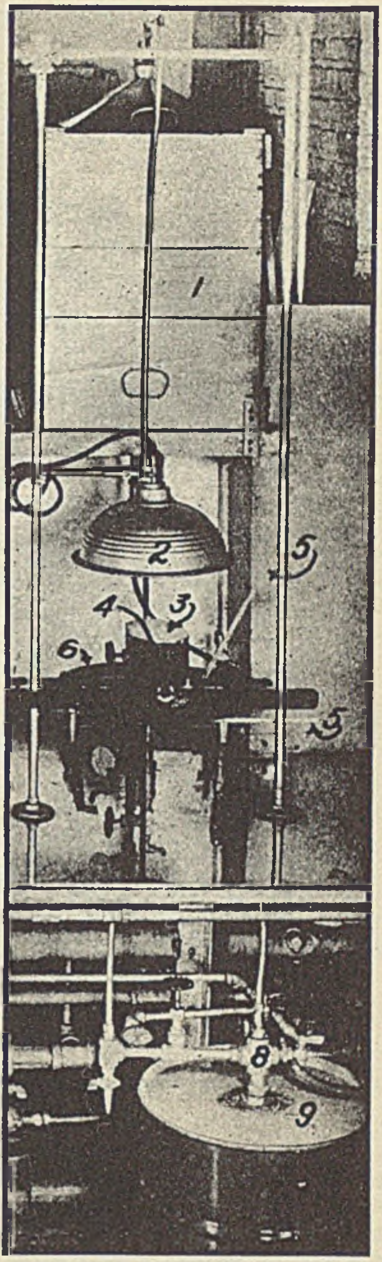

Figure 1. Gravity-Feed Circulating Systems for Accelerated Stability Tests on Furnace Oils

1. Charge container
2. Infrared lamp
3. Float bowl
4. Strainer
5. Thermometers
6. 12-foot copper coil feed line
7. Flow rate regulating valve
8. Low-pressure air line to lift oil from receiver to charge container
9. Receiver

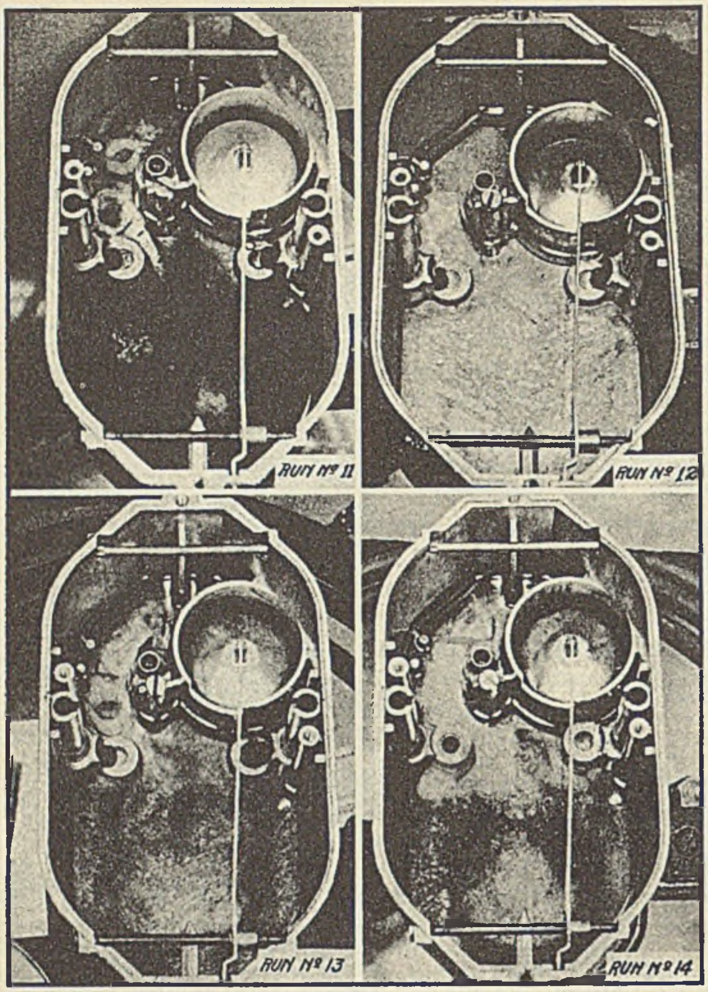

Figure 2. Sediment in Float Bowls of Gravity-Feed Circulating Systems after Operating on Medium Furnace Oils under Test Conditions

Runs 11, 13, and 14, unstable straight-run furnace oil causing corrosion and the formation of sludge: run 12, refined straight-run furnace oil causing no corrosion and the formation of very little sludge.

←

The accumulated sediment in the float bowl was removed with the oil by a suction flask, the bowl being washed with clean furnace oil. The amount of sediment was then determined by centrifuging at 2500 r. p. m. in a 100-cc. pear-shaped A. S. T. M. centrifuge tube for 5 minutes. If the volume of oil exceeded 100 cc., a portion of the oil-sediment mixture was centrifuged and the clear oil decanted; then the remainder of the mixture was added to the sediment in the centrifuge tube and the total volume of sediment determined. The brass pieces placed in the float bowl for corrosion determination were washed with acetone and alcohol, dried, and weighed.

This laboratory arrangement of parts of a burner system and the test method used was considered an adequate substitution for an actual domestic installation since the type of corrosion found and the nature of the sediment deposited in the float bowls were similar to those observed in customer installations.

DISCUSSION OF RESULTS

Oils that formed large amounts of sludge in the stability test were found to corrode parts of the circulating system and to deposit sediment in the float bowl assembly. Frequently the flow of oil through the system was retarded as a result of accumulation of sediment in the valves. Oils that formed only small amounts of sludge in the stability test did not deposit noticeable amounts of sludge in the circulating system or corrode parts, and the rate of flow of oil through the system remained relatively uniform.

Table IV. Accelerated Tests on Medium Furnace Oil

		Stability Test, Mg. Sludge/50 Cc. Oil				Behavior of Oil in Gravity-Feed Systems					
							Corrosion of brass parts				
Run No.	Description of Oil	Fe-Cu	Fe-Pb	Total	Oil rating[a]	Sludge in float bowls[b], cc.	Appearance	% loss in wt.	Strainer conditions	Oil flow through systems[c]	Oil rating[a]
13	Straight run, low S	7	61	68	Un	0.18	Clean	0.04	Clean	NU	Un
38	Straight run, refined, low S	1	9	10	S	0.04	Clean	Slight gain	Clean	U	S
22	Straight run, high S	46	4	50	Un	0.19	Trace corrosion	0.01	Trace sediment	NU	Un
14	Straight run, high S	45	30	75	Un	0.10	Corroded black	0.01	Slight sediment	NU	Un
36	Straight run, refined, high S	5	11	16	S	0.08	Corroded	0.002	Clean	U	S
7	Straight run	21	59	80	Un	0.20	Corroded	....	Slight sediment	NU	Un
11	Straight run	25	68	93	Un	0.22	Corroded	1.50	Slight sediment	NU	Un
10	Straight run	8	35	43	S	0.075	Clean	....	Clean	U	S
35	Straight run, refined	10	22	32	S	0.02	Clean	0.05	Clean	U	S
25	Straight run, refined	9	28	37	S	0.07	Clean	0.03	Clean	U	S
12	Straight run, refined	14	17	31	S	0.08	Slight corrosion	0.052	Clean	U	S
26	Straight run, refined	12	52	64	Un	0.12	Corroded	0.53	Slight sediment	U	Un
32	Straight run, refined	10	31	41	S	0.05	Clean	0.02	Clean	U	S
33	Blend, straight run & cracked, refined	4	12	16	S	0.05	Clean	0.00	Clean	U	S
37	Blend, straight run & cracked, refined	8	12	20	S	0.09	Clean	0.03	Clean	U	S
34	Blend, straight run & cracked, refined (high S)	24	24	48	Un	0.50	Corroded	0.13	Clean	U	Un
39	Blend, straight run & cracked, refined	27	17	44	Un	0.06	Corroded	0.21	Trace sediment	U	Un
28	Blend, straight run & cracked, refined	5	7	12	S	0.15	Clean	0.02	Nearly clogged	NU	Un

[a] S = satisfactory; Un = unsatisfactory.
[b] Volume after centrifuging from oil at 2500 r. p. m. for 5 minutes in regular 100-ml. A. S. T. M. centrifuge tube.
[c] U = uniform flow; NU = nonuniform flow (required frequent adjustment, clogged needle valve).

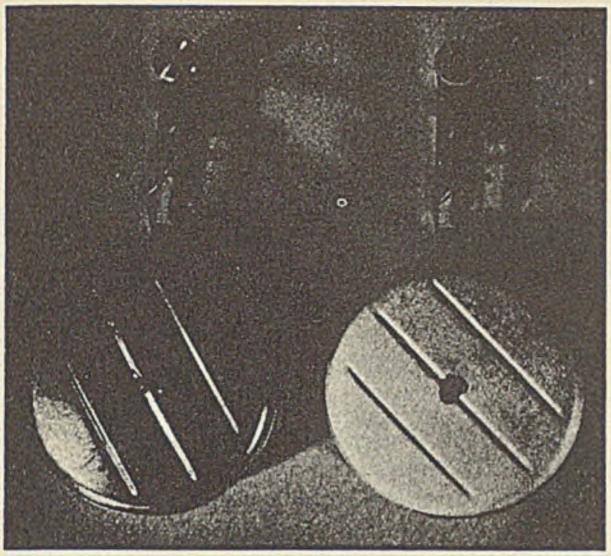

Figure 3. Corrosion of Brass Floats in Contact with Furnace Oils in Float Bowls

Left. Run 12, blend of straight-run refined oil, no corrosion
Right. Run 11, blend of straight-run unrefined oil, corroded

Figure 2 shows four float bowls of systems after operation on oils of various degrees of stability. During run 12 a minimum amount of sludge deposited and there was little evidence of corrosion. There was uniform flow of oil during the 28-day test. In runs 11, 13, and 14 there was greater sludge deposition and nonuniform flow of oil. In runs 11 and 14 there was considerable corrosion. Figure 3 shows the condition of the brass floats used in runs 12 and 11, the latter being corroded. Corrosion sometimes is in the form of a black layer (probably a copper sulfide) over the brass parts rather than an etching effect. This pictorial evidence of one satisfactory oil (run 12) and three unsatisfactory oils (runs 11, 13, and 14) is supported by the data in Table IV.

These results represent four types of oil based on their reaction to the stability test. Run 12 had low iron-copper and iron-lead values. Run 11 had high values in both tests. Run 13 had low iron-copper but high iron-lead values. Run 14 was the opposite, high iron-copper but low iron-lead values. These data show definitely that neither of the individual tests adequately predicts the stability of furnace oil and that a combination of tests is required, each having its maximum value.

To arrive at these maximum values, the data from the laboratory circulating systems and the stability test were correlated and the limits selected were 15 mg. of sludge in 50 cc. of oil for the iron-copper test and 45 mg. of sludge in 50 cc. of oil for the iron-lead test. To avoid being too near the maximum value in both tests, the sum of the two values should not exceed 55 mg.—for example:

	Mg. Sludge			
Oil	Iron-copper	Iron-lead	Total	Rating
A	20	40	60	Unsatisfactory
B	12	40	52	Passes
C	15	45	60	Unsatisfactory

That a general relation exists between the total sludge formed in the stability test and the volume of sludge deposited in the float bowls of the circulating systems is evident in Figure 4. Float bowl sludges of 0.1 cc. and higher correspond to high values in the stability test. However, the total sludge formed in the stability test is not sufficient to judge an oil, as has already been pointed out; the amount of sludge formed in the individual iron-copper and iron-lead tests must be considered.

Table IV gives the results obtained on a variety of oils in both the circulating system and the stability test. Some raw straight-run oils (run 10) are sufficiently stable. The oils labeled "refined" were unstable to the stability test prior to refining. The proper refining method can be selected on the basis of the stability test of the raw oil. The fact that an oil has been refined does not necessarily mean that it is stable. Run 26 is an example, and this is clearly pointed out by the stability test.

Table IV also shows five runs made on blends of straight-run and cracked oils. These blends contained up to 50 per cent of cracked oil. In general, the stability test was indicative of their performance in the circulating systems. However, run 28 which was quite stable to the stability test was unsatisfactory in the circulating system. No cracked oil or blend of cracked and straight-run oils have been found which are unstable to the stability test but stable in the circulating systems.

The failure of the stability test to rate all cracked oils properly is apparently due to formation in service of a varnishlike film (gum precipitation) on valves and strainers that is not picked up by the test. Where cracked oils are used extensively, the stability test probably should be supplemented by a form of potential gum test.

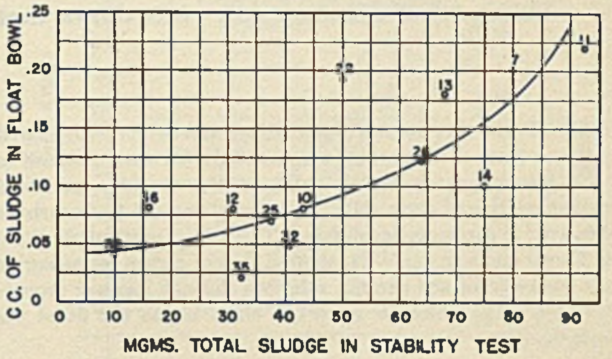

Figure 4. Relation of Total Sludge Formed in Stability Test to Sludge Formed in Float Bowl of Circulating Systems

The stability test presented here has been in use by this company for the past three years as a means of controlling the quality of its domestic furnace oil and the refining operations related to its production. Since its use, trouble experienced by consumers from fouled burner systems has been reduced to a negligible amount.

ACKNOWLEDGMENT

The authors take this opportunity of expressing their indebtedness to S. W. Ferris who directed the work, to H. M. Hancock, K. G. Krech, and J. J. Mulvey for helpful discussion, and to G. E. Irwin whose assistance was invaluable in correlating laboratory experimental work with results obtained in practice.

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Viscosity of *n*-Paraffin Solutions

VISCOSITY AND STRUCTURAL RELATIONS OF LINEAR POLYMERS

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Viscosity measurements of equal base molar solutions of the *n*-paraffins in *n*-hexane have shown good agreement with the Staudinger relation which requires the specific viscosity to be exactly proportional to the number of atoms in the chain. A comprehensive analysis of viscosity molecular weight data on various linear polymers has led to the development of a new viscosity constant, K_{ca}, based on the contribution to viscosity of a chain atom. It is shown that $K_{ca} = \log \eta_r W/\Phi N$. The range for K_{ca} is 0.030 to 0.038, with an average of 0.032. By the use of this average K_{ca} value in the equation, the polymer length can be calculated even in the case of a nonlinear type since the side groups of a branched-chain polymer have little influence on viscosity. This paper gives new emphasis to the correctness of the underlying basis for the measurement of molecular weights of linear polymers by the viscosity method.

THE viscosity studies of Staudinger and Staiger (*10*) as well as those of Meyer and van der Wijk (*6*) were designed to test the fundamental aspect of the viscosity–molecular weight relation of chemically pure normal paraffin hydrocarbons dissolved in carbon tetrachloride. These data, particularly those of Meyer and van der Wijk, showed that in carbon tetrachloride the viscosity of the paraffin solutions did not increase proportionately with molecular weight or chain length but fitted the equation,

$$\eta_{sp} = 145\,MC - 15.981C \tag{1}$$

where M = molecular weight
C = concentration, base moles per liter

rather than the equation

$$\eta_{sp} = KM \tag{2}$$

called for by the Staudinger rule in the case of solutions of equimolar concentration.

In previous investigations (*1–5*), the authors found that the nature of the solvent is frequently as important as the solute. The present investigation was undertaken to determine the influence of different solvents, particularly the lower members of the normal paraffin series which should be more ideal on account of their identical structure.

MATERIALS AND METHODS

The normal paraffins were the chemically pure synthetic products from Eastman Kodak Company. The solvents used were all chemically pure except the *n*-hexane known as Skellysolve B which has a refractive index at 20° C. of 1.3844 and a density at 20°/4° of 0.6822 in contrast with n_D^{20} of 1.3759 and d_4^{20} of 0.6617 for Eastman's C. P. *n*-hexane. Skellysolve, however, is a uniform solvent and readily available at low cost.

The viscometer was of the Ostwald type with a capillary length of 10.5 cm. and a bore of 0.051 cm. The volume of liquid taken was 5.0 cc., measured by a pipet which was filled by the liquid passing through a fine mesh silk gauze to remove any foreign particles or fibers which might be present. The bulb had a capacity of 2.29 cc. and the mean head was 13.6 cm. A large water bath was employed and the temperature was held at 20° ± 0.03° C. The timing was by a high-precision electric timer read to 0.1 and estimated to 0.01 second, and the average reading taken of several runs seldom varied more than ±0.05 second between the extreme readings. In most cases the accuracy was better than ±0.03 second. A smaller-bore viscometer was also used for comparison but gave practically the same relative viscosity of a solution of tetracosane in carbon tetrachloride. The larger bore was selected because of the greater ease in cleaning and the lesser chance of foreign particles clogging the capillary and vitiating the results. All solutions were carefully filtered, and the utmost care taken to eliminate foreign solid matter by using filtered air for drying the pipet and viscometer between each determination.

The time of flow in seconds at 20° C. of the various solvents were: carbon tetrachloride 64.0, benzene 76.4, cyclohexane 130.8, chloroform 41.1, *n*-hexane (Skellysolve) 50.5, C. P. *n*-hexane 50.3, C. P. *n*-heptane 63.2, C. P. *n*-octane 80.4, C. P. *n*-decane 129.4.

