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EDITORIALS

The Insignificance of the Chemist

WHILE the theme and title of this editorial are in sharp contrast with the customary tone of these columns, it is perhaps just as well for the chemist to be reminded from time to time that the forces and quantities which he controls are, after all, rather puny compared with the might and vast resources of Nature.

Probably every chemist appreciates that the combined result of all our mining and chemical activities to date has made but an infinitesimal alteration in the composition of the earth's crust or of the sea water. Taken by and large, the outstanding factor affecting the world's material balance in this chemical and industrial age is the tremendous quantity of mined fuels which are burned every day of the year. It recently occurred to the writer that the enormous quantity of carbon dioxide produced by this combustion should in time have at least an appreciable effect on the tiny percentage of carbon dioxide which is present in as tenuous a substance as our atmosphere. Such a change might, in turn, promote to some degree the growth of vegetation, which depends almost entirely on this trace of carbon-bearing gas in the atmosphere. It even seemed conceivable that we might eventually begin to reverse what took place during the carboniferous era, when a combination of climatic conditions, probably including a high carbon dioxide content in the air, resulted in the fixing and locking up in the earth of most of our tremendous stores of coal.

Using rough figures, it appears that the total world's production of mined fuels during the last 50 years of high activity has contained about 50,000,000,000 tons of carbon—including coal, lignite, crude petroleum, and natural gas, petroleum constituting roughly 7 per cent of the total.

On burning, this mined fuel probably yielded about 180,000,000,000 tons of carbon dioxide, an amount which, if not dissipated in some way, sounds like enough to snuff out most of the animal life in the world, or in any case to make a very substantial change in the 0.03 per cent normal carbon dioxide concentration in the air. Actually, however, calculation indicates that if all this extra carbon dioxide had been dumped into the atmosphere and none removed during this 50-year period it would only raise the carbon dioxide content from 0.03 per cent to about 0.032 per cent.

However, this overlooks another very important factor, namely, the function of the ocean in stabilizing and regulating the carbon dioxide content of the air. Available data indicate that there is 30 or 40 times as much carbon dioxide dissolved in the ocean as is present in the atmosphere, and the average partial vapor pressure of this dissolved carbon dioxide is probably largely what determines the average carbon dioxide content of the air, so that well over 90 per cent of any excess carbon dioxide introduced into the atmosphere eventually finds its way into the ocean, leaving the composition of the former virtually unaffected. Incidentally, it appears that the temperature of the ocean, which is considerably influenced by glacial conditions and polar ice caps, has been, and probably will continue to be, the most significant factor in determining the carbon dioxide content of the air.

It also appears that if the small increase in the concentration of carbon dioxide should occur, another factor would tend to restore about the present balance—namely, a small increase in the rate of growth of at least part of the world's vegetation. The tremendous quantity of carbon dioxide consumed every year by growing vegetation (and practically all returned by its eventual combustion or decay) is more than a thousand times the total amount produced by all the coal and petroleum burned in a year of high industrial activity!

"What is man, that Thou art mindful of him?"

ROBERT E. WILSON

Names Wanted

WE ARE indebted to Jerome Alexander for the rhyme:

> A aids development, saves from sore eyes;
> B (or B_1) beriberi defies;
> C conquers scurvy, and D dodges rickets;
> E gives you heirs who can bowl at Life's wickets;
> G (or B_2) keeps pellagra away—
> These are the vitamins known today.

May we emphasize that last line, for it touches a controversial matter. If we include in our references to the literature articles which have appeared in abundance and which should be collated under the head-ing of advertising, then there is one more letter in the alphabet which has been appropriated by those who wish other substances to be known and accepted as a vitamin.

We are told that when Adam and Eve were naming the animals, it was a relatively simple matter. Thus, Eve said, "That looks like an elephant," and so Adam agreed that "elephant" it should be. At any rate, they could see what they were naming. When vitamins were discovered, the most that could be seen was the effect in animal and some human experiments of the presence or absence of these food accessory substances. When the letters were assigned, F was held in reserve because research then well on the way indicated that there was another substance which had the characteristics of a vitamin that could soon be announced.

In those days little, if anything, was known of the structure of the vitamins. That was years before the classic work on vitamin B_1, reported in detail by Williams at the Chapel Hill meeting, which gave first a reasonable picture of the B_1 molecule, was soon followed by the preparation of a highly purified concentrate, and then in 1936 was crowned with the synthesis of this very important substance. We seem to have come, therefore, to the place when what we have known as vitamins are pretty definite entities, for which names, rather than letters, can be assigned. Some names have already been suggested by authorities. Whereas a decade ago there were relatively few recognized vitamins, today there are some 25 chemically different substances which by their effect may be so classed.

Let us break away from the unsatisfactory letter designations, many now with subscripts, and proceed to identifying names selected in accordance with chemical composition. Such a procedure will be welcome for many reasons, among them the clarification of certain aspects of extreme commercialism in which the vitamins have been exploited.

It was ever thus. Success in some perfectly proper direction always yields its diverse by-products of exploitation, few of which can be justified and all of them designed solely for profit. Unhappy results have occurred when good things have been overdone against the best advice. Overselling may sometimes be the cause.

But what about vitamin F? This designation has been applied, so far as we can ascertain, primarily to linoleic and/or linolenic acid which has been found by those researching in biological chemistry to be essential to the nutrition of rats and presumably other of the higher animals. These fatty acids, however, have never been officially accepted as vitamins. The application of such fatty acids having been shown to prevent or cure scaly rat tails, they have found their way into certain cosmetics, soaps, and similar commercial commodities. Those who discovered that such substances are essential constituents of the diet did not use the term "vitamin F," maintaining that it would only complicate matters to designate with a letter a compound that is already known chemically. It would be just as unsatisfactory to assign vitamin letters to each of the essential amino acids. But this point of view is not acceptable to those who recognize in the word "vitamin" a great popular appeal, and "vitamin F" has been adopted by many manufacturers who are apparently pleased to indicate on their labels something supposedly so important. While these acids have been incorporated in cold creams, nail polishes, and various cosmetics, the benefits that may accrue from their use are probably no greater than those which result when you inadvertently spill paint on your hands when redecorating the old wheelbarrow.

Remembering how many years of careful research with highly purified diets are required to demonstrate the necessity of almost vanishingly small quantities of fat in a complete diet for the rat and that linoleic or linolenic acid will take the place of the natural fat, it would seem almost impossible for man to select a diet from naturally occurring foodstuffs that would be likely to leave it deficient in fatty acids.

Let us, then, not be excited about what may happen to us if we do not get our daily allotment of "vitamin F." However, let us be very much concerned about this further exploitation of science for no good purpose and speed the day when we will insist upon calling things by their right names, utilizing letters or other means of designation only as a temporary and more or less unsatisfactory expedient.

It Has Been Said

What greedy ears receive, loose tongues betray,
But no one can repeat what you don't say.

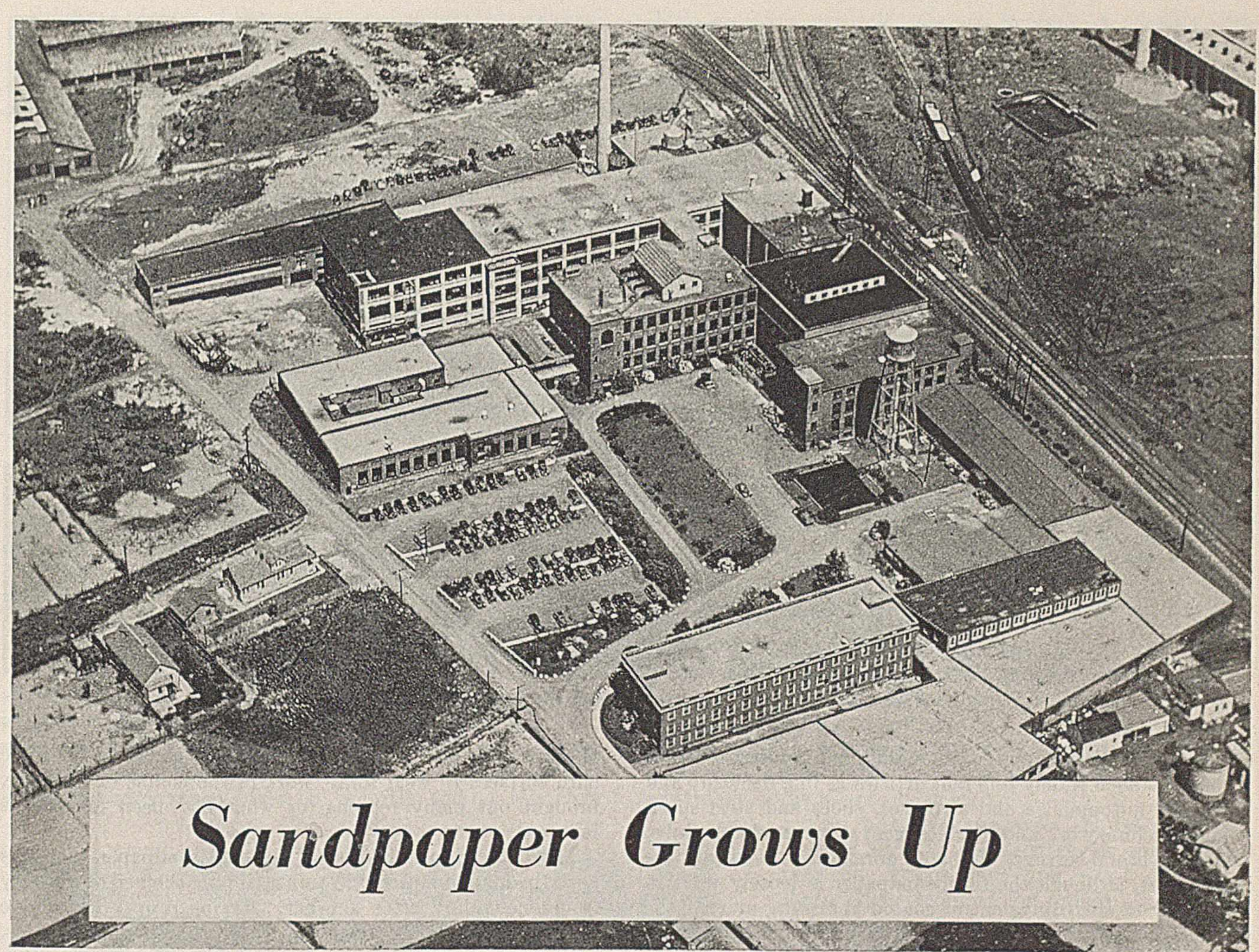
The heaviest burden a man can bear is a chip on his shoulder.

Research is an insurance policy, not a fire department.

According to Charles F. Kettering: "If at any time you should want to stop research, I will tell you how you can do it and save time. Just get a small committee together and have them pass on it. What they will say is that you were foolish for having started; so the first thing you can do is to say 'that is no good' and throw it away. But if you are curious and want to know what was really happening, keep fussing along with it until you find out why. Most things are known somewhere else."

You say the experiment failed. That is just your alibi. It was your own thinking that failed in the experiment. Remember that an experiment is an impartial judge of your thinking.

Knowing how to do a thing and getting it done are two entirely different things.



Sandpaper Grows Up

D. H. KILLEFFER

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

SANDPAPER ceased to be merely grains of sand glued to paper and became a tool of thousands of cutting edges after John Manning[1] failed to sell his rope cylinder paper to sandpaper makers. Whether or not lack of interest by sandpaper makers in a tougher paper was the real cause need not trouble us here. At least it was the proximate one, and the entry into this particular line of work of one accustomed to aid the native ingenuity of the mechanic with the deeper seeing of science did the rest.

Sandpaper, convenience of the workman, had always been a coating of grit cemented to flexible sheets. Nothing much could be done about such an apparently simple thing. The grits, whether of sand, flint, garnet, emery, or what, were sieved for size and dropped more or less evenly on a piece of paper or cloth previously coated with glue. Crushed abrasives were better than ground grit or sea sand. The paper or cloth backing received no special attention so long as the abrasive was held to it with reasonable tightness. The glue was similarly chosen to form a bond between the abrasive grains and the backing. Inspection was a matter of the keenness of vision of the workmen, and as long as everything looked all right it must be all right. Machines were developed to make sandpaper continuously, wonderful machines with huge capacities to apply glue and to drop sand upon it. Mechanical skill of high order went into those machines, and their operation day in and day out was a continuing mechanical triumph for their makers. Everyone who saw them in action was duly impressed. Everyone, that is, but the sandpaper itself.

Despite the elegance and intricacy of the "making" machines, variations of as much as 1000 per cent in the usefulness of the product were common. The traditional obstinacy of the inanimate dogged the sandpaper industry. Paper split, cracked, or disintegrated when it had no business to do so. Glue often separated from the grains and allowed them to drop off without apparent cause. In the efforts to overcome this, so much glue was used that at times it covered the grains and interfered with their cutting, often to the point of burning the work. Even when no such calamities happened, two pieces of presumably identical paper would produce effects quite different both in kind and degree when doing identical jobs.

Complaints were passed around freely, and, as was usual a few decades ago, most of them got nowhere. Mystery shrouded the causes of failure for everyone. If the sand failed to stick it was the fault of the glue, but the glue came from the same maker and the grit from the same source that had always supplied good materials. The paper, too, was always made on the same machines and hence must be uniform. So the whole accumulation of faults was laid on the perversity of nature!

Lest anyone, basing his view on the average person's limited contact with and use for coated abrasives, look upon these problems and the value of their solution as trivial, let it be noted here that literally millions of dollars worth of sandpaper

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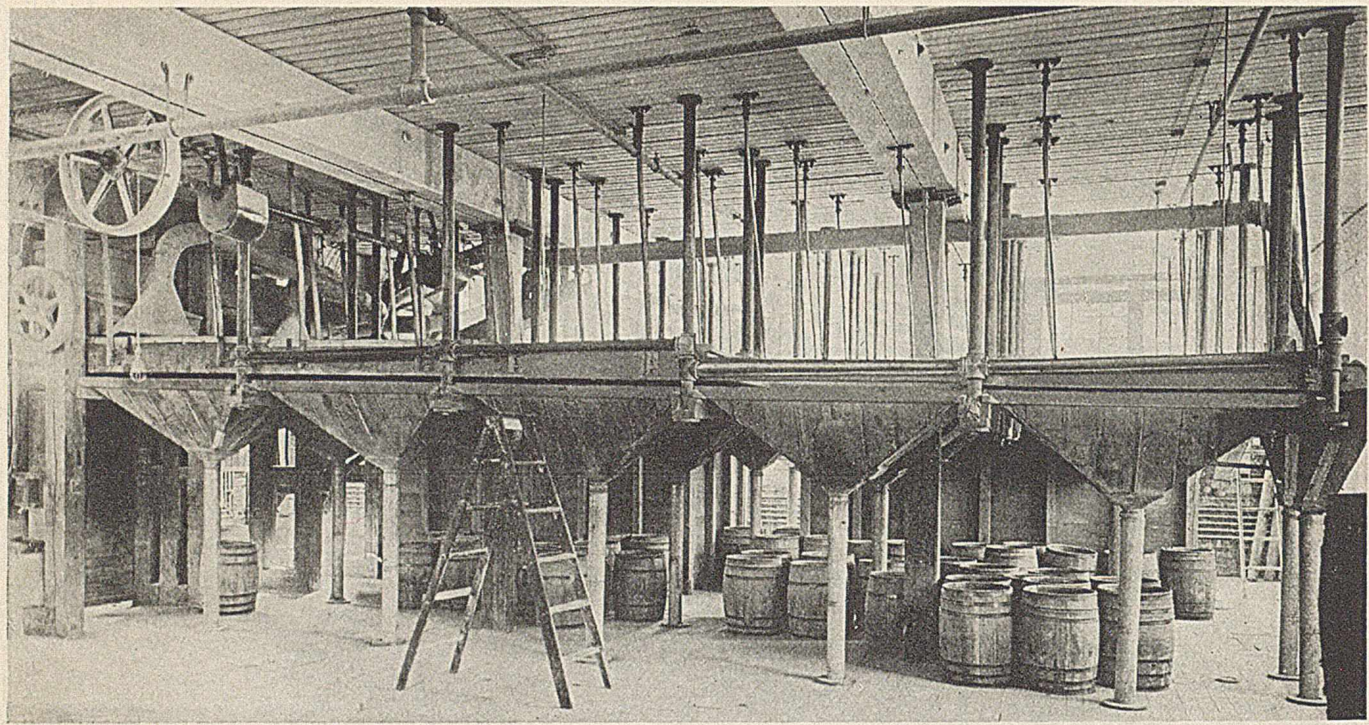
[1] The above photograph shows the plant of the Behr-Manning Corporation at Troy, N. Y., where coated abrasives are made by the acre.



Accurate Sizing of Grit Is Essential to a Uniform Product

are consumed annually in scores of different industries. Production of such widely different articles as fine furniture and felt hats, automobiles and airplanes, shoes and steel specimens, machine work and marbles, gem stones and golf clubs, consumes literal acreages of coated abrasives. Let it also be noted that, although the term sandpaper is loosely used in this story as the equivalent of coated abrasives, much of the product so designated is not made with paper and a minimum proportion of it uses sand, in the sense of silicon dioxide, as its abrasive.

At about the time when industries were beginning to look rather shamefacedly into science as something of possible, but probably remote, use to them and scientists were beginning diffidently to peek outside their laboratories for things to do, John Manning, maker of paper, thought a market for his newly developed rope cylinder paper might exist in the sandpaper industry. Tough and flexible beyond any others then to be had, this rope fiber paper seemed very much the kind of thing sandpaper makers needed, and it was with a distinct shock that reports were received from salesmen that it had failed to sell. Repeated efforts and conferences got nowhere. Sandpaper makers were quite unwilling to add a new complication to their already long list of woes; especially were they reluctant to admit that someone outside their industry might be able to teach them something experience had omitted from its curriculum.

The combined effect of this rebuff and other factors persuaded the papermaker to go farther to prove his point, and soon he was making sandpaper. That was the beginning of what is now the Behr-Manning Corporation. He, too, found it full of major mysteries in the ways of stuff. Fortunately, however, he had already learned that scientists, with aids to deeply penetrating vision at their command, did not believe in mysteries. That was the turning point.

Problems Solved by Science

Examination of the grits, glue, and backing revealed causes back of one mystery after another. A new conception of coated abrasives as methods of utilizing hundreds of thousands of sharp edges simultaneously as tools to cut, instead of mere hard surfaces to wear away, work in the course of finishing, brought out many reasons for what had been mysterious failures.

Microscopic examination of finished sandpaper that was good, bad, and indifferent began stripping the veil of mystery from one failure after another. Grains dropped into glue fell in more different ways than there were kinds of grains. Sometimes their sharp edges were up, but even more often flat surfaces were exposed and expected to cut. Often razor-edged long grains were buried beneath smooth ones. If chance allowed a long slender grain to stick up above the general level, it cut a deep groove into the work until the strain became too great, and it either fractured itself or broke out of the glue that held it in place. Some grains were tightly stuck by the glue and held against even extraordinary strains; others simply lay loosely in the glue coat ready to drop out at the slightest provocation. Even distribution of abrasive particles was attained only by applying such an excess that the great majority became buried too deep ever to be useful abraders.

These insights into the peculiarities of the product were further confirmed by microscopic searches through the dust and detritus removed by the sandpaper in use. Some samples produced long shavings which looked as if they had been made by thousands of tiny planes. Those samples gave good performance from the user's point of view. Others produced no discrete shavings at all, but rather a dust like that which the friction of severe rubbing might yield. That kind had little value.

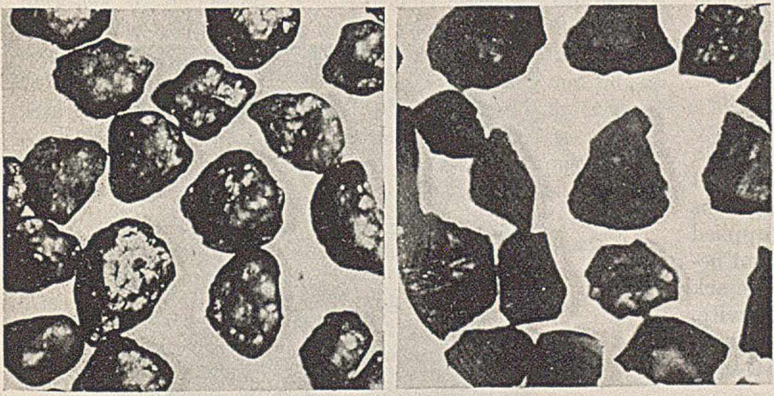
These revelations of things too tiny for the eye of the mechanic to perceive provided the basis for new progress in this industry in directions previously unexplored. Upon them and other related findings, F. E. Gallagher built the new conception of coated abrasives which has literally revolutionized the industry of their manufacture. Myriads of tiny cutting edges arranged and held in orderly array today cut work given them instead of wearing down surfaces by mere friction. By thus thinking of abrasive grains as tools, efficiency in use has been enormously increased and uniformity attained.

Solutions of some of the problems encountered have already been suggested. Others were more recalcitrant. In general, four major problems plague sandpaper makers—grit, glue, backing, and the coördination of all three. Each of them is complicated to an extraordinary degree by the wide variety of services the product is expected to perform. Some three thousand varieties of coated abrasives are required to meet the needs of users, and each must be accurately fitted to certain specific requirements. Above all, each of the three thousand must be made with the greatest possible uniformity and at a unit price that must be kept down.

Abrasives

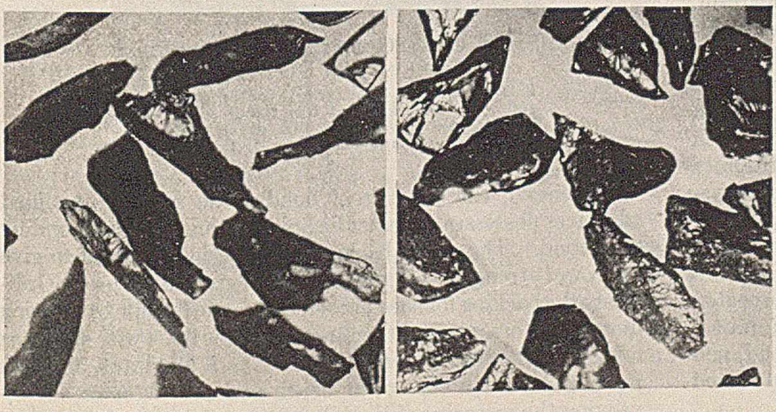
The problems presented by the abrasive grains have to do with size, uniformity, cutting edges, toughness, and hardness primarily, and with adhesion to glue and backing as a vital secondary characteristic. The differences in the material of the grains control hardness and toughness. Characteristic also of the material is its ability to fracture to give sharp or dull edges, and the grinding operation must be so conducted as to produce a maximum number of cutting edges without subsequently injuring them. The size and shape of the product of grinding are also essential to its service character, and finally the separation of particles into uniform sizes adapted to particular purposes is necessary if uniformity is to be expected in the finished product.

Three natural minerals serve as abrasives—flint, garnet, and emery. Latterly, electric furnace practice has supplied the important synthetic abrasives, silicon carbide, and fused aluminum oxide. Each abrasive has its individual character and usefulness. Flint (actually selected quartz of the correct grade) has very sharp edges but is brittle and has relatively little crushing strength. Garnet combines toughness with hardness somewhat higher than that of quartz. Only the hardest and toughest types of garnet can be used. Emery consists of minute crystals of naturally fused aluminum oxide held together by a matrix consisting largely of iron oxide. The particles of fused aluminum oxide in emery are harder than either quartz or garnet, but the soft matrix of iron oxide produces a fine cutting and polishing action. The synthetic abrasives are harder than the natural in the following order: fused aluminum oxide, silicon carbide, and, hardest of all, boron carbide, a recent commercial development not yet used to any great extent in coated abrasives because of its relatively high cost. Although there is naturally much overlapping of fields, flint and garnet are generally used on wood, leather, and other relatively soft materials; emery and artificially fused aluminum oxide are invaluable in finishing metals, minerals, and other harder substances. This classification is not exact, but, in general, garnet has replaced or is replacing flint in most woodworking operations. The introduction of better and higher speed machines is allowing properly crushed fused aluminum oxide to replace a large part of the garnet formerly used in woodworking machines. In general, fused aluminum oxide either has or should replace emery in metal working operations where cutting action is desired. For very fine polishing operations, emery still has certain advantages over the more abrasive synthetic material. Silicon carbide finds extensive use in finishing lacquers, paints in general, and leather, and is employed in some unusual wood and metal finishing operations. For work on metals, fused aluminum oxide is generally the best material, but in rare cases with metals of low tensile strength there may be some advantage in the use of silicon carbide.



A. Sea sand, rounded by wear on itself through tide action

B. A crushed abrasive, too chunky and dull for general use



C. A crushed abrasive, too thin and slivery for hard usage

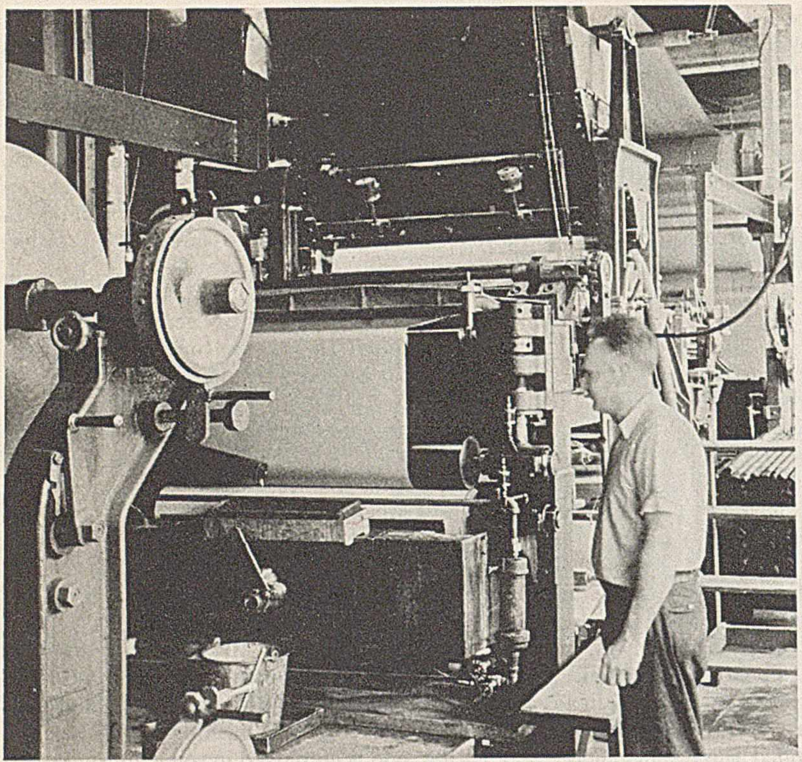
D. Crushed quartz, an excellent shape grain for strength and sharpness

FIGURE 1. PHOTOMICROGRAPHS OF EXTREME SHAPES OF ABRASIVE PARTICLES

The natural abrasives are ground from massive form or coarse particles, since naturally fine grains have dull rather than the sharp edges required for proper abrasive action. Synthetic abrasives must be similarly crushed to substitute sharp fracture edges for the duller ones of crystals. This fracture to grains must be accomplished by crushing or breaking of particles with a minimum of attrition. Roller mills following jaw crushers are satisfactory, but ball and rod mills tend to wear off the essential sharpness.

Adjustment of crushing equipment is critical for each material since shape of particles is equally important with size. Long slender needles are usually too weak to withstand the stresses of use and, by breaking off under strain, lose their value too quickly. Solid chunky particles expose too few edges. Consequently the adjustment of the mills must be so made as to yield a maximum percentage of particles of intermediate shape with good cutting edges but not too slender for strength. Figure 1 illustrates these characteristics of good and poor grains.

The accurate selection of particles to size is the next essential operation. Wire screens, silk screens, and air separators are used in classifying the successively finer particles. For the most accurate separations, water classifiers are employed. Each size is selected to match the percentages of control size, overgrade, and fines in standard samples for each grade of coated abrasive. This method of grading has been adopted in preference to specifying mesh sizes, since it better meets this industry's needs for an accuracy greater than that attainable



The Making Machine Applies Glue and Grit Evenly to the Backing

by mesh specification and avoids personal errors. The finest particles must be graded by special sedimentation methods.

Most remarkable about this industry is that, despite the enormous tonnages of flint ground in its mills to extremely fine and sharp particles, its records show no cases of silicosis. The other abrasives used do not cause this disease.

Adhesives

The adhesive bond between the grains and the backing must possess strength under conditions of use, it must hold grains firmly in position against torsional strains set up when applied to the work under the requisite pressure, and it must not become so brittle under ordinary weather conditions as to crack when bent around the arc that may be required in service. Above all, it must be uniformly strong, so that today's output may not differ from the same product made next week or next year by more than a minimum variation.

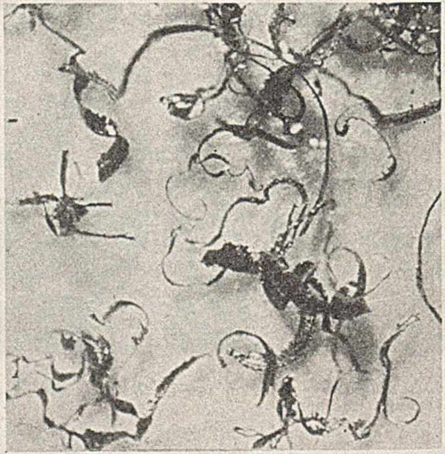
Glue was perhaps the most intricate problem of the industry, for glue itself is by nature difficult to manufacture or control accurately in the region where it is near maximum strain. The effect of weather, too, was long a baffling problem in securing uniform glue performance. Improvements in glue manufacture, as well as careful selection of the glue maker's products for the purpose, vastly improved sandpaper. Even the differences between glue from bone and from hide (which may be more than twice as strong) escaped the attention of early sandpaper makers and contributed much to the mysterious failures they had to face.

By selecting hide glue on rigid specifications and by using it under conditions of carefully controlled temperature and humidity, most of the mystery has been dispelled from the coated abrasive industry. Now it is the largest consumer of animal glue. Attempts to use other adhesives—casein, blood, and bone glues—have been abandoned, and all glue-bonded coated abrasives are now made with hide glue.

That statement must be qualified because of the growing demand for even stronger bonds with high resistance to moisture and solvents. In numerous operations, wet sanding of work drenched with water or oil is required, the specific requirement being the suppression of dust or the need for some lubricating agent to prevent too great accumulation of heat caused by the speed of sanding. Glue bonds resist oils generally, but either heat or moisture soon destroys them. The need for better bonds, resistant to both the heat of rapid work and the water used to lubricate and cool it, was growing as synthetic resinous bonds were being developed.

Now various resins and varnishes made from them are of growing usefulness to the abrasive coaters. Several types of varnishes, adapted initially from the quick-drying vehicles of the printing-ink makers, have been widely used. More recently, synthetic resin varnishes have come into favor and investigations of others are being actively pursued.

In addition to the oil-modified binders or flexible binders, strong thermosetting resin bonds, resistant to water and heat, are used in coated abrasives designed for hard grinding. This type of product is particularly useful for disk grinding, an operation more or less intermediate between grinding with abrasive wheels and with relatively flexible coated abrasives. Using very strong special backings and heat- and water-resistant bonds, such coated abrasives possess strengths approximating those of abrasive wheels and at the same time retain a certain degree of flexibility required in many grinding operations where a rigid wheel cannot be used.



Steel Chips Cut by a Metalite Fiber Combination Disk (×20)

This looked like black dust to the naked eye; under the microscope it was found to be a collection of steel shavings just as clear and distinct as those cut on a planer, milling machine, or lathe.

In general, the waterproof bond made with oil-modified adhesives possesses a greater flexibility than the corresponding glue bond. The paper backings are specially treated to give them wet strength and prevent disintegration in use. Ordinarily the backing for such abrasives is made flexible by soaking in water before use, and then the sanding is done with water as a lubricant. Sometimes oil is used as a lubricant, and this permits a certain control of depth and character of cut by varying the viscosity of the lubricating oil.