The data are presented both with and without application of the Ostwald kinematic correction

$$\eta_r = t_1 d_1 / t_0 d_0$$

due to differences in head pressures caused by differences in density of the solution and the solvent. In very dilute solutions this correction is negligible and does not need to be made in viscosity–molecular weight studies of high polymers. It is very large, however, in the case of the more concentrated carbon tetrachloride and chloroform solutions of the paraffins. In the case of *n*-hexane, cyclohexane, and benzene solutions of the paraffins, the densities of solvent and solute differ so little that the correction is small. The densities of the solutions were calculated, assuming the volume of the paraffin is additive and is 0.78 at 20° C. This correction, however, appears to be excessive in the case of the lower members of the series in carbon tetrachloride.

VISCOSITY OF *n*-PARAFFINS IN SOLVENTS

The data on the paraffins dissolved in various solvents are presented in Table I. A comparison of calculated K_{cm} values before and after correction is shown in Table II. *n*-Hexane is the only solvent which gives practically a constant K_{cm} value for the paraffins $C_{12}H_{26}$ to $C_{28}H_{58}$.

In Figure 1 the data of Table I are plotted to show the relation between η_{sp}/C and $\log \eta_r/C$ and the number of carbon atoms in the paraffin. In Figure 2 data on carbon tetrachloride solutions corrected for density effect are compared with those of Staudinger and Staiger and of Meyer and van der Wijk. In Figure 3 all

Table I. Viscosity of Normal Paraffins in Various Solvents

Hydrocarbon	Base Molarity C	η_r	$\frac{\log \eta_r}{C}$	$\frac{\eta_{sp}}{C}$	$K_{cm} \times 10^{-}$
			Benzene Solutions		
$C_{10}H_{22}$	7.21	1.0026	0.00016	0.00036	10.11
$C_{12}H_{26}$	6.14	1.0393	0.00273	0.0064	6.60
$C_{14}H_{30}$	6.26	1.0733	0.00490	0.0117	4.05
$C_{16}H_{34}$	5.46	1.0864	0.00660	0.0158	3.42
$C_{16}H_{34}$	2.73	1.0303	0.00613	0.0144	3.69
$C_{18}H_{38}$	4.57	1.0903	0.00820	0.0197	3.10
$C_{24}H_{50}$	4.57	1.1453	0.01288	0.0317	2.62
$C_{24}H_{50}$	1.52	1.0485	0.01348	0.0319	2.50
$C_{28}H_{58}$	1.01	1.0393	0.01655	0.0389	2.38
			Carbon Tetrachloride Solutions		
$C_{10}H_{22}$	7.21	1.0453	0.00269	0.00630	6.02
$C_{12}H_{26}$	6.07	1.0781	0.00537	0.0128	3.35
$C_{14}H_{30}$	6.26	1.1250	0.00818	0.0200	2.42
$C_{16}H_{34}$	5.46	1.1375	0.01024	0.0252	2.21
$C_{18}H_{38}$	4.57	1.1422	0.01262	0.0311	2.08
$C_{18}H_{38}$	2.285	1.0672	0.01240	0.0294	2.05
$C_{18}H_{38}$	1.14	1.0328	0.01228	0.0287	2.07
$C_{24}H_{50}$	4.57	1.2063	0.01780	0.0452	1.90
$C_{24}H_{50}$	2.285	1.0984	0.01782	0.0430	1.89
$C_{24}H_{50}$	1.14	1.0469	0.01740	0.0410	1.94
$C_{28}H_{58}$	1.985	1.0969	0.02026	0.0488	1.94
			n-Hexane Solutions		
$C_{10}H_{22}$	7.21	1.1124	0.00642	0.0156	2.52
$C_{12}H_{26}$	6.21	1.1276	0.00840	0.0205	2.14
$C_{14}H_{30}$	6.26	1.1700	0.01088	0.0272	1.83
$C_{16}H_{34}$	5.46	1.1700	0.01248	0.0311	1.81
$C_{16}H_{34}$	2.73	1.0800	0.01222	0.0293	1.85
$C_{18}H_{38}$	4.57	1.1562	0.01380	0.0343	1.84
$C_{24}H_{50}$	4.57	1.2190	0.01880	0.0480	1.80
$C_{24}H_{50}$	1.52	1.0705	0.01941	0.0462	1.75
$C_{28}H_{58}$	1.98	1.1048	0.02180	0.0523	1.81
$C_{28}H_{58}$	1.32	1.0686	0.02178	0.0519	1.81
			Chloroform Solutions		
$C_{10}H_{22}$	7.21	1.1192	0.00678	0.0166	2.39
$C_{12}H_{26}$	6.10	1.1265	0.00846	0.0207	2.13
$C_{14}H_{30}$	6.26	1.1703	0.01089	0.0272	1.83
$C_{16}H_{34}$	5.46	1.1680	0.01234	0.0308	1.83
$C_{16}H_{34}$	2.73	1.0778	0.01190	0.0285	1.90
$C_{18}H_{38}$	4.57	1.1581	0.01391	0.0346	1.83
$C_{24}H_{50}$	4.57	1.2165	0.01860	0.0475	1.82
$C_{24}H_{50}$	1.52	1.0681	0.01880	0.0447	1.81
$C_{28}H_{58}$	1.01	1.0512	0.02150	0.0507	1.83
			Cyclohexane Solutions		
$C_{14}H_{30}$	6.26	1.0604	0.00407	0.0096	4.87
$C_{16}H_{34}$	5.46	1.0818	0.00625	0.0150	3.62
$C_{18}H_{38}$	4.57	1.0963	0.00875	0.0190	2.91
$C_{24}H_{50}$	4.57	1.1628	0.01431	0.0355	2.36
$C_{28}H_{58}$	1.985	1.0826	0.01738	0.0417	2.27

viscosity readings were corrected for the differences in density between the solution and solvent.

Figure 2 shows that the present data on carbon tetrachloride solutions are in perfect agreement with those of Meyer and van der Wijk and of Staudinger and Staiger, an indication that by using somewhat different viscometers and techniques, the results of the different laboratories agree closely.

All n-hexane data, before and after applying the kinematic energy correction, plot a straight line through the origin except for the lowest members of the homologous series which fail to conform. It is well known, however, that the lowest members of various polymeric series give anomalous results. The data, including those of cyclohexane solutions, show that n-hexane is the only solvent of those tried which gives paraffin solutions whose viscosities at equivalent concentration are exactly proportional to the number of carbon atoms in the chain. Figure 3 shows that $\eta_{sp}/C = N \times 0.00203$, whereas $\log \eta_r/C = N \times 0.00833$, where N is the number of carbon atoms in the chain. The relation employing $\log \eta_r$ is more exact since $\log \eta_r/C$ varies less with concentration than η_{sp}/C.

The lower viscosity given by the other solvents may be due either to differences in structural configurations between solvent and solute molecules or to different extensions or degrees of folding of the paraffin chains.

The falling off of the viscosity values for the lower hydrocarbons from the linear relation is the reverse trend from that found in the cases of polyprene, polyisobutylene, and polystyrene recently investigated (*1*, *3*, *4*). Decane, however, is a liquid only about 2.5 times as viscous as n-hexane. The state of solution may differ from that of the higher paraffins, as observed in the case of other polymers with very short chain lengths.

The viscosities of octacosane in several n-paraffin solvents are compared in Table III. The correction of these values for density is negligible. There appears to be a decrease in viscosity in going from octane to decane which indicates a change in the sol-

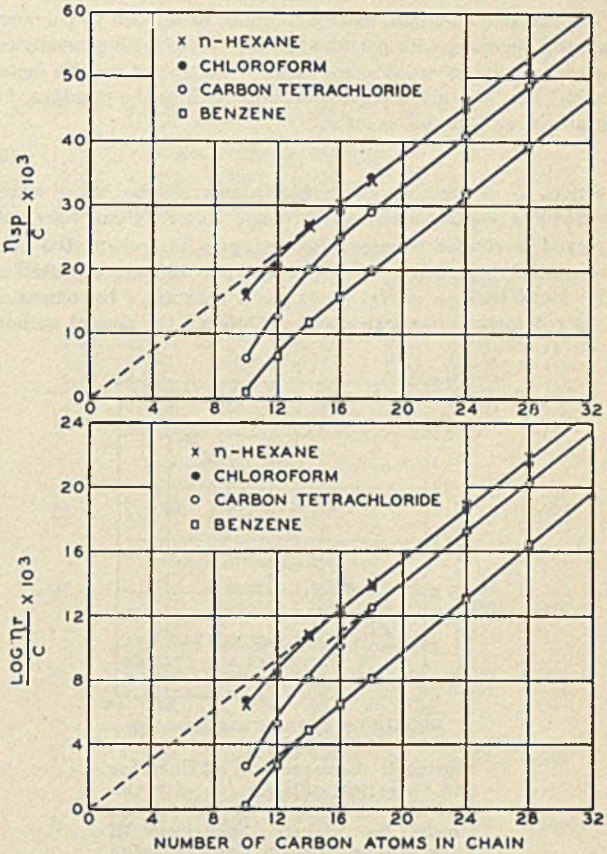

Figure 1. Variation of η_{sp}/C and of $\log \eta_r/C$ with the Number of Carbon Atoms in the Chain for Dilute Solutions of Paraffins in Different Solvents

Table II. Effect of Kinematic Correction on K_{cm} Values for n-Paraffin Solutions in Various Solvents

Hydrocarbon	$K_{cm} \times 10^{-4}$ for Benzene		$K_{cm} \times 10^{-4}$ for CCl_4		$K_{cm} \times 10^{-4}$ for n-Hexane		$K_{cm} \times 10^{-4}$ for Chloroform		$K_{cm} \times 10^{-4}$ for Cyclohexane	
	Calcd.	Cor.	Calcd.	Cor.	Calcd.	Cor.	Calcd.	Cor.	Calcd.	Cor.
$C_{14}H_{30}$	4.05	4.95	2.42	4.51	1.83	1.72	1.83	2.91	4.87	4.87
$C_{16}H_{34}$	3.42	4.09	2.21	3.41	1.81	1.74	1.83	2.66	3.62	3.62
$C_{18}H_{38}$	3.10	3.49	2.08	2.98	1.84	1.72	1.83	2.49	2.91	2.91
$C_{24}H_{50}$	2.62	2.81	1.94	2.47	1.80	1.72	1.82	2.27	2.36	2.36
$C_{28}H_{58}$	2.38	2.56	1.94	2.32	1.81	1.75	1.83	2.18	2.27	2.27

vent-solute structure or to a decrease in the extension of the paraffin chains in the *n*-decane. There is a decrease in solubility of octacosane in *n*-decane as compared with *n*-octane which may be related to this change in some manner.

TABLE III. COMPARATIVE VISCOSITY OF *n*-OCTACOSANE IN C. P. NORMAL PARAFFIN SOLVENTS

Solvent	Base Molarity	η_r	$\frac{\log \eta_r}{C}$	$K_{cm} \times 10^{-4}$	$K_{cm} \times 10^{-4}$ (Cor.)
n-Hexane	1.335	1.0616	0.01962	2.01	1.94
n-Heptane	1.323	1.0633	0.01999	1.98	1.94
n-Octane	1.335	1.0634	0.02000	1.98	1.94
n-Decane	1.335	1.0587	0.01860	2.12	2.11

CALCULATION OF VISCOSITY FROM VOLUME PER CENT SOLUTE

Einstein found, in the case of rigid uniformly dispersed spheres of a solid in a liquid

$$\eta_{sp} = \Phi K$$

where Φ = proportional volume occupied by spheres in liquid
K = a constant, found to be 2.5 under certain specified conditions

The Einstein equation, however, cannot be applied to polymers since K increases with polymer length; this effect is generally regarded as the so-called shape factor. To correct for this factor in the case of a given polymeric series such as the paraffins, for example, an equation is set up:

$$\eta_{sp}/\Phi N = K_1 \tag{3}$$

where N = number of carbon atoms in the chain which reflects a constant change in shape factor. Staudinger employed a similar equation for the paraffins where the concentration was taken as 1.4 grams per 100 cc. of solution. He found that $\eta_{sp} = Ny$, where y is a constant. In comparing one polymeric series with another, however, the present authors found that the use of volume concentration Φ gives more consistent results than weight concentration when employed in Equation 3. The present data for the *n*-hexane solutions of the paraffins and other polymer solutions were treated according to this relation, and the K value was determined as the chain length increased. The data in Table IV show that η_{sp}/Φ increases proportionately to the number of carbon atoms in the chain, and from these calculations the relation $\eta_{sp}/N\Phi = K_1$ is shown to hold. The data in Table IV indicate that $\log \eta_r/N\Phi = K_2$ is also valid.

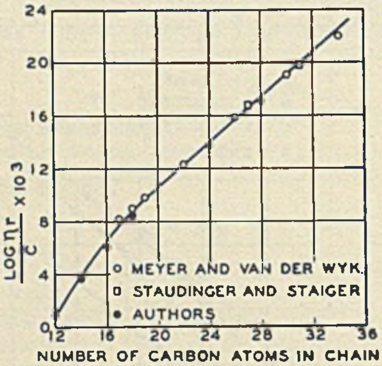

Figure 2. Comparison of Data for the Variation of log η_r/C with the Number of Carbon Atoms in the Chain for Dilute Solutions of Paraffins in Carbon Tetrachloride

Correction $\eta_r = \frac{d_1 \times t_1}{d_0 \times t_0}$ applied to these data.

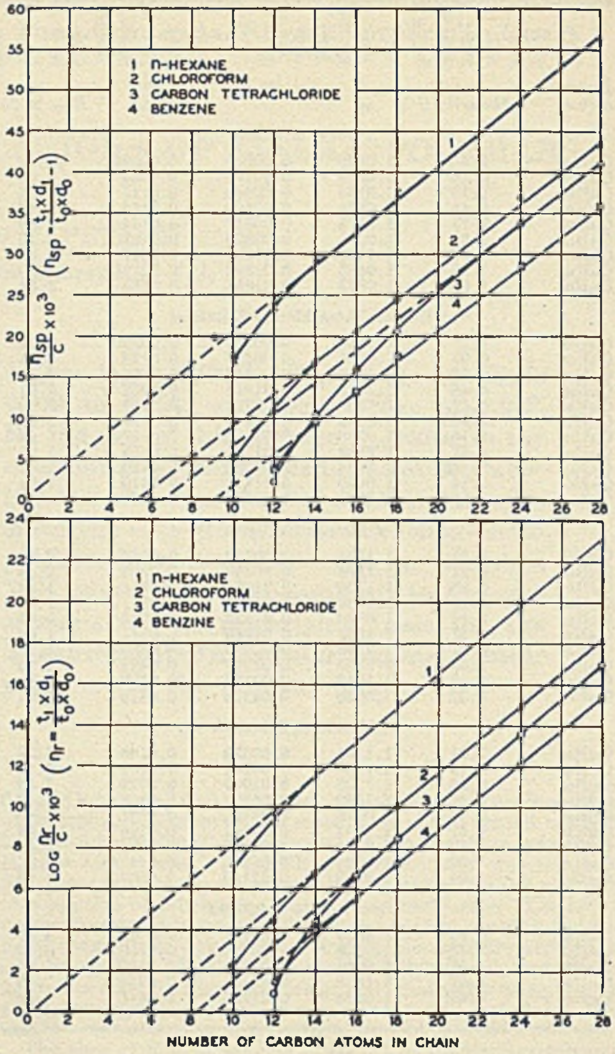

Figure 3. Same Data as Figure 1 with Correction $\eta_r = d_1t_1/d_0t_0$ Applied

The data for hydrosqualene, polyethylene oxide, cellulose acetate, and cellulose nitrate solutions were taken from Staudinger's work (*7*), and the other data were taken from published work by the authors (*1–5*). In all cases the polymers were carefully fractionated and their molecular weights were low enough to avoid serious deviation from Raoult's law in the cryoscopic molecular weight determinations.

Since the data for each member of a given polymeric series agree with the relation $\log \eta_r/N\Phi = K_2$, it is seen that K_2 may have a different value for different polymers. Thus, some other factor besides the number of atoms in the chain of linear polymers must control the viscosity-concentration relation between them.

In a recent paper (*3*) the authors calculated a K_{cm} equivalent for various polymers which depended upon the proportion by weight of the chain atoms in the base molecules to the number of chain atoms in the base molecule:

$$K_{cm} \text{ equivalent} = \frac{\text{No. chain atoms in base molecule} \times K_{cm}}{\text{Wt. proportion of chain atoms in base molecule}}$$

With a wide variety of polymers the K_{cm} equivalent was shown to lie between 2.2×10^4 and 4.8×10^4. In this calculation the specific volume of the solute was not considered, and it was assumed that distances between chain atoms in solution are constant.