The nature and strength of the adhesive bond between the grain and the backing necessarily depend upon the natures of the surfaces of each. Glue readily bonds to paper and to cloth, the principal problem in the latter case being the production of a smooth surface by means of a sizing coat of filler calendered in to support grains evenly. The nature of the adhesive bond to the grains presents serious problems in surface effects and capillarity. In the solution of these, some of the best scientific work in the industry has been done.

The cracked glassy surfaces of the grains of abrasive are often glue repellent and require treatment to permit the bond to form. Among the methods used are controlled heating to high temperatures, chemical etching of bright, smooth surfaces, and treatments which leave materials readily wet by the adhesive tightly bonded to the grain surfaces. The same treatments of grains that permit glue to bond with them are also effective, with a few exceptions, with resinous adhesives. Tests of capillarity of grains are made by measuring the height to which water is raised in a glass tube of standard diameter containing them. With this simple gage of capillarity, standards are maintained for raw and treated grains which have completely overcome the old tendency for grains to drop out of the hardened glue coat.

Backing

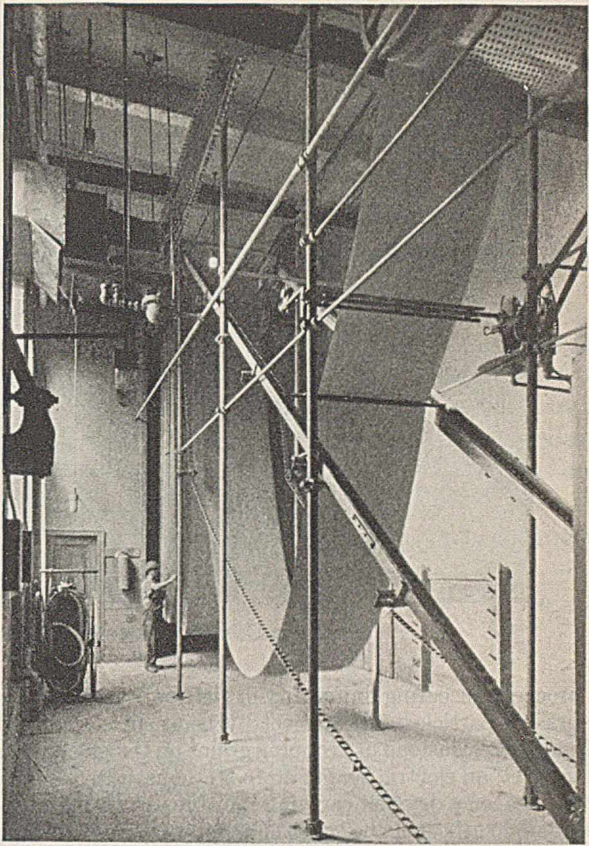
The backing used for abrasive grains must possess high tearing strength. This is generally far more important than actual tensile strength. Several types of papers are adaptable for this purpose, but the superiority of rope paper has been amply demonstrated. Both the Fourdrinier process and the cylinder process are used in manufacturing this important material. Papers varying from 40 to 130 pounds, and even as high as 170 pounds, are required by the industry. To secure even higher tear strengths and greater flexibility, particularly for heavy sanding jobs using hard abrasives, cloth backings are employed. Cloth-backed abrasives are generally used in metal working and to a less extent for finishing wood. The cloth used is of special construction woven with a twill weave and a careful balance between warp and fill, as well as an accurate count of threads. Four weights of cloth meet the industry's present requirements.

Because of the easy penetration of adhesives through cloth, various treatments are given before it is coated. Necessarily the cloth must be shrunk and dried under tension for accurate size. Each type of finished product is made of a definite color to designate its properties. The sizing of the cloth backing is a starch-base filling which gives a glue-proof finish. The properties of the size are adjusted to give the balance between adhesion and flexibility required in final service. Rigid inspection of cloth at all stages in the finishing is essential to a uniform product, because any imperfections in the weave or threads would show up in use. In the cloth-finishing department of this single plant, an average of 750,000 yards of finished cloth per month undergoes three treatments equivalent to the processing of 2,250,000 yards of goods every 30 days.

For special strength, cloth is frequently laid on a backing of paper before the abrasive grains are bonded to the cloth side. For some purposes paper backings are employed, and for others vulcanized fiber in relatively thicker sheets is used.

Coördination of Problems

The actual coating operation, carried out on remarkable automatic machines, consists of first applying a sizing coat of glue to the backing, leveling off this coat, and dropping on it a even layer of abrasive grains. Necessarily the quantity of abrasive is in excess of that required in the finished product, and a whipping machine, consisting of a rotating series of flights, knocks off those particles which are not imbedded in the glue and returns them through screens to the feed of the machine. For fast-cutting products, the web from this operation is suspended in festoons to allow the adhesive to harden. An anchoring adhesive coat may be subsequently applied to hold the abrasive more firmly in place.

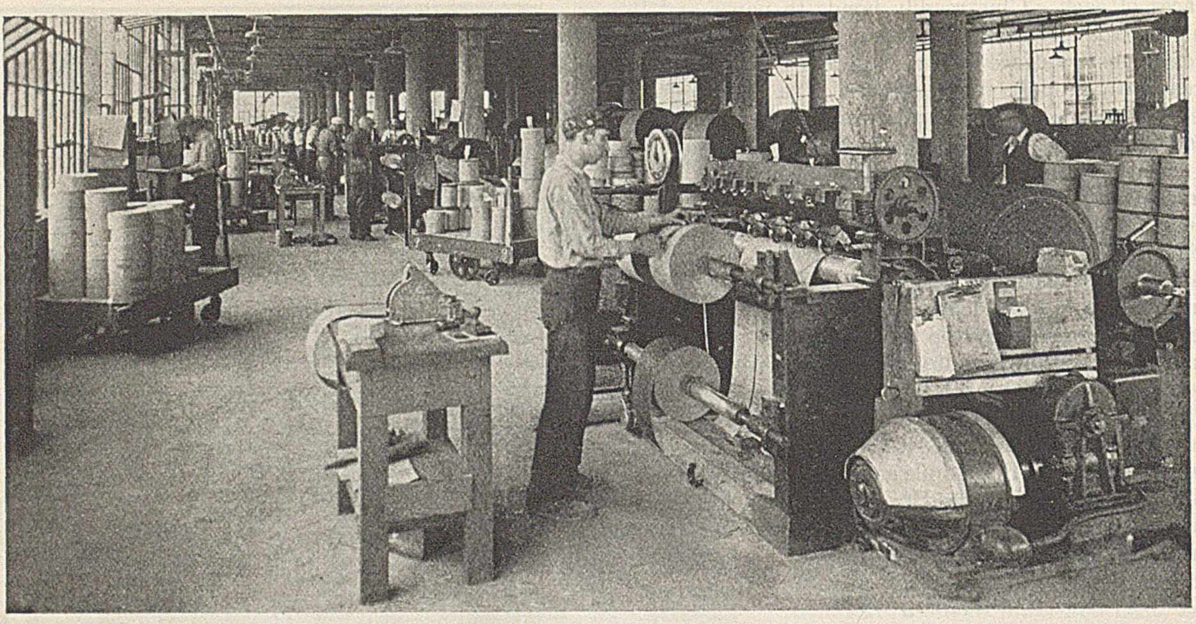


From the Making Machine the Web Is Festooned in a Dryer to Set the Adhesive

For relatively severe grinding, the web with its layer of excess abrasive is often rolled before this excess is whipped off. The objective is to press more abrasive into the adhesive layer and form a denser coating. After this rolling-in operation, the web, whipped free of unattached grains, is festooned to set the adhesive, and a subsequent adhesive coat is applied for anchoring purposes.

From the making machine, the continuous sheet of finished product goes in festoons to a drying room where the bond is set. If a varnish adhesive has been used, the temperature of the drying room is adjusted to harden it. With glue, drying is accomplished in a room where temperature and relative humidity are both carefully controlled. The dried sheet with its coating of abrasive is removed from the festoons and put through a flexing machine to break the adhesive bond evenly to make the product flexible in service. Several methods of breaking or flexing are employed, depending upon the degree of flexibility needed. The most common of these consists in drawing the sheet under controlled tension over a steel mandrel whose diameter is selected to give the desired result. The flexing mandrel may be placed either directly at right angles to the length of the sheet, or two mandrels at angles of 45° to the sheet may be used to flex it in two directions at once. The importance of this flexing operation is evident immediately in the feel and behavior of any sheet of coated abrasive; for having once been through the treatment, a sheet retains its flexibility permanently.

The most important development in this industry has been



Rolls of Coated Abrasive Are Slit to Convenient Widths for Use as Belts

the process of securing uniformity in distribution and position of abrasive particles on the sheet by using an electric field. In this process, instead of dropping grains on the glued surface of the sheet, an electric field of 40 to 50 thousand volts is produced between a dry belt carrying the abrasive grains and the glue-coated surface of the sheet held approximately 0.75 inch above the grains. As the grains and sheet enter this field, the particles are picked up by the charge and carried to the adhesive surface. This accomplishes two useful results. The grains are lifted by the lines of force of the field in the direction of their major axes so that in the finished product sharp edges uniformly stick up. Because each particle is similarly charged and hence repels every other particle, their distribution in the adhesive layer is of the utmost uniformity. In all other ways the treatment of the electrocoated product is the same as that of those mechanically made.

In the making operation, large rolls of backing are handled. For some of the lighter weights of backing for fine abrasive grains, as much as 3 miles of backing form a single roll continuously treated. In the heavier weights the length of the roll is reduced to a few hundred yards to make it convenient to handle. In the coating operation one roll of backing is attached to another as it is drawn through the machine so that rethreading is not required, and the operation proceeds continuously.

For special uses abrasive sheets are frequently required whose grains are widely separated. These products, particularly useful in removing old varnish coats from wood and in other operations where closely coated grains are likely to become quickly clogged by accumulations of detritus, are made by dropping grains on the adhesive layer from corrugated rolls which leave substantial spaces between them.

The final finishing of the abrasive sheets consists in cutting from the rolls pieces or belts of the desired size convenient to the user. For making square sheets, the roll as made is slit to convenient widths by circular rotating knives, and from the narrower strips thus made the desired sheets are cut off. For abrasive belts the slitting operation is similarly conducted and the narrow strips are cut to desired lengths and cemented into continuous belts. Disks are chopped out of the continuous roll for use on disk sanders. The waste from the finishing operation is burned to recover the grains, and they are returned to the operation.

Perhaps the most interesting feature about the industry is the variety of uses of its products and the accuracy of machines for applying them. It is even possible with one type of sanding machine (perhaps there are others) to remove the ink impression from paper on which it is printed without tearing the sheet or wearing through it! With machines of such delicacy, on the one hand, using paper so fine-grained that it holds a hundred thousand particles per square inch and, on the other hand with rugged disks approaching the abrading ability of high-speed grinding wheels, the variety of operations in which these products are useful runs the whole gamut of industry.

Acknowledgment

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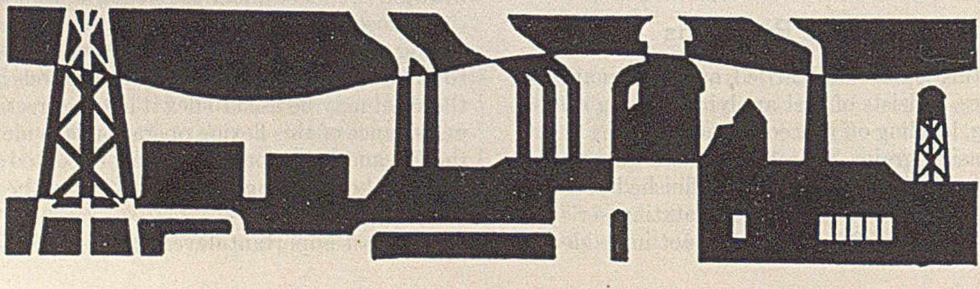

MANILA RESINS

ORIGIN, PROPERTIES, AND APPLICATIONS

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Manila copal is derived from conifers of the *Agathis Alba* Foxw. species which is widespread over the East Indies area. The Netherlands Indies furnishes the bulk of the world's production. Physical and chemical data on the various sorts of Manila resins are summarized. Solubility of these resins in a wide variety of organic solvents is reported. Manila copal apparently consists almost entirely of four different resin acids. Soft or half-hard Manila resin can be made the basis of a substitute for shellac in spirit varnishes by the addition of fatty acids and beeswax or by the addition of nitrocellulose. By proper treatment the same resins can be dissolved in aqueous borax and ammonia solution to give waterproofing sizes for paper for ink vehicles. Treatment with glycerol is discussed, suggesting the possibility of a cheap thermosetting molding resin to be derived from this reaction.

MANILA resins are members of that rather vaguely defined class of natural resins known as copals. They are characterized by a comparatively high acid number, a moderately high melting point, solubility in alcohol, and insolubility in petroleum solvents. They are often referred to as spirit-soluble gums. The resin as gathered soon after its exudation from the tree has a wide application in spirit varnishes of many sorts and has numerous minor uses. Manila copal of a fossilized or semifossilized nature imparts some excellent qualities to oil varnishes. As with other natural resins, for the latter use the Manila copal must first be run or thermally processed. It is heated alone at 300° to 330° C. until sufficiently changed chemically to dissolve in hot drying oils. Except for the brown fossil variety dug from the ground, Manila copal is light in color; commercial grades vary from yellow to almost water-white. It is quite transparent and is not sticky to the touch.

The resin is exuded from a conifer of the Agathis family. Foxworthy's work (*3*) traces it all to a single species, *Agathis Alba* Foxw.

Van de Koppel, chief of the Forestry Service of the Netherlands East Indies Government, who has studied the economically valuable flora of the Netherlands Indies for many years, is of the opinion that other similar species may also supply the resin (*12*). The bulk of the Manila copal of commerce is gathered in and exported from the Netherlands East Indies. Some of that gathered in Borneo is exported from Singapore. The remainder of the world's supply is collected in the Philippines. Currently the Netherlands Indies supplies more than three-quarters of the United States requirements, and the Philippines and Singapore the balance. The annual imports of resins of this class (soft Manilas, Lobas, Pontianaks, and Boeas) are currently of the order of 15,000,000 pounds.

Some study is now being made in Celebes on tapping and collecting this resin in a systematic manner, and closer control is being assumed by the Netherlands Indies Government. Exporters have also been supporting research work in the United States to study the possibilities of standardizing the resin grades, of improving present methods of use, and of finding new uses. In the course of this work some thirty-five samples of commercial grades of Manila copal have been examined. In addition, hundreds of botanical samples of resins from Agathis trees have been studied analytically, physically, and practically.

Constitution of Manila Resin

Several chemists have published reports of research on the chemical constitution of Manila resin, but the results are diverse, and the samples in some cases are so illy defined that it is difficult to say just how much is accurately known (*4, 7–11*).

All are agreed that a large percentage of the resin consists of a resin acid or acids. Tschirch and Koch (*11*) report 12 per cent of resene. No samples contained more than 1.5 per cent of resinous substances insoluble in cold 10 per cent aqueous sodium hydroxide, and as a rule the amount of insoluble material is about 0.5 per cent. Some chemists reported one acid in Manila resin; others report as many as four. In order to study the behavior with glycerol, a preliminary fractionation of the soft and the half-hard Manila resin was carried out and four fractions were obtained; the resin was divisible into a fraction that was soluble in sodium bicarbonate solution and one that was insoluble in bicarbonate solution, but soluble in sodium carbonate or sodium hydroxide solution. Each of these fractions can, in turn, be divided into a fraction whose potassium salt is soluble in alcohol and one whose potassium salt is insoluble in alcohol. Since more precise separation was not required, no attempt was made to purify these fractions, which were obtained as more or less amorphous powders, but the presence of four different acids seems definitely indicated. In addition the resin contains a small amount of essential oils and 1 to 3 per cent of moisture.

Properties of Manila Resins

Manila resins are divided into classes according to the age of the resin. The relationship of the various classes is shown in Figure 1. The softest grades, gathered between 1 and 3 weeks after tapping, and called *melengket* by the natives, are exported from the Netherlands Indies in four qualities. The finest grade, PWS (prime white soft), is nearly water-white in color and almost entirely free from impurities of any sort. WS (white soft) is very clean and quite light in color. MA (or *melengket* A) may contain some bark and wood fiber. The

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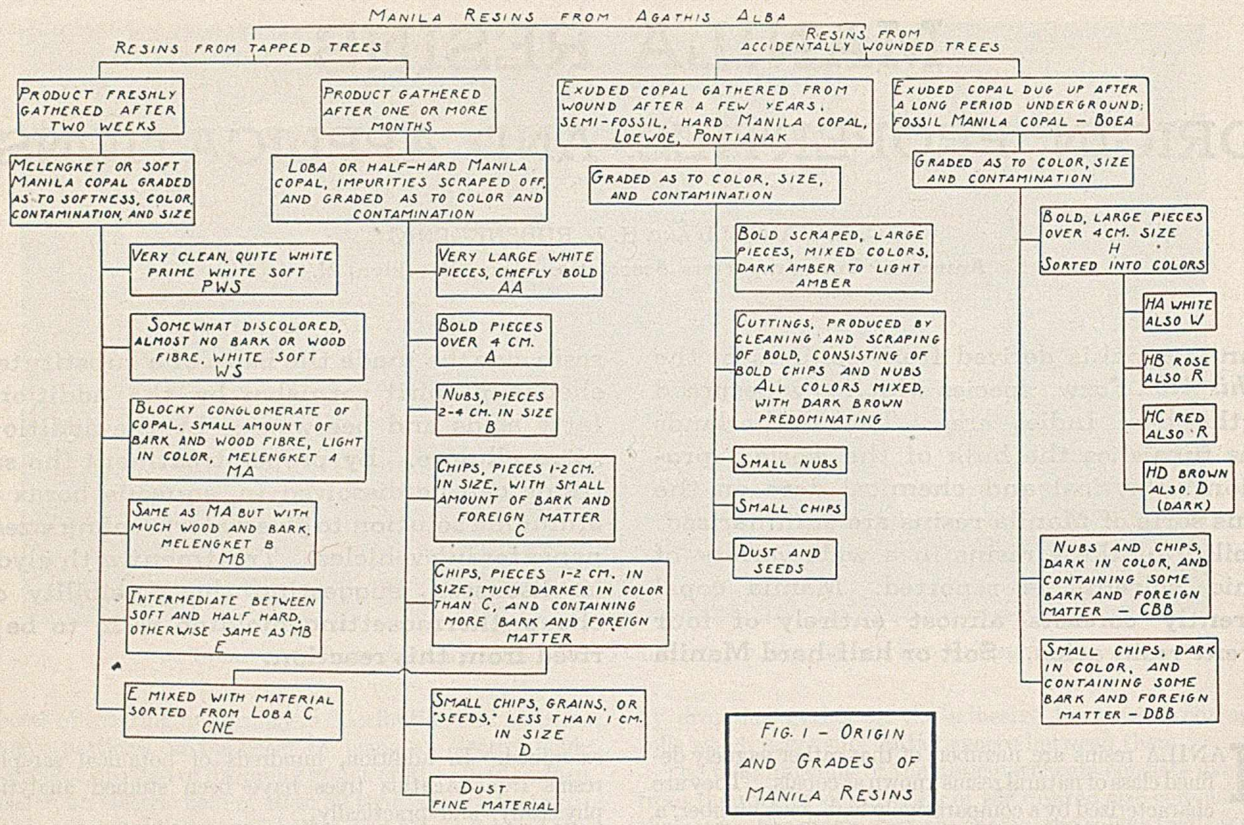

FIG. 1 - ORIGIN AND GRADES OF MANILA RESINS

latter grades are by far the most used in this country. MB (or *melengket* B) may contain considerable amounts of woody impurities. Currently it is not much in demand in the United States but finds outlets abroad. These soft grades arrive on the market as blocky lumps, clear and free from any surface crust. A slightly older and harder grade is called E and is marketed in admixture with the C grade of the Loba type of Manila as Loba CNE.

Half-hard Manila, or Manila Loba, is the designation of material gathered from 1 to 3 months or more after tapping. The resin has become hard enough so that the pieces do not block together as does the soft Manila. It is scraped free of surface impurities and graded according to size of piece, from A (over 4 cm.) to D (less than 1 cm.) and dust. These are Netherlands Indies gradings. Singapore Manila is of the same type. Philippine Manila is also resin of about the same age; it is sorted according to both color and size of piece. *Olmaciga* is a Philippine designation for this resin.

The fossil grade of Manila is derived from the Netherlands Indies and is known as Boea or hard Manila. The light col-

TABLE I. PROPERTIES OF MANILA RESINS FROM DIFFERENT LOCALITIES

Resin	Refractive Index	Softening Point °C.	Melting Point °C.	Specific Gravity	Direct Acid No.	Indirect Acid No.	Saponification No.	Iodine No.
Manila (Macassar):								
WS pale soft	1.526	80–88	115–128	1.06–1.07	135–137	150–165	170–190	118–124
MA soft blocky	1.526	77–78	121	1.06–1.07	127–134	149–165	158–190	121–126
Loba A bold pale	...	82	117	1.08	149	162	176	122
Loba B bold pale nubs	1.539	73–90	120–124	1.07–1.08	136–139	147–162	160–170	116–124
Loba C bold pale chips	1.540	81–88	114–123	1.07–1.08	139–141	152–155	160–170	119–125
Loba D small pale chips	1.539	83–89	114–127	1.07–1.08	127–131	151–164	160–180	114–115
Loba DK dark chips	1.538	71–89	114–130	1.07	127–131	146–161	165–180	107–111
Loba CNE dark nubs	...	79–90	116–127	1.07	125–133	144–163	168–190	104–130
Loba dust	...	78–91	116–125	...	110–131	134–159	160–177	68–87
CBB medium pale nubs	1.538	82–90	119–130	1.06–1.08	134–141	152–164	176–190	114–120
DBB pale chips	1.538	78–88	120–129	1.06–1.07	135–143	154–163	170–179	112–113
Singapore Manila:								
White split chips	...	94	126	1.07	120	139	144	125
Manila (Philippine) spirit-soluble:								
Extra bold pale scraped	...	86	123	1.06	107	138	140	125
Bold pale	...	89	129	1.07	109	130	136	123
Bold extra pale sorts	...	96	128	1.07	111	135	143	124
Bold pale chips	...	91	129	1.07	114	143	154	120
Pale small chips	...	93	130	1.08	113	135	143	116
Bold amber sorts	...	103	128	1.07	110	139	148	113
Seeds and dust	...	110	132	1.08	110	142	157	104
Pontianak:								
Bold scraped	...	87–135	135–161	1.07–1.08	113–118	122–131	149–180	119–142
Mixed bold	...	95	126	1.07	121	135	148	131
Cuttings	...	91	138	1.08	118	135	151	127
Nubs	1.540	99–135	136–169	1.07–1.08	112–118	126–135	151–180	106
Chips	...	82–132	136–156	1.07–1.08	119–120	127–139	154–180	125
Boea Manila:								
Hard bold white	...	79	130	1.07	118	147	143	137
Hard bold amber	1.540	80	131	1.07–1.08	120–123	145–147	159	110–129
Hard bold dark	1.539	80	132	1.07	122–141	147–150	175	110–133

ored variety is found where it has exuded in the crotches of trees still standing. The amber and dark grades are found buried in the ground, often in masses so huge that the botanists are completely at a loss to account for their formation. Manila CBB and Manila DBB are grades consisting of a mixture of Boea with Loba. The excellence of Boea as a varnish resin is outstanding. It is to be hoped that some treatment of the more recent Manila resins may be devised to obtain from them a product of the same qualities. Reference should be made to previous papers for data on tests and characteristics of protective coatings made from this resin (*1, 2, 5*).

A closely related resin used for oil varnishes is Pontianak, also a fossil resin. It originates in Borneo, whereas Boea comes chiefly from Celebes and other parts of the Netherlands Indies. Pontianak behaves more like Kauri gum in the varnish kettle, but otherwise its properties and the properties of its varnishes make it almost indistinguishable from Boea. Not enough is known with certainty about the origin of either resin to explain fully these differences and similarities between Pontianak and Boea.

The specific gravity of Manila resins varies from 1.06 to 1.08. Other properties vary according to the origin and age of the particular shipment examined, but the approximate limits of these variations may be defined as follows:

Resin	Melting Point, ° C.^{a}	Direct Acid No.	Indirect Acid No.	Saponification No.	Iodine No.
Soft and half-hard Manilas	115–135	125–150	140–165	160–190	120–130
Boea Manila	130–135	120–140	145–150	145–175	110–135

^{a} Melting point determined by the mercury method (*6*).

Typical characteristics of the Manila resins from different localities are given in Table I for the commercial grades entering the American market.

The acid and saponification values for Philippine Manila run about ten points lower than the corresponding values for half-hard Manilas from the Netherlands Indies. These same values for Pontianak are lower than those for Boea by about the same amount.

The Manila resins are imported in containers of local origin, in weights which have become standard by long usage. These specifications are as follows:

Resin	Class of Copal	Tree	Country of Origin	Imported from	Package	Net Weight of Package *Lb.*
Boea	Fossil	*Agathis Alba*	Netherlands East Indies	Macassar; Netherlands East Indies	Basket bags	160
Loba Manila	Semirecent	*Agathis Alba*	Netherlands East Indies; Philippines	East Indian ports; Manila	Basket bags and bags	160
Soft Manila	Recent	*Agathis Alba*	Netherlands East Indies; Philippines	East Indian ports; Manila	Basket bags and bags	160
Pontianak	Semifossil	*Agathis Alba*	Borneo	Pontianak; Borneo; Singapore	Cases (bold) and bags	Cases, 224; bags, 160

Solubility Studies

As is well known, resin solutions show no evidence of any saturation point, simply becoming more viscous as the concentration of resin increases, and are probably more in the nature of colloidal sols rather than true solutions. These are generally spoken of as solutions, however, and the dissolving power of a solvent for a particular resin is considered to vary inversely with the viscosity of a solution of the resin in it. Using the term in this sense, some solvents dissolve these resins completely, some dissolve only part of it, some simply swell the resin particles, some mix with it to form a more or less elastic gelatinous mass, and some do not affect the resin at all. The effect on Manila resins of sixty-seven different solvents, including different commercial petroleum solvents, was determined by agitating 100-gram samples of the resins with an equal weight of each solvent overnight.

Petroleum distillates, whether paraffinic or naphthenic in base, whether low- or high-boiling, have no effect on these resins. Hydrogenated petroleum solvents sometimes may attack the resin enough to swell the particles, but have no further effect.

Coal-tar solvents, such as benzene, toluene, and xylene, may swell the particles or even form rubbery, gelatinous masses with Manila resins.

Turpentine and dipentene either swell the particles slightly or do not attack the resin at all. The other terpenic solvents tried, Hercosol 80 and terpineol, formed gelatinous masses and in some cases partly dissolved the resins.

Chlorinated solvents, examples of which are carbon tetrachloride, amyl chloride, monochlorobenzene, tetrachloroethane, either swelled the particles or formed gelatinous masses.

The alcohols tried were: methyl, three anhydrous denatured ethyl alcohol formulas, isopropyl, *n*-butyl, *sec*-amyl, diacetone, and benzyl alcohols. The Boea was largely, but not completely, dissolved by all of these except the benzyl alcohol, with which it formed a gelatinous mass. The remaining Manila resins were completely soluble in all the alcohols, except that one sample of Loba was only swelled by benzyl alcohol and a sample of CBB formed a gelatinous mass with the same solvent. The viscosity of these solutions showed a marked increase with each increase in the length of the chain in the aliphatic alcohols. The benzyl alcohol solutions were the most viscous of all, and the Pontianak solutions were much more viscous than the corresponding solutions of the half-hard Manila resins.

The viscosities of the solutions are given in Table II. Boea was largely but not completely dissolved by acetone and methyl acetone. It was completely dissolved in phenol at 60° C. It was swelled by or formed gelatinous masses with all the other solvents tried.

The other Manila resins, except Pontianak, gave solutions of low viscosity with acetone and methyl acetone. Pontianak also was dissolved, but its solutions were much more viscous. Ethyl ether gave similar results. *n*-Butyl ether either swelled or did not attack the resins. Dichloroethyl ether only swelled the particles.

The alcohol-ethers, Cellosolve and butyl Carbitol, gave viscous solutions.

Ethyl acetate completely dissolved all the samples. Butyl, amyl, and octyl acetates and butyl lactate dissolved some samples and swelled or formed gelatinous masses with the remainder. Diethyl carbonate, methyl salicylate, dimethyl phthalate, and methyl abietate swelled or formed gelatinous masses with the resins.

Dioxane, aniline, Hexalin, and Tetralin completely dissolved some samples and partly dissolved or formed gelatinous masses with the remainder. Nitrobenzene and tricresyl phosphate swelled these resins. All the Manila resins were soluble in phenol at 60° C.

When these resins are run or thermally processed to render

TABLE II. VISCOSITIES AND COLORS[a] OF 50 PER CENT SOLUTIONS OF MANILA RESINS

	Boea Manila, Hard Bold Amber			Manila Loba C			Manila CBB			Manila DBB			Philippine Manila, Bold Pale Chips			Pontianak Bold Scraped		
	Viscosity	*Poises*	Color	Viscosity	*Poises*	Color	Viscosity	*Poises*	Color	Viscosity	*Poises*	Color	Viscosity	*Poises*	Color	Viscosity	*Poises*	Color
Acetone	J	2.50	2	B	0.65	5	C	0.85	5	A–	0.50–	10	A	0.50	8	R	4.70	5
Amyl acetate	..	...	..	..	....	..	..	5.50	6	M	3.20	10	U	6.27	8	Y	17.6	5
sec-Amyl alcohol	X	12.9	3	W	10.70	5	U	6.27	6	R	4.70	10	U	6.27	9	Y	17.6	5
Amyl chloride	..	...	..	..	....	..	T	5.50	9	..	....	..	..	....	..	..	....	..
Aniline	..	...	..	Z3	46.3	17	Z1	27.0	18	..	....	..	Z1	27.0	Da	Z4	63.4	18
Ansol M[b]	J	2.50	4	F	1.40	5	E	1.25	6	B	0.65	10	C	0.85	9	N	3.40	5
Benzyl alcohol	..	...	..	..	....	..	..	....	..	Z1	27.0	12	Z1	27.0	12	Z6	148	8
Butyl acetate	..	...	..	..	....	..	..	....	..	L	3.00	9	T	5.50	9	Y	17.6	4
n-Butyl alcohol	V	8.84	3	T	5.50	5	R	4.70	5	K	2.75	10	N	3.40	10	X	12.9	6
Butyl Carbitol	..	...	..	Y	17.6	5	X	12.9	6	X	12.9	11	E	1.25	8	Z2	36.2	6
Butyl ether	..	...	..	..	....	..	A–	0.50–	2	..	....	..	..	....	..	..	....	..
Butyl lactate	..	...	..	Y	17.6	5	Z	22.7	6	..	....	..	Z1	27.0	10	Z3	46.3	7
Cellosolve	..	...	..	..	....	..	U	6.27	6	J	2.50	10	P	4.0	10	Y	17.6	5
Diacetone alcohol	Z	22.7	6	W	10.70	6	U	6.27	8	Q	4.35	11	U	6.27	10	Z2	36.2	8
Dioxane	..	...	..	..	....	..	V	8.84	5	T	5.50	10	U	6.27	8	Z2	36.2	5
Dipentene	..	...	..	..	....	..	Q	4.35	4	..	....	..	..	....	..	..	....	..
Ethyl acetate	..	...	..	L	3.00	4	G	1.65	6	B	0.65	9	X	12.9	11	W	10.70	4
Ethyl ether	..	...	..	C	0.85	4	E	1.25	4	A	0.50	8	C	0.85	7	R	4.70	4
Hercosol 80[c]	..	...	..	..	....	..	Z1	27.0	6	..	....	..	Z3	46.3	10	..	....	..
Hexalin	..	...	..	Z6	148	5	Z3	46.3	7	Z2	36.2	12	Z6	148	9	Z2	36.2	5
Isopropyl alcohol	U	6.27	4	P	4.00	5	O	8.70	6	H	2.00	10	J	2.50	9	V	8.84	6
Methyl acetone	K	2.75	2	C	0.85	5	C	0.85	6	A–	0.50–	9	A	0.50	8	V	8.84	5
Methyl alcohol	G	1.65	5	A	0.50	7	B	0.65	7	A–	0.50–	11	A	0.50	10	M	3.20	7
Octyl acetate	..	...	..	Y	17.6	5	Z	22.7	5	Z1	27.0	11	Z5	98.5	10	..	....	..
Shellacol[b]	N	3.40	4	H	2.00	6	I	2.25	6	A	0.50	11	E	1.25	10	R	4.70	6
Solox[b]	O	3.70	4	I	2.25	6	I	2.25	7	C	0.85	11	H	2.00	10	Q	4.35	6
Terpineol	..	...	..	..	....	..	Z6	148	7	..	....	..	Z6	148	12	Z5	98.5	9
Tetralin	..	...	..	..	....	..	..	....	..	Z6	148	17	Z5	98.5	18	..	....	..

[a] Viscosities refer to Gardner-Holdt bubble viscosity tubes and colors to Gardner-Holdt standards.
[b] An anhydrous denatured ethyl alcohol.
[c] A special high-boiling solvent for varnishes and lacquers, consisting chiefly of terpene, hydrocarbons, and ketones.

them soluble in drying oils, a number of changes take place in their properties. The Boea and the Pontianak suffer a weight loss of from 15 to 25 per cent in this process. The soft and half-hard Manila resins are somewhat more difficult to render soluble in oils and are more commonly used for spirit varnishes. Samples of each, however, have been run and their physical and chemical properties and solubilities determined. In each case the melting point was not markedly changed by the heat treatment, the acid and saponification values were reduced by 25 to 45 per cent, and iodine values were slightly reduced.

The characteristics of typical run resins are given in Table III. These properties are dependent on the temperatures employed, time of processing, and care exercised by the operator, and may be varied widely.

TABLE III. PROPERTIES OF RUN MANILA RESINS

Resin	Loss	Softening Point	Melting Point	Specific Gravity	Direct Acid No.	Indirect Acid No.	Saponification No.	Iodine No.
	%	° *C.*	° *C.*					
Boea hard bold amber	20–25	105	125–135	1.06	78–85	86	91	106
Manila CBB	25	80–90	115–120	1.06	60	67	70	99
Manila DBB	25	85–90	125–135	1.05	50–60	53	67	96
Manila Loba C	20	85–90	125–130	1.05	55–65	72	89	104
Philippine Manila bold pale chips	20	85	127	1.06	50–55	62	72	93
Pontianak bold scraped	20–25	105	125–130	1.06	75–85	92	86	99

The metal of the varnish kettle is an important factor in its effect on the color of the processed resin after running. The lightest colors were produced either in low-carbon austenitic steel equipment of the 18 per cent chromium–8 per cent nickel type or in nickel kettles. Good results as far as color is concerned could be obtained in Monel metal equipment which, in turn, was superior to copper or its alloys. Iron, even when the time of contact was short, caused undesirable darkening and increase of color when it was allowed to come in contact with Manila resins during running.

Solubility characteristics were strikingly changed by the treatment. The run resins were soluble in all the petroleum and coal-tar solvents, and also in the terpenic and chlorinated solvents listed in Table II. The original untreated resin showed insolubility in the same solvents.

The run resins showed insolubility in methyl, ethyl, isopropyl, and diacetone alcohols. They were soluble in *n*-butyl, *sec*-amyl, and benzyl alcohols. They were soluble in ethyl, *n*-butyl, and dichloroethyl ethers, Cellosolve, butyl Carbitol, and in ethyl, butyl, amyl, and octyl acetates. They were soluble in diethyl carbonate, butyl lactate, and methyl salicylate, and were swelled by dimethyl phthalate and methyl abietate.

The run resins were partly soluble in acetone and methyl acetone and partly or wholly soluble in Hexalin. They were swelled by tricresyl phosphate. They were soluble in dioxane, aniline, Tetralin, nitrobenzene, and phenol at 60° C.

The change in solubility as the result of thermal processing is marked. Material originally soluble in alcohols becomes insoluble because of chemical changes on heating. In contrast, fossil resins such as Congo are converted by running from insoluble materials to soluble ones.

Shellac Substitutes

Shellac used as a spirit varnish resin gives a film that is both hard and tough and has no tackiness. Since soft and half-hard Manila copals have a hardness equal to that of shellac, though their spirit varnish films are much more brittle, some work has been devoted to modifying Manilas so as to provide acceptable substitutes for shellac. A product only slightly inferior to shellac in hardness and toughness of film may be obtained by fusing the copal with as much as 30 per cent of a partially oxidized fatty acid and as much as 10 per cent of beeswax.

A spirit varnish superior to shellac varnish in hardness, flexibility, clarity, and lightness of color may be made by dissolving 3 parts of soft Manila resin, 2 parts of spirit-soluble nitrocellulose, and 1 part of dibutyl phthalate in a 3 to 1 mixture of alcohol and toluene.

Shellac may be dissolved in aqueous borax solution to yield a size, which gives a waterproof finish when coated on paper. It is also a good vehicle to make waterproof inks, using a basic dyestuff such as methyl violet as a coloring matter, which is fixed by the resin acids. Manila copal cannot be held safely in solution with borax alone, but with proper pretreatment of the resin it can be made to dissolve by the addition of ammonia. The raw resin as a rule swells up into a doughy mass when treated with ammonia and borax solution. It may, however, be rendered easily soluble by grinding and exposing to air at a temperature just below its softening point for 100 hours. Several months of exposure in the ground condition to air at room temperature has the same effect. Resin acids which have been precipitated from a sodium hydroxide solution of the resin dissolve readily in ammonia and borax solution. These sizes are about as water- and wear-resistant as the shellac size and also fix the basic dyes as well. If Manila resin acids in alkali solutions are treated with 0.5-gram equivalent of sodium hypochlorite per 100 grams of resin, and then precipitated with mineral acid, the product gives a nearly colorless size. The viscosity of these sizes may be decreased by the addition of a little butyl Carbitol which also improves the flexibility of thick coatings of the sizes.

TABLE IV. APPLICATIONS OF MANILA RESIN

	Adhesives and Cements	Amber Substitute	Chewing Gum	Driers	Dry Colors and Pastes	Finishing Compositions	Inks	Lacquers	Linoleum	Oilcloth	Oil Varnishes	Paints	Paper Sizing	Plastics	Polishes	Rubber Compositions	Spirit Varnishes	Textile Sizing	Wax Compositions
Boea		x			x	x	x				x	x				x			
Loba	x			x		x	x	x	x	x		x	x	x	x		x	x	
Soft Manila	x			x		x	x	x	x	x		x	x	x	x		x		x
Pontianak	x		x		x		x	x	x	x	x	x	x		x	x	x	x	x

Chemical Modification of Manila Copal

Raw Manila copal was treated with glycerol according to procedures similar to those used in making rosin ester. In every case the acid number was slowly reduced a small amount, then with continued heating the reaction mixture suddenly formed an infusible spongy mass somewhat like a China wood oil gel, which on cooling was very hard and tough, and insoluble in organic solvents. Addition of dammar or rosin ester to the reaction mixture delayed this gelation somewhat, but at no time during the reaction was the mixture soluble in linseed oil. The fractionation of Manila copal mentioned earlier in the paper was undertaken with the idea of determining if any one constituent of the resin might be responsible for this gelation with glycerol. Three of the fractions obtained gelled with glycerol even more promptly than the original resin. The fourth fraction which is soluble in sodium bicarbonate solution and whose potassium salt is soluble in alcohol, was readily esterified with glycerol to a clear resin soluble in linseed oil; the acid number was reduced from 145 to 8 and the melting point from 205° to 115° C. This fraction, however, constitutes only 4 to 8 per cent of the original resin, and so has little practical value.

Heating soft or half-hard Manila resin with glycerol and maleic anhydride, with a partially reacted glycerol phthalic anhydride mixture, and with glyceryl mono- and diacetates gave similar infusible, insoluble products. Addition of calcium hydroxide or calcium chloride to molten Manila did not prevent it from gelling with glycerol. The course of this reaction can be fairly accurately followed and it might be possible to develop a thermosetting molding resin from it.

A Manila copal that has been run until thoroughly soluble in oil can be esterified with glycerol, but with present methods so much heating develops an excessive color in the product. This esterified Manila copal imparts a high gloss and good water and weather resistance to an oil varnish.

Heating in a glass-lined autoclave at 300° C. for several hours was found to render a soft Manila oil soluble with only about 20 per cent loss and with comparatively little increase in color. In such a treatment, however, contact with even very small amounts of metallic iron gives a strongly blackened product.

Manila copal at present is chiefly used in oil and spirit varnishes and paints, and also finds some applications in the manufacture of lacquers, sizing materials, plastics, japans, driers, linoleum, oilcloth, waterproofing compositions, printing inks, adhesives, and other miscellaneous uses. The applications of the different classes are shown in Table IV.

The large supply of the resin, the known usefulness of some of its properties, and its uniform botanical origin promise the possibility that further research on the subject will be amply repaid. Supplies are sufficient to meet any demand. The collection, grading, and sorting are economic factors in the life of native populations, their consumption in the United States is a factor in the large field of decorative and protective coatings. They are not competitive with American products, and their properties are specific and individual and not shared with other resins.

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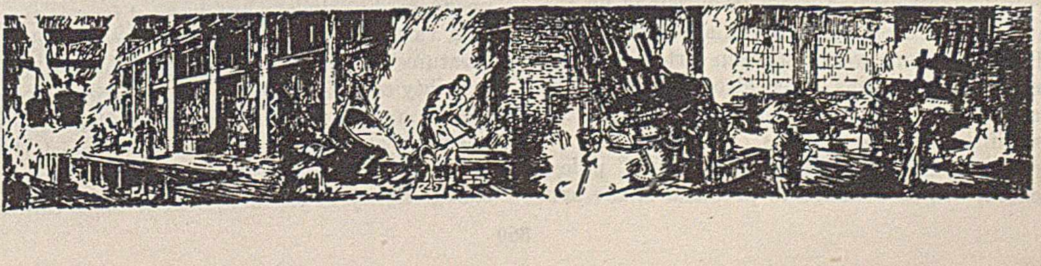

Condensation of Phenols with Formaldehyde

II. Resinification of Phenol Alcohols

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To facilitate a clear understanding of the phenol-formaldehyde condensation process, its component stages are studied separately. The initial simple combination was the subject of the previous article of the series (*5*). The second or resin-forming stage is discussed here. Reaction and product characteristics are described generally and analyzed with reference to the various determining factors, introducing experimental data. Chemical equations are derived for the resinification of the dialcohols of ortho- and paracresol under various conditions. Further condensation is shown to end with the total loss of two molecules of water per molecule of dialcohol in each case.

THE formation of resins by reaction of phenols with formaldehyde may be conveniently studied in two distinct and practically separable steps: (*a*) the formation of phenol alcohols, and (*b*) the condensation of phenol alcohols.

The first of these steps, the foundation of the building-up of the complex resin molecule, was the subject of the previous article of the series (*5*). It consists of attachment of one or more formaldehyde molecules to the benzene ring, to form the grouping -CH_2OH, at positions ortho or para to the phenolic hydroxyl. Reaction may be stopped at this stage by working under alkaline conditions and limiting temperature or time. The phenol alcohols may then be isolated. As a class they are more or less water-soluble, crystallizable substances.

Resinification

These ortho- and paraphenol alcohols are characterized by the property of undergoing condensation readily to form complex products, usually of a resinous nature. This consists in the union of two or more molecules with the elimination of water. In general it is brought about by the agencies of heat and of acidic or basic substances.

This now technically important fact has been known for nearly a century. It was observed when the first known phenol alcohol, saligenin or orthohydroxy benzyl alcohol, was isolated from a natural source by Piria in 1843 (*12*). The process was recognized from the beginning as one of dehydration, involving the elimination of an approximately equimolar quantity of water. The products were called "saliretins." Later as other alcohols of this class were prepared by various synthetic means, the same property was observed.

Reaction between phenols and aldehydes was unknown until many years later. The first known products were of the complex type resulting from the acid condensations of von Baeyer in the seventies (*4*). Twenty years more elapsed before the direct synthesis of phenol alcohols from phenols and an aldehyde (formaldehyde) was discovered by Manasse and Lederer (*8*), establishing the intermediary role of phenol alcohols in the formation of the resinous condensation products.

Curability

Of the amorphous condensation products obtained by the early investigators, either from phenols and aldehydes direct or from phenol alcohols, some were soluble in certain solvents and fusible like the natural resins of recent or current origin; others were partially or wholly insoluble and infusible, resembling the semifossil and fossil resins.

In the present discussion the designation "resin," unless otherwise indicated, will be confined to products of the first class. All such products derived from phenols and formaldehyde are soluble in acetone and practically insoluble in water or petroleum ether. With respect to various other common organic solvents, they vary greatly with the parent phenol.

The classical work of Baekeland, near the beginning of the present century (*1*), opened up the commercialization of this field by a thorough, fundamental investigation. He found that the second class of products, like its natural analogs, results from the further condensation or polymerization of an intermediate product of the first type—i. e., a resin.

This change is brought about or greatly hastened by heating. It has been designated by various names; the word "cure" and its derivatives have been adopted in the present discussion for the sake of simplicity of expression.

Classification of Resins

With respect to this phenomenon, three types of resins were recognized. They will be indicated by the following numbers: type 1, noncurable; type 2, partially or slowly curable; type 3, completely and readily curable.

The resins of the first type had been suggested as shellac substitutes and Baekeland gave them the name "Novolak." They are characterized primarily by permanent solubility and fusibility, by extreme brittleness, usually cracking spontaneously after cooling from a fusion and solidifying as a glass, and by susceptibility to surface oxidation at elevated temperatures. This produces a brown film which is infusible and unaffected by solvents, but does not form in the absence of air. In a vacuum they can withstand prolonged heating at temperatures around 200° C. without losing their solubility and fusibility or suffering much discoloration. Some discolor decidely on aging, however, whereas others do not, depending apparently on the parent phenol from which they are derived.

To the second type belong those resins which, on heating, change slowly to products such as those called "polymerized saliretins" by Baekeland. Such products are softened in various degrees by heat or certain solvents, but are not completely liquefied or dissolved.

The third or completely curable type of resin is represented by the well-known Bakelite A. When heated it passes through an intermediate stage, called Bakelite B, which is physically similar to type 2 products but differs in that further heating rapidly changes it to the completely resistant Bakelite C, which is entirely unaffected by solvents or temperatures short of charring.

Commercially these changes are usually brought about by hot molding under pressure. Bakelite B is sufficiently thermoplastic to be molded in this way. One of the theoretically as well as practically important facts brought out by Baekeland (*2*) is that the change from A to B involves elimination of water whereas the change from B to C is essentially one of polymerization only.

Products in the B stage are slowly gelatinized and disintegrated by acetone, which usually extracts varying quantities of soluble matter; other common resin solvents have comparatively little effect. They may even be dissolved completely by a small quantity of acetone but precipitate on dilution with the same solvent.

Factors Determining Curability

Baekeland, working with phenol, found that the type of resin formed depends primarily on the proportion of formaldehyde to phenol actually entering into the composition. Synthesis, either direct from phenol and formaldehyde or from saligenin and phenol or formaldehyde, and analysis of the resulting products associated the Novolak type of resin with an excess of phenol over the equimolar ratio, and Bakelite with an excess of formaldehyde. Between the two a narrow type 2 zone was found.

Baekeland also found that the proportions entering into the product from a given reaction mixture are, in turn, determined by whether the reaction conditions are acid or alkaline. Alkaline conditions favor the utilization of a larger proportion of formaldehyde and consequently the formation of the Bakelite type of resin. If a Novolak is desired, acid conditions are to be preferred. This applies only to direct resinification.

Baekeland found that metacresol resembles phenol in forming type 3 resins but reacts much faster; ortho- and paracresols are slower, like phenol, but yield products of inferior curability (*3*).

The function of alkaline conditions in favoring the formation of the highly curable type of resin evidently lies solely in bringing about the combination of the phenol with a larger proportion of formaldehyde. When applied to the resinification of phenol alcohols, the method of condensation becomes immaterial, since the phenol and formaldehyde are already combined. The type of resin formed then depends primarily on what phenol alcohol is resinified.

The properties of phenol alcohols, with reference to the curability of their resinification products, depend, in turn, on two factors, the number of formaldehyde molecules combined with one phenol molecule and the parent phenol from which the alcohol is derived. For a given phenol, curability increases with the formaldehyde to phenol ratio, but for the same ratio it varies with different phenols.

Classification of Phenols According to Curability

The writer has numbered the three types of resin, 1, 2, and 3 in the order of increasing curability. The same designation may be applied to the classification of phenols, indicating by the type number the number of free positions on the benzene nucleus ortho or para to the phenolic hydroxyl. If this is done, we find that the type number of each class of phenol is the same as that of the most highly curable resin type which it is capable of producing individually. This is in agreement with the conclusions of other recent investigators (*10*).

Thus, type 1 phenols have only one free active position and form resins only of type 1 or Novolaks in the absence of phenols of the other types—for example, 2,4-xylenol.[1] 2,6-Xylenol and pseudocumenol fail to form resins, owing to condensation of the monoalcohol with a second molecule of the phenol to form the crystalline diphenolmethane (*5*), leaving no active positions free for further condensation.

Type 2 phenols (e. g., ortho- and paracresol, 2,5- and 3,4-xylenols, thymol, carvacrol, and the naphthols) have only two free active positions and form resins of types 1 and 2 but not of type 3, except in conjunction with type 3 phenols.

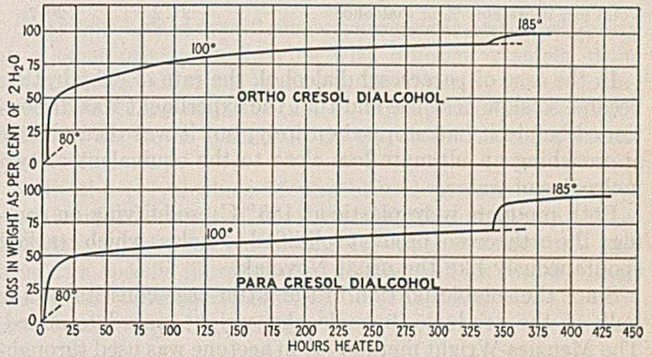

FIGURE 1. EFFECT OF HEAT ON CONDENSATION

Type 3 phenols (e. g., phenol, metacresol, and 3,5-xylenol) have all three active positions free and can form the three types of resins. The dihydric phenol of this class, resorcinol, has attracted attention in recent years in the production of a type 3 product of outstanding properties.

Incident to this classification of phenols, the possibilities of phenol alcohol formation may be mentioned also. Type 1 phenols can form only monoalcohols; type 2 can form mono- and dialcohols; and type 3 can form mono-, di-, and trialcohols. The number of alcohol isomers possible also increases with the type number. With type 2 phenols, we find an approximate coincidence between the type number of the resin obtained and the actual ratio of combination. In the case of type 3 phenols, however, any ratio above equimolar may yield a type 3 resin.

Resinification Process

The contrasting characteristics of the three general methods of phenol alcohol condensation (acid, alkaline, and uncatalyzed) will be described and illustrated specifically by quantitative experiments with the pure dialcohols of ortho- and paracresol, prepared as described in the first article of this series (*5*).

Polyalcohols have received very little attention in the literature, in view of the predominating role which they evidently play as intermediates in the formation of resins of the highly curable type under practical conditions. The behavior of the dialcohols of type 2 phenols is of special theoretical significance, which will appear in a future article.

Resinification by Heat Alone

In the absence of catalysts (acidity or alkalinity), resinification of phenol alcohols occurs on heating, either dry or in aqueous solution, but is comparatively slow. From aqueous solutions the resins precipitate.

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[1] In this discussion, the various xylenols will be distinguished by numbers indicating the positions of the side chains with reference to the phenolic hydroxyl taken as 1.

The rate of condensation, in relation to temperature, was studied quantitatively in the case of the dialcohols of ortho- and paracresol. The very gradual condensation, on merely heating dry samples of these alcohols in an oven, and the sharp increases in the rate, on stepping up the temperature, are shown in Figure 1.

The progress of condensation is indicated by the loss in weight resulting from dehydration. This is expressed in per cent of the equivalent of two molecules of water per molecule of dialcohol, showing the ultimate close approach to this theoretically significant limiting value, which amounts to 21.43 per cent of the weight of original dialcohol. Little, if any, odor of formaldehyde could be detected at any time.

	Dialcohol	
	Orthocresol	Paracresol
Total loss in weight, % of dialcohol	21.2	20.7
% of product soluble in acetone	94.65	11.5

In the case of paracresol dialcohol, the rate of dehydration became so slow near the end that the experiment was discontinued before it had stopped entirely, but it was then plainly approaching an ultimate loss close to the equivalent of two molecules of water.

Both products were plastic at 185° C., solidifying on cooling; the orthocresol product solidified to a glass which cracked spontaneously like the usual Novolak.

Since the soluble portion in the latter case constituted the bulk of the product, its molecular weight was determined. The Menzies-Wright method (*9*) in acetone was used throughout this work. With phenol-formaldehyde products, in general, it was found to give consistent values at widely varying concentrations.

The value obtained in the present instance was 981 = 7.43 units. The term "unit" is used here to represent the yield of resin per mole of phenol alcohol. For cresol dialcohols,

$$1 \text{ unit} = \frac{\text{wt. of product}}{\text{wt. of alcohol}} \times 168$$

corresponding in the present case closely to $C_9H_{12}O_3 - 2H_2O = 168 - 36 = 132$. Thus, the number of units in the molecular weight of the resin expresses the number of phenol alcohol molecules condensing to form the resin molecule. In the present case the results approximate the following equation:

$$7C_9H_{12}O_3 \longrightarrow C_{63}H_{56}O_7 + 14H_2O$$

Characteristics of Alkaline Resinification

While resinification of phenol alcohols, on heating, is definitely accelerated by substances of a basic nature, the situation is peculiar in that the effect appears to be independent of the hydroxide-ion concentration beyond a low minimum. Thus resinification velocity at 100° C. was found to be practically the same in the presence of a quantity of sodium hydroxide equimolar to the phenol as with one-twentieth of that quantity.

Holmes and Megson (*7*) recently compared the resinification velocities of various phenols with formaldehyde in aqueous solution in the presence of varying proportions of various bases at 100° C. Their interesting curves show, in general, a rapid increase in velocity with the proportion of catalyst up to a very low alkalinity, beyond which the reaction velocity remains nearly constant.

The physical behavior with high and low alkalinities, however, is quite different. This is due to the phenolic character of the resin. With high alkalinity, equimolar to the phenol or phenol alcohol (phenolate proportions) or considerably less (sometimes down to about one-fifth that quantity), the resins usually remain in solution until liberated by neutralization. Exceptions will be noted later.

With low alkalinity, on the other hand, the resin precipitates when the reaction has progressed to a certain point—namely, when the solvent effect of the diminishing concentration by phenol alcohols is exceeded by the increasing concentration of resin.

The velocity of resinification under alkaline conditions, in contrast to its indifference to the degree of alkalinity, shows great variation with different phenols, as in certain instances by various investigators (*3*, *7*, *11*).

At room temperature the more slowly resinifying phenol alcohols, such as those of phenol, ortho-, and paracresol, etc., are quite stable in alkaline solution in phenolate proportions, standing for days without appreciable resinification. Those from metacresol and phenols of faster characteristics, on the other hand, undergo considerable resinification under these conditions.

With low alkalinity there appears to be an increase in the resinification rate at room temperature so that some resinification occurs even with the slower phenols.

Phenolate Method

When a solution of a phenol in equimolar quantities of say 10 per cent sodium hydroxide solution and the usual approximately 40 per cent formaldehyde solution (known as formalin) is boiled under reflux, phenol alcohol formation is completed in the first few minutes of heating, with relatively little resin formation. From that point on, if the heating is continued the process is essentially the resinification of phenol alcohols which, under phenolate conditions, is much slower than their formation.

With increasing proportions of formaldehyde up to the limit of combination for the phenol in question, a longer time is required for complete consumption of the aldehyde. Consequently there is more overlapping of the two stages. Loss of formaldehyde by Cannizzaro's reaction (see under section on "Loss of Formaldehyde by Polyalcohols") also occurs to a minor but increasing extent, and any excess over the limit of combination is eventually consumed in that way.

In the writer's investigation of various phenols by this method, the reaction mixtures, after varying resinification or refluxing times, were diluted (usually about ten times) and neutralized (usually by titration with normal hydrochloric acid). In the cases of phenol, ortho-, and metacresol, 2,5-, 2,4-, and 3,5-, xylenols and α-naphthol (with equimolar formaldehyde), which may be termed normally acting phenols in this respect, no precipitation occurs until the addition of acid.

Precipitated Forms

Here an interesting phenomenon is encountered, which is convenient as an index of the progress of resinification. The physical form of the resin precipitating on neutralization varies according to the extent to which resinification has progressed or, for any one phenol, with the reaction time. As between one phenol and another, the time required to produce a given form will vary, but the same series of forms is obtained in every case.

This series comprises a gradual progression from definite liquid to gelatinous solid, the two extremes. Ten definitely distinguishable forms were observed. Of these, the following five may be regarded as the principal forms and the others intermediate: (1) liquid, (2) gummy, plastic, or solid mass, (3) loose, compact, fine, sandy granular, unhydrated, (4) bulky, claylike, soft, hydrated granular, (5) gelatinous.

Forms 4 and 5, pressed solid, still contain about 90 per cent of water and are therefore characterized by great shrinkage on drying, yielding a typically resinous mass.

TABLE I. RESINIFICATION OF ORTHOCRESOL DIALCOHOL

Experiment No.	1	2
Molar scale	1/100	1/20
Reaction mixture:		
Orthocresol dialcohol, grams	1.680	8.400
Water, cc.	4	15
5 *N* NaOH, cc.	2.00	10.00
Hours boiled	1	2
Subsequent dilution, total cc.	75	300
Formaldehyde elimination millimoles:		
Original NaOH	10.0	50.0
Titration (HCl)	7.5	38.5
Loss in alkalinity	2.5	11.5
Loss in HCHO	5.0	23.0
Dehydration, grams:		
Original dialcohol	1.680	8.400
Total resin	1.305	6.641
Total loss in weight	0.375	1.759
HCHO	0.150	0.690
H_2O (by difference)	0.225	1.069
Moles per mole dialcohol:		
HCHO	0.50	0.46
H_2O	1.25	1.19

Gelatinous form 5 is definitely the final form. Continuing the heating of the reaction mixture beyond this point gives no further change in form on precipitation. The only further effect is to cure the resin in the case of highly curable resins. When this occurs, the whole alkaline reaction mixture sets to a jelly, the skeleton of which is insoluble in alkali or other solvents.

These precipitated forms are by no means peculiar to phenol-formaldehyde resins. They are found also, for instance, when acid constituents of natural resins are dissolved in alkali and precipitated with acids. In general, they appear to be determined directly by the relation of the softening or melting point of the resin to the temperature of precipitation.

In the present instance prevailing conditions which may affect the above relation are as follows. As resinification proceeds, we have a diminishing concentration of phenol alcohols accompanied by an increasing concentration of resin. Thus, each successive form represents the precipitation of the resin, in larger yield, in the presence of a lower concentration of phenol alcohols. Furthermore, a certain physical affinity exists between phenol alcohols and resins, as indicated by their miscibility and the solubility of the latter in concentrated aqueous solutions of the former.

In view of these conditions, it is conceivable that, in this instance, the variation in melting point, as indicated by the series of forms precipitated at room temperature, may result from the carrying down of diminishing proportions of phenol alcohols by the resins on precipitation. The final gelatinous form which at moderate dilutions is obtained only when the phenol alcohols are nearly exhausted, thus signifying the practical completion of resinification, would be the form of purely resinous material according to the above view.

This view is further supported by the following facts. If any one of the intermediate forms, after filtration and washing, is redissolved in dilute alkali and reprecipitated by neutralization, it will come out in one of the more advanced forms with a loss in weight, and soluble resinifiable material is found in the filtrate. The higher the dilution, the greater will be the change in form. Starting with any form, the gelatinous form will be attained eventually by repeated precipitations after which there is no further effect.

Velocity Comparison

On the basis of these effects, whatever their mechanism may be, resinification velocities can be indicated and compared. Thus under these conditions in the case of phenol with equimolar formaldehyde, about 8 hours are required to reach the gelatinous form; with the fastest phenols this result is obtained in about 8 minutes. Metacresol is about ten times as fast as phenol.

From the same phenol under alkaline conditions the polyalcohols generally resinify faster than the monoalcohols. Thus in the cases of phenol and metacresol, which can form tri- as well as dialcohols, the mixed alcohols formed from a 2 to 1 formaldehyde-phenol alkaline reaction mixture by allowing it to stand for several days at room temperature, were found to resinify on subsequent heating about four times as fast as those from an equimolar mixture. With type 2 phenols, forming only mono- and dialcohols, the velocity ratios were about 2 or 3 to 1; with 2,4-xylenol, structurally capable of forming only a monoalcohol, there was practically no increase in velocity on doubling the formaldehyde ratio. In the latter case the additional formaldehyde did not take part in the reaction.

Loss of Formaldehyde by Polyalcohols

The dialcohols of type 2 phenols are characterized by giving up a substantial part, varying with different phenols, from half to nearly all of the second molar quantity of formaldehyde on alkaline resinification in boiling aqueous solution. This will be shown specifically in the cresol dialcohol examples.

With the polyalcohols of phenol and metacresol, on the other hand, nearly all of the formaldehyde is retained. The following experiment, involving the phenol trialcohol, will serve as a specific illustration of this as well as various other items which have been mentioned in connection with the subject of resinification generally:

A reaction mixture, made up of 0.39 mole of formalin to 0.1 mole of phenolate solution, was allowed to stand at room temperature for 18 days to provide ample time to complete the formation of the trialcohol. It was then boiled under reflux for a half-hour, resinifying the trialcohol nearly completely as shown by precipitation of the gelatinous form upon titration with normal hydrochloric acid which followed.

In strongly alkaline solution, at boiling temperature, free formaldehyde is rapidly consumed by Cannizzaro's reaction,

$$2HCHO + NaOH \longrightarrow NaOCHO + CH_3OH$$

and therefore can be determined by loss of alkalinity. The results, interpreted on this basis, were as follows.

	Millimoles
Original alkalinity	100.0
Residual alkalinity	46.8
Alkalinity consumed	53.2
Formaldehyde lost	106.4
Formaldehyde total	390.0
Formaldehyde retained	283.6 (94.5% of 3:1)
Moles retained per mole of phenol	2.836

The resin was filtered off, washed, and dried at room temperature over a period of several days, finally in a desiccator. It was then insoluble in acetone and infusible, showing the high curing tendency of the trialcohol resin.

Alkaline Resinification of Orthocresol Dialcohol (Phenolate Method)

Reaction mixtures were prepared by dissolving the dialcohol in water and adding its equivalent of 5 *N* sodium hydroxide solution. Resinification was effected by boiling under reflux. The solutions were then diluted with water and titrated with normal hydrochloric acid.

In both experiments (Table I) the resin precipitated in gelatinous form on titration, indicating nearly complete resinification. The little remaining dialcohol was then resinified by strong acidification with hydrochloric acid. In experiment 1 this was done before removing the main resin but had no visible effect upon it; complete resinification occurred after 2 days at room temperature. In experiment 2 the main resin was removed first and the completion of resinification was hastened by boiling down the acidified filtrate and washings. The main resin was 97.8 per cent of the total.

The resins were filtered off on fritted glass filters, washed thoroughly with water, and dried to constant weight at room temperature, finally in a desiccator, requiring several days.

The precipitation of the final gelatinous form in the first experiment indicates that the conversion of dialcohol to resin was near completion at the end of the first hour. This was anticipated from previous experience. The second experiment shows no further dehydration or deformalization of the resin on further exposure to the same conditions. Thus there is no evidence of progressive condensation of the same type under these conditions beyond the state reached in the first hour.