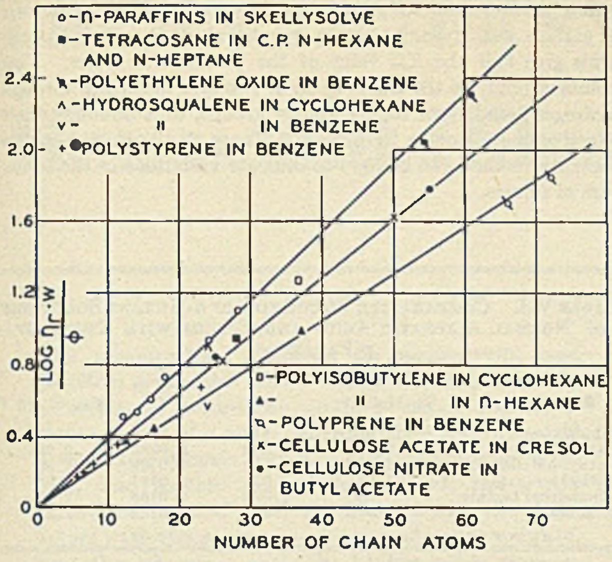

Figure 4. Variation of (log $\eta_r/\phi)W$ with Number of Chain Atoms for Dilute Solutions of Linear Polymers

If the proportion by weight of chain atoms to the base molal concentration is considered in the relation log $\eta_r/\Phi N = K_2$, it is possible to calculate a viscosity-concentration equivalent per chain atom for different linear polymers. The distances between chain atoms in solution are assumed to be the same. Such a chain atom viscosity equivalent K_{ca} can then be calculated by:

$$K_{ca} = \frac{\log \eta_r \times W}{N\Phi} \tag{4}$$

where W = proportional weight of chain atoms in repeating unit to base molecular weight. By assigning an average value of 0.032 to K_{ca} when good solvents are employed, the average number of atoms in any linear polymer chain can be estimated by measuring the viscosity of the polymer in dilute solution, using a good solvent and the following equation:

$$N = \frac{\log \eta_r \times W}{\Phi \times 0.032} \tag{5}$$

If the polymer is strictly linear, its molecular weight can be obtained by multiplying N by the chain atom equivalent weight of the polymer. Examples of these equivalent weights follow:

Polymer	Equivalent Weight per Chain Atom
Paraffins	14
Polyprene	17
Polyisobutylene	28
Polystyrene	52
Cellulose acetate	57.6

Where the polymer chains are branched or cyclized in an unknown manner, the value for N cannot be employed to estimate molecular weight since the equivalent weight per chain atom is not known. In these cases some other independent method must be employed to determine molecular weights. However, where significant nonlinearity in the polymer exists, viscosity measurements may be employed in Equation 5 as an index of polymer length since Staudinger and others have shown that in highly dispersed systems the side groups have a relatively small effect on viscosity.

The low K_{ca} value for depolymerized and partly oxidized polyprene may be due to nonlinearity in its chain, possibly due to oxygen cross linkages. The other equivalent values show fairly good agreement when good solvents are employed. In the case of polyisobutylene in n-hexane and hydrosqualene in benzene, the equivalent values are low, an indication of lack of full chain extension in these solvents. The type of solvent is very important since the solvent which gives the highest relative viscosity value is usually considered as the one which extends the chain most. In view of the complexity of the problem and the many factors affecting viscosity, the agreement in the chain equivalents of the different polymers is considered very good. The viscosity data on various linear type polymer solutions are further analyzed in

TABLE IV. VISCOSITY-CONCENTRATION RELATIONS OF VARIOUS POLYMER SOLUTIONS

M	N	C, Gram per Cc.	Φ	η_{sp}	$\frac{\eta_{sp}}{\Phi}$	$K_1 = \frac{\eta_{sp}}{N\Phi}$	$K_2 = \frac{\log \eta_r}{\Phi N}$
		n-Paraffins $C_{12}H_{26}$ to $C_{28}H_{58}$ in n-Hexane (Skellysolve)					
170.2	12	0.0869	0.1161	0.1446	1.24	0.103	0.042
198.2	14	0.0876	0.1147	0.1857	1.62	0.115	0.045
226.3	16	0.0765	0.0988	0.1801	1.82	0.114	0.045
254.3	18	0.0640	0.0822	0.1720	2.09	0.116	0.047
338.4	24	0.0640	0.0822	0.2316	2.81	0.117	0.046
394.5	28	0.0278	0.0356	0.1114	3.14	0.112	0.046
394.5	28	0.0185	0.0237	0.0686	2.90	0.104	0.044
		$C_{28}H_{58}$ in C. P. n-Hexane					
394.5	28	0.0187	0.0240	0.0616	2.57	0.092	0.040
		$C_{28}H_{58}$ in C. P. n-Heptane					
394.5	28	0.0185	0.0237	0.0633	2.67	0.096	0.040
		$C_{28}H_{58}$ in C. P. n-Octane					
394.5	28	0.0187	0.0240	0.0634	2.65	0.094	0.040
		Polyisobutylene in n-Hexane					
353	12.6	0.1624	0.1805	0.434	2.41	0.190	0.070
460	16.4	0.1624	0.1805	0.534	2.97	0.184	0.062
1030	36.8	0.0448	0.0498	0.306	6.14	0.177	0.063
		Polyisobutylene in Cyclohexane					
1030	36.8	0.0448	0.0498	0.408	8.16	0.226	0.080
		Polystyrene in Benzene					
293	5.64	0.0661	0.0608	0.145	2.38	0.425	0.131
352	6.76	0.0655	0.0603	0.151	2.53	0.378	0.125
393	7.56	0.0661	0.0608	0.167	2.75	0.372	0.143
600	11.54	0.0666	0.0612	0.240	3.94	0.343	0.132
1200	23.1	0.0402	0.0370	0.279	7.56	0.300	0.125
2360	45.4	0.0659	0.0607	1.148	18.9	0.420	0.122
		Polyprene (Rubber) in Benzene					
1120	66	0.0140	0.0150	0.084			0.036
1120	66	0.0280	0.0301	0.178			0.036
1220	72	0.0789	0.0850	0.662			0.036
		Cellulose Acetate in Cresol					
1520	26	0.0288	0.0205	0.193	9.4	0.362	0.144
2890	50	0.0144	0.0101	0.186	18.4	0.368	0.147
		Cellulose Nitrate in Butyl Acetate					
1485	25	0.0270	0.0156	0.155	10	0.400	0.160
3265	55	0.0130	0.0079	0.166	21	3.378	0.154
		Hydrosqualene ($C_{30}H_{62}$) in Benzene					
422	24	0.0280	0.0311	0.058	1.9	0.078	0.033
		Hydrosqualene in Cyclohexane					
422	24	0.0280	0.0311	0.078	2.5	0.104	0.043
		Hydrosqualene in Carbon Tetrachloride					
422	24	0.0280	0.0311	0.078	2.5	0.104	0.043
		Polyethylene Oxide Dihydrate, $H(C_2H_4O)_xH$, in Benzene					
790	54	0.044	0.035	0.20	5.7	0.105	0.042
895	61	0.044	0.035	0.23	6.6	0.108	0.042
1170	80	0.044	0.035	0.32	9.1	0.114	0.043

TABLE V. RELATION BETWEEN VISCOSITY AND EQUIVALENT CHAIN LENGTH OF LINEAR POLYMERS

Polymer	$\frac{\log \eta_r}{N\Phi}$	W*	$K_{ca} = \frac{\log \eta_r \times W}{N\Phi}$
n-Paraffins in Skellysolve	0.045	0.85	0.038
Octacosane in c. p. hexane, heptane, or octane	0.040	0.86	0.034
Polyisobutylene in n-hexane	0.065	0.43	0.028
Polyisobutylene in cyclohexane	0.082	0.43	0.035
Polystyrene in benzene	0.130	0.23	0.030
Hydrogenated polyindene in benzene	0.150	0.20	0.030
Polyprene in benzene	0.030	0.71	0.021
Hydrosqualene in benzene	0.033	0.70	0.023
Hydrosqualene in cyclohexane	0.043	0.70	0.030
Hydrosqualene in CCl_4	0.043	0.70	0.030
Cellulose acetate in cresol	0.145	0.22	0.032
Cellulose nitrate in butyl acetate	0.157	0.21	0.033
Polyethylene oxide dehydrate in benzene	0.042	0.21	0.037

* Proportional weight of chain atoms in repeating unit to base molecular weight.

Figure 4 where it is shown that the average K_{ca} value is 0.032 with a spread of about ±17 per cent in this value. Some of this spread can be attributed to solvent effects. In some cases lack of perfect linearity may be a contributing factor.

The use of base molar concentration C in the Staudinger equation,

$$M = \eta_{sp}/CK_m \tag{6}$$

has led to considerable confusion. Also, Staudinger calculated what he terms K_{eq} by dividing his K_m values for different polymers by the number of chain atoms in the base molecule. If this be done in the case of the polymers listed in Table V, the Staudinger K_{eq} values are found to range from 0.82×10^{-4} for the polyprene to 3.12×10^{-4} for polystyrenes as shown in Table VI. In the present authors' analysis the concentration is based on the same chain atom concentration obtained by employing the ratio W/Φ in Equation 4.

TABLE VI. COMPARISON OF STAUDINGER'S K EQUIVALENT FOR VARIOUS POLYMER SOLUTIONS

Polymer Solution	Staudinger's $K_m \times 10^4$	Staudinger's $K_{eq} \times 10^4$
n-Paraffins in n-hexane	1.20	1.20
Polyisobutylene in n-hexane	3.71	1.85
Polyisobutylene in cyclohexane	4.92	2.46
Polyprene in benzene	3.30	0.82
Cellulose acetate in cresol	12.7	2.54
Cellulose nitrate in butyl acetate	11.6	2.32
Polystyrene in benzene	6.25	3.12
Hydrosqualene in benzene	3.52	0.88
Hydrosqualene in cyclohexane	4.72	1.18
Hydrosqualene in CCl_4	4.72	1.18
Polyethylene oxide in benzene	2.73	1.36

It is recognized that the above estimates of the viscosity of linear polymers on an equivalent chain atom basis is not complete and should be explored further for other cases. However, this analysis is presented as evidence that the viscosity method for molecular weight determinations of strictly linear polymers of moderate molecular weights is basically sound if proper consideration is given to the choice of solvent and to the accurate establishment of the viscosity–molecular weight relation in the lower polymers. In the case of extremely high molecular weight polymers, independent methods of sufficiently proven accuracy are not available to establish the soundness of the viscosity method. However, the simplicity and reproducibility of results by the viscosity method makes it a valuable tool for comparing high polymer fractions.

As a check on the paraffins it was of interest to compare the viscosities of n-hexane solutions of certain normal aliphatic acids and esters which are given in Table VII. The molarity was calculated by employing a base molecular weight obtained by dividing the molecular weight of the substance by the total number of carbon and oxygen atoms in the chain. It is noted that the acids give half the K_{cm} value of the paraffins or esters. This points strongly to the chaining up of two acid molecules through hydrogen bonding of their carboxyl groups, thus doubling their effective chain lengths in solution. These results show how the viscosity method can be used to indicate variations in the structure of solutes.

TABLE VII. COMPARATIVE VISCOSITIES OF n-HEXANE SOLUTIONS OF NORMAL ALIPHATIC ACIDS AND ESTERS WITH THOSE OF n-PARAFFINS

Substance	Molarity	η_r	$\frac{\log \eta_r}{C}$	$K_{cm} \times 10^{-}$
Palmitic acid	1.997	1.114	0.0238	1.07
Stearic acid	0.485	1.032	0.0286	0.99
Methyl palmitate	1.993	1.063	0.0137	1.98
Methyl stearate	1.931	1.074	0.0161	1.85
n-Octadecyl acetate	1.930	1.076	0.0165	1.89
Octadecane	4.570	1.116	0.0138	1.84

CONCLUSIONS

1. Data are presented on the viscosity of a series of pure normal paraffins in carbon tetrachloride, benzene, chloroform, and cyclohexane which confirm previous investigators' work and show nonconformity to the Staudinger rule that viscosity increases proportionately with increase in carbon atoms in the chain.

2. Data presented on n-hexane solutions of the paraffins confirm the Staudinger rule in the case of all paraffins above $C_{14}H_{30}$, showing that $\eta_{sp} = NK$, where $K = 0.00190$. In the same manner the data agrees with the formula $\eta_r = 1 + (NK)$, where $K = 0.00183$.

3. In the case of the paraffins and other fractionated polymers where reliable experimental data are available, it is shown that $\eta_{sp} = K_1N\Phi$ and that $\log \eta_r = K_2N\Phi$.

4. The relation $K_{ca} = (\log \eta_r \times W)/N\Phi$ is shown to hold between the values for K_{ca} of 0.030 and 0.038 for a wide range of linear polymers in good solvents. The value for K_{ca} will be lowered as in the case of depolymerized and partly oxidized rubber, possibly due to poor solution or cross linking.

5. It is shown that stearic and palmitic acids dissolved in n-hexane contribute to viscosity in agreement with a dimolecular chain length, whereas esters of these acids behave like the paraffins.

6. The present work provides evidence of the basic soundness of the viscosity method for molecular weight estimation of linear polymers when proper procedure is followed and a suitable solvent is chosen.

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LIGNIN ESTERS OF Mono- and Dibasic Aliphatic Acids

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The preparation, methods of purification, and physical properties are described of a large number of aliphatic monobasic esters of alkali hardwood lignin, from the acetyl through the stearoyl, and also of the dibasic esters of succinic, adipic, suberic, and azelaic acids. In general, the penta esters are formed with the lower acids, the tetra esters with the acids of medium molecular weights, and the tri esters with the higher acids such as palmitic and stearic acids. As a rule, the melting points of the products decrease with increasing chain length of the acid group as the products become more waxlike. All the esters of alkali hardwood lignin are quite soluble in acetone, chloroform, dioxane, and ethyl acetate. Solubility in methanol and ethanol decreases with increasing chain length of the fatty acid, whereas the solubility in ether and petroleum ether increases with increasing chain length. Esters of benzoic acid and *p*-toluenesulfonic acid have also been prepared, purified, and studied. One ester (the stearate) has proved to be an excellent mold lubricant for wood plastics. It is also soluble in drying and semidrying oils, and has been successfully incorporated in ink and paint formulations.

ACYLATION of lignin and lignin derivatives has been used for some time as a means for determining the presence of hydroxyl groups in lignin and for their estimations. Thus, Willstätter lignins of various sources have been acetylated by Pringsheim and Magnus (*15*), Heuser and Ackermann (*11*), and Fuchs and Horn (*9*). Freudenberg lignin from spruce and beech was acetylated by Freudenberg and co-workers (*5*), and Brauns and Hibbert (*3*) acetylated partially methylated Willstätter and Freudenberg lignin. Freudenberg and Hess (*7*) reacted Freudenberg lignin with toluenesulfonyl chloride. All these lignin esters are as insoluble as the original materials from which they were prepared. Alkali lignin prepared from corncobs was acetylated by Phillips (*13*); that obtained from winter rye straw was benzoylated by Beckmann, Liesche, and Lehmann (*1*); and Marshall, Brauns, and Hibbert (*12*) acetylated alkali lignin from spruce. These acetylated alkali lignins are soluble in organic solvents. Lignin derivatives, such as methanol, glycol, and phenol lignins, have been acylated to acetyl, benzoyl, *p*-bromobenzoyl, *p*-nitrobenzoyl, and *p*-toluenesulfonyl lignin esters (*4*), which are also soluble in organic solvents such as dioxane, pyridine, and acetone.

A lignin of comparatively high purity (Meadol) is now available on the market (*14*). It is prepared from a soda black liquor from hardwood cooks. The crude black liquor is evaporated to a specific gravity of 1.1 and then contains 19–20 per cent total solids, of which about 60 per cent is organic matter and the remainder is soda ash. A portion of the lignin is precipitated from this solution by passing carbon dioxide obtained from flue gases into the solution until a pH of 8.5–8.6 is reached. This flue gas is obtained from coke burned in a Spencer boiler and cooled to 25–30° C. by means of two Struthers-Wells gas coolers in series. After cooling, the gas, which averages 15 to 18 per cent carbon dioxide, is passed through the black liquor in a tank, operating at approximately 5 pounds per square inch positive pressure, which greatly increases the rate of carbon dioxide adsorption. During the carbonation cycle the black liquor is continuously recirculated by means of a pump, and is sprayed into the gas space in the upper third of the tank. The Meadol separates in the form of an extremely fine precipitate which is coagulated by heating to 90° C. and immediately cooling to 40°. The lignin is then filtered on an acidproof Oliver vacuum filter, and thoroughly washed with water until the wash water has a light straw color and then with dilute sulfuric acid to reduce the ash content. The filtrate is returned to the pulp mill for recovery of soda ash, and the wash water and acid are discarded. The lignin is dried on a double-drum dryer. It is powdered and has a moisture content between 2 and 4 per cent and an ash content of 0.5 per cent. Its methoxyl content of 21.5 per cent agrees with that usually found for lignins from hardwood (*10*). The carbon content of 64.35 per cent and the hydrogen content of 5.93 are also within the range usually found for hardwood lignins. Meadol is soluble in pyridine and partially soluble in dioxane, acetone, and alcohol; it is insoluble or only slightly soluble in ether and petroleum ether. It is thermoplastic, with a melting point of 230° C.

Lignin itself is a poor material for plastics, even in combination with other plastic bases. This may be because of the presence of various types of hydroxyl groups which make it a relatively hydrophilic compound. Although in the condensation of lignin with formaldehyde, furfural, or other compounds the phenolic hydroxyl groups in the lignin may be covered, there still remain aliphatic (alcoholic) hydroxyl groups which will affect the water resistance of plastics made from it. Covering these hydroxyl groups by acylation should make the lignin less hydrophilic and, by using higher fatty acids, even water repellent.

Because Meadol is now available in large quantities and because it can be considered a hardwood lignin of relatively high purity, a series of Meadol esters have been prepared and their physical properties determined. In general, the esters are prepared by the dropwise addition of 5.5 moles of acid chloride to a solution of 1 mole of Meadol (molecular weight 860), previously dried in a vacuum desiccator over sodium hydroxide, in dry pyridine with vigorous stirring at room temperature. The addition requires 30–60 minutes. The temperature is increased to approximately 65–75° C. and kept at that point, with continuous stirring, for 2 hours. The mixture is then poured into 1.5–2 liters of ice water with vigorous stirring, whereby the

Table I. Characteristics of Aliphatic Monobasic Acid Esters of Hardwood Alkali Lignin

Acyl Group	No. C Atoms in Acids	Yield of Purified Ester, %	Methoxyl in Purified Ester, %	No. of Acid Groups	Theoretical Methoxyl, %	Melting Point, ° C.
Acetyl	2	98	17.2	5	17.4	197–204
Propionyl	3	96	16.3	5	16.3	183–193
Butyryl	4	96	16.2	4	16.3	124–129
Isobutyryl	4	92	16.1	4	16.3	152–162
Valeryl	5	94	15.2	4	15.6	140–155
Isovaleryl	5	96	14.8	5	14.5	130–140
Caproyl	6	96	14.1	5	13.8	135–140
Isocaproyl	6	90	14.8	4	14.9	130–145
Heptoyl	7	89	14.3	4	14.2	120–135
Decanoyl	10	40	12.5	4	12.6	80–95
Undecanoyl	11	78	12.5	4	12.1	80–110
Lauroyl	12	54	11.6	4	11.5	60–85
Tridecanoyl	13	91	10.5	4 5	11.3 10.1	65–70
Myristoyl	14	64	11.2	4	10.9	100–108
Palmitoyl	15	46	11.4	3	11.8	90–105
Stearoyl	16	56	11.4	3	11.2	140–150
Oleoyl	16	60	8.5	5	8.5	130–140

acylated product separates and is filtered. If a part of the pyridine is to be recovered, the mixture is distilled under reduced pressure and the residue extracted with ice water to remove the pyridine hydrochloride. The isolated crude products are then purified as described under the individual compounds.

ESTERS OF MONOBASIC ALIPHATIC ACIDS

Acetyl and propionyl Meadol were prepared by the action of acetic anhydride or propionyl chloride and pyridine on Meadol. For purification, 5 grams of the dry crude acylated Meadol were dissolved in 40 cc. of dioxane and precipitated by dropping the dioxane solution into vigorously stirred ether. The product was washed twice with fresh ether and once each with high-boiling and with low-boiling petroleum ether. The product was dried in a desiccator over sulfuric acid.

Butyryl and isobutyryl Meadol were prepared from their respective acyl chlorides. The crude products, obtained by pouring the reaction mixtures into ice water and drying in a desiccator, were purified by the dropwise addition of a solution of 5 grams in 35 cc. of benzene into well-stirred petroleum ether.

Valeryl, isovaleryl, caproyl, and isocaproyl Meadol were prepared from their corresponding acyl chlorides. The crude products, obtained by precipitation with water, were dried and purified by the addition of their solutions in benzene to petroleum ether.

Heptoyl Meadol was prepared by the action of 25 grams of heptoyl chloride upon a solution of 25 grams of Meadol in 80 cc. of pyridine. After the reaction was complete, 60 cc. of the pyridine were distilled off *in vacuo*, and the residue was extracted with water. The crude sticky product was milled for several hours in a ball mill, which gave a fine brown powder. In spite of thorough washing and drying in a desiccator over sulfuric acid for several days, it still had a strong odor of heptoic acid. A 5-gram sample was purified by dropping its solution in 25 cc. of benzene into a mixture (1:1) of high- and low-boiling petroleum ether (75–95° and 30–45° C., respectively).

Decanoyl Meadol was prepared by the method used for butyryl Meadol. Because the crude product was sticky even after milling with water in a ball mill, it was dissolved in a mixture of acetone and dioxane and the solution was added dropwise to vigorously stirred water. It was filtered, washed with fresh water, and dried. For further purification, a solution of 5 grams in 25 cc. of absolute ether was centrifuged, filtered, and dropped into absolute methanol, followed by a precipitation of its solution in acetone into water.

Undecanoyl Meadol was obtained by the action of 32 grams of undecanoyl chloride upon 25 grams of Meadol in 80 cc. of pyridine. The crude product, even after milling in a ball mill, was sticky. It was a dark brown crumbly mass which, on drying, fused together to form a hard cake. When its solution in benzene was dropped into low-boiling petroleum ether, it was precipitated as a fine brown powder; when the centrifuged product was dried, it partly fused and became hard and almost black.

Lauroyl Meadol, which separated as a sticky product on pouring the reaction mixture into ice water, was purified by dropping its solution in a mixture of acetone and dioxane into water, followed by a precipitation of its ether solution into methanol.

Tridecanoyl Meadol was isolated from the reaction mixture by distilling off the excess pyridine and dissolving the residue in ether. The pyridine hydrochloride was centrifuged off the solution; it was washed twice with a saturated calcium chloride solution containing 10 per cent of hydrochloric acid, with a neutral saturated calcium chloride solution, and finally with a suspension of calcium carbonate in saturated calcium chloride. The ether solution was dried with calcium chloride and the ether distilled off, leaving the tridecanoyl Meadol as a hard waxy product.

Myristoyl and palmitoyl Meadol separated as oils when the reaction mixture was poured into ice water; after treatment with water in a ball mill, the oils became solid. They were filtered, washed with water, and dried. Each of these esters was purified by dropping its solution in ether into absolute methanol, followed by precipitation of the dioxane solution of the methanol-insoluble product into water.

Stearoyl Meadol was prepared and purified by the method used for tridecanoyl Meadol, except that the ether solution was washed with sodium carbonate solution. This may have partially saponified the stearoyl Meadol because the methoxyl content agrees with that calculated for a tristearate.

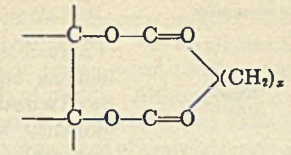
Stearoyl Meadol was prepared on a semicommercial scale by vigorously stirring 40 pounds of Meadol with a solvent mixture consisting of 30 pounds of pyridine and 100 pounds of dioxane. Eighty pounds of stearoyl chloride were quickly added. The temperature of the reaction mixture rose to 90° C. which was sufficiently high to keep the reaction mixture fluid. After stirring for a short time, the ester was precipitated by pouring the reaction mixture into cold water. The product was filtered and washed with water. It was ball-milled with water to break up the lumps; the product was filtered and dried. The yield was approximately 110 pounds.

Oleoyl Meadol was isolated from the reaction mixture by extraction with ether. The ether solution was washed twice with 10 per cent hydrochloric acid, once with water, and then quickly with ice-cold 5 per cent sodium hydroxide solution. As a separation of the aqueous solution occurred slowly, it was saturated with calcium chloride. The ether solution was dried with calcium chloride and evaporated.

The yields, analytical data, and melting point data are given in Table I.

ALIPHATIC DIBASIC ACID ESTERS

With monobasic fatty acids, tri-, tetra-, or penta-acyl compounds of Meadol are formed, but with dibasic acids the reaction is more complicated. If two hydroxyl groups in the lignin building unit are linked to two adjacent carbon atoms, as in glycol, or even if two hydroxyl groups are in the 1,3 position to each other, as in 1.3-propanediol, it might be possible that one acyl dichloride would react with those hydroxyl groups to form heterocyclic ring systems containing two oxygen atoms.



The formation of such ring systems also depends upon the size of x because with an increasing number of carbon atoms in the chain of the dibasic acid, the formation of such ring systems would become more improbable.

None of the structural formulas, with the exception of the hypothetical ones proposed by Fuchs (*8*), contains a glycol or 1,3-propanediol grouping of hydroxyl groups. On the basis of Freudenberg's structural formula (*6*), each lignin building stone with a C_6—C_3 skeleton contains one hydroxyl group; because these building stones are linked together from the side chain of one stone to the benzene nucleus of the next, it is obvious that the hydroxyl groups in the lignin building unit must be quite a distance from one another. If it is assumed that, of the five hydroxyl groups present in the lignin building stone, two pairs are covered by two dibasic acyl groups and one hydroxyl group would still be free. Two such partially acylated lignin building stones could then react with a fifth acyl dichloride, with the formation of a penta-acyl di-Meadol derivative of the structure shown in formula I (Figure 1).

As mentioned above, it is improbable that the hydroxyl groups in the lignin building unit are located in such a way as to favor the formation of heterocyclic ring systems. It is much more probable that one molecule of acyl dichloride would react with two hydroxyl groups of two lignin building units to form a two-membered chain. The simplest chain which can be formed in this way is that in which five acyl dichlorides have reacted with two lignin building units to form a compound of the structure shown in formula II (Figure 1).

Even for the formation of a compound of such a structure, the position of the hydroxyl groups must be stereochemically located in such a way as to allow the formation of ring systems. It is possible that, in a tridimensional molecule such as lignin, two hydroxyl groups may be in such relation to each other that ring formation may occur; however, that will happen only if the same acid chloride molecule has a chance to react with these hydroxyl groups before one has been taken by another acyl chloride molecule. It is possible, therefore, that two hydroxyl groups of a lignin building unit are combined with the same acyl group, although this seems unlikely. It is much more probable that, in the reaction between Meadol and a dibasic acid chloride, the latter combines with the most reactive hydroxyl group in its vicinity and thus forms chain molecules of various size and unknown structure. The physical properties of the dibasic esters of Meadol seem to support this view, because in most cases products are obtained which are insoluble or only partially soluble in any organic solvent. In some cases it is possible to separate the reaction products into fractions of various solubility, but even the more soluble portions are less soluble than the esters of the monobasic acids.

TABLE II. CHARACTERISTICS OF ALIPHATIC DIBASIC ACID ESTERS OF HARDWOOD ALKALI LIGNIN

Acyl Group	No. C Atoms in Acids	Yield of Purified Ester, %	Methoxyl in Ester, %	Ratio of Acid to Meadol	Theoretical Methoxyl, %	Melting Point, ° C.
Succinyl	4	90	18.2	4:2	18.0	195–200
Adipyl	6	52	18.2	3:2	18.0	165–180
Suberyl[a]	8	98 (crude)	..	..	..	.....
Azelayl	9	68	16.6	4:2	16.6	165–180

[a] Not yet purified and tested.

The following Meadol esters of dibasic esters were prepared by using the general method with the exception that more pyridine was used as solvent, because soon after the addition of the acyl chloride, the reaction mixture becomes more and more viscous. In some cases, with the progressive addition of the acyl chloride, the reaction mixture becomes gummy or even solid.

Succinyl Meadol was prepared from 25 grams of Meadol in 100 cc. of pyridine and 12 grams of succinyl chloride. A portion of the crude product was soluble in a mixture of dioxane and cyclohexanone (1:1), and was precipitated by pouring the solution into ether.

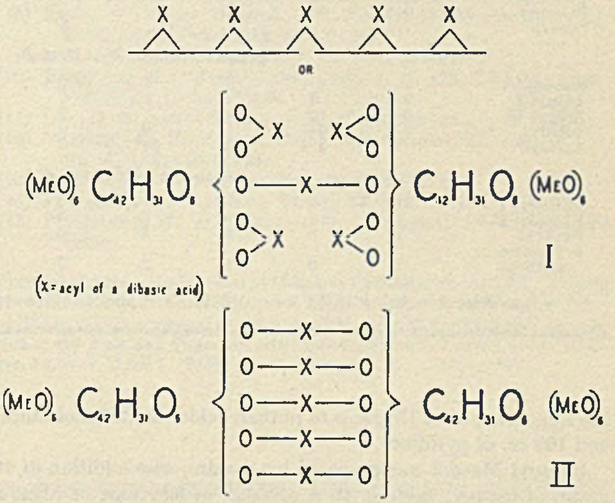


Figure 1. Structural Formulas of Dibasic Acid Esters

Adipyl Meadol I was obtained by the addition of 29 grams of adipyl chloride to a solution of 25 grams of Meadol in 75 cc. of pyridine. After about 60 per cent of the chloride had been added, the mixture became solid and an additional 50 cc. of pyridine was added. The remainder of the chloride was diluted with 25 cc. of dioxane. At the end of the reaction, the product in the reaction flask formed a crumbly mass. Adipyl Meadol II was prepared with only half the above amount of adipyl chloride.

Suberyl Meadol was prepared by using only 2 molecules of suberyl chloride instead of 2.5, as calculated for a completely acylated Meadol.

Azelayl Meadol was made in the same way as adipyl Meadol II, using 25 grams of Meadol in 100 cc. of pyridine and 18 grams of azelayl chloride.

The yields, analytical data, and physical characteristics of the dibasic acid esters are listed in Table II.

ESTERS OF AROMATIC ACIDS

Phthalyl Meadol I was obtained by the addition of 12 grams of phthalyl chloride (2 molecules) to a solution of 25 grams of Meadol in 80 cc. of pyridine. When half the chloride had been added, the mixture soon became viscous and the reaction mixture finally formed a rubberlike mass. The main portion of the pyridine was then distilled off under reduced pressure, and a hard residue remained. This was milled with water in a ball mill to a fine light brown powder. Phthalyl Meadol II was prepared in

TABLE III. SOLUBILITIES[a] OF ESTERS OF HARDWOOD ALKALI LIGNIN

Acyl Group	Methanol	Ethanol	Acetone	Chloroform	Ether	Dioxane	Benzene	Petroleum Ether	Ethyl Acetate
Monobasic Acid Esters									
Acetyl	1	1	3	3	0	3	2	0	3
Propionyl	1	1	3	3	0	3	2	0	3
Butyryl	1	1	3	3	1	3	3	0	3
Isobutyryl	1	1	3	3	1	3	3	0	3
Valeryl	1	1	3	3	1	3	3	0	3
Isovaleryl	1	1	3	3	1	3	2	0	3
Caproyl	0	0	3	3	2	3	2	0	3
Isocaproyl	1	1	3	3	2	3	3	0	3
Heptoyl	0	0–1	3	3	2–3	3	3	0	3
Decanoyl	0–1	0	...	...	2–3	...	...	0–1	...
Undecanoyl	0	0	3	3	2	2–3	2–3	0–1	3
Lauroyl	0	0	3	...	2–3	3	3	1	3
Tridecanoyl	0	0	3	...	2	2–3	2–3	2–3	...
Myristoyl	0–1	0–1	3	3	3	3	3	2–3	3
Palmitoyl	1	1	...	...	3	3	3	...	3
Stearoyl	0–1	0–1	3	...	3	3	3	3	3
Oleoyl	...	...	3	...	3	3	3	2–3	...
Aliphatic Dibasic Acid Esters									
Succinyl	...	...	2	1	0	2	0	...	...
Adipyl I	0–1	0	0–1	...	0	0–1	0	0	...
Adipyl II	0–1	0	2–3	...	0	2–3	0	...	...
Suberyl	0–1	0–1	1	0	0	2	0	0	...
Azelayl	1	0–1	2	0–1	0	2	0	0	0–1
Aromatic Acid Esters									
Phthalyl I	0	0	1–2	0–1	0	1–2	0	0	0
Phthalyl II	0	0	1–2	0	0	1–2	0	0	0
Benzoyl	0	0	2	3	0	3	2	0	1
p-Toluenesulfonyl	0	0	1	2	0	3	0	0	0

[a] 0 = insoluble; 1 = below 10%; 2 = 10–50%; 3 = above 50% (very soluble).

the same way, from 15 grams of phthalyl chloride (2.5 molecules) and 105 cc. of pyridine.

Benzoyl Meadol was prepared by the dropwise addition of 40 grams of benzoyl chloride to a solution of 50 grams of Meadol in 100 cc. of pyridine. The reaction mixture was poured into water, and the crude benzoyl Meadol was washed with water, 5 per cent sodium bicarbonate, 2 per cent acetic acid, and finally water. A dried sample was purified by the addition of a solution in dioxane to anhydrous ether.

p-Toluenesulfonyl Meadol was obtained under the same conditions, from 25 grams of Meadol in 75 cc. of pyridine and 30 grams of *p*-toluenesulfonyl chloride.

SOLUBILITY AND MELTING POINT

The solubilities of the crude products are given in Table III. All the fatty esters of Meadol are quite soluble in acetone, chloroform, dioxane, and ethyl acetate, but the solubility in methanol and ethanol decreases with increasing chain length of the fatty acid; the solubility in ether and in petroleum ether increases with the chain length.

The solubility of the benzoyl and *p*-toluenesulfonyl derivatives is similar to that of the fatty acid esters; the toluenesulfonyl ester is the less soluble compound. The esters of the dibasic acid are, in general, only slightly soluble, probably because of the formation of complicated high molecular compounds; for this reason their purification is difficult.

The melting points of the purified esters are given in Tables I and II. As would be expected of these amorphous and relatively high molecular compounds, the melting points are far from being sharp. Most of the products sinter long before they begin to melt, and the melting itself often occurs over a wide range. In general, the melting points decrease with increasing chain length of the acid group, because the products become more waxlike with the higher fatty acids. The melting points of the benzoyl, the *p*-toluenesulfonyl, and the dibasic acid derivatives are considerably higher than those of the fatty acid derivatives having the same number of carbon atoms.