The product of experiment 1 was used for the determination of ultimate dehydration under curing conditions. The standard procedure, adopted throughout this series of cresol dialcohol experiments, consisted of heating in an oven at about 180° C. until no further loss in weight occurred. Minimum weight was usually reached in the first hour, followed by a slight increase due probably to surface oxidation. The minimum weight was corrected accordingly.

The resins fused and frothed or puffed up without noticeable odor and eventually reached a semisolid rubbery or plastic state while hot, hardening on cooling. All were completely soluble in acetone before subjection to the curing temperature. The percentage of the final product insoluble in acetone is given in each case as a measure of cure, further illustrating type 2 curability.

In the present case the total time at 180° C. was 2 hours, and 93.2 per cent of the resulting product was insoluble in acetone. The dehydration results were as follows.

	Grams	% of Dialcohol
Original dialcohol	1.680	...
Corrected minimum weight	1.259	...
Total loss in weight	0.421	...
HCHO	0.150	...
H_2O	0.271	16.13
H_2O lost in HCHO	0.090	5.36
Total H_2O lost	0.361	21.49
Theoretical for $2H_2O$	...	21.43

Molecular weight determinations on the main resin from experiment 2 at widely different concentrations completed the data for formulation of the resinification reaction, as follows:

Molecular weight	1450, 1454
Unit weight = 6.641 × 20	132.8
Units per molecule = 1452/132.8	10.94
Moles liberated per 10.94 moles dialcohol:	
HCHO = 0.46 × 10.94	5.03
H_2O = 1.19 × 10.94	13.02

$$11C_9H_{12}O_3 \rightarrow C_{94}H_{96}O_{15} + 5HCHO + 13H_2O$$

Alkaline Resinification of Paracresol Dialcohol (Phenolate Method)

Paracresol is one of the most slowly resinifying phenols under alkaline conditions; it is second only to phenol in this respect among the phenols investigated. Furthermore, its resins even precipitate from strongly alkaline solutions when resinification reaches a certain point.

Therefore in the present instance no attempt was made to carry the resinification to completion. Instead the progress of condensation, after different reaction times, was compared by means of two parallel experiments, boiling 1 and 4 hours, respectively.

The reaction mixtures were the same in both cases: dialcohol, 1.68 grams; 5*N* sodium hydroxide, 2.00 cc.; water, 5 cc.

The procedure was the same as with orthocresol dialcohol, except in the following respects. After resinification, the solution was diluted with hot water and kept hot during titration and filtration to prevent the unresinified dialcohol from crystallizing.

In experiment 1 (Table II) the resin precipitated in plastic form on titration. It was filtered by decantation and thoroughly washed by repeated boiling with water to free it of dialcohol. This converted it eventually into a friable solid which was ground up for further washing.

TABLE II. RESINIFICATION OF PARACRESOL DIALCOHOL

Experiment No.	1	2
Hours boiled	1	4
Original NaOH, millimoles	10.0	10.0
Titration (HCl)	9.0	8.0
Loss in alkalinity	1.0	2.0
HCHO	2.0	4.0
Residual dialcohol, grams:		
Recovered	0.663	....
Determined	0.271	0.244
Total	0.934	0.244
Resin	0.582	1.128
Total recovery	1.516	1.372
Loss in weight (resinification)	0.164	0.308
HCHO liberated, grams	0.060	0.120
H_2O liberated, grams	0.104	0.188
Further dehydration at 185° C.	0.026	0.033
Dialcohol resinified, grams	0.746	1.436
% of original	44.4	85.5
Moles per mole of dialcohol consumed:		
HCHO liberated (resinification)	0.450	0.468
H_2O liberated (resinification)	1.302	1.221
H_2O liberated at 185° C.	0.327	0.214
Total H_2O + CH_2O liberated	2.079	1.903
% cure (1.5 hr. at 185° C.)	15.7	40.3

Copious crystallization of the dialcohol occurred from the filtrate on cooling. The bulk of it was recovered in this form after concentrating by evaporation, and the remainder was determined as resin by acidification, etc., as already described. The resin so obtained was dehydrated to constant weight at about 180° C., and the equivalent weight of dialcohol was calculated by assuming the elimination of two molecules of water.

In experiment 2 some of the resin precipitated in granular form in the later part of the refluxing period. The further procedure was like experiment 1 except that, because of the smaller quantity of residual dialcohol, it was all determined by the acid resinification method.

The original (alkaline condensation) resins from both experiments were used for determination of ultimate dehydration, as already described.

As in the orthocresol dialcohol experiments, these results show no further dehydration, etc., of the resin on continued boiling in alkaline solution, in this case even during the progress of resinification. Thus the progressive condensation which would be expected in the building of the complex resin molecule is evidently a much more rapid process, up to the state that is stable under the resinification conditions, than the initial condensation of the phenol alcohol molecules starting the formation of the resin molecule.

The product which is stable under these conditions undergoes further dehydration on dry heating at 185° C. Thus, we see two distinct stages or kinds of condensation which may be designated, respectively, as resinification and curing (according to the limitations of the resin type). Some indication of this can be seen also in Figure 1. Again we find the ultimate dehydration (including formaldehyde) approximating two molecules of water per molecule of dialcohol or one molecule of water per molecule of original formaldehyde.

Unfortunately time was not available for repetition of these experiments on a larger scale for molecular weight determination and formulation, to see whether simple polymerization (i. e., without dehydration) occurred after the resin formation under the resinification conditions. This is suggested as a subject for theoretical investigation.

Characteristics of Acid Resinification

Under acid conditions, in contrast to alkaline, the velocity of resinification is a direct function of the hydrogen-ion concentration, and no such variation of velocity, with reference to different phenols or between mono- and polyalcohols, is found as under alkaline conditions. In fact, the monoalcohols appear to resinify somewhat more rapidly than the polyalcohols.

The reaction starts at room temperature with sufficient acidification and is highly exothermic, causing a rise in temperature with corresponding cumulative acceleration, varying with the degree of acidification, concentration, thermal insulation conditions, scale, etc. At sufficiently high concentrations the boiling point may be reached with more or less violent effects, but the reaction is easily controlled by dilution.

The variation of velocity with hydrogen-ion concentration is very apparent when either different quantities of a strong acid or equivalent quantities of strong and weak acids are compared. Thus the addition of a moderate quantity of hydrochloric acid to a dilute solution of a phenol alcohol at room temperature produces almost immediate turbidity, followed by increasing precipitation; with acetic acid the solution may remain clear for weeks. Acids of intermediate strengths give intermediate results.

The precipitation starts as a turbidity, coagulating on stirring or as the reaction progresses to either a white, pink, or pale yellowish, flaky solid or a liquid, according to conditions. The liquid solidifies on standing according to temperature and curability, at a rate varying with the intensity of the resinification reaction as determined by conditions.

When polyalcohols in aqueous solution are resinified at elevated temperatures under neutral or acid conditions, formaldehyde is usually liberated, but this does not occur noticeably when the resinification is effected at ordinary room temperatures by acidification.

Acid Resinification and Curability

Acid condensation is not usually associated with the production of curable resins, for reasons which have been indicated under "Factors Determining Curability." If, however, we first allow the phenol and formaldehyde to combine in the necessary proportions by the formation of phenol alcohols in alkaline solution, and then resinify by acidification (*6*), we obtain the same curability types as are obtained by alkaline condensation.

Thus resins are obtained from phenol which are not only highly curable but cure as far as the B state on merely standing at room temperature for periods of time varying widely with the degrees of acidification.

The resulting B product is easily pulverized and washed (to remove acid, etc.) and converted to a C product of high quality in 5 minutes or less by molding under pressure at temperatures in the neighborhood of 180° C. without the excessive thermofluidity and vaporization associated with the A state. Since the curing does not go further than the B state, at room temperature, this is a convenient means of producing a material of the B type for molding. It is difficult to obtain a similar effect by heat precuring, in which the changes from A to B and from B to C go on simultaneously.

A and B products obtained as above from the acid condensation of the alcohols of phenol gradually develop a pink to coral surface discoloration which is associated with a brown discoloration in the C state. If the material is molded before this discoloration has developed or after it is scraped off, a creamy white C product is obtained which gradually turns brown on aging.

This particular discoloration phenomenon appears to be confined to acid condensation products of the highly curable type. It was found to a less extent with metacresol but not with any of the other phenols investigated nor in Novolak from phenol or metacresol. It appears also to be a function of the formaldehyde-phenol ratio, reaching its maximum with the equimolar ratio, whether from a monoalcohol or a mixture of dialcohol and phenol.

The solution of phenol alcohols obtained as above from an equimolar or greater formaldehyde ratio less than trimolar (the limit of combination) contains a mixture of mono- and polyalcohols and free phenol (*5*). When the monoalcohols and phenol are removed from the polyalcohols by extraction of the former with ether and the latter are then resinified separately by acidification, this discoloration phenomenon disappears.

If the monoalcohols are freed of the phenol extracted with them and then resinified by acidification, products are obtained which exhibit both the cold-curing and discoloration phenomena in question. If the phenol is not removed or if phenol is added to the purified monoalcohols, the resinification products are Novolaks which do not turn pink. A mixture of a dialcohol and an approximately equimolar quantity of phenol yields a cold-curing resin which turns an intense pink.

Acid Resinification of Type 2 Dialcohols

The dialcohols were dissolved in water and resinified by strong acidification with hydrochloric acid. In the case of paracresol, hot water was used for solution because of the sparing solubility of the dialcohol when cold. Probably for this reason there was a slight odor of formaldehyde on acidification. This did not occur with the cold orthocresol dialcohol solution.

The orthocresol resin (Table III) precipitated gradually in white granular form. The paracresol resin precipitated immediately and soon settled out as a yellow liquid solidifying on cooling. The mixtures were allowed to stand for several days at room temperature and were then filtered off, washed, and dried as usual. The little remaining dialcohol was resinified by evaporation of the filtrates.

Molecular weights and ultimate dehydration were determined on different samples of the main resins.

Table III. Resinification of Type 2 Dialcohols

Cresol dialcohol	Ortho	Para
Moles taken	1/50	1/20
Grams taken	3.360	8.400
Days standing	3	5
Yields:		
Main resin	2.835	7.260
Filtrate resin	0.010	0.067
Total resin	2.845	7.327
Loss in weight (dehydration)	0.515	1.073[a]
Formulation:		
Unit weight	142.25	146.54
Molecular weight	967	1002, 1002
Units in resin molecule	6.8	7.0
Moles H_2O liberated per mole resin	9.7	7.1[a]
Equations:		
Ortho: $7C_9H_{12}O_3 \rightarrow C_{63}H_{64}O_{11} + 10H_2O$		
Para: $7C_9H_{12}O_3 \rightarrow C_{63}H_{70}O_{14} + 7H_2O$		
Ultimate dehydration:		
Temperature, ° C.	178	185
Time, hours	3	2.25
% of original dialcohol:		
Further dehydration	6.14	8.90
Previous	15.33	12.77[a]
Total	21.47	21.67[a]
Theoretical for $2H_2O$	21.43	
Cure (insoluble in acetone)		82.7%

[a] Includes a little formaldehyde.

Summary

The present article is restricted to the empirical facts relating to resinification considered alone—i. e., as applied to the products of the preliminary combination in which the formaldehyde-phenol ratio is already fixed. Consideration of direct resinification of phenol-formaldehyde mixtures, where the ratio of combination is determined by the resinification conditions, and the speculative question of molecular structure is reserved for later articles.

Much of the material presented is stated collectively in the form of generalizations covering numerous individual observations. The principal items are the following:

Resinification is promoted slowly by heat alone and accelerated by alkalinity or acidity, giving rise to the two contrasting general methods of condensation. The characteristics of each are described.

Under alkaline conditions, the velocity of resinification is largely independent of the concentration of catalyst (hydroxyl ion) but varies greatly with the parent phenol and ratio of combination; under acid conditions the reverse is the case.

Three types of resins are obtained—noncurable, semicurable, and highly curable. When the ratio of combination is already fixed, the degree of curability is independent of the method of condensation and is determined by the ratio of combination and the number of free ortho and para positions in the molecule of the parent phenol.

The more elaborate experiments, made possible by the availability of the pure dialcohols of ortho- and paracresol, are described specifically in detail. In addition to illustrating various items of the general discussion, these furnish special data, such as the empirical formulations of resinification reactions and resin molecules, and the extent of ultimate dehydration, in every instance closely approximating two molecules of water per molecule of dialcohol, or one per molecule of formaldehyde originally combined.

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Studies in the Vulcanization of Rubber

VII. Unsaturation of Rubber Vulcanized with Nitro Compounds and Benzoyl Peroxide[1]

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RUBBER is primarily an unsaturated hydrocarbon. Sulfur adds to its double bonds during vulcanization to form soft and hard vulcanizates. In the formation of soft vulcanized rubber, unsaturation is reduced several per cent by the chemical addition of sulfur. Spence and Scott (*10*) showed that the proportion of combined sulfur corresponds exactly to the decrease in unsaturation, and therefore that sulfur combination consists entirely of addition to the double bonds of rubber.

The studies of one of the authors (*1*) on the vulcanization of rubber with nitro compounds indicate that these substances or their decomposition products combine with rubber. Van Rossem (*8*) also showed that vulcanization with benzoyl peroxide is accompanied by a decrease in extractable material, indicating that either the reagent or its decomposition products combine chemically with the rubber. The natural expectation would be that addition to the double bonds occurs and that the unsaturation decreases correspondingly.

Van Rossem's proposed mechanism for the vulcanization with benzoyl peroxide would involve no change in unsaturation. Fisher and Gray (*2*) applied Kemp's method (*4*) in determining the iodine numbers of a single vulcanizate of each of four compounds. The vulcanizing agents involved were *m*-dinitrobenzene, trinitrotoluene, and benzoyl peroxide. Their unsaturation values agreed closely with calculated values for the unvulcanized compounds. They concluded from their results that "Ordinary vulcanization is an unknown or undetermined type of change in the hydrocarbon involving no change in the unsaturation and that chemical union of sulfur is a secondary reaction." If true, this evidence is a serious blow to the chemical theory of vulcanization which postulates that a chemical reaction is essential for the process. The present paper offers evidence that the vulcanization of rubber with these reagents does involve change in its unsaturation.

Experimental Procedure

There are a number of methods of determining the unsaturation of rubber. The early ones involved reacting it with an excess of bromine and titrating the excess reagent with potassium iodide and thiosulfate after a definite time period. Various authors have recommended differing conditions (*6, 9, 11*). The reaction is complicated, however, by the substitution of some of the hydrogen of the rubber by bromine. Lewis and McAdams (*7*) suggested that the hydrogen bromide formed by the substitution be titrated with potassium iodate and sodium thiosulfate. If this correction is applied to the total bromine absorption, values are obtained that are approximately correct, but conditions have to be controlled carefully if precise results are to be obtained. Kemp suggested the reaction of rubber with iodine chloride at 0°. Under these conditions satisfactory results are obtained, and this is probably the best method yet offered.

Nitro compounds react with rubber so weakly that only

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[1] Previous papers in this series appeared in 1930 (pages 737, 740, 744, 748), 1932 (page 549), and in 1934 (page 1283).

soft vulcanized rubber can be formed. Ebonite cannot be produced with this reagent. It was thought at first that, since iodine chloride is sufficiently active to react completely with rubber at 0° C., the reagent might displace any combined nitro compound to give the impression that no combination had occurred. This might explain the anomalous results of Fisher and Gray. The first part of this paper contains work with iodine bromide, a reagent less vigorous than iodine chloride, with the idea of overcoming the above difficulty. The second part contains work with iodine chloride. Substantially the same results were obtained in both cases.

Iodine Bromide

Iodine is too inactive a reagent to add completely and saturate all the double bonds in rubber. Iodine bromide is intermediate in activity between iodine and iodine chloride. Gorgas (*3*) claimed that iodine bromide makes a very satisfactory agent for determining unsaturation. The regular Hanus reagent consists of a solution of iodine bromide in glacial acetic acid. Gorgas found that this gave low values, perhaps because of the coagulating effect of the acid on the rubber solution. With carbon tetrachloride as the solvent, better results were obtained, but a rapid increase occurred in unsaturation values with reaction time. Kemp found that at 0° C. the rate of addition of this reagent was too slow to make its use feasible. At room temperatures following Gorgas' procedure, Kemp and Mueller (*5*) obtained low values, but by using a larger excess of reagent and a longer reaction time they obtained better results. The results were sufficiently variable, however, so that they believed the method could not be relied upon for a high degree of accuracy.

Previous work in this field indicated that the vulcanization of rubber with dinitrobenzene and benzoyl peroxide is not accompanied by a decrease in unsaturation. This implies that a chemical reaction is unnecessary for the formation of vulcanized rubber and deals a serious blow to the chemical theory of vulcanization. Other evidence indicates that nitro compounds and benzoyl peroxide do react with rubber during vulcanization.

The unsaturation of such vulcanizates has been studied by means of iodine chloride and iodine bromide. The results indicate that vulcanization with these agents is accompanied by a decrease in unsaturation and that it is proportional to the combined material. Calculations of the number of double bonds saturated per molecule of reagent give results that are not readily explained.

Gorgas used 0.2 *N* solutions but in the present work reagents of half this strength were used. The carbon tetrachloride was purified by treating with alcoholic sodium hydroxide, washing with water, drying with C. P. calcium chloride, and distilling fractionally. Exactly 0.1 *N* solutions of iodine and bromine in this solvent were then prepared and standardized with aqueous sodium thiosulfate. Equal volumes were mixed to form the iodine bromide solution. This was standardized against sublimed arsenious oxide.

The determination of the unsaturation of unvulcanized rubber was carried out by refluxing the sample for 2 hours in C. P. carbon tetrachloride. Vulcanized samples were not dissolved sufficiently by this treatment. *p*-Dichlorobenzene was used as the solvent since it disintegrates most vulcanized samples at its boiling point (172° C.) and does not react with the reagent. Since it is a solid at room temperature, carbon tetrachloride must be added after cooling to maintain a liquid solution.

A study of the suitability of the method involved an investigation with a substance of known behavior. Samples of smoked sheet of known weight were swelled in the solvent in covered Erlenmeyer flasks. A measured amount of the iodine bromide solution was added, and the mixture was allowed to stand in darkness for a definite period at room temperature (22° to 25° C.), 50 cc. of 10 per cent aqueous potassium iodide were added, and the excess halogen was titrated with aqueous sodium thiosulfate. As the end point approached, starch solution was added and small amounts of acetic acid were used to destroy the emulsion. With practice, reproducible results can be easily obtained.

A series of determinations was made on 0.1-gram samples from a single batch of smoked sheet with varying times of reaction and with different excesses of reagent. Each sample was extracted with acetone after weighing, and the acetone was removed in a vacuum desiccator before solution in the solvent. It is generally accepted that rubber hydrocarbon is composed of C_5H_8 units, each containing one double bond. The theoretical iodine number of this hydrocarbon is then 372.8. Since the hydrocarbon content of rubber is 93 to 96 per cent, the iodine number of raw rubber should be 347 to 358:

Reaction Time	Excess IBr	Iodine No.	Reaction Time	Excess IBr	Iodine No.
Min.	%		*Min.*	%	
15	39	265	60	110	348
	64	290		135	345
				138	351
30	65	310		188	354
	308	359		210	356
				356	366
60	56	312			
	92	340	120	250	378
			180	241	388

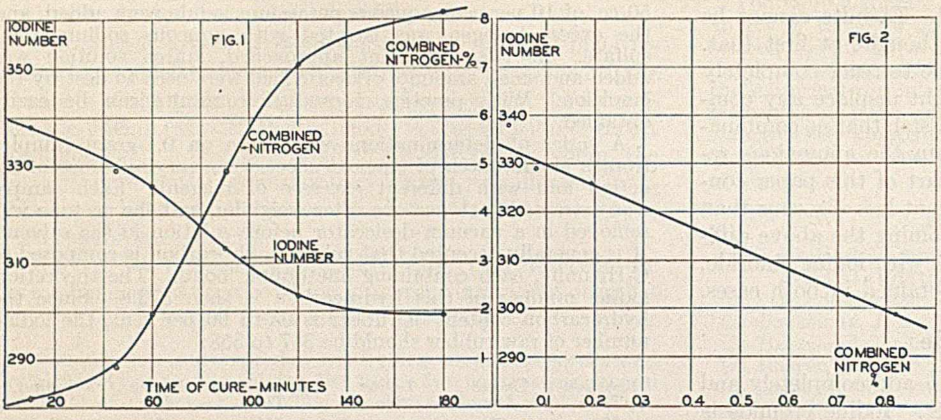
From these results it may be concluded that, if less than 100 per cent excess reagent is used and if the reaction time is less than 60 minutes, the action is incomplete. Increasing the excess beyond 200 per cent and the time beyond 60 minutes gives values which are too high.

Compound A (smoked sheets 100, litharge 5, and *m*-dinitrobenzene 10) was vulcanized for varying periods of time at 132° C. (270° F.). Unsaturation values were determined as above, using 200 per cent excess reagent, a 60-minute reaction time, and *p*-dichlorobenzene as the solvent. Experiments showed that neither *m*-dinitrobenzene nor litharge is affected by iodine bromide.

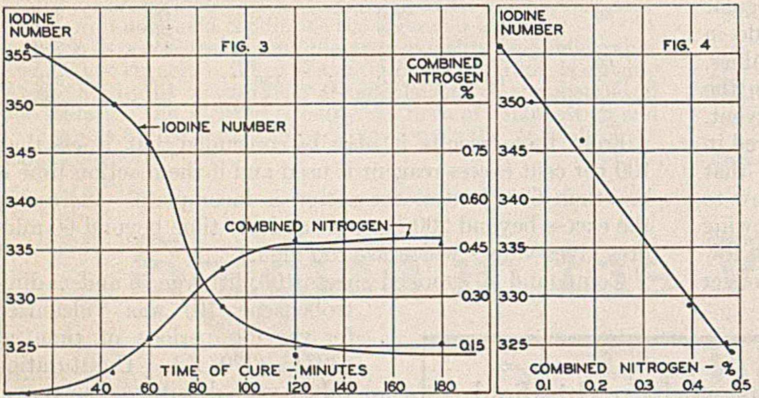
In order to compare the change in unsaturation with the chemical effect of the reaction with dinitrobenzene, combined nitrogen values were determined on other samples of the same cures after similar acetone extraction. The nitrogen values were corrected for the blank on the raw unvulcanized rubber after acetone extraction and calculated on the base of rubber in the compound:

270° F. Vulcanization	Iodine No.	Combined N
Min.		%
10	338	0.027
45	329	0.082
60	326	0.197
90	313	0.483
120	306	0.720
180	299	0.822

There seems to be a progressive decrease in unsaturation during vulcanization as determined by this method, and this is accompanied by an increase in combined nitrogen. In Figure 1 both sets of values are plotted against the time of vulcanization. If the theory is correct that the two



FIGURES 1 AND 2. COMPOUND A, *m*-DINITROBENZENE



FIGURES 3 AND 4. COMPOUND B, *m*-DINITROBENZENE

effects are proportional, plotting the iodine number against combined nitrogen should give a straight line. These data are delineated in Figure 2 and produce a straight line within the limits of the experimental error.

Iodine Chloride

Iodine chloride was used in following the unsaturation for several compounds. The composition of these compounds is as follows:

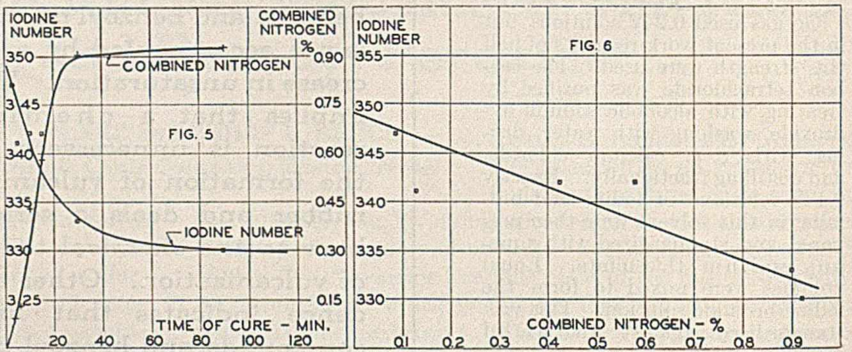
	B	C	D	E	F
Smoked sheet	100	100	100	100	100
Litharge	5	5	...	...	...
m-Dinitrobenzene	6	...	...	...	...
sym-Trinitrobenzene	...	6	...	...	...
Benzoyl peroxide	...	...	7	11.1	25

These vulcanizates had tensile strengths of 1000 to 2000 pounds per square inch.

In Kemp's procedure for determining the unsaturation with iodine chloride, tetrachloroethane was used as the solvent for disintegration of the samples. A number of blanks were run on this material, heating them exactly as Kemp prescribed. No matter how carefully the tetrachloroethane was purified, enough decomposition was found at its boiling point to introduce serious errors. Tests on C. P. *p*-dichlorobenzene indicated that this material is completely stable at its boiling point. Tests lasting up to 5 hours indicated that the time of boiling of this reagent with rubber has no effect on the unsaturation determination. Therefore, this reagent was substituted for the tetrachloroethane in the present determinations.

One-tenth-gram samples of the vulcanizates were acetone-extracted and added to 50 grams of *p*-dichlorobenzene, and the mixture was boiled until disintegration was complete. After cooling, 50 cc. of C. P. carbon disulfide were added to assure a liquid solution. The mixture in watch-glass-covered flasks was chilled in ice for 30 minutes. One hundred per cent excess of 0.2 *N* iodine chloride in glacial acetic acid was added with stirring. After a 2-hour reaction period at 0° C., 25 cc. of 15 per cent aqueous potassium iodide and 50 cc. of water were added. The excess halogen was determined with 0.1 *N* aqueous sodium thiosulfate. Emulsions were broken with small amounts of ethyl alcohol. Tests indicated that ethyl alcohol had no effect on the determination. Blanks were run on the reagents in the usual manner. The iodine numbers on duplicate samples normally checked to within less than four units. It was found that the acetone remaining in the rubber sample after extraction was completely volatilized in the disintegration so that the acetone did not need to be removed previously. It was also determined that during the reaction period with iodine chloride no vapors of halogen were lost from the covered flasks.

The nitrogen content of the various cures of compounds B and C was determined by a micro-Kjeldahl method on acetone-extracted samples. The amount of acetone-soluble material was determined on compounds D, E, and F, and from these values the amount of products from the benzoyl peroxide which combined with the rubber was calculated. In the following



FIGURES 5 AND 6. COMPOUND C, *sym*-TRINITROBENZENE

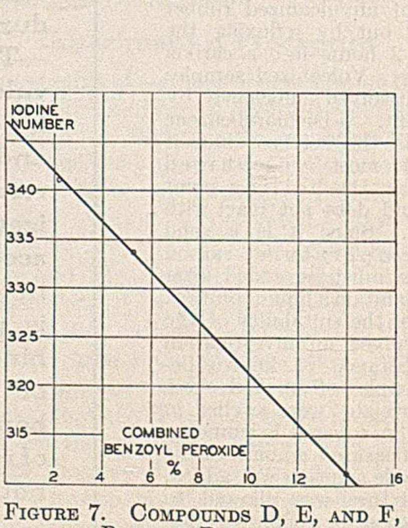


FIGURE 7. COMPOUNDS D, E, AND F, BENZOYL PEROXIDE

table these values are listed as combined benzoyl peroxide. All analytical data are calculated on the basis of the raw rubber in the compound.

Compound B			Compound C		
270° F. vulcanization	Combined N	Iodine No.	245° F. vulcanization	Combined N	Iodine No.
Min.	%		*Min.*	%	
10	0.000	356	3	0.089	347
45	0.070	350	5	0.129	341
60	0.174	346	10	0.427	342
90	0.395	329	15	0.581	342
120	0.480	324	30	0.900	333
180	0.466	325	90	0.921	330

Benzoyl Peroxide Compounds Vulcanized 20 Min. at 275° F.

Compound	Benzoyl Peroxide Total	Benzoyl Peroxide Combined	Iodine No.
D	7.0	2.31	341
E	11.1	5.31	333
F	25.0	13.97	311

These data are plotted in Figures 3 to 7. The procedure used in the present work is somewhat different from that of Fisher and Gray. They swelled the vulcanizates in carbon disulfide for 24 hours at room temperature and then allowed the iodine chloride to react for 24 hours at 0° C. in the dark, or twelve times as long as the above experiment.

The effect of this long reaction period was examined by allowing iodine chloride to act on vulcanizates of compound B for 24 hours at 0° C. The iodine numbers showed that the long time of treatment changes the absolute values somewhat, but the slope of the line relating combined nitrogen and unsaturation was almost exactly the same as that in Figure 4. An unusually long time of acetone extraction had no effect on the iodine number or the per cent combined nitrogen.

The possibility that the decrease in unsaturation might be attributed to a reaction of the double bonds of the rubber with one another or, in the case of compounds B and C, a reaction of the double bonds with litharge was investigated. The following table contains the results of these experiments:

Compound Rubber	Compound PbO	270° F. Heat Treatment	Iodine No. (Not Acetone-Extd.)
%	%	*Min.*	
100	0	None	352
100	0	120	350
95	5	None	350
95	5	120	351

An increase in unextractable nitrogen during the vulcanization with nitro compounds might be explained as being due to a reaction of the nitro compound and the nonrubber constituents, or a reaction between the nitro compound and the litharge to form a material insoluble in acetone. These possibilities cannot be rejected definitely. It was shown, however, that on heating a mixture of litharge and *m*-dinitrobenzene no acetone-insoluble nitrogenous material was formed.

Discussion

The data show an approximately linear relation between the per cent combined vulcanizing agent and the unsaturation of the rubber in the compound. These results obtained through the use of two independent analytical methods are at variance with those of Fisher and Gray. The present experiments seem to indicate that during the vulcanization of rubber with polynitro compounds or benzoyl peroxide, the reagents or products from them add chemically to the double bonds of the rubber hydrocarbon. There is no evidence in these experiments nor is there any in the case of sulfur vulcanization to indicate whether the vulcanizing agents add to the double bonds in a single molecule or bridge between double bonds in adjacent molecules, thereby increasing molecular size.

It is possible that, contrary to the experiments with sulfur, a single molecule of the present vulcanizing agents adds to more than one double bond. The double bonds saturated per molecule of vulcanizing agent may be calculated by the following formula:

$$\frac{100\,(I_0 - I_t)M}{68\,(I_0)W} = \text{double bonds saturated per molecule of nitro compound or benzoyl peroxide, or atom of sulfur or selenium}$$

where I_0 and I_t = iodine numbers at vulcanization times of 0 and t, respectively

M = molecular weight of nitro compound or benzoyl peroxide, or atomic weight of sulfur or selenium

W = weight of vulcanizing agent combined with 100 grams of rubber

The number of double bonds saturated per molecule of vulcanizing agent was calculated as follows:

Vulcanizing Agent	Unsaturation Reagent	Double Bonds Satd. per Mol. of Reagent
m-Dinitrobenzene	IBr	5.4
m-Dinitrobenzene	ICl	7.5
sym-Trinitrobenzene	ICl	3.2
Benzoyl peroxide	ICl	2.6

Preliminary data indicate that an atom of selenium saturates about 6 double bonds.

A molecule of *m*-dinitrobenzene appears to saturate a fairly large number of double bonds. It was perhaps to be expected that a molecule of trinitrobenzene would saturate more double bonds than the dinitro compound, but this does not seem to be true. A molecule of benzoyl peroxide also saturates more than one double bond. It is possible that these results may be explained by the theory that vulcanizing agents produce some sort of cyclization. The quantitative implications of the data need more study.

The qualitative implications of these data are important, indicating that we have yet to find a vulcanization in which a chemical reaction does not take place and thereby give more support to the chemical theory of vulcanization.

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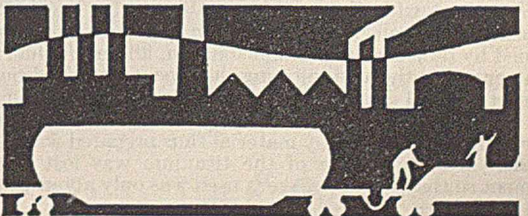

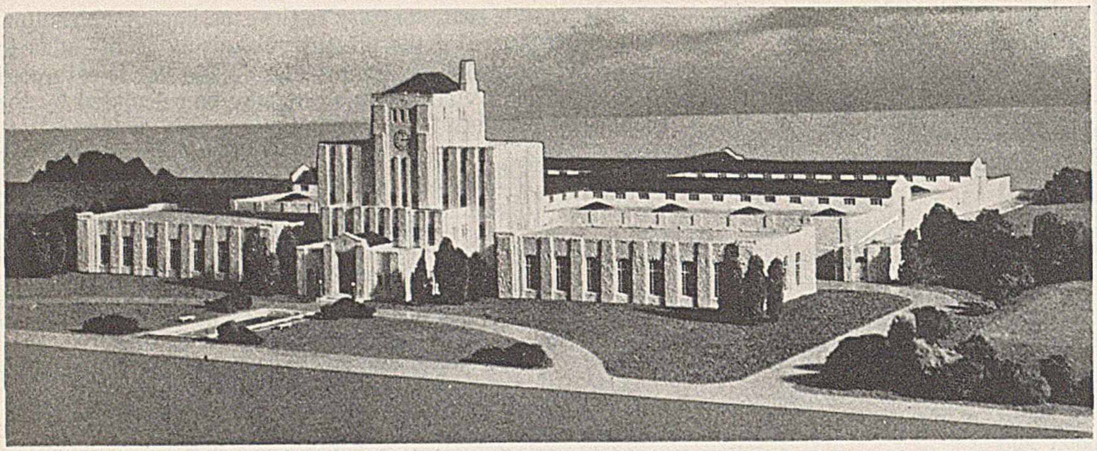

New Milwaukee Filter Plant with a Capacity of 200 Million Gallons per Day

Courtesy, Alvord, Burdick & Howson

Titanium Salts in Water Purification

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THE possibility of using titanium compounds as coagulants in water treatment was suggested by the inadequate removal of fluorides from drinking waters with filter alum (*3*, *4*). Some removal was obtained with this coagulant, and it appeared that better fluoride removal might be obtained by use of a salt having a quadrivalent cation instead of the trivalent aluminum ion (*5*). Titanium salt appeared feasible from the standpoint of cost, and an investigation of these compounds was made (*2*).

Two types of reagent were studied, one a mixture of iron and titanium sulfates prepared from ilmenite and the other pure titanium sulfate. The mixture was studied because such a reagent could be more cheaply obtained from ilmenite than a pure titanium salt.

Preparation of Reagent

The ilmenite extract was prepared from a Norwegian sample. Twenty-five grams of the ore, ground to pass a 200-mesh sieve, were mixed in a beaker with 30 cc. of concentrated sulfuric acid and heated with occasional stirring until the mixture became stiff (*8*). Three 5-cc. portions of sulfuric acid were added alternately with two portions (3 and 10 cc., respectively) of concentrated nitric acid, heating after each addition and driving off the nitric acid as nitrogen dioxide. The mass was cooled, 50 cc. of water were added, and the solution was stirred. Chlorine was allowed to pass through the solution for 12 hours to oxidize the ferrous iron present. In one case this treatment was not sufficient and it was necessary to add barium persulfate to complete the oxidation, removing the precipitated barium sulfate by centrifuging.

The considerable excess of acid in these reagents caused the waters treated with them to have abnormally low pH values. To remedy this fault, a mixture of iron and titanium sulfates was obtained by diluting the original solution, adding sodium carbonate to neutralize the acid, filtering the precipitated hydrous oxides with suction, and dissolving them in the minimum amount of sulfuric acid. This solution was evaporated to dryness at room temperature, and the glassy material thus prepared was powdered and analyzed (*7*). Some of the titanium was lost during the treatment so that the dry reagent used was only about 20 per cent titanium sulfate.

Pure titanium sulfate was also tried as a coagulant. Ten grams of hydrated titanium dioxide (Eimer and Amend c. p. grade) were dissolved with heating in 10 cc. of concentrated sulfuric acid to which about 20 cc. of water had been added. A small amount of colored matter, insoluble in the acid, was removed by filtration; and the solution was evaporated to a small volume and placed in a refrigerator for several days. A white solid precipitated and was freed from the supernatant liquid by filtration. The product thus obtained dissolved in water (but hydrolyzed in dilute solution) fairly readily. This salt appeared from an analysis of its constituents to be largely $Ti(SO_4)_2 \cdot xH_2O$ (*9*).

Coagulation Experiments with Fluorides

In all experiments the water samples to be treated were placed in gallon battery jars. If in solution, the coagulant was fed from a buret; if dry, it was fed in small portions with a spatula. The waters were stirred mechanically by wooden paddles which revolved about one-third of the way down in the liquid at a speed of 45 to 60 r. p. m. Tap water with a residue of 380 p. p. m., alkalinity of 375 p. p. m., and hardness of 296 p. p. m., was used in all experiments unless otherwise stated.

The first step in studying the behavior of the ilmenite extracts as water coagulants was to test their ability to form a floc over the pH range in which coagulants might find use. Using a reagent containing about equal parts of iron and titanium sulfates in solution with excess sulfuric acid, good flocs were obtained in waters with pH values in the treated waters ranging from 2.9 to 8.2, which were the extreme limits studied. All flocs settled well except those at the extreme lower end of the range. There was no residual titanium in any treated water with a pH of 3.5 or greater.

The relative abilities of the titanium reagents and of filter alum to remove fluorides from water were compared. The water treated was tap water to which about 4 p. p. m. of fluoride (*6*) had been added in the form of calcium fluoride. Only slight removal of fluoride was effected either with the titanium reagents or with aluminum sulfate. Treatment of three portions of water containing 4.5 p. p. m. of fluoride with 10 grains per gallon of aluminum sulfate, titanium sulfate, and the ilmenite extract containing 20 per cent titanium sulfate and 80 per cent ferric sulfate, gave a removal of only 0.5 p. p. m. of fluoride in each case. Varying the pH of the waters treated had little effect on the removal of fluorides by titanium compounds. Filter alum gave somewhat better removal in the pH range around 7.0, as found by Boruff (*3*); the best removal was obtained in an experiment where the final pH was 7.0 and the fluoride content of the water was reduced from 3.8 to 1.0 p. p. m.

Since the titanium sulfate appeared to hydrolyze so rapidly it seemed possible that the coagulative and adsorptive properties of the floc for the fluoride ions or complexes might not be as great as if the floc formed more slowly and uniformly throughout the liquid. To try to obtain slower coagulation, a water containing fluoride ion was cooled by an ice-salt bath to 1.0° ± 0.5° C., and 10 grains per gallon of titanium sulfate were added. This cooling slowed hydrolysis and caused a somewhat better floc to form but no removal of fluoride was obtained from a water containing 2.5 p. p. m. of fluoride with a final pH of 7.6.

Coagulation Experiments with Colored Water

A series of experiments was made to compare the color-removing ability of the ilmenite extract with those of aluminum sulfate and ferric sulfate. Color was produced in the water by adding a dark brown trade waste whose color was due to vegetable organic matter. The liquid had a high inorganic salt content, mostly as sodium chloride, but no analyses to determine the concentration were run.

The organic and inorganic matter in the water made flocculation impossible with liquid ilmenite extract, aluminum sulfate, or ferric sulfate in dosages of 14.7 grains per gallon (250 p. p. m.). In the low pH range, however, the ilmenite extract gave good flocs and considerable color removal. In water treated with ilmenite extract amounting to 7.6 grains per gallon of $TiOSO_4 \cdot 2H_2O$ and 7.1 grains per gallon of ferric sulfate, an initial color of 43 on the platinum-cobalt scale (*1*) was reduced to 10. The initial pH was 7.2 and the final pH 4.3.

To obtain less dissolved and suspended material, a water was colored by soaking oak leaves in it. Titanium sulfate was substituted for the ilmenite extract in order to find the effect of the titanium salt. The pH had a great effect on the flocculating power of the titanium sulfate; above a pH of 5 it was impossible to obtain a floc that settled completely at room temperature. The rate of hydrolysis of the titanium sulfate was so great that part of the hydrous titanium oxide formed remained colloidally dispersed instead of precipitating. Below this pH better color removal was obtained with titanium sulfate than with aluminum sulfate or ferric sulfate.

Initial pH	Final pH	Grains Coagulant per Gal.	Initial Color	Final Color
5.2	3.3	2 $Fe_2(SO_4)_3$	40 ± 2	15
5.2	4.5	2 $Al_2(SO_4)_3 \cdot 18H_2O$	40 ± 2	20
5.2	3.7	2 $Ti(SO_4)_2$	40 ± 2	6

Titanium sulfate has advantages and disadvantages as a coagulant for water treatment. The reagent is hard to feed and hydrolyzes readily in the feed solution unless it is kept concentrated. Feeding the titanium sulfate solution with aluminum or iron sulfate, however, makes it much easier to handle by inhibiting hydrolysis in the feed solution. Titanium sulfate cannot be dry-fed since it will not hydrolyze completely in very dilute solution. It shows no advantage over aluminum sulfate in fluoride removal but removes color from water more efficiently. The hydrous titanium oxide floc is much more bulky and opaque than the alum floc but settles somewhat more slowly at ordinary temperatures. The pH range for good floc formation with titanium sulfate is considerably broader than that for alum. The titanium floc forms much more rapidly and in a bulkier condition at temperatures near 0° C. Ilmenite extract gives much better coagulation in the colored water high in colloidal matter and dissolved salts than aluminum or ferric sulfates.

To be sure that the color removal was not due merely to bleaching as a result of increased acidity, the pH of each of the treated waters was adjusted to 5.2 and the color was again read. The final colors from the treatments were as follows: ferric sulfate, 38; aluminum sulfate, 22; titanium sulfate, 7.

Effect of Temperature

The fact that good flocculation was obtained with titanium sulfate at a temperature near the freezing point of water suggested the study of low-temperature coagulation comparing titanium sulfate with aluminum. Two runs were made at 1.5° to 2.0° C. Dosages of 2 grains per gallon of aluminum sulfate and of titanium sulfate were used at pH values of 8.5 and 8.4, respectively. The waters were stirred for 3 hours; a floc appeared in half an hour in the titanium sulfate run but not at the end of the stirring period in the aluminum sulfate run. Standing overnight at 3.0° to 4.0° C. caused a bulky hydrous titanium oxide floc to settle completely. The aluminum-sulfate-treated water was still milky and had a turbidity of 10 p. p. m., and what floc had formed was of a granular, pin-point character.

A series of six similar low-temperature experiments was tried using mixtures of the two coagulants. A total of 2 grains per gallon of coagulant was used in each case; the titanium sulfate dosages for the six runs were 0, 0.10, 0.13, 0.20, 0.33, and 0.50 grain per gallon. The larger the proportion of titanium sulfate, the less tendency there was to form pin-point floc and the faster the floc settled.

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Influence of Metallic Oxides

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The use of compounding ingredients is not essential to the conversion of plastic to nonplastic neoprene, but the addition of suitable materials does affect the properties of both the plastic and the cured neoprene. In this paper data are presented showing the influence of metallic oxides on the stability of uncured neoprene and on the stress-strain properties, hardness, and water absorption of cured neoprene. Proper mixtures are more effective than single oxides. The best compounds for general use contain zinc oxide and magnesia. Calcium oxide cannot be substituted for magnesia. Mixtures of litharge and magnesia or zinc oxide give compounds which have low moduli and tensile strengths, but which, with the proper selection of oxides, possess superior water resistance.

POLYMERIZED chloroprene (*2*) or neoprene resembles natural rubber in that it can be obtained as a plastic material which is converted into an elastic, essentially nonplastic material by heating in the presence of various compounding ingredients. Neoprene differs from natural rubber in that the use of compounding ingredients is not essential to the conversion of the plastic to the elastic form. However, the properties of neoprene can be varied to a considerable extent by the proper selection of the compounding ingredients.

A fundamental investigation of factors influencing the properties of neoprene is being made at this laboratory. This particular paper deals with the influence of metallic oxides on the stability of compounded, uncured neoprene type E and on the stress-strain properties, hardness, and water resistance of the cured product. This paper reports the results obtained, and defers a discussion of possible theories until a more nearly complete picture of the mechanism of the curing of neoprene is obtained. Bridgwater and Krismann (*1*) showed the desirability of compounding neoprene type F with zinc oxide and magnesia. In the present paper the influence of metallic oxides, alone and in various combinations, upon the properties of current plant production of neoprene type E is considered.

Metallic oxides have quite different effects, and can be classified according to their influence on the rate of cure of neoprene. When used singly, the oxides of magnesium, zinc, mercury, and calcium have a strong accelerating action while the oxides of antimony, barium, cadmium, aluminum, lead, manganese, iron, and beryllium have a comparatively mild influence on cure. The oxides of copper, chromium, vanadium, tungsten, and titanium have a neutral effect; that is, the stress-strain properties remain unchanged when up to 10 parts of these oxides per 100 parts of neoprene are added. The oxides of arsenic and molybdenum appear to retard the cure, especially during the shorter cures. The actual test data on which these conclusions are based are given in Table I.

Typical plant neoprene type E was used in these tests. The different oxides with a fineness of at least 100 mesh were mixed with the neoprene on a 15 × 30 cm. experimental rubber mill; the temperature of the rolls was maintained at 50° C. Mixed stocks were slabbed from the mill about 0.22 cm. thick, and cured in a 7.5 × 15 cm. mold 0.20 cm. deep. All cures were made at 153° C. (307° F.). The vulcanized specimens were aged 24 hours in the constant-temperature (28° C.) testing room before testing on a Scott rubber tensile testing machine. A. S. T. M. methods were used in the preparation and testing of samples.

Combinations of metallic oxides, such as magnesia and zinc oxide, and litharge and magnesia were shown by Bridg-

TABLE I. EFFECT OF INORGANIC OXIDES ON THE CURE OF NEOPRENE

Oxide	Cure at 153° C.	Stress at 600% Elongation		Tensile Strength		Elongation at Break	
		5 parts oxide[a]	10 parts oxide[a]	5 parts oxide[a]	10 parts oxide[a]	5 parts oxide[a]	10 parts oxide[a]
	Min.	*Kg. per sq. cm. (lb. per sq. in.)*				%	%
MgO	10	25 (350)	35 (500)	163 (2325)	81 (1150)	1050	900
	30	54 (775)	56 (800)	104 (1475)	120 (1700)	720	810
	60	.....	.....	44 (625)	63 (900)	510	510
ZnO	10	37 (525)	.....	72 (1025)	35 (500)	700	300
	30	.....	.....	44 (625)	33 (475)	480	360
	60	.....	.....	60 (850)	42 (600)	430	360
HgO	10	19 (275)	32 (450)	97 (1375)	116 (1650)	970	840
	30	19 (275)	51 (725)	107 (1525)	92 (1300)	860	670
	60	.....	79 (1125)	37 (525)	79 (1125)	550	600
CaO	10	18 (250)	19 (275)	109 (1550)	114 (1625)	1080	1110
	30	37 (525)	.....	100 (1425)	......	760	..
	60	63 (900)	44 (625)	84 (1200)	116 (1650)	640	770
Sb_2O_3	10	9 (125)	12 (175)	77 (1100)	101 (1450)	1000	1020
	30	19 (275)	33 (475)	62 (875)	54 (775)	800	670
	60	.....	.....	47 (675)	......	590	..
BaO_2	10	9 (125)	5 (75)	40 (575)	65 (925)	1000	1100
	30	19 (275)	26 (375)	88 (1250)	81 (1150)	900	760
CdO	10	12 (175)	11 (150)	70 (1000)	81 (1150)	1200	1260
	30	19 (275)	23 (325)	114 (1625)	144 (2050)	1010	1060
	60	33 (475)	28 (400)	125 (1775)	146 (2075)	820	910
Al_2O_3	10	12 (175)	12 (175)	60 (850)	86 (1225)	1010	1010
	30	12 (175)	.....	65 (925)	......	920	..
	60	19 (275)	33 (475)	62 (875)	63 (900)	800	690
PbO	10	14 (200)	16 (225)	60 (850)	77 (1100)	1000	1050
	30	16 (225)	21 (300)	100 (1425)	121 (1725)	1020	1060
	60	23 (325)	.....	107 (1525)	......	900	..
PbO_2	10	19 (275)	9 (125)	72 (1025)	70 (1000)	1090	1150
	30	23 (325)	26 (375)	72 (1025)	83 (1175)	860	860
	60	47 (675)	51 (725)	54 (775)	84 (1200)	620	700

[a] Per 100 parts neoprene by weight.

on Neoprene Properties

water and Krismann (*1*) to give much better results with neoprene type F than those obtained with any one oxide alone. The influence on neoprene type E of combinations, of the strong accelerators magnesia, zinc oxide, and calcium oxide, and the mild accelerator litharge have been studied in some detail.

For all the tests on combinations of the oxides reported, master batches of the following composition were used:

Neoprene type E	100
FF wood rosin	5
Phenyl-β-naphthylamine	2
Sulfur	1

FF wood rosin, sulfur, and phenyl-β-naphthylamine were used because they are employed in a wide variety of practical formulas and, so far as is known, except with regard to the effect of sulfur on the stability of litharge compounds, do not mask or interfere with the characteristic behavior of combinations of metallic oxides in neoprene. Sulfur and rosin (*1, 3*) improve the curing properties of neoprene, although it is possible to obtain good cured products from neoprene without the use of either. High-temperature aging of neoprene type E[1] has shown that sulfur should not be used in compounding heat-resistant stocks. It has been demonstrated repeatedly that rosin improves the stability of the compounded uncured stock. Phenyl-β-naphthylamine is a valuable antioxidant for use with neoprene (*1, 2, 3*).

Magnesia and Zinc Oxide

Magnesia (extra light calcined, with not over 2 per cent carbon dioxide calculated as magnesium carbonate) was used in combination with varying amounts of zinc oxide (St. Joe Black Label) in such quantities as are given in Table II. The compounds were mixed on the laboratory rubber mill and cured in the manner described for testing the different metallic oxides singly. Four 2-cc. pellets were punched from the compounded, uncured stocks for plasticity and stability measurements. Table II summarizes the stress-strain properties of the compounds. Figure 1 is a graphic representation of the alteration of the stress at 600 per cent elongation and the tensile strength for the 10-, 30-, and 60-minute cures at 153° C. as both the zinc oxide and magnesia are varied. The influence of increased quantities of magnesia on the stress at 600 per cent elongation of compounds with different fixed amounts of zinc oxide is given in Figure 2; Figure 3 shows the variation in the stress with increased amounts of zinc oxide for different quantities of magnesia.

Figures 2 and 3 exhibit the range over which the stiffness of the 30-minute cure of this master batch may be varied by controlling the amounts of zinc oxide and magnesia. A notable effect is the sharp decrease in the modulus when 1 part of zinc oxide is added to compounds containing less than 15 parts of magnesia. With the use of more than 1 part of zinc oxide in these compounds there is a gradual increase in the modulus. In compounds that contain more than 15 parts of magnesia, the modulus gradually increases as zinc oxide is added. Table II and Figure 1 show that the tensile strength is mainly 3400 ± 200 pounds per square inch (240 ± 14 kg. per sq. cm.), and the elongation at break for the 30-minute cure falls mainly within the limits of 850 ± 50 per cent, for a variation in zinc oxide from 1 to 20 parts and in magnesia from 5 to 40 parts per 100 parts of neoprene. Variation in the hardness parallels the change in the stress. The hardness varies from 37 (Shore Durometer, type A), without metallic oxides, to 55 with 20 parts zinc oxide and no magnesia, to 65 with 40 parts magnesia and no zinc oxide, and to 70 with 20 parts zinc oxide and 40 parts magnesia.

The plasticity and stability of the compounded, uncured stock are important considerations in practice. A compound must be sufficiently plastic to mold, calender, or tube well, must exhibit a minimum recovery when sheeted or tubed and retain these properties during processing and storage. A measure of the tendency of a compound to scorch on the mill and to "setup" during storage before it is cured is obtained by aging pellets of the stock at 50° C. and comparing the plasticity and recovery figures obtained at fixed intervals with the initial figures. The plasticity was determined at 80° C. in the Williams parallel plate plastometer (*4*). The thickness of 2-cc. samples, which had been preheated for 15 minutes, was measured in thousandths of an inch after 3 minutes under a load of 5 kg. at 80° C. and again after a rest interval of 1 minute at room temperature. The difference in the two thickness readings was taken as the recovery. The actual results obtained are presented in Table III and in Figure 4. Compounds containing as little as 1 part of zinc oxide alone are extremely unstable and scorch very readily on the mill. On the other hand, while

TABLE I. (*Continued*)

Oxide	Cure at 153° C.	Stress at 600% Elongation: 5 parts oxide[a]	Stress at 600% Elongation: 10 parts oxide[a]	Tensile Strength: 5 parts oxide[a]	Tensile Strength: 10 parts oxide[a]	Elongation at Break: 5 parts oxide[a]	Elongation at Break: 10 parts oxide[a]
	Min.	*Kg. per sq. cm. (lb. per sq. in.)*				%	%
Pb_3O_4	10	14 (200)	9 (125)	69 (975)	83 (1175)	1100	1250
	30	16 (225)	26 (375)	90 (1275)	58 (825)	980	800
	60	19 (275)	26 (375)	93 (1325)	81 (1150)	860	820
MnO_2	10	9 (125)	14 (200)	30 (425)	81 (1150)	980	960
	30	18 (250)	19 (275)	79 (1125)	83 (1175)	960	930
	60	23 (325)	33 (475)	107 (1525)	105 (1500)	850	810
Fe_2O_3	10	4 (50)	5 (75)	40 (575)	39 (550)	1160	1020
	30	7 (100)	11 (150)	62 (875)	69 (975)	950	940
	60	46 (650)	49 (700)	65 (925)	54 (775)	650	610
BeO	10	5 (75)	.....	63 (900)	......	1220	..
	30	11 (150)	.....	97 (1375)	......	1090	..
	60	19 (275)	.....	104 (1475)	......	970	..
Blank	10	4 (50)		44 (625)		1140	
	30	12 (175)		63 (900)		980	
	60	12 (175)		74 (1050)		960	
CuO	30	5 (75)	11 (150)	51 (725)	67 (950)	1180	1000
	60	9 (125)	11 (150)	58 (825)	63 (900)	1000	940
CrO_3	30	9 (125)	.....	46 (650)	......	1040	..
V_2O_4	60	11 (150)	.....	47 (675)	......	930	..
WO_3	30	.....	7 (100)	......	84 (1200)	..	1140
	60	.....	12 (175)	......	65 (925)	..	900
TiC_2	10	2 (25)	5 (75)	46 (650)	54 (775)	1320	1250
	30	5 (75)	12 (175)	65 (925)	79 (1125)	1110	1000
	60	9 (125)	14 (200)	83 (1175)	98 (1400)	960	965
As_2O_3	10	2 (25)	2 (25)	47 (675)	56 (800)	1180	1340
	30	2 (25)	7 (100)	49 (700)	60 (850)	1080	1010
	60	18 (250)	23 (325)	65 (925)	58 (825)	780	730
MoO_3	10	2 (25)	2 (25)	35 (500)	26 (375)	1140	1260
	30	4 (50)	7 (100)	67 (950)	69 (975)	1160	1110
	60	9 (125)	11 (150)	60 (850)	58 (825)	1010	1010

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[1] Unpublished data.

Table II. Effect of Magnesia and Zinc Oxide on Stress-Strain Properties of Neoprene

MgO/ 100 Parts Neoprene	Cure, at 153° C.	0.0 Part ZnO				1.0 Part ZnO				5.0 Parts ZnO				10 Parts ZnO				20 Parts ZnO			
		Stress[a]	Tensile strength	Elongation[b]	Hardness[c]	Stress[a]	Tensile strength	Elongation[b]	Hardness[c]	Stress[a]	Tensile strength	Elongation[b]	Hardness[c]	Stress[a]	Tensile strength	Elongation[b]	Hardness[c]	Stress[a]	Tensile strength	Elongation[b]	Hardness[c]
Parts	*Min.*	*Kg./sq. cm.*	*(lb./sq. in.)*	%		*Kg./sq. cm.*	*(lb./sq. in.)*	%		*Kg./sq. cm.*	*(lb./sq. in.)*	%		*Kg./sq. cm.*	*(lb./sq. in.)*	%		*Kg./sq. cm.*	*(lb./sq. in.)*	%	
0.0	10	2 (25)	37 (525)	1200	..	53 (75)	62 (875)	980	..	141 (200)	63 (925)	860	..	18 (250)	76 (1075)	860	..	......	51 (725)	500	..
	30	4 (50)	65 (925)	1080	37	11 (150)	56 (800)	800	40	25 (350)	35 (500)	660	45	39 (550)	92 (1300)	840	50	65 (925)	65 (925)	600	55
	60	9 (125)	40 (575)	860	..	32 (450)	49 (700)	660	..	......	35 (500)	560	..	40 (575)	46 (650)	640	..	......	62 (875)	420	..
2.5	10	33 (475)	199 (2825)	940	..	32 (450)	151 (2150)	1000	..	33 (475)	195 (2775)	1060	..	37 (525)	167 (2375)	1000	..	42 (600)	202 (2875)	1060	..
	30	84 (1200)	109 (1550)	650	55	30 (426)	179 (2550)	970	52	33 (475)	204 (2900)	1020	50	51 (725)	211 (3000)	970	55	54 (775)	243 (3450)	1000	55
	60	......	89 (1275)	580	..	60 (850)	118 (1675)	780	..	44 (625)	186 (2650)	950	..	49 (700)	206 (2925)	950	..	63 (900)	218 (3100)	910	..
5.0	10	49 (700)	223 (3175)	930	..	32 (450)	209 (2975)	1080	..	37 (525)	195 (2775)	1040	..	44 (625)	236 (3350)	1040	..	53 (750)	251 (3575)	1040	..
	30	95 (1350)	181 (2575)	720	56	44 (625)	206 (2925)	960	58	47 (675)	206 (2925)	1000	55	51 (725)	253 (3600)	1000	55	58 (825)	241 (3425)	960	58
	60	116 (1650)	153 (2175)	640	..	54 (775)	234 (3325)	920	..	56 (800)	200 (2850)	920	..	74 (1050)	265 (3775)	920	..	76 (1075)	244 (3475)	920	..
10	10	60 (850)	207 (2950)	900	..	46 (650)	225 (3200)	1010	..	46 (650)	229 (3250)	1060	..	67 (950)	250 (3550)	1020	..	69 (975)	264 (3750)	1000	..
	30	86 (1225)	197 (2800)	820	57	76 (1075)	232 (3300)	880	60	69 (975)	234 (3325)	900	56	79 (1125)	243 (3450)	920	56	88 (1250)	258 (3675)	900	57
	60	90 (1275)	181 (2575)	780	..	92 (1300)	225 (3000)	770	..	90 (1275)	204 (2900)	800	..	97 (1375)	243 (3450)	860	..	102 (1450)	241 (3425)	840	..
15	10	76 (1075)	255 (3625)	940	..	70 (1000)	244 (3475)	940	..	70 (1000)	239 (3400)	1000	..	74 (1050)	255 (3625)	1000	..	76 (1075)	250 (3550)	960	..
	30	90 (1275)	230 (3275)	820	60	109 (1550)	258 (3675)	800	63	102 (1450)	257 (3650)	900	60	97 (1375)	255 (3625)	880	61	105 (1500)	243 (3450)	820	61
	60	120 (1700)	179 (2550)	680	..	114 (1625)	218 (3100)	740	..	111 (1575)	229 (3250)	800	..	111 (1575)	229 (3250)	800	..	127 (1800)	239 (3400)	760	..
20	10	86 (1225)	267 (3800)	960	..	88 (1250)	265 (3775)	900	..	92 (1300)	267 (3800)	900	..	84 (1200)	244 (3475)	940	..	88 (1250)	230 (3275)	900	..
	30	97 (1375)	264 (3750)	860	60	105 (1500)	225 (3200)	780	63	120 (1700)	223 (3175)	780	61	112 (1600)	218 (3100)	800	63	116 (1650)	265 (3775)	860	65
	60	114 (1625)	206 (2925)	780	..	118 (1675)	230 (3275)	790	..	141 (2000)	243 (3450)	740	..	125 (1775)	202 (2875)	740	..	134 (1900)	227 (3225)	740	..
25	10	84 (1200)	286 (4075)	930	..	92 (1300)	262 (3725)	900	..	70 (1000)	214 (3050)	960	..	92 (1300)	255 (3625)	940	..	83 (1175)	241 (3425)	960	..
	30	93 (1325)	253 (3600)	840	62	116 (1650)	246 (3500)	780	62	102 (1450)	227 (3225)	820	63	116 (1650)	243 (3450)	800	65	116 (1650)	234 (3325)	800	65
	60	104 (1475)	250 (3550)	790	..	127 (1800)	239 (3400)	760	..	116 (1650)	218 (3100)	760	..	120 (1700)	216 (3075)	750	..	123 (1750)	229 (3250)	760	..
30	10	95 (1350)	267 (3800)	880	..	97 (1375)	267 (3800)	900	..	84 (1200)	246 (3500)	960	..	100 (1425)	267 (3800)	930	..	105 (1500)	243 (3450)	860	..
	30	104 (1475)	221 (3150)	800	62	112 (1600)	236 (3350)	800	64	118 (1675)	246 (3500)	780	64	123 (1750)	236 (3350)	790	66	123 (1750)	218 (3100)	760	68
	60	112 (1600)	216 (3075)	770	..	118 (1675)	234 (3325)	760	..	123 (1750)	225 (3200)	740	..	125 (1775)	213 (3025)	740	..	135 (1925)	202 (2875)	720	..
40	10	109 (1550)	248 (3525)	850	..	107 (1525)	255 (3625)	900	..	81 (1150)	202 (2875)	960	..	104 (1475)	232 (3300)	900	..	104 (1475)	221 (3150)	900	..
	30	112 (1600)	227 (3225)	800	65	132 (1875)	248 (3525)	790	65	114 (1625)	223 (3175)	810	65	134 (1900)	237 (3375)	780	67	125 (1775)	206 (2925)	760	70
	60	123 (1750)	204 (2900)	740	..	146 (2075)	230 (3275)	740	..	127 (1800)	218 (3100)	760	..	142 (2025)	216 (3075)	720	..	132 (1875)	202 (2875)	720	..

[a] At 600% elongation. [b] At break. [c] Shore Durometer, type A.

magnesia is a strong accelerator for the cure of neoprene at 150° C., compounds containing up to 40 parts of this material are relatively stable under normal storage conditions and at 50° C. Furthermore, the addition of magnesia to compounds containing zinc oxide improves the stability of these compounds. Thus, by using 10 parts or more of magnesia in a compound containing zinc oxide, the tendency to scorch is greatly reduced and the storage life increased many times.

In addition to the fact that zinc oxide improves the curing range and the stress-strain properties of compounds containing magnesia, it increases the water resistance of neoprene compounded with magnesia. The results of the water absorption tests are expressed as percentage volume increase of the compound after immersion in boiling distilled water for 48 hours. The testing apparatus used for determining the water absorption and the procedure adopted was as follows: A rectangular tin-coated iron can, 14 × 22 cm. on top and 32 cm. deep, was equipped with a tight cover 9.5 cm. in diameter and a reflux condenser. Inside the cans, 7.5 cm. from the top and 5 cm. from the sides on the 22 × 32 cm. faces, were soldered two grooved Monel metal cross bars to support the test specimens. The test specimens, 1.5 × 7.5 cm., were cut from the slabs cured for 30 minutes, coded by trimming corners and cutting notches, and weighed to a centigram in both air and water. The specimens were then placed on Monel metal hooks and suspended from the cross bars in the can in boiling distilled water. After 48 hours the specimens were removed and cooled in water. The excess water on the surface of each specimen was removed by blotting with

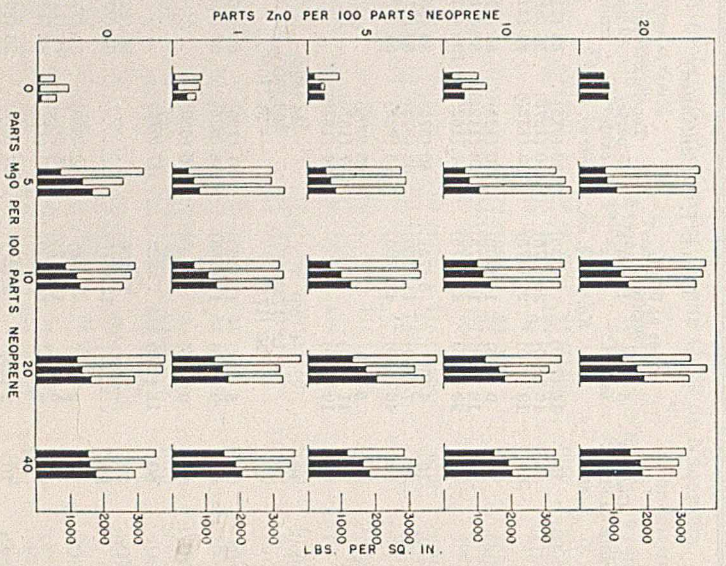


Figure 1. Effect of Varying Amounts of Magnesia and Zinc Oxide on Stress at 600 Per Cent Elongation and Tensile Strength

Cures, 10, 30, and 60 minutes at 153° C.; stress shown by solid portions, tensile strength by whole column.