DISCUSSION OF RESULTS

Assuming for the lignin building unit of Meadol (a hardwood lignin) a unit molecular weight of 860, its methoxyl content for six methoxyl groups per building unit is calculated to be 21.6 per cent. The methoxyl content found agrees well with the calculated value. On the basis of this molecular weight and the presence of five free hydroxyl groups per lignin building unit (*2*), the methoxyl values for the tri-, tetra-, and penta-acyl derivatives were calculated (Table IV). It is evident that the acetyl and propionyl Meadol esters are penta-acyl derivatives. As these compounds are insoluble in ether, whereas acetic and propionic acids are very soluble in this solvent, they can be easily purified. With increasing chain length of the acyl group, tetra-acyl derivatives are formed for the most part; in the case of palmitoyl and stearoyl chlorides, triacyl esters are obtained. This may be partially explained by steric hindrances (*5*) or by the fact that the esters of the higher fatty acids are difficult to purify because of their high solubility in solvents such as ether and petroleum ether; these solutions give homogeneous solutions with aqueous alkali. The latter are used to remove the excess acid; because this procedure requires a long time, partial saponification of ester groups (especially of those combined to a phenolic or enolic hydroxyl group) may take place. On the other hand, the methoxyl value of the oleoyl ester agrees well with a penta-oleate if the method of purification can be considered sufficient. Whereas the Meadol benzoate is a penta ester, the *p*-toluenesulfonate is a tetra ester (found, 8.3 per cent; calculated for a tri ester, 7.3 per cent; for a tetra ester, 8.6 per cent; for a penta ester, 9.8 per cent). The methoxyl content also agrees well with that of a tetra ester. As the benzoyl and the *p*-toluene-

TABLE IV. NUMBER OF ESTER GROUPS PER LIGNIN BUILDING UNIT

Acyl Derivative	MeO Found, %	Methoxyl Content Calcd. for: 3 acyl groups	4 acyl groups	5 acyl groups	No. Acyl Groups per Lignin Unit
Acetyl	17.23	...	19.0	17.4	5
Propionyl	16.3	...	17.17	16.33	5
Butyryl	16.23	...	16.32	15.4	4
Isobutyryl	16.1	...	16.32	15.4	4
Valeryl	15.24	...	15.56	14.54	4
Isovaleryl	15.05	...	15.56	14.54	4.5
Caproyl	14.06	...	14.87	13.8	5
Isocaproyl	14.77	...	14.87	13.8	4
Heptoyl	14.25	...	14.23	13.1	4
Decanoyl	12.47	...	12.6	11.4	4
Undecanoyl	12.5	...	12.14	10.95	4
Lauroyl	11.6	...	11.45	10.51	4
Tridecanoyl[a]	(10.48)	...	11.3	10.1	(5)
Myristoyl	11.2	12.5	10.94	9.7	4
Palmitoyl	11.4	11.8	10.27	...	3
Stearoyl	11.37	11.23	9.67	...	3
Stearoyl	9.52	11.23	9.67	...	4
Oleoyl	8.45	11.3	9.73	8.5	5

[a] This product was not further purified.

sulfonyl Meadol esters are easily purified, there seems to be no doubt as to their composition. As mentioned above, the Meadol esters of the dibasic acids are relatively insoluble and for that reason are difficult to purify. Although in some cases (succinyl, suberyl, and azelayl esters) tetra esters seem to be formed, the main product with 2 moles of phthalyl chloride is a tetra ester and with 2.5 moles is a penta ester.

INDUSTRIAL APPLICATIONS

A study of the industrial application of the Meadol esters was recently initiated. It has been found that Meadol stearate is an excellent mold lubricant for woody plastics such as redwood, hydrolyzed wood, and the like. Because this product is also soluble in drying and semidrying oils, it may be successfully incorporated in ink and paint formulations. A solution of Meadol stearate in linseed oil is buttery in consistency, as compared with the stringy solutions obtained with drying oil varnishes. Thus, its use as a modifier of the flow characteristics of inks is indicated.

Meadol suberate also appears to be an excellent resin with some possibilities in the field of injection molding.

Molding compounds in which various Meadol esters have been substituted for Meadol have shown a reduction in water absorption of the finished molded articles, especially when the higher esters are used. This would be expected from the hydrophobic nature of the acid group.

Other possible applications of the various esters are suggested by their solubility and melting point behavior. By selection of the proper ester, it is now possible to utilize Meadol in many applications where it could not be used otherwise. Studies of these uses are currently underway, and the full picture of their potential field of application is still incomplete.

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ROYAL LABORATORY

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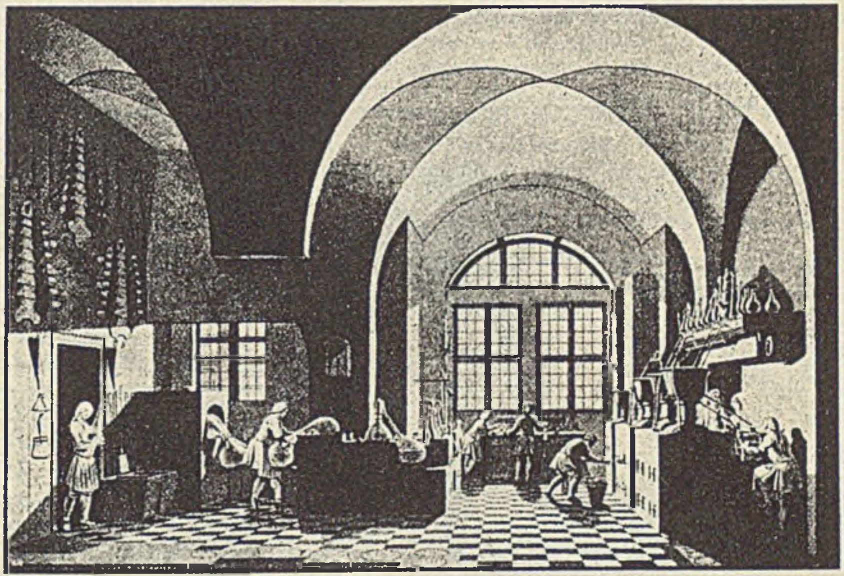

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Surface Consistency Characteristics of ASPHALTS

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The need for studying the surface consistency characteristics of asphalts, as well as bulk flow properties, is pointed out. A modification of the A. S. T. M. asphalt penetration method, used to investigate consistency characteristics of asphalt surfaces ranging in thickness from 0.04 to 0.30 cm., is described. The modified procedure is based upon the load in grams required to force the A. S. T. M. needle into the asphalt to a given depth in a constant time. It avoids several shortcomings of the A. S. T. M. penetration procedure and is identified as constant depth penetration. Data are given to illustrate the application of constant depth penetration measurements to show the progressive increase of hardness of roofing asphalt in the accelerated weathering test. Data are also given to illustrate application of the method to the measurement of the effect of various storage conditions on surface consistency of asphalt, and from this work a storage test was set up at 125° F. (51.7° C.) whereby the tendency of asphalts from various sources to undergo surface hardening was determined. The conclusion is reached that certain properties of asphalt surfaces can be studied by application of constant depth penetration measurements, and that the results supplement information currently obtained by bulk flow consistency measurements.

A GREAT deal of information has been published during the last few years on the flow characteristics of asphalts (*1, 2, 3, 6*). However, in all of this work the consistency measurements have been applied in such a manner that they reflect the flow properties of asphalt in bulk. In practice, asphalts are applied in relatively thin layers or coatings which become progressively harder with time and severity of service conditions. Hence, it would be desirable to study the flow properties of such relatively thin layers of asphalts since they might be significant in relation to performance of the asphalt in service.

In making such a study, it would be essential to measure consistency of undisturbed layers of asphalt in order to preserve any so-called structural effect on consistency (*5*). To attain this objective, it has been necessary to develop a method suitable for measuring the consistency of relatively thin layers of asphalts; the object of this paper is to describe the method used and to present some resulst on the flow characteristics of asphalt surfaces.

Several requirements were set up: (*a*) The procedure should be applicable to such thin layers of asphalt as are tested in accelerated weathering tests on roofing asphalts; (*b*) the unit of measurement should permit direct comparison between determinations of widely different magnitude; (*c*) the method should be applicable over a wide temperature range, such as 0° to 46.1° C. (32° to 115° F.); (*d*) the method should be applicable to asphalts of a wide consistency range; and (*e*) the method should require a minimum of time.

On the basis of these requirements, a penetration procedure was developed in which the weight required to force the A. S. T. M. penetrometer needle into a layer of asphalt to a given depth in a constant time is determined. By keeping the penetration depth constant,. numerous shortcomings of the A. S T. M. as-

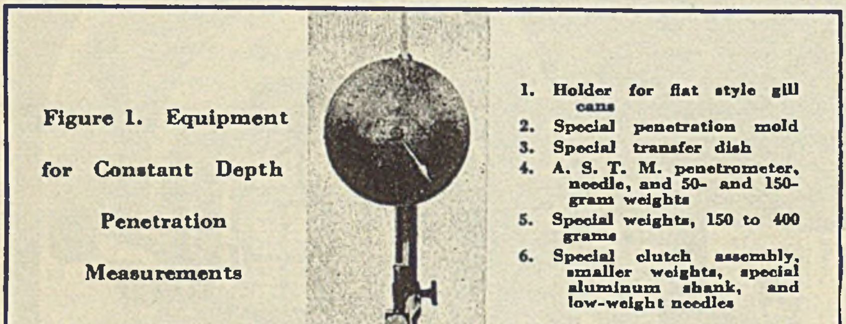

Figure 1. Equipment for Constant Depth Penetration Measurements

1. Holder for flat style gill cans
2. Special penetration mold
3. Special transfer dish
4. A. S. T. M. penetrometer, needle, and 50- and 150-gram weights
5. Special weights, 150 to 400 grams
6. Special clutch assembly, smaller weights, special aluminum shank, and low-weight needles

phalt penetration procedure (D-5-25) are avoided. These points may be summarized as follows:

1. The variable amount of asphalt displaced for each different A. S. T. M. penetration on the conical portion of the needle is kept constant.
2. The effect of the asphalt adhering to the needle is kept substantially constant since the same surface area is in contact with the asphalt.
3. Because of the small penetration depth, the difference in the depression around the needle is kept approximately constant, whereas in the A. S. T. M. procedure there are pronounced variations depending on the type and consistency of the asphalt.
4. By keeping penetration depth and time constant, the rate of asphalt displacement is kept substantially constant, which means that the degree of "working" of the asphalt is essentially constant.
5. Under the foregoing conditions, the weight required to give a constant depth penetration is a means of expressing asphalt consistencies which permits ready comparison of any two determinations.

APPARATUS

The A. S. T. M. penetrometer was employed in this investigation with certain modifications which were necessary to obtain a much wider range of loading weights on the needle. These loading weights were obtained as follows:

Weights of 250 to 600 grams were obtained by installing a special compression spring in the regular clutch assembly of the A. S. T. M. penetrometer and using a series of graduated weights (Figure 1, item 5).

Weights in the range 50 to 250 grams were obtained by using the regular A. S. T. M. penetrometer and series of graduated weights (Figure 1, item 4).

Weights in the range 10 to 50 grams were obtained by using a special tubular aluminum shank with the same dimensions as the regular shank, which weighed 10 grams including the needle. This shank was loaded with weights up to 50 grams (Figure 1, item 6).

Weights in the range 1 to 20 grams were obtained by welding an A. S. T. M. needle into an aluminum rod 0.24 cm. in diameter and 6.5 cm. long. This needle weighed 1 gram, and weights of 0.5, 1, 2, and 5 grams were added. Special guides on the A. S. T. M. penetrometer support arm were used for this needle (Figure 1, item 6).

Weights in the range 0.5 to 1 gram were obtained by welding 6 cm. of 20-gage spring steel wire to the regular penetrometer needle. A special clutch assembly, which was essentially a miniature replica of the regular assembly, was inserted in the penetration support arm for these measurements (Figure 1, item 6).

Weights in the range of 0.2 gram up to 0.5 gram were obtained by welding 6 cm. of 26-gage spring steel wire to 2 cm. of the conical end of the regular penetration needle. Additional 0.1 and 0.2 gram weights were used. The special clutch assembly was used to release the needle (Figure 1, item 6).

PENETRATION DEPTH LEVELS

Upon completing constant depth penetration measurements on a series of asphalts of varying degrees of hardness and at various temperatures, it was evident that a single penetration depth level would not be sufficient for all the contemplated applications of the procedure. Three penetration depth levels—namely, 0.04, 0.15, and 0.30 cm., corresponding to 4, 15, and 30, respectively, on the A. S. T. M. penetrometer scale—were finally selected as suitable for general use. All three of the selected depths were on the 0.54-cm.-long conical portion of the needle. The use of three penetration depths may appear to be inconsistent with the term "constant depth penetration", but in practice no confusion has resulted when the standardized depth levels were used.

Procedure. It is apparent that the selection by trial of a weight to give one of the above penetration depths would not be practical. Accordingly, at least three penetration measurements are made with different loads, such that at least one penetration is above and one below the selected depth. These results are plotted, a curve is drawn, and the weight required to give the specified penetration is obtained by interpolation. This value is identified as constant depth penetration. The procedure is illustrated graphically in Figure 2, which shows penetration measurements on an asphalt at 0°, 25°, and 46.1° C. (32°, 77°, and 115° F.).

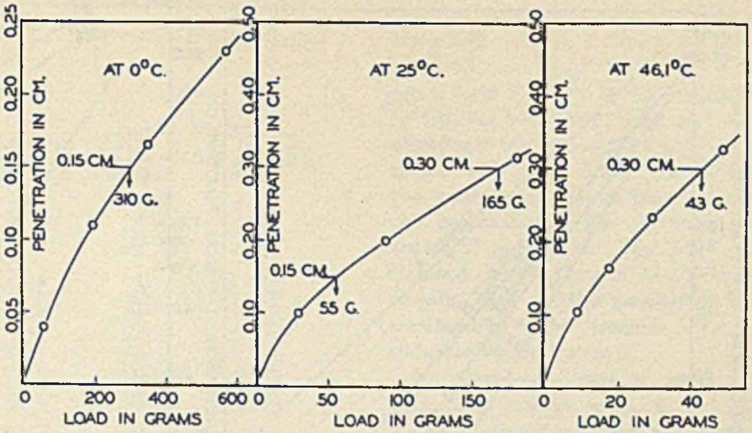

Figure 2. Penetration Depth *vs.* Load

In the case of regular asphalt samples, the method of preparing the sample, bringing it to the test temperature, and making the penetration measurements follows the procedure prescribed in A. S. T. M. Standard Method D-5-25, with the exception that a constant time of 5 seconds is used regardless of the test temperature. In the case of panels for accelerated weathering tests certain modifications are necessary in the technique of making the penetration measurements. These modifications will be discussed later in the paper.

ADAPTABILITY OF CONSTANT DEPTH PENETRATIONS

A comparison between constant depth and regular A. S. T. M. penetration on a group of asphalts is shown in Table I. The A. S. T. M. values are expressed in decimillimeters, and since the needle has a conical shape up to 54 dmm., the volume of asphalt displaced per unit depth of penetration varies over the penetration range of 0 to 54. Hence, in this range A. S. T. M. penetrations cannot be directly compared with each other. On the other hand, constant depth penetrations, expressed in grams, are in comparable units, and a value of 19.6 compared with 118 grams indicates approximately a sixfold increase of consistency.

Table I. Comparison of A. S. T. M. with Constant Depth Penetrations

Asphalt	Ball & Ring Softening Point[a] ° C.	° F.	Penetration, 25° C. A. S. T. M., dmm.	Constant depth[b], grams
Mexican flux	37.8	100	257	1.8
Air-blown Mexican	53.3	128	80	19.6
	67.2	153	38	72
	76.7	170	27	118
	98.9	210	15	275
	111.7	233	11	368

[a] A. S. T. M. Method D-36-26.
[b] 0.3-cm. depth in 5 seconds.

To determine the adaptability of the method over a wide range of consistency and temperature, tests were performed at 0°, 25°, and 46.1° C. on a group of asphalts varying in melting point from 54.4° to 112° C. (130° to 234° F.), ball and ring. The con-

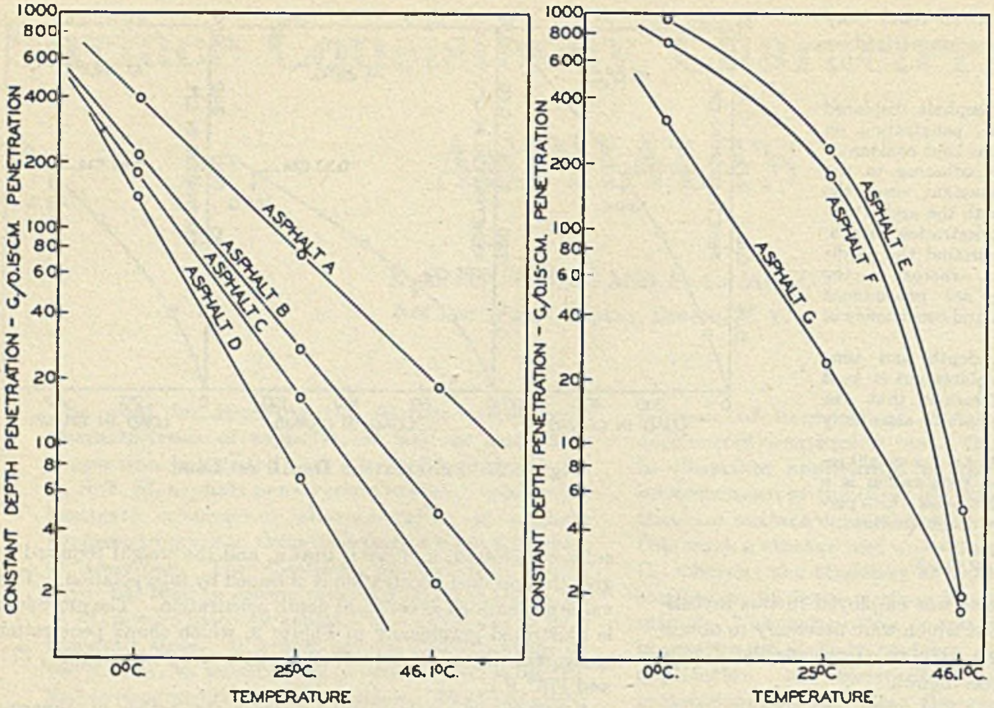

Figure 3. Effect of Temperature on Constant-Depth Penetration of Air-Blown Coastal Asphalts (*left*) and of Mexican Asphalts (*right*)

ventional physical tests on these asphalts are shown in Table II. In this series a constant depth of 0.15 cm. was used, since it was the only one of the three selected penetration depths suitable for measurements over the wide range of consistencies involved. Furthermore, at 0° C. the 0.30-cm. penetration could not be attained on the higher-melting-point asphalts without the use of excessive loads, which tend to crack the asphalt surface. On the other hand, the 0.04-cm. depth would not be suitable for the softer asphalts, particularly at 46.1° C., since the required load would be less than could be attained even with the modified apparatus.