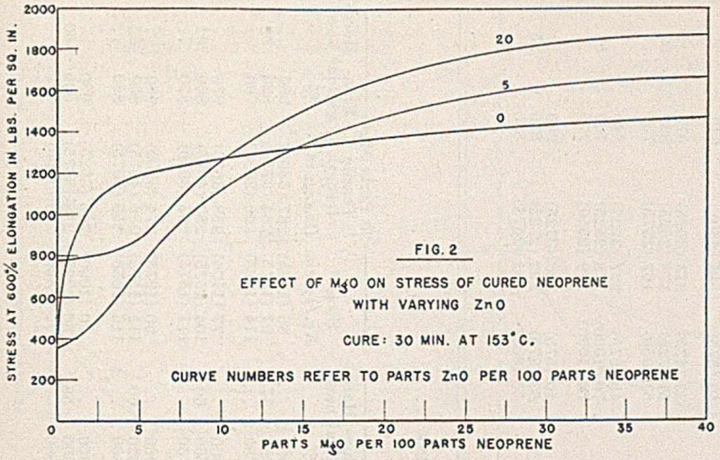


FIG. 2

EFFECT OF MgO ON STRESS OF CURED NEOPRENE WITH VARYING ZnO

CURE: 30 MIN. AT 153°C.

CURVE NUMBERS REFER TO PARTS ZnO PER 100 PARTS NEOPRENE

absorbent cloth, and the specimen was weighed at once. From the weight measurements, the percentage volume increase was calculated by the equation:

$$\text{Per cent volume increase} = \frac{\text{gain in weight}}{(\text{original weight in air}) - (\text{original weight in water})} \times 100$$

This per cent volume increase is volume of water absorbed per hundred volumes of neoprene stock; it does not take into account contraction in volume due to hydration of MgO.

The relative effects of magnesia and zinc oxide on the water resistance of neoprene compounds containing them is demonstrated by the curves of Figures 5 and 6. Compounds containing magnesia alone have low water resistance, but it is much improved by the addition of zinc oxide. On the other hand, the water resistance of zinc oxide compounds is improved by the addition of magnesia.

Magnesia and Zinc Oxide in a Stock Loaded with Soft Carbon Black

To determine the influence of these oxides in a typical compound loaded with soft carbon black, 25 parts by weight of P-33 were added to the neoprene master batch. Varying amounts of magnesia and zinc oxide were added, and the stress-strain properties, hardness, and water absorption of the cured compounds, and the stability of the uncured compounds were determined. The change in the stress-strain properties, as the magnesia and zinc oxide are varied, is shown by the summary given in Table IV and Figure 7. The behavior of magnesia and zinc oxide in varying amounts in a compound loaded with soft carbon black is similar in character to their action in the gum compound just described. In both cases a small amount of zinc oxide added to a magnesia-containing compound lowers the modulus considerably. Magnesia has a greater effect on the modulus than zinc oxide in any given series of these compounds. In the stock loaded with carbon black there is a greater tendency for the magnesia to cause a lowering of the percentage elongation at break, with attendant decrease in tensile strength, than in the case of the gum stock. The variation in hardness of the 30-minute cure with variation in the amounts of magnesia and zinc oxide used is much the same as the variation with the gum stock. In each case the carbon black stock is slightly harder (5 ± 3) than the gum stock.

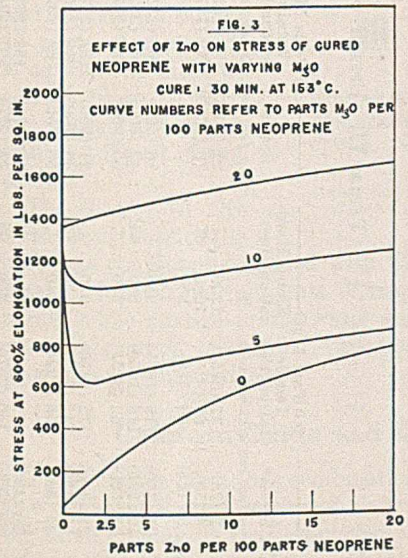


FIG. 3

EFFECT OF ZnO ON STRESS OF CURED NEOPRENE WITH VARYING MgO

CURE: 30 MIN. AT 153°C.

CURVE NUMBERS REFER TO PARTS MgO PER 100 PARTS NEOPRENE

TABLE III. STABILITY OF UNCURED STOCK COMPOUNDED WITH MAGNESIA AND ZINC OXIDE

MgO/100 Parts Neoprene	Aging Period at 50° C.	Plasticity Recovery in 0.001 In. (0.025 Mm.): 0.0 part ZnO	1.0 part ZnO	5.0 parts ZnO	10 parts ZnO	20 parts ZnO
Parts	*Hr.*					
0	0	90–2	103–5	100–5	103–5	111–9
	24	89–0	380	317	412	356–128
	48	90–0	....	....	....	355–128
	96	89–3	....	....	....	370–123
5	0	102–6	89–5	101–7	101–6	96–8
	24	111–10	95–6	113–6	114–5	108–9
	48	117–8	97–6	139–9	145–13	113–8
	96	125–12	116–11	292–151	318–143	325–159
10	0	112–8	99–6	109–7	113–8	112–8
	24	124–9	108–6	115–8	117–7	123–9
	48	127–13	116–5	123–7	127–5	132–7
	96	143–32	135–15	170–92	178–92	171–93
20	0	111–7	122–14	123–13	140–13	136–13
	24	121–7	132–13	131–13	132–11	145–23
	48	129–11	141–11	136–9	138–14	152–13
	96	144–16	160–39	155–48	163–53	175–73
30	0	117–10	121–10	110–8	122–14	125–13
	24	129–12	135–9	119–8	132–12	132–15
	48	137–9	147–13	131–8	141–12	146–17
	96	149–22	160–30	145–25	156–26	157–52
40	0	120–10	145–14	121–14	141–19	140–20
	24	133–12	161–39	139–16	149–23	152–21
	48	....	165–58	151–24	160–34	166–48
	96	156–44	181–64	170–65	180–62	178–67

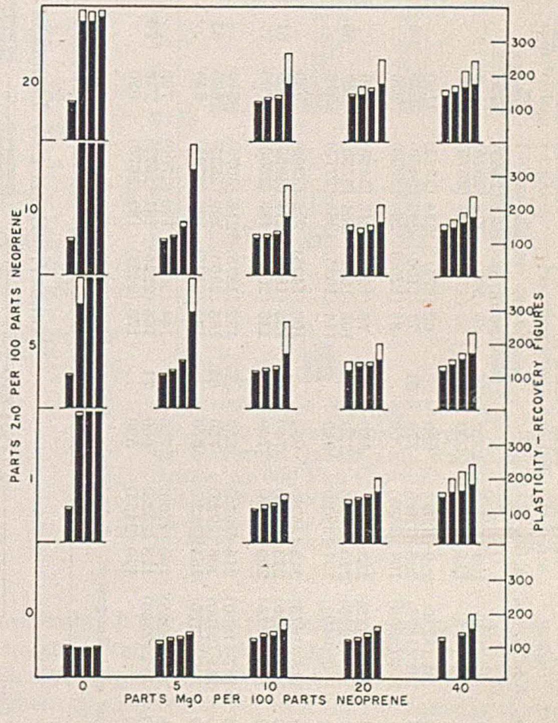


FIGURE 4. EFFECT OF VARYING AMOUNTS OF MAGNESIA AND ZINC OXIDE ON THE STABILITY OF UNCURED NEOPRENE

Aging periods, 0, 24, 48, and 96 hours at 50° C.; plasticity shown by solid portions, recovery by unshaded portions.

TABLE IV. EFFECT OF MAGNESIA AND ZINC OXIDE ON STRESS-STRAIN PROPERTIES OF NEOPRENE LOADED WITH SOFT CARBON BLACK

MgO/100 Parts Neoprene	Cure at 153°C.	0.0 Part ZnO				1.0 Part ZnO				5.0 Parts ZnO				10 Parts ZnO				20 Parts ZnO			
		Stress[a]	Tensile strength	Elongation[b]	Hardness[c]	Stress[a]	Tensile strength	Elongation[b]	Hardness[c]	Stress[a]	Tensile strength	Elongation[b]	Hardness[c]	Stress[a]	Tensile strength	Elongation[b]	Hardness[c]	Stress[a]	Tensile strength	Elongation[b]	Hardness[c]
Parts	*Min.*	*Kg./sq. cm.*	*(lb./sq. in.)*	%		*Kg./sq. cm.*	*(lb./sq. in.)*	%		*Kg./sq. cm.*	*(lb./sq. in.)*	%		*Kg./sq. cm.*	*(lb./sq. in.)*	%		*Kg./sq. cm.*	*(lb./sq. in.)*	%	
0.0	10	......	......	..	..	26 (375)	172 (2450)	1200	..	53 (750)	165 (2350)	970	..	47 (675)	218 (3100)	1030	..	47 (675)	216 (3075)	1100	..
	30	35 (500)	109 (1550)	1020	46	35 (500)	178 (2525)	1120	47	56 (800)	202 (2875)	980	55	60 (850)	192 (2725)	980	55	56 (800)	200 (2850)	1000	56
	60	51 (725)	114 (1625)	900	..	33 (475)	181 (2575)	1100	..	67 (950)	204 (2900)	950	..	76 (1075)	192 (2725)	920	..	69 (975)	202 (2875)	970	..
2.5	10	81 (1150)	229 (3250)	980	..	62 (875)	234 (3325)	1100	..	72 (1025)	250 (3550)	1020	..	65 (925)	232 (3300)	1050	..	67 (950)	221 (3150)	1050	..
	30	132 (1875)	225 (3200)	770	61	77 (1100)	243 (3450)	1020	56	83 (1175)	246 (3500)	980	57	76 (1075)	241 (3425)	1030	57	83 (1175)	220 (3125)	980	59
	60	141 (2000)	199 (2825)	700	..	88 (1250)	260 (3700)	990	..	95 (1350)	244 (3475)	930	..	90 (1275)	200 (2850)	910	..	95 (1350)	230 (3275)	940	..
5.0	10	104 (1475)	253 (3600)	930	..	76 (1075)	243 (3450)	1090	..	79 (1125)	243 (3450)	1050	..	77 (1100)	223 (3175)	1040	..	88 (1250)	230 (3275)	1020	..
	30	156 (2225)	220 (3125)	720	60	105 (1500)	264 (3750)	960	56	90 (1275)	246 (3500)	990	57	86 (1225)	225 (3200)	980	58	100 (1425)	227 (3225)	960	60
	60	169 (2400)	197 (2800)	640	..	114 (1625)	265 (3775)	910	..	104 (1475)	225 (3200)	890	..	109 (1550)	223 (3175)	890	..	114 (1625)	202 (2875)	850	..
10	10	118 (1675)	248 (3525)	900	..	100 (1425)	225 (3200)	930	..	93 (1325)	234 (3325)	990	..	104 (1475)	216 (3075)	940	..	104 (1475)	221 (3150)	960	..
	30	148 (2100)	213 (3025)	740	62	132 (1875)	214 (3050)	800	61	127 (1800)	221 (3150)	830	62	137 (1950)	197 (2800)	770	63	142 (2025)	209 (2975)	800	64
	60	160 (2275)	209 (2975)	700	..	146 (2075)	183 (2600)	700	..	142 (2025)	207 (2950)	770	..	148 (2100)	206 (2925)	740	..	149 (2125)	211 (3000)	740	..
20	10	127 (1800)	216 (3075)	850	..	132 (1875)	216 (3075)	840	..	139 (1975)	218 (3100)	820	..	132 (1875)	216 (3075)	840	..	128 (1825)	192 (2725)	830	..
	30	148 (2100)	206 (2925)	750	65	165 (2350)	199 (2825)	680	65	172 (2450)	202 (2875)	680	67	170 (2425)	181 (2575)	640	68	148 (2100)	189 (2675)	730	68
	60	160 (2275)	185 (2625)	670	..	174 (2475)	192 (2725)	640	..	......	183 (2600)	580	..	......	179 (2550)	580	..	169 (2400)	174 (2475)	610	..
40	10	156 (2225)	190 (2700)	720	..	144 (2050)	190 (2700)	700	..	155 (2200)	189 (2675)	740	..	160 (2275)	195 (2775)	750	..	162 (2300)	185 (2625)	700	..
	30	165 (2350)	178 (2525)	660	71	156 (2225)	181 (2575)	710	70	185 (2625)	185 (2625)	600	73	......	192 (2725)	580	73	......	183 (2600)	580	75
	60	......	170 (2425)	590	..	170 (2425)	189 (2675)	620	..	......	179 (2550)	520	..	......	185 (2625)	520	..	......	186 (2650)	520	..

[a] At 600 per cent elongation. [b] At break. [c] Shore Durometer, type A.

TABLE V. EFFECT OF LITHARGE AND ZINC OXIDE ON STRESS-STRAIN PROPERTIES OF NEOPRENE

PbO/100 Parts Neoprene	Cure at 153° C.	0.0 Part ZnO				1.0 Part ZnO				5.0 Parts ZnO				10 Parts ZnO			
		Stress[a]	Tensile strength	Elongation[b]	Hardness[c]	Stress[a]	Tensile strength	Elongation[b]	Hardness[c]	Stress[a]	Tensile strength	Elongation[b]	Hardness[c]	Stress[a]	Tensile strength	Elongation[b]	Hardness[c]
Parts	*Min.*	*Kg./sq. cm.*	*(lb./sq. in.)*	%		*Kg./sq. cm.*	*(lb./sq. in.)*	%		*Kg./sq. cm.*	*(lb./sq. in.)*	%		*Kg./sq. cm.*	*(lb./sq. in.)*	%	
0.0	10	2 (25)	37 (525)	1200	..	5 (75)	62 (875)	980	..	14 (200)	65 (925)	860	..	18 (250)	76 (1075)	860	..
	30	4 (50)	65 (925)	1080	37	11 (150)	56 (800)	800	40	25 (350)	35 (500)	660	45	39 (550)	92 (1300)	840	50
	60	9 (125)	40 (575)	860	..	32 (450)	49 (700)	660	..	....	35 (500)	560	..	40 (575)	46 (650)	640	..
5.0	10	25 (350)	118 (1675)	950	..	18 (250)	170 (2425)	990	..	33 (475)	178 (2525)	940	..	33 (475)	213 (3025)	970	..
	30	19 (275)	116 (1650)	860	45	30 (425)	167 (2375)	890	45	54 (775)	165 (2350)	800	52	51 (725)	178 (2525)	800	50
	60	35 (500)	62 (875)	710	..	35 (500)	137 (1950)	920	..	72 (1025)	121 (1725)	700	..	67 (950)	167 (2375)	750	..
10	10	28 (400)	172 (2450)	950	..	32 (450)	132 (1875)	860	..	33 (475)	197 (2800)	960	..	40 (575)	227 (3225)	960	..
	30	32 (450)	142 (2025)	830	45	46 (650)	163 (2325)	800	48	53 (750)	174 (2475)	800	52	70 (1000)	178 (2525)	760	53
	60	35 (500)	156 (2225)	840	..	46 (650)	132 (1875)	740	..	56 (800)	98 (1400)	690	..	70 (1000)	179 (2550)	770	..
20	10	30 (425)	172 (2450)	980	..	33 (475)	183 (2600)	960	..	40 (575)	181 (2575)	970	..	40 (575)	220 (3125)	960	..
	30	39 (550)	146 (2075)	900	48	49 (700)	139 (1975)	800	50	56 (800)	132 (1875)	740	53	62 (875)	192 (2725)	830	55
	60	37 (525)	148 (2100)	900	..	46 (650)	123 (1750)	700	..	54 (775)	158 (2250)	810	..	56 (800)	181 (2575)	830	..

[a] At 600 per cent elongation. [b] At break. [c] Shore Durometer, type A.

TABLE VI. EFFECT OF LITHARGE AND MAGNESIA ON STRESS-STRAIN PROPERTIES OF NEOPRENE

PbO/100 Parts Neoprene	Cure at 153°C.	0.0 Part MgO				2.0 Parts MgO			5.0 Parts MgO				10 Parts MgO				20 Parts MgO			
		Stress[a]	Tensile strength	Elongation[b]	Hardness[c]	Stress[a]	Tensile strength	Elongation[b]	Stress[a]	Tensile strength	Elongation[b]	Hardness[c]	Stress[a]	Tensile strength	Elongation[b]	Hardness[c]	Stress[a]	Tensile strength	Elongation[b]	Hardness[c]
Parts	*Min.*	*Kg./sq. cm.*	*(lb./sq. in.)*	%		*Kg./sq. cm.*	*(lb./sq. in.)*	%	*Kg./sq. cm.*	*(lb./sq. in.)*	%		*Kg./sq. cm.*	*(lb./sq. in.)*	%		*Kg./sq. cm.*	*(lb./sq. in.)*	%	
0.0	10	2 (25)	37 (525)	1200	..	21 (300)	185 (2625)	1075	49 (700)	223 (3175)	930	..	60 (850)	207 (2950)	900	..	86 (1225)	267 (3800)	960	..
	30	4 (50)	65 (925)	1080	37	70 (1000)	132 (1875)	700	95 (1350)	181 (2575)	720	56	86 (1225)	197 (2800)	820	57	97 (1375)	264 (3750)	860	60
	60	9 (125)	40 (575)	860	..	......	......	..	116 (1650)	153 (2175)	640	..	90 (1275)	181 (2575)	780	..	114 (1625)	206 (2925)	780	..
5.0	10	25 (350)	118 (1675)	950	..	16 (225)	165 (2350)	1140	44 (625)	218 (3100)	1000	..	58 (825)	232 (3300)	1000	..	77 (1100)	258 (3675)	970	..
	30	19 (275)	116 (1650)	860	45	42 (600)	163 (2325)	860	76 (1075)	225 (3200)	800	58	90 (1275)	250 (3550)	860	60	104 (1475)	283 (4025)	860	61
	60	35 (500)	62 (875)	710	..	63 (900)	125 (1775)	720	83 (1175)	211 (3000)	780	..	104 (1475)	216 (3075)	760	..	111 (1575)	253 (3600)	820	..
10	10	28 (400)	172 (2450)	950	..	21 (300)	181 (2575)	1120	51 (725)	232 (3300)	970	..	62 (875)	237 (3375)	960	..	90 (1275)	274 (3900)	980	..
	30	32 (450)	142 (2025)	830	45	49 (700)	218 (3100)	880	72 (1025)	230 (3275)	850	55	90 (1275)	236 (3350)	820	60	111 (1575)	286 (4075)	860	65
	60	35 (500)	156 (2225)	840	..	53 (750)	163 (2325)	770	72 (1025)	227 (3225)	840	..	84 (1200)	206 (2925)	800	..	116 (1650)	258 (3675)	850	..
20	10	30 (425)	172 (2450)	980	..	26 (375)	189 (2675)	1180	47 (675)	229 (3250)	990	..	56 (800)	223 (3175)	950	..	70 (1000)	248 (3525)	980	..
	30	39 (550)	146 (2075)	900	48	54 (775)	207 (2950)	880	63 (900)	237 (3375)	900	57	72 (1025)	237 (3375)	900	58	86 (1225)	258 (3675)	900	60
	60	37 (525)	148 (2100)	900	..	62 (875)	158 (2250)	820	65 (925)	236 (3350)	890	..	72 (1025)	216 (3075)	880	..	92 (1300)	253 (3600)	900	..

[a] At 600 per cent elongation. [b] At break. [c] Shore Durometer, type A.

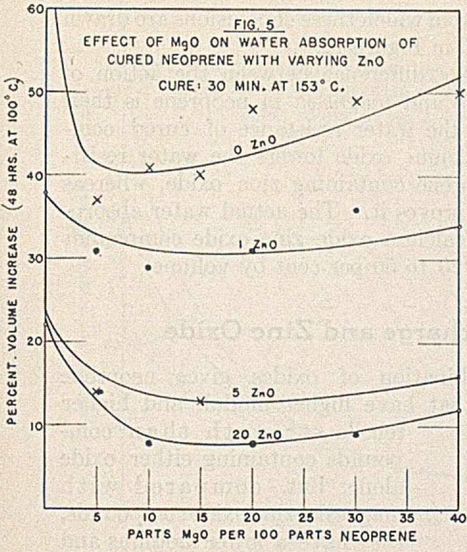


FIG. 5

EFFECT OF MgO ON WATER ABSORPTION OF CURED NEOPRENE WITH VARYING ZnO

CURE: 30 MIN. AT 153° C.

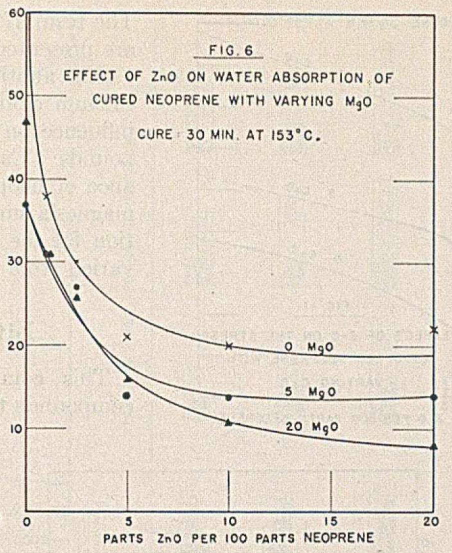


FIG. 6

EFFECT OF ZnO ON WATER ABSORPTION OF CURED NEOPRENE WITH VARYING MgO

CURE: 30 MIN. AT 153° C.

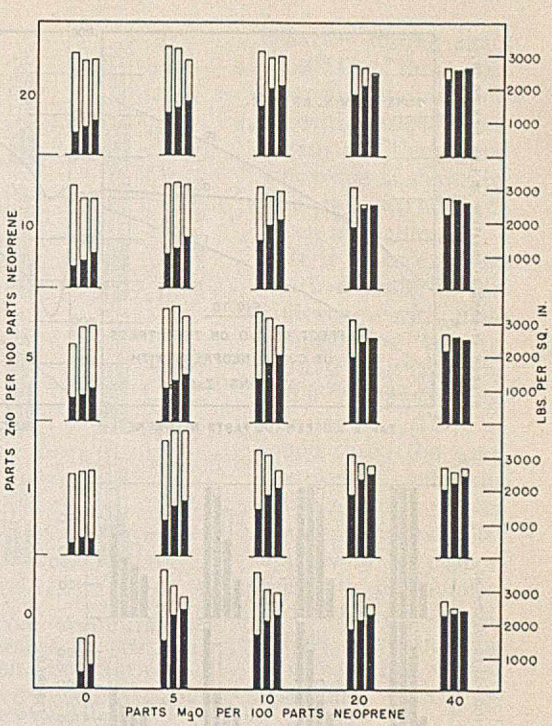


FIGURE 7. EFFECT OF VARYING AMOUNTS OF MAGNESIA AND ZINC OXIDE ON STRESS AT 600 PER CENT ELONGATION AND TENSILE STRENGTH OF CURED NEOPRENE CONTAINING 25 PARTS OF P-33 CARBON BLACK

Cures, 10, 30, and 60 minutes at 153° C.; stress shown by solid portions, tensile strength by whole column.

The stability of compounded, uncured neoprene containing P-33 carbon black, FF wood rosin, sulfur, phenyl-β-naphthylamine and varying amounts of magnesia and zinc oxide is shown in Figure 8. Again the use of magnesia strongly inhibits the premature curing of compounds containing zinc oxide, particularly in amounts of 10 to 20 parts. Similarly, as in the case of the gum stock, an increase of the magnesia to 40 parts makes the compounds less stable than when 20 parts are used, and a stock containing 10 parts of zinc oxide is as well stabilized by adding 10 to 20 parts of magnesia as one containing 1.0 part of zinc oxide.

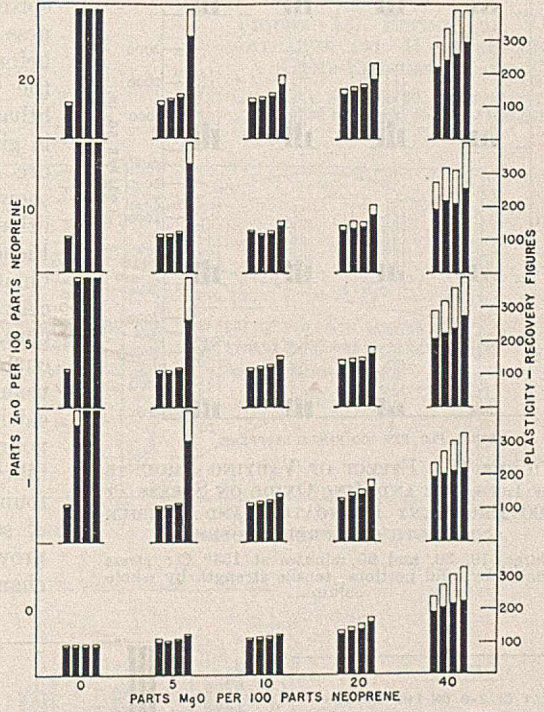


FIGURE 8. EFFECT OF VARYING AMOUNTS OF MAGNESIA AND ZINC OXIDE ON THE STABILITY OF UNCURED NEOPRENE CONTAINING 25 PARTS P-33 CARBON BLACK

Aging periods, 0, 24, 48, and 96 hours at 50° C.; plasticity shown by solid portions, recovery by unshaded portion.

The change in the water resistance of the neoprene compounds, loaded with 25 parts of P-33 carbon black, with varying amounts of magnesia and zinc oxide, parallels the change in the water resistance of the neoprene gum compounds for similar variations in the quantities of magnesia and zinc oxide.

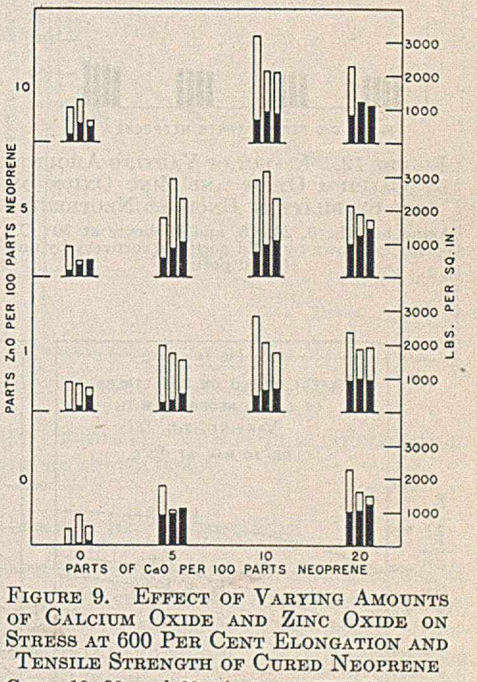
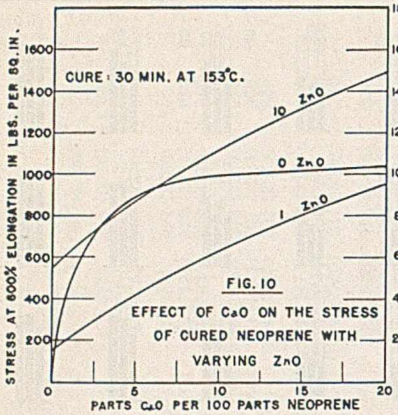


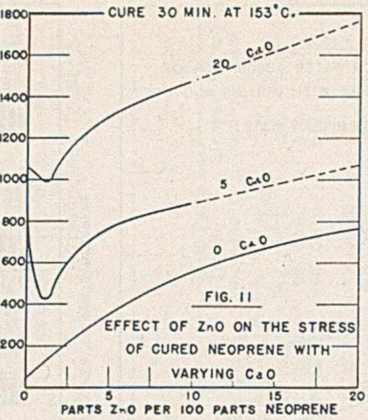
FIGURE 9. EFFECT OF VARYING AMOUNTS OF CALCIUM OXIDE AND ZINC OXIDE ON STRESS AT 600 PER CENT ELONGATION AND TENSILE STRENGTH OF CURED NEOPRENE

Cures, 10, 30, and 60 minutes at 153° C.; stress shown by solid portions, tensile strength by whole column.

Calcium Oxide and Zinc Oxide

The influence of various combinations of calcium oxide and zinc oxide on the properties of neoprene was determined in the same manner as that employed with magnesia and zinc oxide. The summary of the stress-strain properties given in Figure 9 shows that the calcium oxide–zinc oxide compounds are much inferior to the corresponding compounds in which the calcium oxide is replaced by magnesia. The tensile strength of the compounds containing calcium oxide is considerably lower than that of the compounds prepared with magnesia, and the percentage elongation at break decreases more rapidly as the curing time is increased. However, there is a similarity between the two series in the lowering of the modulus of compounds containing the alkaline earth oxides by the addition of small amounts of zinc oxide. The effect of zinc oxide in combination with calcium oxide is better shown by the curves of Figures 10 and 11.





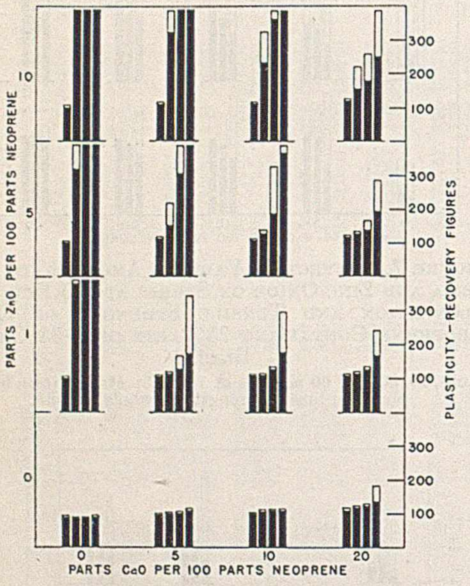


Figure 12. Effect of Varying Amounts of Calcium Oxide and Zinc Oxide on the Stability of Uncured Neoprene

Aging periods, 0, 24, 48, and 96 hours at 50° C.; plasticity shown by solid portions; recovery by unshaded portion.

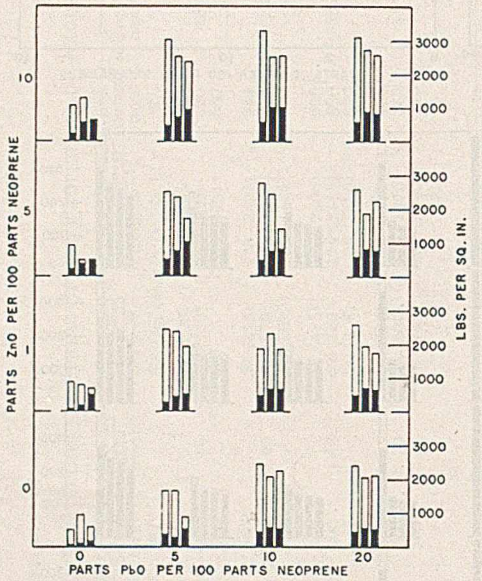
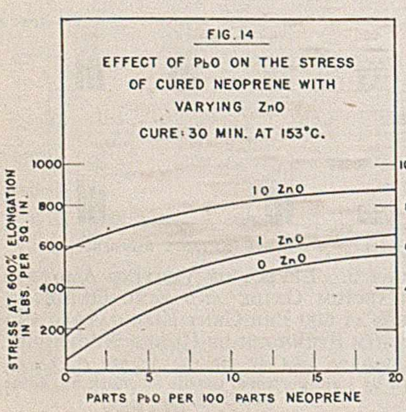
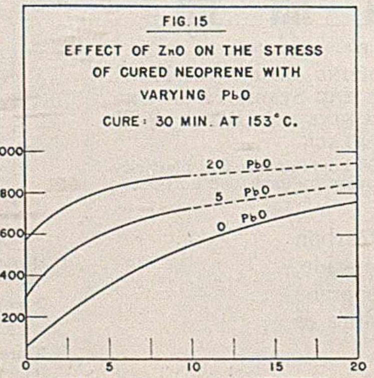


Figure 13. Effect of Varying Amounts of Litharge and Zinc Oxide on Stress at 600 Per Cent Elongation and Tensile Strength of Cured Neoprene

Cures, 10, 30, and 60 minutes at 153° C.; stress shown by solid portions, tensile strength by whole column.





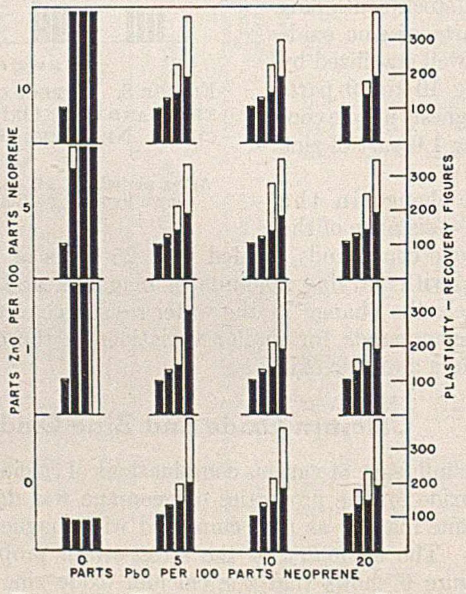


Figure 16. Effect of Varying Amounts of Litharge and Zinc Oxide on the Stability of Uncured Neoprene

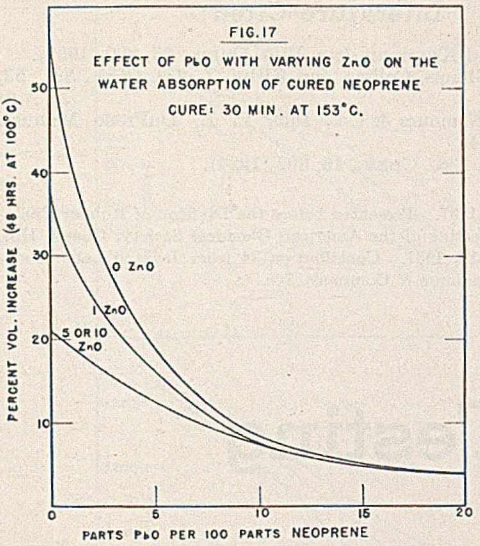
Aging periods, 0, 24, 48, and 96 hours at 50° C.; plasticity shown by solid portions, recovery by unshaded portion.

Another pronounced difference between the calcium oxide and magnesia compounds containing zinc oxide is found in the stability of the uncured compounds. Calcium oxide itself does not seriously impair the stability of neoprene and improves the stability of neoprene containing zinc oxide, but it is far less effective in this respect than magnesia. No quantity of calcium oxide has been found to stabilize neoprene containing zinc oxide sufficiently for general use. The results from which these conclusions are drawn are presented in Figure 12.

Still another difference between the action of calcium oxide and magnesia in neoprene is their influence on the water resistance of cured compounds. Calcium oxide lowers the water resistance of neoprene containing zinc oxide, whereas magnesia improves it. The actual water absorption for the calcium oxide–zinc oxide compounds varied from 20 to 50 per cent by volume.

Litharge and Zinc Oxide

This combination of oxides gives neoprene compounds that have higher moduli and higher tensile strength than compounds containing either oxide alone, but, compared with magnesia–zinc oxide compounds, they have a lower modulus and lower tensile strength with correspondingly lowered hardness and they are less stable before curing. A summary of the stress-strain properties of litharge–zinc oxide compounds is given in Table V and Figure 13. Figures 14 and 15 show the relative effects of litharge (sublimed, Eagle-Picher) and zinc oxide, in combination, on the stress at 600 per cent elongation for the 30-minute cure. The stability of the uncured compounds, while better than that of the corresponding calcium oxide–zinc oxide compounds, is poor. This poor stability, in part at least, has been found to be due to the presence of sulfur, and its omission improves the stability. The change in plasticity and in the



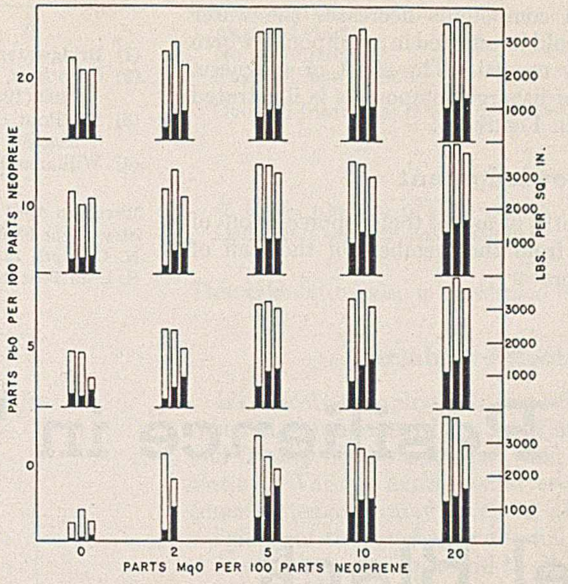
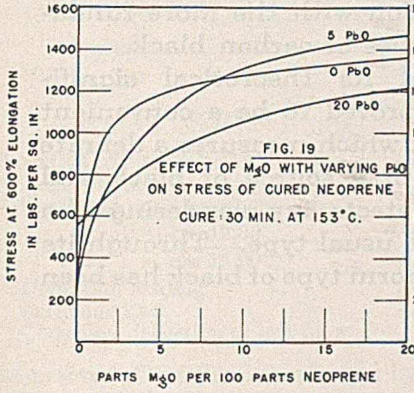


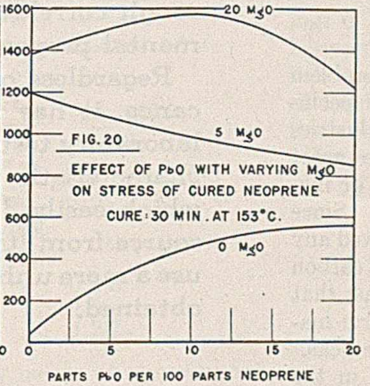
Figure 18. Effect of Varying Amounts of Litharge and Magnesia on Stress at 600 Per Cent Elongation and Tensile Strength

Cures, 10, 30, and 60 minutes at 153° C.; stress shown by solid portions, tensile strength by whole column.

recovery during aging at 50° C. of these compounds containing sulfur with various quantities of litharge and zinc oxide is shown by the measurements given in Figure 16.

It is to be expected that a material like litharge, with little affinity for water, would improve the water resistance of neoprene. This is found to be the case. Compounds containing litharge alone possess a water resistance that appears to be proportional to the amount of litharge used. Added zinc oxide improves the water resistance of litharge compounds slightly (Figure 17). This is quite different from the action of magnesia shown below.





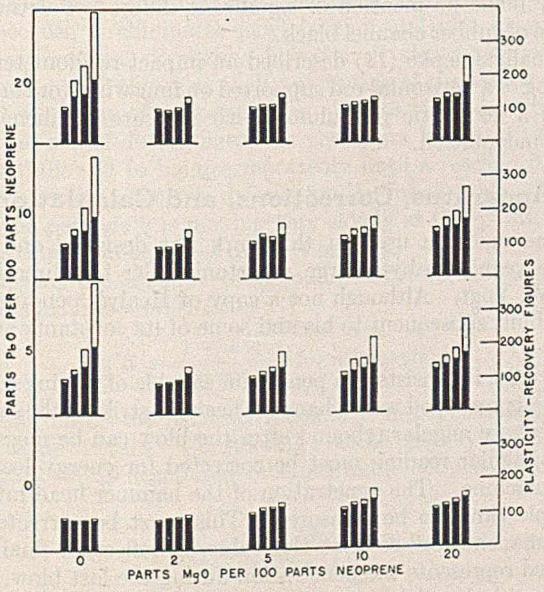
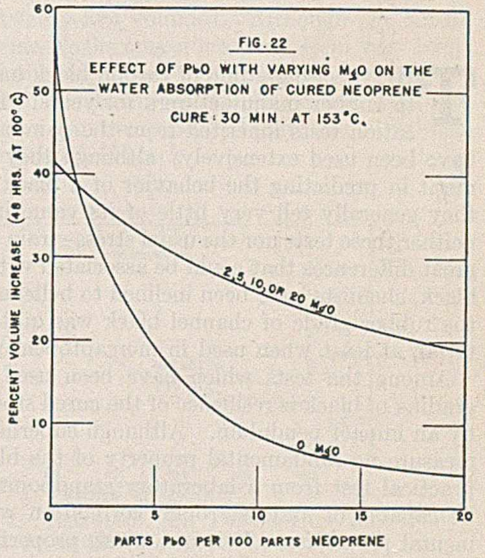


Figure 21. Effect of Varying Amounts of Litharge and Magnesia on the Stability of Uncured Neoprene Containing 25 Parts P-33 Carbon Black

Aging periods, 0, 24, 48, and 96 hours at 50° C.; plasticity shown by solid portions, recovery by unshaded portion.



Litharge and Magnesia

In order to raise the moduli and tensile strengths and to improve the stability of compounds containing litharge, magnesia may be added. A summary of the actual stress-strain data obtained for compounds containing varying amounts of litharge and magnesia is given in Table VI and Figure 18; and the relative effects of these oxides on the stress at 600 per cent elongation for the 30-minute cure are illustrated by Figures 19 and 20. Litharge, an accelerator of the curing of neoprene, retards the cure of neoprene compounds containing magnesia in a manner that may be related to that in which zinc oxide retards the cure of neoprene compounded with magnesia or with calcium oxide. The stabilizing action of magnesia in unstable compounds containing litharge is shown by the plasticity data given in Figure 21.

The magnesia which may be used in litharge compounds to improve the stability of the uncured stock and to stiffen the moduli of the cured compounds decreases the water resistance. Magnesia should be omitted in a compound where a high water resistance is needed. The effect of magnesia on the water absorption of litharge compounds is illustrated by the results presented in Figure 22.

Acknowledgment

The writers express with pleasure their appreciation of the coöperation received from the members of the staff of the du Pont Rubber Laboratory.

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Impact Resilience in Testing Channel Black

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An old test, impact resilience, has been given a new application, that of grading carbon black. Although an empirical property itself, it is capable of at least rough correlation with the more fundamental properties of carbon black.

Regardless of its theoretical significance, it has proved to be a convenient laboratory test which measures a definite characteristic of a source of black and which easily detects any wandering of a source from its usual type. Through its use a more uniform type of black has been obtained.

THE precise grading of carbon black has been a problem to rubber manufacturers for years. Empirical specification tests inherited from the paint and ink industries have been used extensively; although they may have great merit in predicting the behavior of a black in paint or ink, they generally tell very little of its value in rubber. Since neither these tests nor the usual stress-strain data showed any great differences that could be associated with type of carbon black, chemists have been inclined to believe in the past that the rubber grade of channel black was quite a uniform material, at least when used in mercaptobenzothiazole stocks.

Among the tests which have been used recently in the grading of black is resilience of the cured stock as determined by an impact pendulum. Although superficially it seems to measure no fundamental property of the black, it is a very practical test from a laboratory standpoint and appears to be capable of at least rough correlation with more fundamental properties. It is not a new property; the fact that it is influenced by carbon black is not new; but its application to the separation of blacks within the range of rubber channel black is new, and this phase will be discussed here.

History

As the term implies, impact resilience involves rapid deformation and forces which are largely compressive. More specifically, it is a measure of the amount of energy which can be returned by the rubber after a rapid blow. There have been several publications on the subject.

Memmler (*13*) described several falling-ball methods and a pendulum hammer for determining resilience, all of which dates back to before 1920.

Healy (*9*) referred to a pendulum impact tester that is capable of measuring both the resilience and the penetration under impact. He reported maximum resilience in the neighborhood of 212° F. (100° C.) and its increase after repeated impacts. He illustrated the deadness and hardness brought about by carbon black.

Goodwin and Park (*8*) applied the present pendulum to the evaluation of carbon black over a broad range extending all the way from the soft blacks to the high-color blacks. They made no mention of significant differences within the range of rubber channel black.

Finally Luepke (*12*) described an impact resiliometer consisting of a horizontal rod supported on four wires (or cords) to form a geometric pendulum which measures resilience but not indentation.

Apparatus, Corrections, and Calculations

The machine used in this work was designed and built some years ago by George Albertoni under the direction of W. W. Vogt. Although not a copy of Healy's pendulum, it was built subsequent to his and some of its constants are the same (*1*).

Briefly, it consists of a pendulum capable of storing energy, which is equipped with a hammer head for striking the sample, and whose angular rebound after the blow can be measured. The angular reading must be corrected for energy losses in the machine. The penetration of the hammer head into the sample can also be measured. This must be corrected for "permanent set" so that the value of deflection finally reported represents the penetration during the last blow.

Considering that when the pendulum is at rest it contains a certain amount of potential energy which depends solely upon the angle made with the vertical, α, and defining per cent rebound (*RB*) as the percentage of striking energy that is returned to the sample, it can easily be shown that:

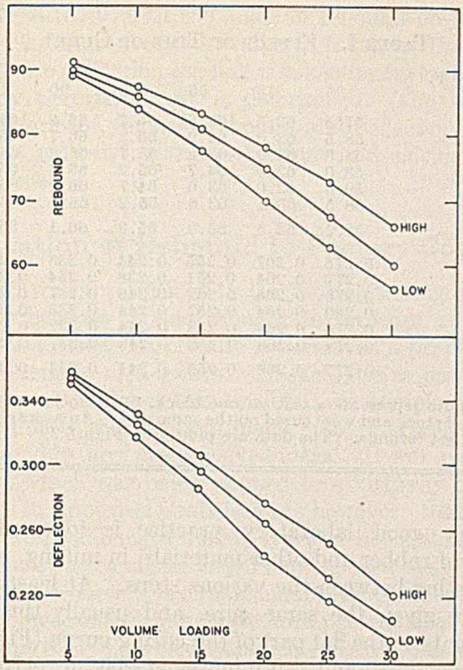

Figure 1. Per Cent Rebound and Inches of Deflection *vs.* Black Loading in Volumes per 100 Volumes of Rubber

Three types of black were used.

$$\% RB = \frac{1 - \cos \alpha}{1 - \cos \alpha_0} \times 100$$

Sample Calculation 1.

Angle of start	15.00°
Corrected angle of rebound, α	12.05°

$$\% RB = \frac{1 - \cos 12.05°}{1 - \cos 15.00°} \times 100 = \frac{0.02209}{0.03407} \times 100 = 64.8\%$$

Deflection reading	0.261
Permanent set	0.006
Corrected deflection of last blow	0.255

In practice all of this is performed by means of convenient tables.

Another method of using the pendulum is worthy of mention because it eliminates pawl friction and also magnifies small differences. Probably, however, it also magnifies errors due to such things as faulty mounting of the sample and lateral vibration of the pendulum. The pawls are tied back, and after a half-dozen blows the pendulum is released from 15° and allowed to bounce repeatedly until a reading is obtained between some two definite limits—for example, 4° and 5°. The pendulum is moving very slowly at this point, and the maximum value is not difficult to read.

Following the same line of reasoning as before, let the over-all fractional rebound (FR) be:

$$FR = \frac{1 - \cos \alpha}{1 - \cos 15°} \text{ for } n \text{ impacts}$$

Within limits the per cent rebound is nearly independent of the angle of start. Considering it to be entirely independent, the over-all fractional rebound for n bounces is given by:

$$FR = \left(\frac{\% RB}{100}\right)^n$$

Hence, by this method the per cent rebound is found by taking the nth root of the over-all fractional rebound and multiplying by 100. Since the relation is not rigorously exact, it is advisable always to take the final reading between the same narrow limits (e. g., between 4° and 5°).

Sample Calculation 2.

Angle of start	15.00°
No. of impacts	6
Angle of last rebound, α	4.1°

$$\text{Over-all fractional rebound, } FR = \frac{1 - \cos 4.1°}{1 - \cos 15°} = \frac{0.00256}{0.03407} = 0.0744$$

$$\% RB = 100 \sqrt[6]{0.0744} = 64.9\%$$

Deflection same as calculation 1

This calculation also is performed easily by the use of tables.

Variables Affecting Test

Like most other physical tests which are applied to rubber, rebound is influenced by a great many factors such as type and history of raw materials, and conditions of curing and testing. Various experimental errors, some accidental and some systematic, may creep in at any point between the weighing of the batch and the final recording of the result. A few of these variables will be discussed.

Figure 1 shows three curves of per cent rebound *vs.* black loading. All three curves tend to intercept the zero loading axis at 92 to 93 per cent rebound, which is the value usually obtained with a pure gum stock. They proceed downward to the right, spreading apart at the higher loadings. Hence, for accurate separation of blacks it is advisable to use loadings of at least twenty-five volumes. Although the spread between the extreme blacks may not at first seem very large, it is easily seen from the curves that if twenty-five volumes of the high-rebound black will produce a certain deadness, that same deadness can be produced with only eighteen volumes of the low-rebound black.

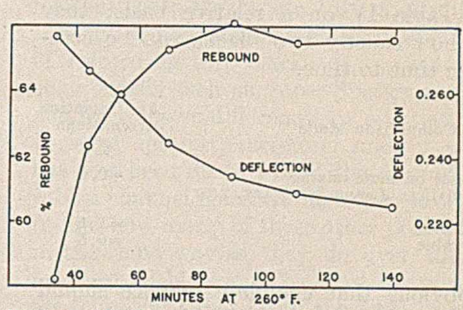

Figure 2. Rebound and Deflection *vs.* Time of Cure (Data of Table I)

Rebound is comparatively insensitive to state of cure (Figure 2) after the condition of undercure has been passed. But this is not true of deflection. Insensitivity to state of cure is a distinct advantage because it means that no error is introduced when comparing fast- and slow-curing carbon blacks.

On the other hand, rebound is quite sensitive to the temperature of testing (Figure 3). For that reason it has been found essential to condition samples in a constant-temperature bath for some time before testing.

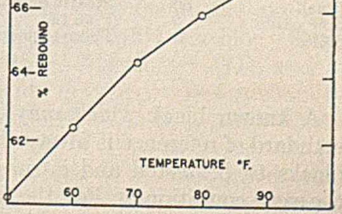

Figure 3. Rebound *vs.* Temperature

As a sample is struck repeatedly, it becomes more resilient. The biggest change is between the first and second blows, and after five or six blows it levels off to a fairly constant value. This is not due to the heating of the sample as might be supposed at first but rather is analogous to the change from the first to the *n*th hysteresis loop of a stress-strain curve. In order to eliminate this as a source of error, the practice has been to strike the block until the reading becomes constant.

After precautions have been taken either to eliminate these sources of error or to keep them constant, there is still an irregular day-to-day variation. It is of such magnitude that it is impractical to use the absolute value of per cent rebound as a means of factory control. In this respect the rebound pendulum is not unique, for many other rubber tests have met with the same difficulty. On the other hand, samples of black which have passed through the laboratory as a group should all be subject to the same systematic errors, which would not affect the test when viewed in a relative sense. For want of a better method, we have dealt in terms of "per cent standard;" that is, assigning a value of 100 to the standard, ratings are found for the other samples by direct proportion. This eliminates the systematic error but has the disadvantage that any chance error in the standard is automatically transferred to the relative ratings of all the other samples.

As an example of the errors of testing, the figures of the tables were subjected to a rough analysis. In Table I each figure represents an individual test, and an analysis of this table illustrates the duplicability of tests of the same mixing. In Tables II and III each figure represents an average of several tests. An analysis of these data, therefore, illustrates the exactness with which the absolute value of rebound can be duplicated from mixing to mixing when sufficient tests are run to give a good average. Finally, the same data are given in Table IV on a relative basis; they illustrate how exactly two blacks can be compared from time to time.

Comparison Made	Av. Deviation from Mean %
Duplicate tests on same mixing	±0.6
Duplicate mixings of same black (av. 2 to 4 tests):	
Absolute value	±1.1
Relative value	±0.6

It is obvious that complete reliance should not be placed in a test on a single block, and that the relative value is more reliable than the absolute.

Recommended Procedure for Black Testing

Giving due consideration to the variables dsscussed, the following procedure has been worked out as being good practice:

In order to obtain differences between blacks which are of sufficient size to measure accurately, the test formula has been:

Rubber	100	Mercaptobenzothiazole	1
Black	50	Stearic acid	4
Zinc oxide	5	Pine tar	5
Sulfur	3	Phenyl-β-naphthylamine	1
			169

A known black which may be considered a standard of reference is always included with the blacks to be tested and is subjected to exactly the same conditions. For the sake of both efficiency and accuracy the number of unknown samples is usually held between three and seven.

TABLE I. EFFECT OF TIME OF CURE[a]

Min. at 260° F. (126.7° C.)	35	45	55	70	90	100	140
% rebound	57.5	62.5	63.6	65.7	65.2	64.2	65.7
	58.5	62.0	64.2	65.2	66.7	65.7	65.7
	58.5	62.0	63.6	65.7	66.2	66.2	65.2
	58.0	62.0	64.7	65.2	66.2	65.2	65.7
	59.0	62.0	63.6	64.7	66.2	66.2	65.2
	58.5	63.1	63.6	65.2	66.2	65.7	66.2
Av.	58.2	62.3	63.9	65.3	66.1	65.5	65.6
Deflection	0.275	0.267	0.255	0.244	0.233	0.226	0.225
	0.277	0.264	0.261	0.238	0.234	0.230	0.224
	0.276	0.266	0.262	0.246	0.237	0.230	0.224
	0.280	0.264	0.257	0.244	0.233	0.227	0.223
	0.276	0.264	0.258	0.244	0.232	0.232	0.227
	0.278	0.268	0.258	0.245	0.237	0.231	0.226
Av.	0.277	0.266	0.259	0.244	0.234	0.229	0.225

[a] Each figure represents a test on one block. All blocks were from the same batch of stock and were cured on the same day. An average black was used in the test formula. The data are plotted in Figure 2.

Customary good laboratory practice is followed in the selection of rubber and other materials, in milling, in curing, and in resting between the various steps. At least two test blocks are given the same cure, and usually this is done at two points on the flat part of the curing curve (Figure 2)—for example, at 85 and 140 minutes at 260° F. (126.7° C.).

Just prior to test, the blocks are conditioned for 2 hours in water at 82° F. (27.8° C.). They are removed singly from the water, dried, and mounted in the test piece holder. This must be done carefully to avoid distortion. The pendulum is released at least six times from an angle of 15°, and then

TABLE II. REPEAT TESTS ON SAME SERIES OF BLACKS

	Black A	Black B	Black C	Black D	Black E	Black F	No. of Tests
				Set I[a]			
% rebound:							
85 min. at 260° F.	65.2	61.8	67.3	69.9	65.7	68.5	2
140 min. at 260° F.	65.0	61.5	67.1	69.6	65.7	68.8	2
Deflection:							
85 min. at 260° F.	0.238	0.230	0.244	0.254	0.239	0.253	2
140 min. at 260° F.	0.227	0.218	0.232	0.235	0.231	0.235	2
Nigrometer reading:[b]							
Red	82.4	81.8	82.1	86.3	83.3	84.8	2
Green	85.3	84.6	85.0	89.0	86.0	87.7	2
% net volatile	6.8	4.7	5.9	5.4	4.8	6.4	2
% DPG adsorption[c]	50.8	42.5	38.4	24.9	31.1	53.0	2
				Set II			
% rebound:							
85 min. at 260° F.	66.6	...	...	70.8	66.9	70.0	4
140 min. at 260° F.	66.3	...	...	70.6	66.5	70.7	4
Deflection:							
85 min. at 260° F.	0.246	...	...	0.251	0.242	0.256	4
140 min. at 260° F.	0.229	...	...	0.237	0.228	0.242	4
Nigrometer reading:							
Red	82.1	...	...	85.8	82.8	83.9	2
Green	85.2	...	...	88.8	85.8	87.0	2
% net volatile	5.4	...	...	4.6	4.0	6.4	2
% DPG adsorption	54.4	...	...	25.4	33.4	53.4	2
				Set III			
% rebound:							
85 min. at 260° F.	65.5	...	65.7	68.0	...	68.2	2
140 min. at 260° F.	64.5	...	65.0	69.9	...	69.9	2
Deflection:							
85 min. at 260° F.	0.245	...	0.244	0.253	...	0.254	2
140 min. at 260° F.	0.226	...	0.230	0.241	...	0.239	2
Nigrometer reading:							
Red	81.8	...	83.9	86.7	...	84.5	2
Green	84.8	...	86.8	90.3	...	87.5	2
% net volatile	6.8	...	6.0	4.8	...	6.6	2
% DPG adsorption	53.4	...	36.5	25.3	...	48.8	2
				Set IV			
% rebound:							
85 min. at 260° F.	65.8	63.7	66.6	68.9	...	...	4
140 min. at 260° F.	65.2	63.7	66.3	69.6	...	...	4
Deflection:							
85 min. at 260° F.	0.234	0.230	0.242	0.249	...	...	4
140 min. at 260° F.	0.224	0.215	0.226	0.233	...	...	4
K_3[d]	462	458	412	407	...	...	9

[a] Each set of data is entirely comparable within itself; that is, the processing of the stocks and the running of the tests were so carried out that the relative comparison of each black with black A is reliable.

[b] Nigrometer readings according to Johnson (*11*), using red and green filters.

[c] DPG (diphenylguanidine) adsorption according to Amon and Estelow (*2*).

[d] K_3 determined on a Williams plastometer.

released repeatedly until the angle of rebound no longer increases. The most frequent value is taken as the angular reading. The deflection reading is taken for several impacts, and finally permanent set is determined. The results in their final form of per cent rebound and deflection are read from tables embodying the corrections and calculations already outlined.

Application of Rebound to Factory Control

Rebound was applied first to the routine testing of carbon black, not because it was thought to measure a desirable property of a black but because it measured a property that was characteristic of a source. In fact, it was used at first merely as an additional test to obtain as complete data as possible on daily shipments of black. Its interpretation was not hampered by any preconceived ideas. It was considered a new test which was being applied to a virtually unknown material. It appeared statistically, however, that certain sources were producing different types of black than others. Figure 4 shows a few distribution curves, each one representing a source. Source *Y* is of particular interest since its curve has two humps, one forming a definite peak at about 98 and one at about 89. This clearly indicates two producing units so far apart in type of product that their distribution curves are almost entirely separated. Curve *Z* is a recent curve taken on a typical source. It has a higher peak than the others and is spread between narrower limits. There is no question but that it represents a far greater degree of uniformity than the others.

TABLE II. (*Continued*)

	Black A	Black B	Black C	Blank D	Black E	Black F	No. of Tests
				Set V			
% rebound:							
85 min. at 260° F.	66.5	63.2	68.7	70.2	...	...	4
140 min. at 260° F.	65.1	63.1	67.1	69.6	...	...	4
Deflection:							
85 min. at 260° F.	0.236	0.228	0.239	0.245	...	...	4
140 min. at 260° F.	0.223	0.220	0.227	0.233	...	...	4
K_3	470	490	457	415	...	...	12
Nigrometer reading:							
Red	82.8	80.5	83.4	85.0	...	...	1
Green	84.0	82.5	85.8	88.0	...	...	1
% net volatile	6.1	7.1	6.2	4.9	...	...	1
% DPG adsorption	57.1	52.6	42.9	29.1	...	...	1
				Set VI			
% rebound:							
85 min. at 260° F.	67.3	63.5	68.1	71.0	...	...	4
140 min. at 260° F.	66.1	64.7	67.6	71.0	...	...	4
Deflection:							
85 min. at 260° F.	0.236	0.230	0.235	0.247	...	...	4
140 min. at 260° F.	0.222	0.222	0.225	0.233	...	...	4
K_3	472	488	469	436	...	...	12
Nigrometer reading:							
Red	81.2	81.0	84.4	86.2	...	...	1
Green	83.2	83.3	86.4	88.6	...	...	1
% net volatile	6.0	4.1	5.7	4.4	...	...	1
% DPG adsorption	55.1	42.1	38.1	24.7	...	...	1
				Set VII			
% rebound:							
85 min. at 260° F.	65.6	...	...	...	65.1	...	4
140 min. at 260° F.	64.0	...	...	...	65.0	...	4
Deflection:							
85 min. at 260° F.	0.232	...	...	...	0.234	...	4
140 min. at 260° F.	0.219	...	...	...	0.222	...	4
Nigrometer reading:							
Red	82.0	...	...	...	82.0	...	1
Green	84.3	...	...	...	84.5	...	1
% net volatile	6.5	...	...	...	4.1	...	1
% DPG adsorption	53.5	...	...	...	35.0	...	1
				Set VIII			
% rebound:							
85 min. at 260° F.	65.8	64.2	67.8	...	...	69.2	7
140 min. at 260° F.	66.2	63.4	67.8	...	...	68.3	7
Deflection:							
85 min. at 260° F.	0.239	0.233	0.240	...	...	0.250	7
140 min. at 260° F.	0.229	0.222	0.226	...	...	0.233	7
Nigrometer reading:							
Red	83.0	81.6	83.5	...	...	84.0	1
Green	85.0	84.0	85.8	...	...	86.2	1
% net volatile	5.1	4.2	4.6	...	...	6.0	1
% DPG adsorption	50.4	38.3	33.9	...	...	46.8	1

The interpretation of the test came after its use as a routine test. Because of its practical nature it was comparatively easy to use it in selecting type blacks which were then subjected to other tests such as those described below.

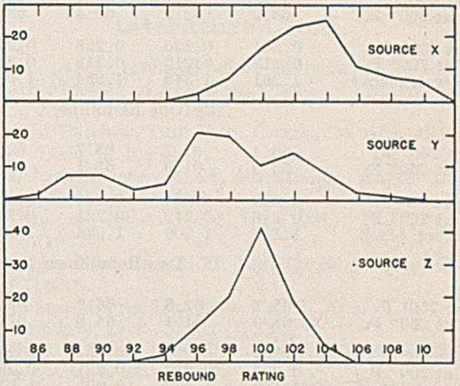

FIGURE 4. FREQUENCY IN PER CENT OF SAMPLES FALLING WITHIN A 2 PER CENT RANGE OF REBOUND RATING, PLOTTED AT THE MIDPOINT OF THAT RANGE

Meaning of Rebound as Applied to Black

For years certain blacks—for example, Thermax—have been classed as soft blacks, and various investigators have reported that such soft blacks are of large particle size, gray, relatively nonadsorptive, and capable of incorporation to very high loadings, and that they produce soft uncured stocks and resilient cured stocks, etc. (*6, 7, 8, 11, 14*).

Many papers have been based upon the idea of comparing soft blacks at one extreme with color blacks such as Super Spectra at the other, and have shown differences by a variety of tests. It is of interest, therefore, since a separation has now been made within the normal range of rubber channel black through the use of rebound, to find how many of these other properties vary in the same way as they do over the broader range of all blacks. The most instructive data are found in Table IV in the form of ratings in which black A has been assigned an arbitrary value of 100.

Plasticity of the uncured tread stock as measured by the Williams plastometer is definitely influenced by type of black. Although the correlation of rebound with some properties is doubtful, as will be shown below, no exception has yet been found in the case of plasticity. Low rebound and toughness go hand in hand (Figure 5).

Blackness of the black, as viewed by reflected light either in the dry state or when dispersed in oil, has been found to be related to rebound. It is a rather difficult property to measure, but, considering the number of tests made, the average ratings of Table IV are probably reliable. They were obtained with a Nigrometer (*11*), and a high figure represents grayness. It seems obvious that a low-rebound black is a black black (Figure 5).