Table II. Summary of Physical Tests on Asphalts Shown in Figure 3

Source	Asphalt	Penetration[a] (25° C.)	Ductility[b], (25° C.), Cm.	Ball & Ring M. P.[c] ° C.	Ball & Ring M. P.[c] ° F.
Air-blown coastal	A	16	0	112	234
	B	32	3	76.6	170
	C	43	5	65.5	150
	D	70	48	54.4	130
Steam-refined Mexican	E	16	17	69.4	157
	F	20	50	66.7	152
Air-blown Mexican	G	38	22	67.2	153

[a] A. S. T. M. Method D-5-25.
[b] A. S. T. M. Method D-113-39.
[c] A. S. T. M. Method D-36-26.

The results of these tests are shown graphically in Figure 3. Constant depth penetration on asphalts A, B, C, and D, which have relatively low susceptibilities, is substantially a logarithmic function of temperature over the range 0° to 46.1° C. On asphalt G, which is considerably more susceptible, the straight-line relation is only approximate over the range 0° to 46.1° C. In the case of highly susceptible asphalts E and F, there is a marked deviation from the straight-line relation, particularly in the range 25° to 46.1° C.

APPLICATION TO SURFACE HARDENING

The hardening of asphalts during service is well known, and this increase in hardness is undoubtedly closely related to service performance. Therefore, the ability of an asphalt to resist change of physical properties under service conditions may be more significant than initial physical tests themselves as a criterion of probable service behavior. In order to study this phenomenon it was considered necessary to measure the increase in the surface hardness of the asphalt under test without disturbing the surface in any way—for example, by melting or dissolving in solvents—in order to retain any so-called structural hardness (*5*).

The first step was to determine whether the proposed method of surface hardness measurement would distinguish between the effects of various storage conditions on increase of surface hardness. Samples of asphalt were stored in ordinary 2-ounce flat style gill cans under a variety of conditions, and constant depth penetration measurements were made after various storage periods. The cans were placed in a special brass holder (Figure 1, item 1) for the penetration measurements to prevent any movement under high loads. In these experiments a penetration depth of 0.30 cm. was used throughout. The results (Table III) indicate that the method distinguished definitely between the effects of the various storage conditions employed and therefore should be suitable for the proposed investigation.

It should be emphasized that the data in Table III are very preliminary in nature, and nothing more than very general conclusions are justified regarding the effect of the various storage conditions on surface hardening. Thus it would appear, from the results on asphalt A samples stored in air and in nitrogen at 25° C., that oxidation did not play an important part in surface hardening. However, it may have been that, in the process of melting and pouring the nitrogen-stored sample, sufficient oxygen

Table III. Effect of Storage Conditions on Surface Hardening of Asphalt

Storage Conditions	Asphalt[a]	Constant Depth (0.3-Cm.) Penetration at 25° C., Grams Initial	3 days	95 days
Air, light, 25° C.	A	36.5	46	69
Nitrogen, dark, 25° C.	A	36.5	48	75
	B	160	160	188
Nitrogen, dark, −12.2° C.	A	36.5	40	51
	B	160	160	163
Nitrogen, dark, 79.4° C.	B	160	175	350
Under water, 25° C.	A	36.5	44	46

[a] A = air-blown mid-continent asphalt of 65.6° C. (150° F.) ball & ring softening point; B = air-blown mid-continent asphalt of 98.9° C. (210° F.) softening point.

Table IV. Comparison of Surface Hardening Characteristics with Asphalt Aging Index

	Original Asphalts					Aged Asphalts	
	Ball & ring softening point						
Asphalt	° C.	° F.	Penetration at 25° C.	Viscosity[a] at 51.7° C., poises × 10^{-1}	Viscosity index[b] at 20–30° C.	% increase in surface hardness[c]	Asphalt aging index[d]
1. Air-blown	55	131	57	40	19	76	0.141
2. Air-blown	52.8	127	61	386	14	95	0.183
3. Air-blown	47.2	117	63	6.11	23.5	118	0.050
4. Air-blown	52.8	127	56	23.6	21.0	123	0.108
5. Vacuum-tube-still reduced	53.9	129	58	23.6	20.5	157	0.088
6. Air-blown	51.1	124	57	26.0	23.5	162	0.073
7. Steam-reduced	46.1	115	59	4.1	27.0	190	0.017
8. Air-blown	51.1	124	57	68.0	17.5	209	0.092
9. Steam-reduced	54.4	130	57	31.6	19.0	267	0.054
10. Steam-reduced	51.1	124	57	29.2	21.5	279	0.056
11. Air-blown	52.2	126	56	15.6	23.0	333	0.023
12. Air-blown	48.3	119	47	6.28	25.5	352	0.038
13. Steam-reduced	48.9	120	56	9.18	23.0	400	0.027

[a] Determined by Traxler and Schweyer method (*6*).

[b] Percentage change of viscosity (in poises) for 1° C. rise in temperature (determined by method of Schweyer, Coombs, and Traxler, *4*).

[c] Based on increase of surface hardness after 42-day storage at 51.7° C. in open 0.795-cm.-diameter brass molds.

[d] Slope of log viscosity *vs.* log time curve (based on increase of viscosity after 100-hour storage at room temperature, *7*).

was adsorbed at the surface to have been a factor in surface hardening even though the sample was stored in an atmosphere of nitrogen.

Apparently temperature has a profound effect on surface hardening, whereas storage under water tends either to inhibit the hardening process or to counteract it by a softening action due possibly to absorption of water.

Before this method of surface hardening was extended, the increase in hardness noted in Table III was shown to be actually a surface phenomenon. Information as to this point was obtained by shearing successive layers, approximately $^1/_{16}$ inch (1.59 mm.) thick, from the surface of a sample of asphalt which had been in storage 95 days at 25° C. The results were as follows:

Surface Hardness	Constant Depth (0.3-Cm.) Penetration at 25° C., Grams
Original	72
After 95 days	117
$^1/_{16}$-in. layer removed	98
Second $^1/_{16}$-in. layer removed	82
Third $^1/_{16}$-in. layer removed	82

These data illustrate that the type of hardening observed in the asphalts shown in Table III is substantially a surface phenomenon and does not extend throughout the total depth of the asphalt.

From the data in Table III it is apparent that temperature is one of the most severe factors in promoting increase of hardness of asphalt surfaces. Some work was therefore carried out to select a storage temperature which would give a fairly large increase in surface hardness in a reasonable time—that is, about 30–40 days. At the same time, it was necessary to keep the temperature low enough so that no fluxing of the surface layer with the remainder of the sample would occur when testing asphalts in the lower softening-point range. With these considerations in mind, a temperature of 51.7° C. (125° F.) was finally selected for general use.

During this work it was observed that the conventional 2-ounce friction-top can was not a suitable container for certain asphalts which exhibit a surface shrinking or drawing effect toward the center. This difficulty was overcome by the use of a small mold 0.795 cm. ($^5/_{16}$ inch) in diameter. Before this mold was adopted, it was determined that constant depth penetration measurements were substantially the same as in the regulation size A. S. T. M. container. Molds used in this work were made by drilling eighteen holes of the above size to a depth of 0.635 cm. ($^1/_4$ inch) in a cylindrical brass block 6.35 cm. (2.5 inches) in diameter and 1.59 cm. ($^5/_8$ inch) in depth (Figure 1, item 2). The molds were filled by pouring hot asphalt into the holes, allowing it to cool, and cutting off the excess with a hot knife. In making the penetration measurements, only one determination was made in the center of each hole. The mold was clamped into a special heavy brass transfer dish for the penetration determination. The transfer dish is shown in Figure 1, item 3.

In considering surface hardening data from storage tests, it was desirable to determine whether this phenomenon was similar to, or distinct from, the age hardening effect evaluated by the falling coaxial-cylinder method of viscosity measurements, as developed by Traxler and Schweyer (*7*). Accordingly, a series of asphalts was tested for both surface hardening and age hardening properties. The results are shown in Table IV, where increase in surface hardness after 42 days' storage at 51.7° C. is compared with asphalt aging index as determined by the method of Traxler and Schweyer. The fact that no definite correlation exists between the two series of observations is evident from a comparison of results on asphalts 3 and 9, for example. They have about the same aging index, but their rates of increase in surface hardness are very different. Similarly, asphalt 7 which has the lowest aging index of the series is intermediate in increase of surface hardness.

This lack of correlation is not surprising when it is considered that the asphalt aging index takes into account principally the increase of consistency due to development of internal structure in the entire bulk of the sample. On the other hand, it was previously shown that the increase in surface hardness as meas-

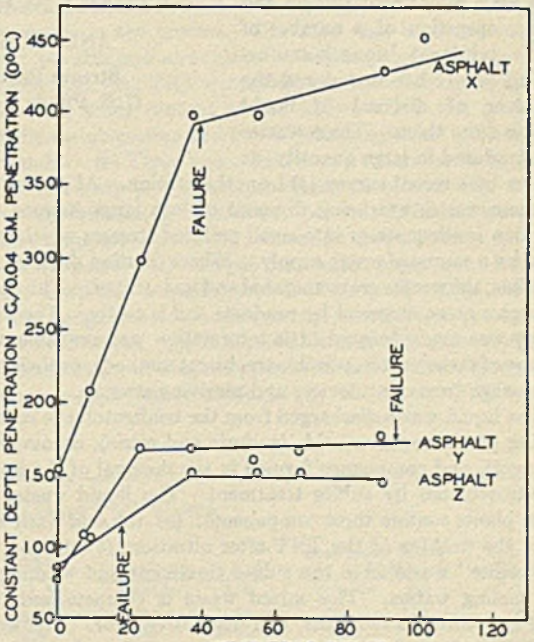

Figure 4. Effect of Weathering on Hardness of Asphalt

ured by constant depth penetration is primarily a surface phenomenon which affects only a relatively thin upper layer of asphalt.

APPLICATION TO ROOFING TEST PANELS

One interesting application of the new method was the study of the rate of hardening of asphalt in accelerated weathering tests. It is well known that asphalts increase in hardness under normal or accelerated aging conditions, and it is commonly believed that this increase in hardness is closely related to failure in service. It has been found possible to follow this hardening phenomenon by means of periodic constant depth penetration measurements on panels undergoing accelerated aging tests. Since the hardening determinations require only a few penetration measurements on each panel, the asphalt under test may be considered to be practically undisturbed.

In applying the test to weathering panels, the panel, prepared in the usual manner, was placed on a heavy brass plate embedded in the bottom of a low-form metal transfer dish. The dish was then filled with crushed ice. The usual technique for setting the penetrometer needle on the surface of the sample by reflection could not be used on the weathered panels; hence the following procedure was used on new and weathered panels:

> The needle was brought to within a few millimeters of the asphalt surface, and the nut which holds it in the shank was loosened. The needle was allowed to come to rest on the asphalt surface, after which the nut was tightened and the penetration measurement made in the usual manner. This technique is permissible only on the assumption that the weight of the needle causes no perceptible penetration prior to the actual determination. This condition is met by using the procedure only on the harder asphalts and by conducting the test at 0° C.

Typical results are shown in Figure 4. The choice of 0.04-cm. penetration depth in this case was governed by the fact that the thickness of asphalt on the test panels ranged from 0.0635 to 0.076 cm. As illustrated in Figure 1, penetrations were made under at least three different loads so that a load-penetration curve could be set up; from this curve, the weight required to give a penetration of 0.04 cm. was read.

From Figure 4 it is evident that various asphalts harden quite differently when exposed to identical weathering conditions. The few data given here suggest that failure under exposure to weathering is not related, at least in any simple manner, to increase in hardness.

ACKNOWLEDGMENT

The authors are indebted to R. N. Traxler and personnel at the Port Neches Laboratory of The Texas Company for the data in Table IV, involving falling coaxial-cylinder viscosity measurements.

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TNT WASTES

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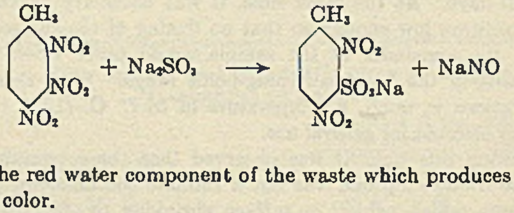
THE recent construction and operation of a number of trinitrotoluene manufacturing plants has introduced the problem of disposal of liquid wastes from them. These wastes are produced in large quantity, as shown by a recent survey (*4*) from this station. At present some of these wastes are being disposed of into large streams where dilution is adequate or into small polluted streams which are not used as a source of water supply. Where dilution disposal is impossible, the wastes are evaporated and incinerated. This method produces no commercial by-products and is costly. The present study was made because little information was available on the nature of these wastes, possible treatment methods, or their effects on sewage treatment devices and receiving streams.

The liquid waste discharged from the trinitrotoluene manufacturing plants contains acids (sulfuric and nitric), decomposition products, and compounds formed in the removal of the isomeric trinitrotoluenes by sulfite treatment. The liquid wastes from most plants contain three components: (*a*) the acid wash waters from the washing of the TNT after nitration, (*b*) the red water or "sellite" waste from the sulfite treatment and washing, and (*c*) cooling waters. This mixed waste is characterized by its acidity, yellow to red color, and distinctive odor. The average analytical data obtained on composite samples of waste representing periods of operation of two weeks each at three plants are given in Table I. These data indicate that mixed composite wastes have a low pH with a high color and are relatively high in total solids, sulfates, and acid dichromate oxygen consumed (*1*). In contrast, the red water from the sulfite treatment is alkaline (pH 8.0) with a very high color (about 100,000 to 300,000 p. p. m.) and practically no odor, and is three to six times higher in total solids, oxygen consumed, nitrites, and nitrates than the combined wastes. The reaction that takes place on treatment of the isomers of α-trinitrotoluene with sodium sulfite results in the formation of soluble nitrotoluene sulfonic acids and sodium nitrite, as indicated by the following equation (*2*):



It is the red water component of the waste which produces most of the color.

The following experiments were directed toward determining whether TNT wastes can be treated best biologically or chemically. The wastes used for the various experiments to be described were grab samples of mixed waste containing cooling water, although in a few experiments sellite waste alone was used. Consequently, the analyses for some of the experiments do not check those given in Table I. It is believed, however, that the experiments performed on the grab samples are, qualitatively at least, indicative of what might be expected from the composite waste.

Large quantities of wastes from TNT plants present a difficult waste disposal problem. The high color of the waste due to soluble nitrotoluene sulfonic acids make dilution disposal difficult unless ample dilution into large streams is available. Self-purification of the principal organic constituent of the waste does not take place in streams, and biological treatment in domestic sewage treatment devices has been unsuccessful. Most of the standard chemical methods of treating dilute industrial wastes, such as neutralization, chemical precipitation, fractionation, extraction, ozonation, and electrolytic reduction proved ineffective or not very promising. Chlorination and bromination alone show promise as practical treatment procedures.

BIOLOGICAL TREATMENT

When properly determined, the biochemical oxygen demand of a waste is considered a good criterion of the organic pollution contributed by it when discharged into a stream. The biochemical oxygen demand data may also be used to indicate the extent to which a waste can be purified in a stream or successfully treated in one of the biological sewage treatment devices. The first B. O. D. tests were hampered by the interference of the waste with the Winkler method for dissolved oxygen. As little as 4 or 5 per cent of the waste raised the apparent dissolved oxygen of the dilution with this method. By using the Rideal-Stewart modification dissolved oxygen could be determined accurately in as high as 8 per cent concentrations of the waste in dilution water. When 8 per cent or less of the waste was neutralized, diluted in the phosphate-buffered mineralized dilution water, and seeded with a small quantity of the aerated sewage seed regularly used in this laboratory, no biochemical oxygen demand was obtained in the standard 5-day incubation period at 20° C. When concentrations of 10 per cent of the waste were put up, the oxygen depletions obtained in 5 days were less than those from the seed control. From these observations it is inferred that the presence of 10 per cent or more waste interferes with the normal biochemical reaction. To determine whether a flora could be developed from the seed which would attack the dilutions of the waste, long-time B. O. D. series were incubated. These long-time studies were made on 2 and 4 per cent dilutions in the standard dilution water containing phosphorus and nitrogen seeded as before. No appreciable oxygen depletion was observed at any intermediate time, and after 129 days the depletions were as follows: seed control, 1.38 p. p. m.; 2 per cent TNT waste, 1.48 p. p. m.; and 4 per cent waste, 2.08 p. p. m. After deducting the control depletion in the conventional way, these observations represent a mean 129-day B. O. D. of 11.2 p. p. m. This is a very low B. O. D. considering that the waste has a relatively high oxygen consumed value (200 to 2000 p. p. m.). In these long-time B. O. D. studies the pH and oxygen consumption of the dilutions were also followed. The initial pH was 7.2, and after 129 days this value was reduced to 6.4 in the 2 per cent waste dilutions and to 6.2 in the 4 per cent waste dilutions; these reductions are not sufficient to influence the B. O. D. reaction. The oxygen consumed value of these B. O. D. dilutions did not change appreciably during the 129-day incubation period. These experiments indicate that the sodium salts of the nitrotoluene sulfonic acids in these wastes cannot be oxidized biochemically and that biochemical self-purification of such waste cannot be expected following its discharge into streams.

EFFECT OF WASTE ON ACTIVATED SLUDGE PURIFICATION

As the organic constituents of the TNT waste were not attacked biochemically, it was of interest to determine whether the waste discharged into sewage would affect sewage treatment devices. In the first experiment 12 liters of activated sludge mixed liquor were divided equally into three 4-liter bottles. The sludge solids were allowed to settle, and 3 liters of the supernatant liquor were siphoned off. The three sludge samples were each redosed for 2 consecutive days with 3 liters of the following: settled sewage, 5 per cent TNT waste (neutralized) in settled sewage, and 50 per cent TNT waste (neutralized) in settled sewage. After dosing, each bottle was aerated continuously at room temperature After 2 days of the dosing procedure, the three bottles were redosed with sewage and the aeration continued for another 24 hours. During this experiment the usual data on B. O. D. of the sewage and supernatant, sludge solids, ash, pH, and sludge settling volumes were collected. These data are given in Table II.

Although these experiments with activated sludge were not so complete as might be desired, they definitely indicate interference of this waste in the process. The data may be interpreted as follows: (*a*) although no evidence of bulking was noted, the dilutions of sewage with TNT waste fed to activated sludge tended to decrease the solids content of the sludge. This was probably caused by disintegration and loss of some suspended solids in the supernatant. (*b*) There was evidence of a reduction in B. O. D. removal efficiency on the second treatment of activated sludge with sewage containing as little as 5 per cent TNT waste. This efficiency is apparently rapidly reduced as the percentage of TNT waste is increased. (*c*) The pH data in the experiment indicate that the nitrification qualities of the activated sludge are lost when the sludge was dosed with sewage containing 5 per cent or more of TNT waste. (*d*) It is probable that difficulties would be encountered in any attempt to operate an activated sludge system continuously on sewage containing 5 per cent or more TNT waste

Table I. Average Analytical Results on TNT Waste

Plant	Color, P. P. M.	Odor, Concn.	pH	Acidity (Methyl Red), P. P. M.	Nitrogen, P. P. M.			Sulfate (SO_4), P. P. M.	Total Solids, P. P. M.		Suspended Solids, P. P. M.		Oxygen Consumed, P. P. M.
					NH_3	NO_2	NO_3		Volatile	Ash	Volatile	Ash	
A	7,100	70	2.4	291	5.3	15	107	672	1004	1273	22	144	795
B	6,300	16	2.7	134	...	20	...	604	868	1123	14	15	551
C[a]	34,000	11	1.2	3230	2.8	62	310	2923	5490	4685	17	0	1057

[a] This waste contained no cooling water.

TABLE II. ACTIVATED SLUDGE PERFORMANCE WHEN FED SEWAGE CONTAINING TNT WASTE

	Aeration Time after Dosing, Hr.	Suspended Solids, P. P. M.			Sludge Index, (Mohlman)			pH			5-Day B. O. D. of Supernatant			Oxygen Consumed, P. P. M.			% B. O. D. Removed in 24 Hr.			% O. C. Removed in 24 Hr.		
		A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
First day, dosed as indicated in A, B, and C[a]	Initial	4232	4268	4392	37.8	32.8	33.0	7.6	7.6	7.4	428	372	198	338	397	362	....	....	....	....	....	....
	4	4216	4456	4560	35.6	33.7	30.7	6.7	7.1	7.4	....	....	....	....	...	...	....	....	....	....	....	....
	24	4132	4284	4124	36.8	36.2	34.4	5.5	5.9	5.9	14.1	13.8	45.2	66.4	247	129	96.7	96.3	77.2	80.4	37.8	64.3
Second day, redosed as on first day	Initial	3152[b]	4284	4124	36.8	36.2	34.4	7.2	7.1	7.1	233	192	96	192	202	272	....	....	....	....	....	....
	4	....	4176	....	35.5	32.5	....	...	...	...	....	....	....	.....	...	...	....	....	....	....	....	....
	24	3124	4048	3656	35.9	37.5	32.8	5.8	7.0	7.0	16.4	27.4	57.8	77.6	229	...	93.0	85.7	39.8	59.6	0.0	....
Third day, redosed with sewage only	Initial	3124	4048	3656	35.9	37.5	32.8	...	...	...	495	495	495	....	...	...	....	....	....	....	....	....
	4	....	....	....	....	....	....	...	...	...	....	....	....	....	...	...	....	....	....	....	....	....
	24	3084	3988	3612	34.0	32.6	34.6	5.4	5.4	8.2	6.19	13.1	41.3	....	...	...	98.7	97.4	91.7	....	....	....

[a] A = dosed with sewage only; B = dosed with sewage plus 5% neutralized TNT waste; C = dosed with sewage plus 50% neutralized TNT waste.
[b] One fourth of the solids of the previous day were wasted before this sample was dosed.

EFFECT OF WASTES ON TRICKLING FILTERS

A wooden experimental trickling filter was set up in the basement of the main laboratory. The filter was 3.5 feet high and had a cross sectional area of 10 square inches. The filter was filled with stones covered with biological slime from a larger experimental trickling filter which had been operating on settled sewage. It was necessary to store the sewage feed in a 16-liter bottle so that some type of aeration was necessary to prevent septicity. As this aeration reduced the B. O. D. of the sewage in the feeding bottle, samples were taken for analysis when the fresh sewage was put into the bottle and again before the bottle was refilled. After considerable experimentation a suitable dosing devise (Figure 1) was built which fed the sewage at 5-minute intervals on to the filter for 30-second periods.

Although sewage feeding was started in the latter part of November, 1941, analytical data were not collected regularly until January 13, 1942, after all the difficulties with the dosing apparatus had been overcome. Apparently because of the development of large numbers of Psychoda flies, the stones never acquired a heavy coating of slime throughout the course of the experiment. The filter was examined several times during the feeding of TNT waste dilutions, and except for a lowering of the numbers of organisms, the filter growth was not appreciably affected.

The data obtained during the operation of the filter on domestic sewage and on sewage containing 5, 10, and 25 per cent neutralized TNT waste are shown in Table III. These data indicate that, when dosed at a rate of about a million gallons per acre per day, the sprinkling filter was capable of treating sewage containing 10 per cent of TNT waste without appreciable decrease in the percentage of B. O. D. removed. When dosed with sewage containing 25 per cent TNT waste at the same rate, the purification efficiency was noticeably decreased. In both the activated sludge and trickling filter experiments there was no apparent reduction in color of the waste dilutions by these processes. The biological treatment experiments seem to show that not only is it impossible to treat the wastes biologically, but the waste actually interferes with the biological treatment of sewage, even after pH correction and the activated sludge process is more sensitive to the waste than the trickling filter.

CHEMICAL TREATMENT

Chemical treatment experiment at first did not appear to be any more promising than biological treatment. Upon neutralization of the waste, a flocculent precipitate was noted which redissolved upon acidification. To determine whether the precipitate carried down any of the organic compounds present, oxygen consumed determinations were made on the waste when neutralized and filtered. The experiment indicated that neutralization alone did not affect the oxygen consumed value materially. When the waste was neutralized to pH 8.1 and filtered, an oxygen consumed reduction of about 25 per cent was obtained. If the waste was made alkaline to a pH of 12.2 and filtered, the oxygen consumed value was reduced only about 10 per cent.

In the next experiment, precipitation reactions with ferrous sulfate, lime, and sodium hydroxide were carried out to determine the effect on the oxygen consumed value:

Treatment of TNT Waste	Oxygen Consumed, P. P. M.	% O.C. Removed by Treatment
Untreated	208	0
1000 p. p. m. $FeSO_4$ + NaOH to pH 6.5	179	13.9
Same, to pH 10.2	185	11.1
1000 p. p. m. $FeSO_4$ + $Ca(OH)_2$ to pH 11.5	161	22.6
Same, to pH 6.7 with boiling	161	22.6
Same, to pH 11.7 with aeration overnight	188	9.6
Same, to pH 12.5 + 1000 p. p. m. activated C	156	25.0

These data indicate that the oxygen consumed values were not reduced satisfactorily even by the extremely high doses of coagulant. The coagulant dose was equivalent to about 58 grains per gallon, which is many times that used in chemical coagulation of most sewages and industrial wastes. The above treatment also had no measurable effect on the color of the waste. A number of other coagulation and precipitation experiments were tried without satisfactory results. Theoretically, insoluble salts of the nitrotoluene sulfonic acids may exist, but none have been found here.

Stirring comparatively large quantities of activated carbon with the waste also produced little reduction of the oxygen consumed values (original O. C. 208 p. p. m.):

Dose, P. P. M.	Form of Activated C	Brand	Oxygen Consumed	
			P. P. M.	% reduction
1000	Granular	Nuchar	155	25.4
2000	Granular	Nuchar	132	36.5
1000	Powdered	Darco	179	14.0
2000	Powdered	Darco	175	15.8

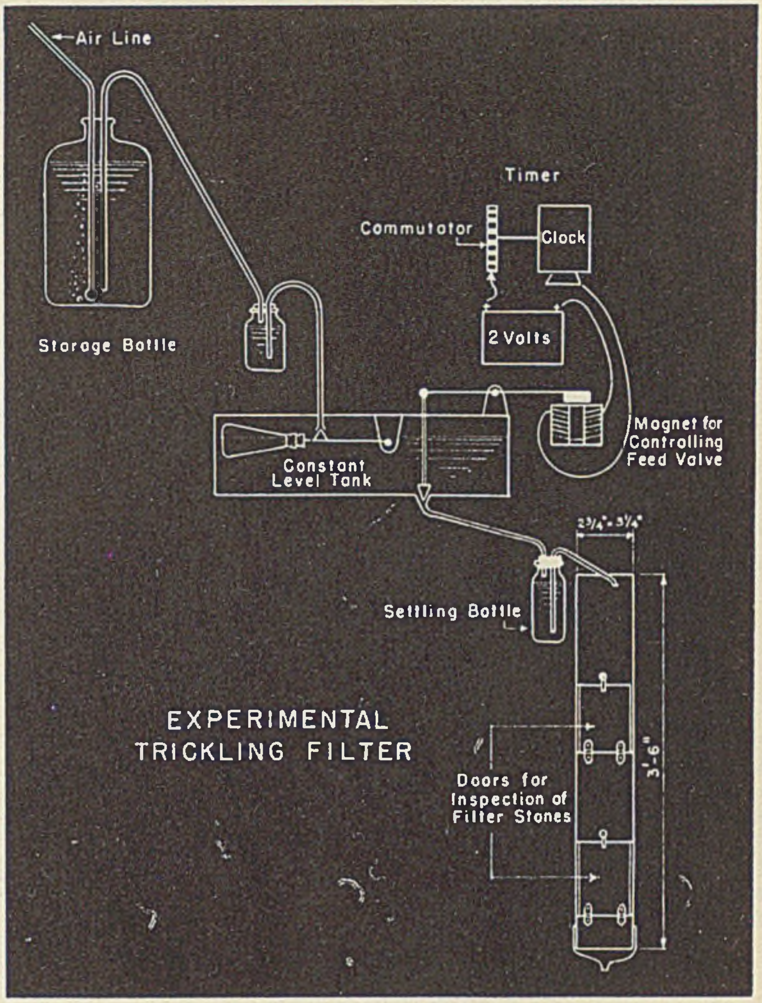


Figure 1

As about 116 grains of granular activated carbon per gallon, or better than 8 tons (cost about a hundred dollars per ton) per million gallons of waste would be required to obtain a 36 per cent removal of the oxygen consumed value, it is evident that such treatment is out of the question.

Ozonation as a method of treatment was next attempted. A laboratory ozonizer (3) was set up, and 25 per cent dilutions of the waste were ozonated for 24 hours. This treatment gave only a 30 per cent color reduction which was disappointing. Ozonation of the waste under various conditions, such as acid to alkaline, room temperature to boiling temperature, and in the presence of various materials as catalysts, failed to improve the efficiency.

Experiments were carried out in which 2 liters of combined waste were distilled at atmospheric pressure and five fractions, each 15 per cent by volume, were collected. In different experiments the waste was adjusted to pH 3.0, 7.3, and 10.8, and distilled as described. Although there was little difference in the results obtained, the acid distillation gave slightly higher oxygen consumed values in the distillate. Even in this case only 3 per cent of the oxygen consumed value was recovered in the first 15 per cent fraction, and the five 15 per cent fractions or 75 per cent of the distillate contained less than 10 per cent of the oxygen consumed of the original waste. There was little difference in the boiling points of the first five fractions, which ranged around 99° C. These fractions from the acid distillation had a slight nitrobenzene odor, were not toxic to fish, but were toxic to Daphnia. The experiments indicate that the large percentage of the oxygen-consuming organic matter in the waste remains in the residue upon distillation, regardless of the pH.

REDUCTION OF NITRO COMPOUNDS

The treatment of the waste to produce aminotoluene sulfonic acids offers another approach. An insoluble salt of these compounds might be found or they might be subject to biological attack. Conversion of the nitro to the amino compounds should take place on reduction with acid and iron or zinc, or by electrolytic reduction.

In one reduction experiment with acid and zinc it was found that both the oxygen consumed value and the color of the waste was increased considerably. The waste so treated was still not subject to biological attack. Electrolytic reduction of the acidified waste was carried out using platinum electrodes and an electromotive force of 3 to 5 volts. After 24 hours of electrolysis the color of the waste was reduced from 120,000 to 60,000 p. p. m. There was a slight reduction in the Kjeldahl nitrogen and a reduction in nitrite nitrogen from 40 p. p. m. to 0, but there was no measurable change in the oxygen consumed value. Experiments indicated that the electrolyzed material was still not appreciably oxidized biochemially. Precipitation and coagulation experiments on the reduced waste were not materially more successful than on the original waste. Therefore the only benefit of the electrolytic treatment was a reduction of about 50 per cent of the color. Additional experimental work indicated that a much greater color reduction could be obtained with prolonged electrolysis.

COLOR REMOVAL

Experiments were carried out to extract the coloring matter from the TNT wastes with organic solvents including chloroform, benzene, toluene, xylene, hexane, and ethyl ether. Attempts to extract any part of the color were negative or unsatisfactory in in both acid and alkaline solutions. This result was not surprising, considering the high solubility of these colored nitrotoluene sulfonic acids in water. Later experiments indicated that amyl and butyl alcohols could be used to extract some of the coloring matter from the combined acid waste but not from the alkaline sellite waste. *n*-Butyl alcohol was by far the better solvent of the two. When an acid sample of a combined waste with a color of 120,000 p. p. m. was extracted once with *n*-butyl alcohol, the color was reduced to 37,000 p. p. m. Extraction with fresh butyl alcohol did not appreciably reduce the color further. Acidified sellite waste can also be extracted with a similar percentage reduction in color by *n*-butyl alcohol. Butyl alcohol extraction of the combined acid sample that was electrolyzed further reduced the color from 55,000 to 30,000.

COLOR REMOVAL BY ACTIVATED CARBON

A sample of the red water waste was made up to a one per cent concentration in distilled water. The diluted waste was then stirred and boiled with definite amounts of activated carbon for 15 minutes, the carbon filtered off, and the residual color measured. The best results were obtained by boiling with a powdered acti-

Table III. Data for Trickling Filter Performance with TNT Waste (Neutralized) Sewage Dilutions

Date	Hour	Influent Av. B. O. D.	Influent Av. pH	Effluent Av. B. O. D.	Effluent Av. pH	Rate of Flow, Million Gal. Acre/Day	Efficiency, % B. O. D. Removed	
				No TNT Waste Added				
1/13	9 A. M. to 3 P. M.	274	...	30.5	...	1.21	88.9	Average
1/13–1/14	3 P. M. to 9 A. M.	296	...	44.1	...	1.01	85.1	
1/14	9 A. M. to 3 P. M.	246	...	47.3	...	1.00	80.8	
1/14–1/15	3 P. M. to 9 A. M.	201	7.6	29.6	7.4	1.11	85.3	
1/15	9 A. M. to 3 P. M.	259	7.7	36.6	7.5	1.18	85.9	87.3
1/15–1/16	3 P. M. to 9 A. M.	277	7.6	35.0	7.3	1.13	87.4	
1/16	9 A. M. to 3 P. M.	313	7.7	46.3	7.6	0.94	85.2	
1/16–1/17	3 P. M. to 10:30 A. M.	238	7.6	17.5	7.5	1.10	92.6	
1/17–1/18	10:30 A. M. to 1 P. M.	378	7.6	34.2	7.9	1.04	91.0	
1/18–1/19	1 P. M. to 10 A. M.	302	7.6	30.5	7.3	Feed line clogged	....	
1/19–1/20	10 A. M. to 1:30 P. M.	378	7.6	34.4	7.4	0.95	90.9	
				5 Per cent TNT Waste				
1/20–1/21	1:30 P. M. to 9 A. M.	340	7.5	30.5	7.3	0.85	91.0	Average
1/21	9 A. M. to 2:30 P. M.	236	7.5	25.3	7.5	1.06	89.3	
1/21–1/22	3 P. M. to 9 A. M.	500	7.4	53.4	7.3	1.07	89.3	
1/22	9 A. M. to 3 P. M.	259	7.7	35.7	7.6	0.94	86.2	
1/22–1/23	3 P. M. to 9 A. M.	251	7.5	13.2	7.3	1.04	94.7	89.5
1/23	9 A. M. to 3 P. M.	371	7.8	39.6	7.4	....	89.3	
1/23–1/24	3 P. M. to 11:30 A. M.	251	7.5	20.4	6.8	0.84	91.5	
1/24–1/25	11:30 A. M. to 1 P. M.	311	7.5	32.9	7.5	0.97	89.4	
1/25–1/26	1 P. M to 10 A. M.	125	7.6	18.7	7.4	0.87	85.0	
				10 Per Cent TNT Waste				
1/26–1/27	10 A. M. to 8:30 A. M.	529	7.3	62.3	7.3	0.80	88.2	Average
1/27	8:30 A. M. to 3:30 P. M.	210	7.7	31.6	7.5	0.79	85.0	
1/27–1/28	3:30 P. M. to 8:30 A. M.	302	7.4	18.4	7.5	0.93	93.9	
1/28	9 A. M. to 3:30 P. M.	195	7.7	14.6	7.1	0.87	92.5	
1/28–1/29	3:30 P. M. to 9 A. M.	241	7.1	27.6	7.1	1.04	88.5	
1/29	9 A. M. to 3 P. M.	425	7.6	51.0	7.5	0.97	88.0	86.0
1/29–1/30	3 P. M. to 9 A. M.	267	7.6	39.3	7.5	1.23	85.3	
1/30	9 A. M. to 3 P. M.	269	7.6	47.4	7.6	1.09	82.4	
1/30–1/31	3 P. M. to 10 A. M.	314	7.5	37.8	7.3	1.13	88.0	
1/31–2/1	10 A. M. to 2 P. M.	386	7.5	51.8	7.8	1.04	86.7	
2/1 –2/2	2 P. M. to 2:30 P. M.	286	7.6	66.6	7.7	....	76.7	
2/2 –2/3	2:30 P. M. to 3 P. M.	255	7.4	58.1	7.5	1.05	77.2	
				25 Per Cent TNT Waste				
2/3 –2/4	3 P. M. to 8:30 A. M.	202	7.9	57.4	7.6	1.17	71.6	Average
2/4 –2/5	8:30 A. M. to 8:30 A. M.	153	7.8	34.7	7.7	0.97	77.3	
2/5	8:30 A. M. to 3 P. M.	249	7.9	69.2	7.7	0.58	72.3	75.5
2/5 –2/6	3 P. M. to 1 P. M.	281	7.7	19.4	7.6	0.96	93.1	
2/6 –2/7	1 P. M. to 8:30 A. M.	97	7.7	35.9	7.6	1.06	63.0	

vated carbon, but the dose required for satisfactory removal was so large (5 to 10 grams per liter) that such treatment was impractical.

In a second activated carbon experiment a sample of combined waste was diluted to 0.5 per cent concentration with distilled water and buffered at pH 7.2 with phosphate buffer. To three portions of this sample, activated carbon was added in amounts of 5, 10, and 15 grains per gallon. The suspensions were mechanically stirred for 15 minutes and filtered, and color readings were made. The following results were obtained:

C Added, Grains/Gal.	Color Remaining, P. P. M.
0	60
5	15
10	0
15	0

COLOR REDUCTION BY CHLORINATION

In an experiment to determine whether chlorination of water containing these wastes accentuated tastes, it was noted that the chlorinated sample showed a decided color reduction. Experiments with 1 to 18 p. p. m. of chlorine in a 1 to 50 dilution of the waste were carried out. A marked reduction in color was noted in all cases, but quantitative evaluation was impossible because of a difference in the colors produced. Repetition of the experiment with higher concentrations of the waste also gave color reductions, but the same visual color difficulties were encountered. Consequently, the extinction values for a series of waste concentrations in distilled water were determined with a Bausch & Lomb spectrophotometer, using wave lengths between 500 and 800 millimicrons. Although the extinction maxima lie outside the range of the instrument, the curves obtained were of value for intensity measurements.

A 50 per cent dilution of waste treated with 17.8 p. p. m. of chlorine was examined with the spectrophotometer in the manner of the above series. The plotted curve of the extinction values of the treated 50 per cent waste fell very close to that produced by the 37.5 per cent dilution of untreated waste, showing a 25 per cent reduction in color. The results are plotted in Figure 2. A similar decrease in extinction value was obtained with a 10 per cent waste treated with 4.4, 8.9, and 17.8 p. p. m. of chlorine. Results are plotted Figure 2.

Additional experiments on color reduction of the waste with chlorination were carried out using a camera attachment to the spectrophotometer to photograph the spectrum. While this method was not so effective for judging efficiencies of color reduction, it relieved eyestrain, and examination of the plates showed a sizable increase in light transmitted with increasing doses of chlorine for the same waste concentration. A 5 per cent waste after a dose of 4.4 p. p. m. of chlorine gave the same light intensity as an untreated 3 per cent waste. Similarly, a 3 per cent waste treated with 2.2 p. p. m. of chlorine equaled a 2 per cent untreated sample, and a 1 per cent waste treated with 1.1 p. p. m. of chlorine equaled a 0.5 per cent untreated sample.

Later experiments showed that bromine treatment of the waste was also effective in color reduction. Using visual methods only, comparative tests indicated that in concentrations equal to chlorine, bromine was roughly twice as effective in reducing color. Economic factors and further experimental work is necessary to determine whether bromine or chlorine could be most effectively used. In any case, no more economical or satisfactory way of reducing the color of these wastes is available at present than bromination or chlorination.

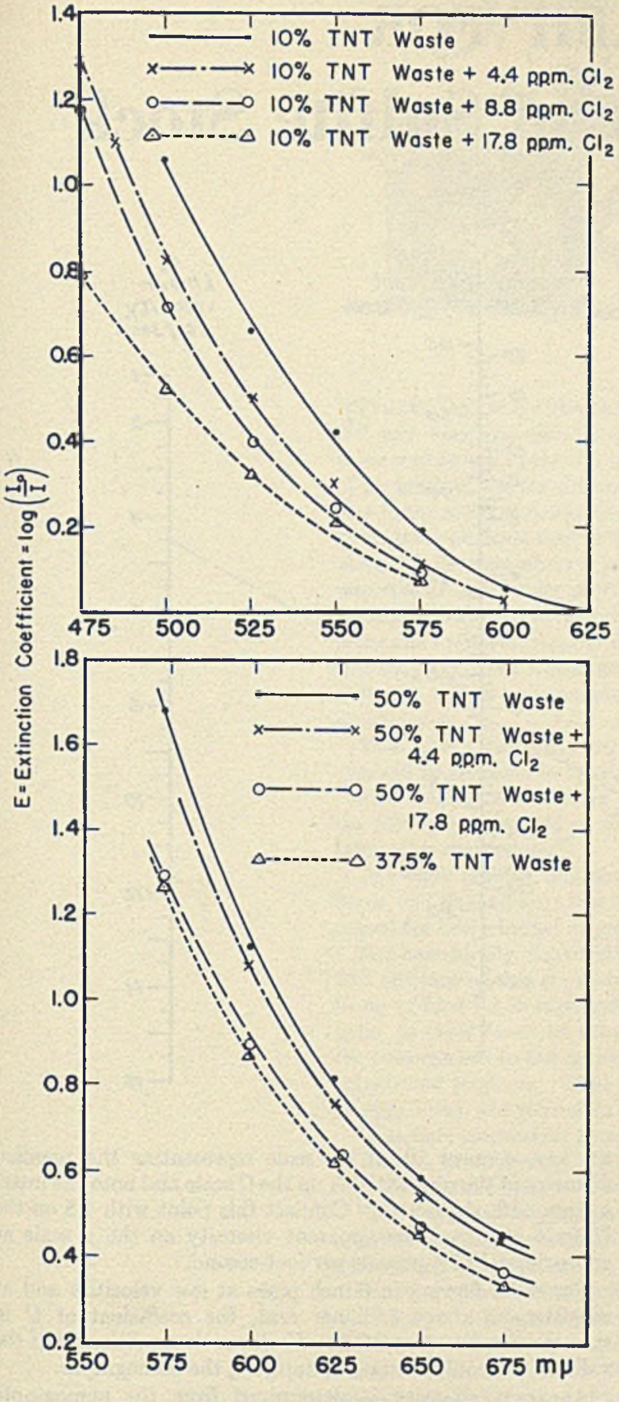


Figure 2. Effect of Chlorine on Color of 10 Per Cent and 50 Per Cent TNT Wastes

TASTE

The experiment already mentioned, to determine whether chlorination enhanced the taste of water containing TNT waste, will be discussed briefly. It indicated that twenty persons who did not know the contents of the samples tasted gave Cincinnati tap water, containing 1000 p. p. m. of the combined TNT waste, a score almost as high as straight tap water and slightly higher than tap water containing 1 p. p. m. of chlorine. Water containing 1000 p. p. m. of TNT waste and 1 p. p. m. of chlorine showed a definite enhancement of taste and received a somewhat lower score from the same judges.

SUMMARY

An exploratory study of the combined TNT waste containing the acid wash, the sulfite or sellite liquor, and cooling waters was carried out. The waste is characterized by its low pH, high color, and relatively high total solids, sulfates, and oxygen consumed value. The waste interferes with the Winkler method for dissolved oxygen. However, dilutions up to 4–8 per cent, depending upon the strength of the original waste, may be examined for dissolved oxygen by the Rideal-Stewart modification. Although the waste has a considerable oxygen consumed value, no 5-day B. O. D. was found. Extended incubation tests indicated no appreciable biochemical demand, from which it was concluded that the principal organic constituents (the nitrotoluene sulfonic acids) were not subject to biochemical breakdown and self-purification in streams. It was found that the wastes interfere with the activated sludge process when present in sewage in concentrations greater than 5 per cent and with the sprinkling filter in concentrations in sewage of more than 10 per cent.

Experiments on chemical treatment of the waste proved it to be stable and difficult to treat. Neutralization and precipitation experiments were fruitless due to the high solubility of the nitrotoluene sulfonic acids. Fractional distillation produced little organic distillate, and ozonation was ineffective. Activated carbon treatment although somewhat effective requires excessive quantities of carbon and would be prohibitive in cost.

Butyl alcohol was the only solvent of the many tried which successfully extracted considerable organic color. The method does not appear promising due to economic factors of solvent recovery. Electrolytic reduction also proved quite effective in reducing the color of the waste, but due to economic factors the process does not appear promising. Of all the procedures studied, chlorination or bromination seems most promising. Although bromination is the more effective in reducing color, economic factors would determine which of these halogens should be used. Additional studies on the course of the reaction and the products formed with halogen treatment of the waste should be made and should be followed by pilot plant experiments.

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Presented before the Division of Water, Sewage, and Sanitation Chemistry at the 105th Meeting of the American Chemical Society, Detroit, Mich.

Deterioration of Lubricating Oils (Correction)

We regret to have to call attention to an error in the above article which appeared in Figure 1, page 884, of the August issue, because an uncorrected drawing was inadvertently submitted for publication. On the figure as printed the dimensions are given in millimeters and the over-all length, 325 mm., is correct. The other dimensions should all be indicated in centimeters. Thus the dimensions are:

Over-all length of cell	32.5 cm.
Diameter	5.0 cm.
Length of steel sleeve	19.0 cm.
Diameter	3.8 cm.
Diameter of air bubbler tube	0.8 cm.
Length of steel tube above jet	14.0 cm.
Inside diameter of steel tube	1.0 cm.
Outside diameter of steel tube	1.3 cm.
Length of copper strip	9.0 cm.

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NOMOGRAPH FOR Apparent Viscosity of Sulfite Stock

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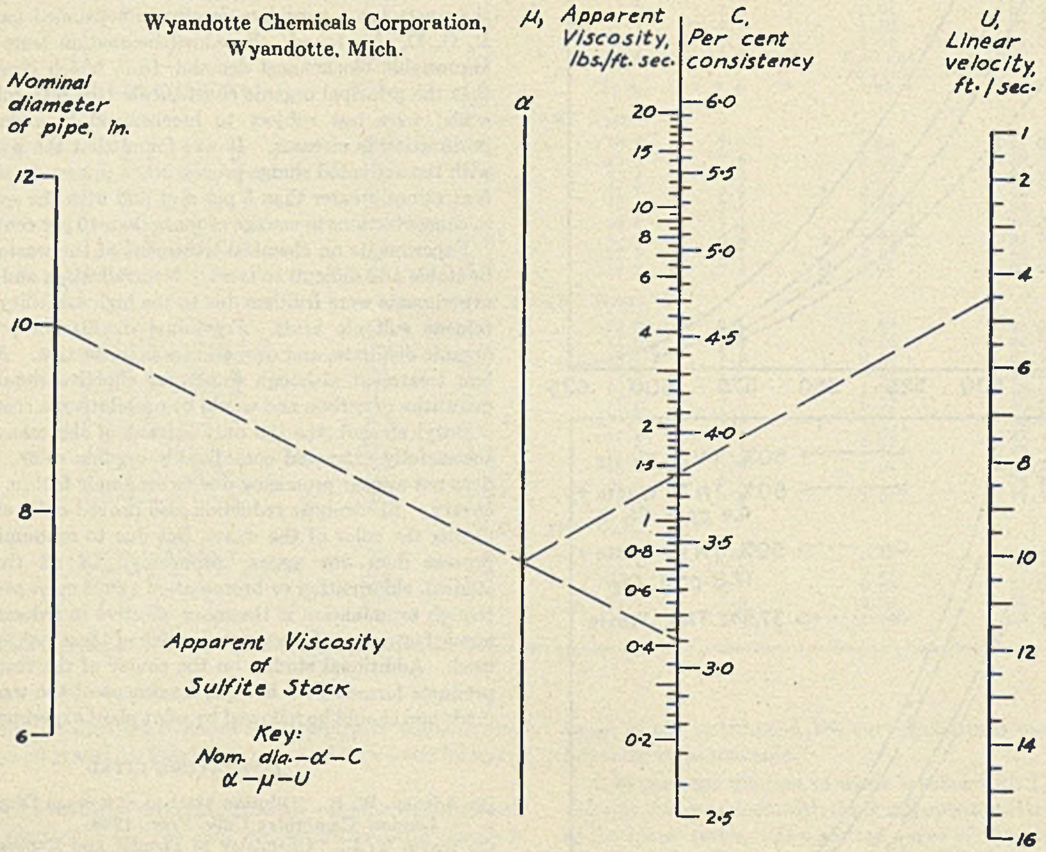

THE standard friction factor plot (*1, 4, 5, 6*) in general use for the correlation of data on the flow of Newtonian liquids also serves for the flow of suspensions in the turbulent range when the Reynolds numbers are above 20,000, if the viscosity of the suspension is taken to be that of the suspending medium (*2*). Under prevailing circumstances in the paper mill, sulfite stocks exhibit viscous flow and require some other value to be used for the viscosity.

From determinations of the pressure drops in the pumping of sulfite stock at various consistencies and velocities in 6–12 inch pipes under conditions of viscous flow, Cooper (*3*) calculated the apparent viscosities of the suspensions. He correlated extensive data by an expression which enabled head losses to be computed within the usual tolerance of ±15 per cent:

$$\log \mu = \log 0.095DC^3 - 0.05U$$

where μ = apparent viscosity, lb./ft.-sec.
D = internal diameter of pipe, ft.
C = moisture-free consistency, per cent
U = average linear velocity, ft./sec.

The use of the nomograph, which enables convenient solution of the equation, is illustrated as follows: What is the apparent viscosity of sulfite stock under conditions such that a linear velocity of 4.5 feet per second is attained in a standard 10-inch pipe when the consistency is 3.1 per cent? Following the key, connect 10 on the scale representing the nominal diameter of the pipe with 3.1 on the C scale and note the intersection with the α axis. Connect this point with 4.5 on the U scale and read the apparent viscosity on the μ scale as approximately 1.4 pounds per foot-second.

For stock flowing in 6-inch pipes at low velocities and at consistencies above 3.75 per cent, the coefficient of U in the equation becomes 0.025. Under such conditions half the value of U should be used in applying the nomograph.

Apparent viscosity μ, determined from the nomograph, is used in computing an apparent Reynolds number from which head losses are calculated from the standard friction factor plot.

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Spying!

Events on world battlefields alternately lift our spirits with hope and dash them with despair. Nevertheless when these wild sweeps of the tide of battle are viewed with a modicum of perspective, the trend toward victory is unmistakable. Even now in the midst of production for combat most of us realize that plans must be made against the dislocations of peace. Furthermore, the dangers inherent in a sudden peace that may catch us unprepared to meet its problems are more and more impressed upon us. Thus in November we plan to survey the production scene and to suggest some of the new points of departure in chemical industry from which we must approach the future. Our objective will be to stimulate thinking rather than to outline a specific plan.

Vital after victory, as now, will be our petroleum industry, and this will be analyzed in "past, present, and future" for us.

Also looking to the future is a report of late developments in the relatively new field of nitroparaffins and their increasingly interesting derivatives.

The water problem of grain alcohol distilleries will be reviewed for us, and we shall learn how hundreds of gallons of water are consumed for every bushel of grain processed.

Not unnaturally, dehydration of foods comes next on the list. The advance of this art under war's stimulus is providing new forms of food for storage and shipment and lending new importance to older forms of dehydration. Problems important for the future relate to the nutritive, particularly vitamin, values of dehydrated products. Thus we shall find significant new data on eggs, meat, and spinach in our November issue.

Especially emphasized by recent developments is the widening utilization of soybeans. Their protein, we shall learn, makes dispersions which may be useful in vehicles for printing inks.

Pectin's emulsifying powers for oils have been determined under a variety of conditions and are compared with those of tragacanth, karaya, and acacia gums.

Behavior of synthetic anionic detergents in the presence of soap and hard water has been examined for us to learn how and why the use of both soap and synthetic is better than either alone. Fatty oils, and particularly their fatty acids, have been oxidized catalytically in the vapor phase to maleic acid, a process of which we shall learn.

Catalytic hydrogenation of high sulfur gasolines has been studied as a method of removal of this objectionable element and the results reported suggest important values in the method, particularly since complete removal of sulfur improves the tetraethyllead susceptibility of the product. Cobalt molybdate is the catalyst.

New data on water-binding properties of cellulose will be presented, based on researches in which hydroxyl groups are blocked off by acetylation.

There will, of course, be much more, and the stimulus to thinking of the whole should keep our minds at useful work in such moments as we can spare them from our urgent jobs of war production. And that suggests our important avocation: "Buy *more* war bonds."

Your Humble Spy