Volatile matter which is a measure of the oxygen content of the black (*10, 18*) seems to be entirely unrelated to rebound. This is not difficult to believe since there is no rea-

TABLE III. EFFECT OF REMILLING[a]

	Black A	Black B	Black C	Black F	No. of Tests
			Regular Milling		
% rebound:					
85 min. at 260° F.	65.1	62.4	65.7	68.9	2
140 min. at 260° F.	63.2	62.2	65.4	68.4	2
Deflection:					
85 min. at 260° F.	0.231	0.220	0.228	0.240	2
140 min. at 260° F.	0.218	0.212	0.218	0.231	2
Vol. rubber/vol. black[b]	1.261	1.345	1.234	1.080	3
			One Remilling		
% rebound:					
85 min. at 260° F.	65.4	61.7	65.7	69.2	2
140 min. at 260° F.	63.0	61.9	65.1	68.9	2
Deflection:					
85 min. at 260° F.	0.232	0.224	0.233	0.241	2
140 min. at 260° F.	0.218	0.212	0.221	0.235	2
Vol. rubber/vol. black	1.176	1.200	1.036	1.017	3
			Two Remillings		
% rebound:					
85 min. at 260° F.	65.1	62.8	66.0	68.1	2
140 min. at 260° F.	63.0	61.4	64.8	67.6	2
Deflection:					
85 min. at 260° F.	0.234	0.227	0.234	0.248	2
140 min. at 260° F.	0.221	0.217	0.221	0.230	2
Vol. rubber/vol. black	1.159	1.198	0.992	1.012	3
			Three Remillings		
% rebound:					
85 min. at 260° F.	65.4	61.9	65.4	67.8	2
140 min. at 260° F.	63.7	60.6	63.7	68.1	2
Deflection:					
85 min. at 260° F.	0.233	0.226	0.233	0.253	2
140 min. at 260° F.	0.222	0.212	0.220	0.233	2
Vol. rubber/vol. black	1.139	1.195	0.967	0.994	3
			Four Remillings		
% rebound:					
85 min. at 260° F.	63.0	62.7	64.8	67.6	2
140 min. at 260° F.	62.7	61.6	63.8	67.6	2
Deflection:					
85 min. at 260° F.	0.231	0.226	0.235	0.250	2
140 min. at 260° F.	0.218	0.213	0.222	0.233	2
Vol. rubber/vol. black	1.076	1.128	0.923	0.942	3

[a] A master batch was made of each black, and portions of it were remilled at 24-hour intervals; 24 hours after each remilling, a set of complete tread stocks was milled and an extraction experiment was started. In this way all samples had the same resting period between the last remilling and the final milling or extraction.

[b] Extraction experiment: A 2-gram sample of black master batch was covered with 50 cc. of benzene. Each day for 6 weeks the clear cement was poured off and renewed with fresh benzene. At the end of this time the pellets were dried at room temperature and weighed. Results are reported as volumes of rubber per volume of black. For example,

Initial weight, 2.000 grams containing 0.800 gram black	
Weight after extraction	1.336 grams

$$\frac{1.336 - 0.800}{0.800} \times \frac{1.75}{0.93} = 1.261 \text{ vol. rubber/vol. black}$$

son why oxygen content should have any relation to particle size, shape, or any other physical characteristic of a black. It is generally conceded that volatile matter has its biggest influence on such things as rate of cure and adsorptive capacity.

Diphenylguanidine adsorption from benzene (*2*) may be placed with volatile matter as having no connection with rebound. This, too, is not difficult to believe, considering the profound effect of oxygen content on acid or basic adsorption (*15*, *17*, *18*).

Particle size measurements unfortunately are not available. However, over the broad range of black from Thermax to Super Spectra, low rebound, toughness of uncured stock, and blackness all mean fine particle size. It is possible, then, that within the range of rubber channel black, particle size and rebound may be related. Two other facts may be used to throw some light on this point.

It has been reported before (*4*, *5*, *7*, *16*) that, when a mixture of black and rubber is extracted with benzene, a pseudoequilibrium may be reached beyond which rubber is extracted only very slowly. The data of Table III show that this property is definitely influenced both by type of black and by the degree of milling the rubber has received. It seems reasonable to believe that this rubber is held by forces of adsorption (*3*, *4*) and, if so, the amount held should be a function of the specific surface of the black and hence a function of particle size. Considered in a relative sense, as in Table IV, it appears to agree broadly with per cent rebound (Figure 5).

Finally, it is no doubt possible to go farther in this interpretation of diphenylguanidine adsorption. Diphenylguanidine adsorption should be a function both of specific surface and of the activity of that surface toward diphenylguanidine. The latter is controlled by the oxygen content and is indicated by volatile matter. If there were a quantitative relation between these three quantities (diphenylguanidine adsorption, specific surface, and volatile matter), it would be possible to predict any one of them knowing the other two. In other words, knowing diphenylguanidine adsorption and volatile matter, we could predict specific surface. Although such a quantitative relation is not available, these blacks can be lined up at least qualitatively by such a line of reasoning. Black F has higher volatile matter content than black A. If it had the same specific surface as A it should be more adsorptive. Actually it is less. Therefore, it has less specific surface than A or larger particle size. By a similar line of reasoning other comparisons can be made: F is larger than A, C is larger than B, D is larger than B, and D is larger than E.

Summing up the data of Table IV, therefore, it appears that a black which produces a resilient cured stock (i. e., high rebound) also (*a*) produces a soft uncured stock, (*b*) is a gray black, (*c*) binds a relatively small amount of rubber and consequently has low specific surface, and (*d*) is less adsorptive toward diphenylguanidine than its volatile content requires and hence has low specific surface. The last two relations are distinctly qualitative, and for that reason there is no intention of stating that rebound is a direct measure of particle size.

Ability to Separate Blacks

Entirely apart from its significance or its correlation with other properties, if a test cannot separate blacks clearly, it is of no practical use. This ability to give a clear separation does not depend solely upon the size of the experimental error. It depends rather upon how much larger than the experimental error the total range of readings is.

To be more specific, the total spread in rebound ratings which we find in rubber black is about 20 per cent (Figure 4). The experimental error may be represented by twice the average deviation from the mean, or 1.2 per cent. The total spread, therefore, is seventeen times the experimental error. In order to compare this with the other tests, we may extrapolate the curves of Figure 5 to obtain the

TABLE IV. RELATIVE COMPARISON OF VARIOUS TESTS[a]

	Black A	Black B	Black C	Black D	Black E	Black F	Av. Deviation from Mean
Rebound rating (direct):							
Original mix	100	96.2	102.1	106.4	100.6	105.5	±0.6
After remilling	100	96.6	101.6	...	...	106.6	
Williams rating (inverse)	100	97.8	105.2	111.7	...	...	±3.0
Nigrometer rating (direct)	100	98.9	101.6	105.0	100.6	102.4	±0.8
Bound rubber rating (inverse)	100	95.9	113.0	...	...	115.2	±1.9
Volatile rating (direct)	100	84	92	78	69	107	±8.2
DPG rating (direct)	100	82	71	48	63	97	±3.6
Particle size predicted from volatile matter and DPG adsorption	...	...	Larger than B	Larger than B and E	...	Larger than A	...

[a] These are average ratings taken from Tables II and III. Black A is arbitrarily assigned a rating of 100 and all others are found by proportion, either direct or inverse.

spread in their ratings corresponding to a spread of 20 in rebound rating as follows:

Test	Total Spread, *A*	Av. Deviation from Mean, *B*	Ratio *A/2B*
Rebound	20	±0.6	17
Plasticity	30	±3.0	5
Nigrometer	11	±0.8	7
Bound rubber	46	±1.9	12

Therefore, of these four tests, rebound seems to give the clearest separation.

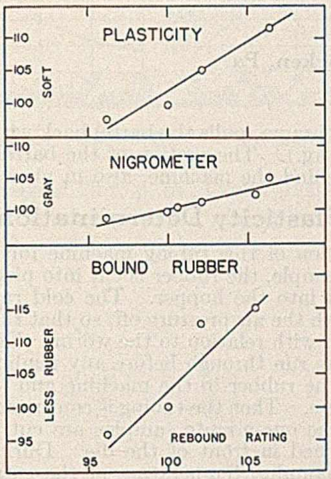

FIGURE 5. CORRELATION OF REBOUND WITH OTHER PROPERTIES (DATA OF TABLE IV)

Acknowledgment

The author wishes to express his thanks to G. K. Hinshaw, chief chemist of The Goodyear Tire & Rubber Company, for permission to publish this paper; to W. W. Vogt who has been in constant touch with the problem from the start and who has always taken a vital part in its discussion; and to H. V. Powers who has engineered the daily testing of blacks and has kindly consented to the publication of the distribution curves.

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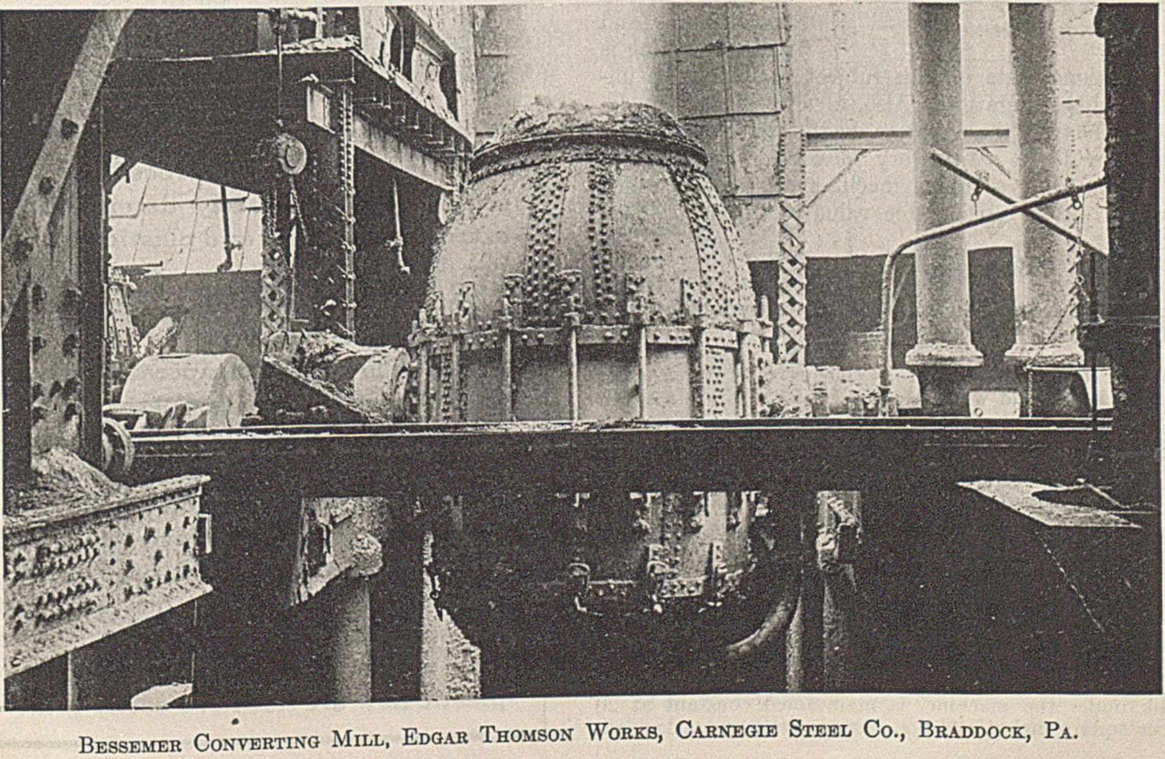

BESSEMER CONVERTING MILL, EDGAR THOMSON WORKS, CARNEGIE STEEL CO., BRADDOCK, PA.

Extrusion Qualities of Rubber

EFFECT OF TEMPERATURE AND MILL ROLL OPENING

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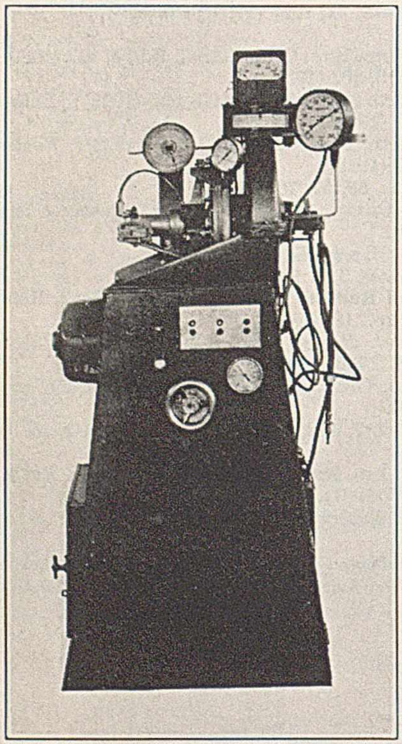

TUBING MACHINE

EVERYDAY milling practice shows that rubber becomes softer when milled on a cold mill than when milled for the same length of time on a hot mill, and also that a tight mill will produce softer rubber than an open mill, using the same number of passes. Although this may seem obvious to one who is experienced in rubber milling, the published work on variations in the softness of rubber resulting from differences in roll temperatures and mill roll setting is meager; additional data on this subject would not be unwelcome in rubber literature. Also, a series of tests to determine the effects of these factors on the working qualities of rubber provides a satisfactory means for describing a method for operating a tubing machine plastometer which has proved to be of considerable value in this laboratory.

Tubing Machine

In this method a small tubing machine was specially built for the purpose:

The temperature is regulated by means of water passing through both barrel and worm at 180° F. (82.2° C.) in a closed system with thermostatic control, and temperature variations of this circulating water are indicated on a dial thermometer plainly visible to the operator. Speed is held constant at 35 r. p. m. of the worm, which is 1.25 inches (3.2 cm.) in diameter with progressively decreasing pitch; the power consumed is indicated on a wattmeter, also in front of the operator. A $^3/_{32}$-inch (2.38-mm.) orifice is used for the extrusion, and built into the head is a thermocouple around which the rubber must pass before extruding. This is connected to a temperature indicator, also in position over the machine. The barrel of the tubing machine is free to move back and forth a short distance (0.75 inch, or 19 mm.) and is rigidly attached to a diaphragm operated by air pressure. This air pressure, obtained from a small tank under the machine, is maintained constant at 20 pounds per square inch (1.406 kg. per sq. cm.) and, when applied to the diaphragm, pulls the barrel back with a force of 1380 pounds (625.97 kg.). The motion of the barrel is indicated on a dial placed behind the machine, also in view of the operator.

Plasticity Determinations

In the operation of this tubing machine for determining the plasticity of a sample, the rubber is cut into pieces small enough to be easily fed into the hopper. The cold rubber is fed at a uniform rate with the air pressure off, so that the barrel is in the forward position with relation to the worm. Exactly 200 grams of the rubber are run through before any readings are taken, in order to bring the rubber in the machine and the die to a constant temperature. Then the tubing is continued with additional rubber, and three one-minute samples are cut off by means of the cutter fastened in front of the die. During the extrusion of these three samples, temperature of the extruding rubber is recorded and average power readings are taken. Any variations in the circulating water temperature are also noted. The three samples are weighed individually, and the average is taken and recorded as "grams extruded per minute," which for brevity is called G_x. The worm is then stopped with the machine loaded and held for exactly 3 minutes. Then the air valve is opened, and the 20 pounds per square inch pressure is applied to the diaphragm which forces the die back against the rubber in the space between the die and screw with a pressure of 1380 pounds. The movement of the barrel backward as the rubber is forced out of the die is indicated on the dial back of the machine, and the divisions on the dial correspond to the volume of rubber extruded. With a stop watch the number of minutes to extrude 5.4 cc. are taken and recorded as M. This completes the test, and the machine is cleaned out; each test is started with an empty machine.

The factor G_x is a direct measure of tubeability or tubing speed, and M is an inverse measure of plastic flow. G_x/M, for want of a better word, is called "plasticity."

An apparatus and procedure are described for accurately determining the extrusion qualities and plastic flow of rubber.

Between 90° and 210° F. on a laboratory mill when temperature is the only variable, the lower the temperature the softer the rubber. At any temperature between 90° and 210° F. on a laboratory mill when the rubber is passed through an equal number of times, the tighter the mill, the softer the rubber. Between 120° and 200° F. in a tube machine used as a rubber plasticizer, the lower the temperature, the softer the rubber.

In rubber compounds tubeability and plastic flow are not necessarily related.

Figure 1 and the following table give results on four 400-gram samples taken from the same slab of factory milled and blended smoked sheet which were ground for 4, 6, 8, and 10 minutes on a 12 × 6 inch (30.48 × 15.24 cm.) laboratory mill, front roll speed 22 r. p. m., back roll speed 32 r. p. m., ratio 1.45 to 1, roll temperature maintained at average of 90° F. (32.2° C.), and opening between rolls 0.010 inch (2.54 mm.):

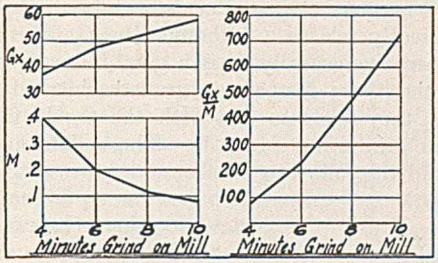

FIGURE 1. RESULTS OF EXTRUSION TESTS

Grinding Time Min.	G_x	M	G_x/M
4	37.02	0.4	92.6
6	47.07	0.2	235.4
8	52.81	0.11	480.5
10	57.21	0.08	715.0

These figures serve to illustrate the magnitude of differences in plasticity readings, even when samples are taken with only 2-minute variations in grinding.

Effect of Temperature and Roll Setting

In order to determine the effect on the rubber tubing qualities and plastic flow of the variations in roll temperature and roll settings, fifteen 400-gram samples, taken from a slab of factory milled and blended smoked sheet, were treated on the same laboratory mill as follows: Each passed through the rolls exactly ten times. Five samples were subjected to a roll temperature of 90° F. (32.2° C.) and openings between the rolls of 0.010, 0.020, 0.040, 0.080, and 0.120 inch (0.25, 0.51, 1.02, 2.03, and 3.05 mm.), respectively; five to a roll temperature of 165° F. (73.9° C.) and the same openings; and five to a roll temperature of 210° F. (98.9° C.) and the same openings. Samples were tested approximately 24 hours after milling.

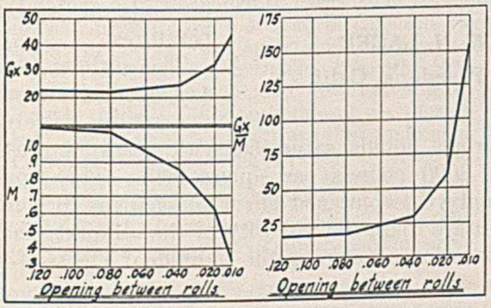

FIGURE 2. EFFECT OF SIZE OF MILL OPENING ON EXTRUSION QUALITIES

The time for making the ten passes decreased as the mill opening increased. Also, the time increased as the roll temperature increased, as the spring of the rolls brought them closer together when the rubber on the mill was hot and soft. Table I gives data on samples milled at the three temperatures.

Figure 2 shows the effect of variations in mill openings, in each case the average of the three temperatures; Figure 3 shows the effect of temperature, in each case the average of the five mill openings.

TABLE I. EFFECT OF TEMPERATURE AND ROLL SETTING ON RUBBER PROPERTIES

Mill Opening	Mill Temp. at End	Time of Ten Passes	G_x	M	G_x/M		
					Original	Increase from original[a]	% increase from original
Mm.	° C.	Min.					
Mill Temp. at Start, 32.2° C.							
0.25	46.1	6	45.97	0.20	230	213.5	1293
0.51	40.6	3	35.90	0.44	81.5	65.0	393
1.02	37.2	2	28.21	0.75	37.6	21.1	128
2.03	33.3	1	24.34	1.04	23.4	6.9	42
3.05	32.2	0.9	23.89	1.03	23.2	6.7	41
Mill Temp. at Start, 73.9° C.							
0.25	81.1	7.7	44.71	0.27	165.5	149.0	903
0.51	79.4	3.8	32.22	0.56	57.5	41.0	248
1.02	76.7	2.1	25.77	0.86	29.9	13.4	81
2.03	73.9	1.2	24.07	1.09	22.1	5.6	33
3.05	73.9	1.0	23.39	1.13	20.7	4.2	25
Mill Temp. at Start, 98.9° C.							
0.25	98.9	11.5	35.67	0.45	79.3	62.8	381
0.51	98.9	5.7	24.93	0.83	30.1	13.6	82
1.02	98.9	2.3	23.76	0.97	24.5	8.0	48
2.03	98.9	1.3	22.44	1.14	19.7	3.2	19
3.05	98.9	1.1	23.93	1.30	18.4	1.9	12

[a] G_x/M on original factory slab, 16.5.

Another test was run to determine the effect of temperature by using the tubing machine as a plasticizer and running samples of the same smoked sheet through the machine once each with the circulating water temperature varying between 120° F. (48.9° C.) and 200° F. (93.3° C.). After passing 400 grams of the rubber through the machine, it was run through the laboratory mill twice with the 3.05-mm. opening and a temperature of 210° F. (98.9° C.) to sheet it out; it was then held approximately 24 hours before testing for plasticity. The following table gives the data obtained in running the rubber through the machine at the various temperatures:

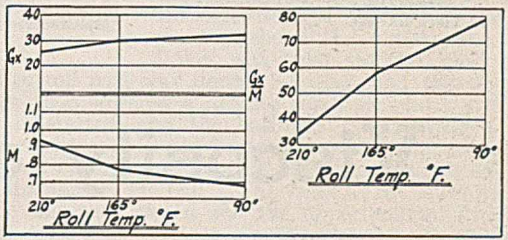

FIGURE 3. EFFECT OF TEMPERATURE ON EXTRUSION QUALITIES

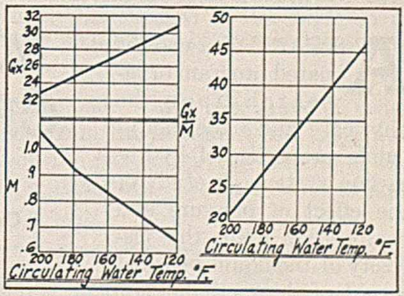

FIGURE 4. EFFECT OF WATER TEMPERATURE ON EXTRUSION QUALITIES

Sample No.	Circulating Water Temp. ° C.	Temp. of Extruding Rubber ° C.	Temp. Rise ° C.	Av. Watts
1	48.9	73.9	25	450
2	60.0	83.9	23.9	350
3	71.1	88.3	17.2	250
4	82.2	94.4	12.2	170
5	93.3	103.9	10.6	140

As is to be expected, the lower the temperature of the barrel and worm, the greater the temperature rise between the water temperature and that of the rubber extruding through the die, and the greater the power consumption.

Figure 4 and the following table show the effect on the extrusion qualities of the variation in circulating water temperature:

Sample No.	G_x	M	G_x/M Original	G_x/M Increase from original[a]	G_x/M % increase from original
1	30.42	0.65	46.8	30.3	183
2	29.02	0.77	37.7	21.2	128
3	27.05	0.84	32.2	15.9	96
4	25.50	0.91	28.0	11.5	70
5	22.41	1.07	20.9	4.4	27

[a] G_x/M on original rubber, 16.5.

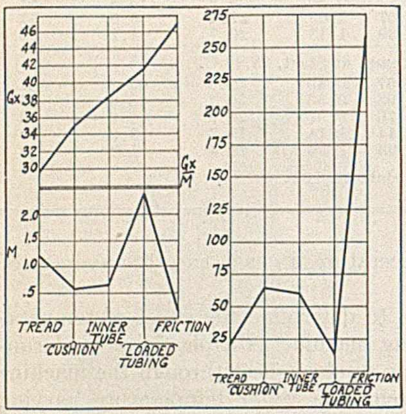

FIGURE 5. RELATION OF TUBEABILITY AND PLASTIC FLOW

Relation of Tubeability and Plastic Flow

All of the data presented thus far show a direct relation between tubeability and plastic flow, and conclusions would be identical if either G_x or M were used and G_x/M omitted. However, G_x and M have a direct relation when the same type of rubber or compound is compared, but not always when different types of rubber or different compounds are compared. For example, if we draw a curve of the G_x values of five different types of rubber compounds and then below this show the M values, it becomes evident that tubeability and plastic flow are not directly related. Although the G_x/M figure may mean little mathematically, it is a good index of the actual softness of the stock; if stocks are graded arbitrarily by "feel" on the mill, they fall into line with the G_x/M figure more closely than with either G_x or M. These data are given in Figure 5 and the following table:

	G_x*	M	G_x/M
Tread compound	29.7	1.23	24.2
Cushion	35.2	0.51	68.6
Inner tube	38.2	0.58	65.8
Loaded tubing	41.5	2.44	17.0
Friction	46.9	0.18	260.5

* Corrected to 0.92 specific gravity.

In this paper only one procedure for the successful operation of this tubed machine plastometer has been described. A discussion of other procedures designed for factory control of stocks which permit of rapid testing of samples, for development of stocks of certain desired characteristics, for determination of tubing and plastic properties of pigments, for scorch tests of compounds would provide data enough for a number of papers.

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Viscosity of Hydrocarbon Solutions

METHANE–PROPANE–CRYSTAL OIL SYSTEM

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AS PART of a coördinated program of research upon the physical and thermodynamic properties of hydrocarbon systems, a study of the effect of pressure and composition upon the viscosity of the liquid phase of a part of the methane–propane–crystal oil system was made. The work was primarily limited to a temperature of 100° F. and to liquid compositions containing less than 5 per cent methane and 20 per cent propane by weight. The viscosity of the liquid phase of numerous mixtures in this composition range was determined in both the two-phase and condensed-liquid regions at pressures up to 3000 pounds per square inch absolute.

Experimental investigation of the effect of pressure and composition upon the viscosity of hydrocarbon liquids has not progressed sufficiently to permit correlation of the viscosity as a function of state. Bridgeman (*1*) made measurements of the effect of pressure upon the viscosity of several hydrocarbons. His pressure range (17×10^4 pounds per square inch) was many times that recorded in the present paper, but no attempt was made to study systematically the effect of composition upon the changes in viscosity of such liquids. Hersey and Shore (*4*) also determined the effect of pressure upon the viscosity of lubricating oils at several temperatures.

The authors (*6*, *8*, *9*, *10*, *11*) reported measurements upon the viscosity of hydrocarbon liquids saturated with gases at pressures as high as 3000 pounds per square inch. This work determined only the combined effect of changes in composition and pressure upon the viscosity of these liquids and offered no information concerning the individual effects of the variables.

Materials

The oil used in this investigation was a water-white paraffin-base oil refined from Pennsylvania crude stock. The average molecular weight, as determined by the freezing point lowering of benzene, was 342. Its specific gravity at 100° F., relative to water at its maximum density, was 0.8244, and the viscosity-gravity constant (*5*) was found to be 0.7979. The results of an aniline extraction analysis upon similar material indicated that it was primarily composed of constituents of a narrow range of high molecular weights, which accounted for the oil's low volatility (10^{-3} inch of mercury at 100° F.). Throughout the remainder of this paper this oil will be called "crystal oil," but it is quite different from the water-white oil used in other phase-equilibrium and viscosity studies by the authors. The latter was refined from western crude stock. The propane used in this investigation was obtained from the Philgas Company, together with a special fractionation analysis showing that the propane contained less than 0.05 mole per cent of impurities. Investigation showed that the vapor-pressure of this material varied by less than 0.3 pound per square inch between dew and bubble points at 100° F. The methane was prepared from natural gas by methods previously described (*7*). The methane was purified by charcoal adsorption and partial solidification at liquid air temperature, and it is the authors' belief that the material contained less than 0.05 mole per cent ethane and heavier constituents, and probably not more than 0.2 mole per cent nitrogen or other noncondensable constituents.

The effect of pressure upon the viscosity of the liquid phase of eighteen mixtures of methane, propane, and crystal oil was determined at 100° F. The work included measurements at bubble point and throughout the condensed liquid region at pressures up to 3000 pounds per square inch. The results are presented in tabular form, and several diagrams illustrating the behavior of the system are included.

Experimental Methods

The instrument employed was a revised form of the rolling ball viscometer, previously described (*6*), which was adapted from earlier forms used by Flowers (*2*) and Hersey (*3*, *4*). In principle the method consisted of measuring the time for a close-fitting steel ball under the influence of gravity to move down a closed inclined liquid-filled tube through a fixed distance. Figure 1 is a schematic diagram of the instrument as used for these measurements:

The liquid under investigation filled the entire system, except when measurements in the two-phase region were made; under these circumstances the upper part of saturation cell *A* was filled with gas. The liquid was circulated through chamber *B*, up through the flow tube of the viscometer proper, and back to saturation cell *A* by means of the small cam pump mounted in the lower part of the saturation cell. This circulation, in addition to the action of a stirrer in saturation cell *A*, permitted the rapid attainment of equilibrium between the gas and the liquid portions of the system. The effective volume of the system could be varied approximately 25 per cent by the addition or withdrawal of mercury from chamber *B*. This variation in volume permitted the investigation of the change in viscosity of the liquid phase with changes in pressure for a system of constant composition.

The roll time of the ball was ascertained by means of an electrically driven chronograph actuated through contacts *C* and *D*. The upper contact *C* was movable to permit release of the ball. The chronograph was of such a design that the lapse of time between the breaking of the upper contact and the making of the lower one could be determined with a precision of 0.01 second. However, an uncertainty in the roll time as great as 0.2 per cent may have existed because of irregularities in the frequency of the alternating current supply used for driving the chronograph.

The temperature of the viscometer was maintained by means of an oil thermostat in which the maximum variation in temperature was 0.05° F. The pressure on the system was measured by means of a pressure balance connected to the mercury in cell *B*. The pressure within the apparatus was known within 0.3 pound per square inch at pressures below 300 pounds per square inch and within 1.5 pounds per square inch at higher pressures.

The instrument was calibrated by use of a series of hydrocarbon liquids of known viscosity. The viscosity of these calibrating liquids was determined at atmospheric pressure by means of a quartz Ostwald pipet. It is believed that the uncertainty introduced as a result of the calibration was less than 0.5 per cent. For a discussion of the parameters involved in these calibrations, the reader is referred to the work of Flowers (*2*) and Hersey (*3*), and to an earlier paper of this series (*6*). The effect of pressure upon the calibration of the instrument was determined by a comparison of the measured increase in the viscosity of several organic liquids with that found by Bridgeman (*1*). This comparison indicated that changes in calibration of as much as 0.5 per cent might be encountered at the higher pressures. Because of the limited over-all accuracy of the measurements (2 per cent), it was not considered worth while to correct the measured viscosity for this small change in calibration.

For this work on binary and ternary mixtures, the crystal oil was first added to the apparatus, and then the desired amount of propane was distilled into it from a small steel bomb. The quantities of crystal oil and propane, which were determined by counterpoise weighing, were known with an uncertainty of less than 0.1 per cent. The methane was measured into the apparatus by volumetric means, and it is believed that the quantity of methane added to the apparatus was determined within 0.3 per cent. After the addition of the requisite amount of the components, the viscometer was allowed to come to thermal equilibrium at the desired temperature.

After the attainment of thermal and of phase equilibrium, the liquid was circulated through the roll tube forcing the ball to the top above the outlet tube. Circulation was then stopped, the ball was allowed to roll part way down the tube, and the upper contact was then lowered a definite small amount. Circulation was again started, and the ball was gently wedged against the upper contact. It was found that small inaccuracies (0.001 inch) in setting the upper contact caused a negligible effect upon the roll distance of the ball. The valve at the lower end of the roll tube was then closed and the upper contact lifted. The break in the upper contact circuit actuated the chronograph pen, thus automatically recording the beginning of the roll time. The end of the period was recorded by the pen as the ball touched the lower contact. The valve at the bottom of the roll tube was then opened, circulation started, and the measurement repeated. The pressure on the system was changed by the addition or withdrawal of mercury, and another set of measurements was taken.

The density of the liquid phase, which is required in order to determine the viscosity from the measured roll time, was calculated from data upon the partial specific volume of the components. These latter data were obtained from experi-

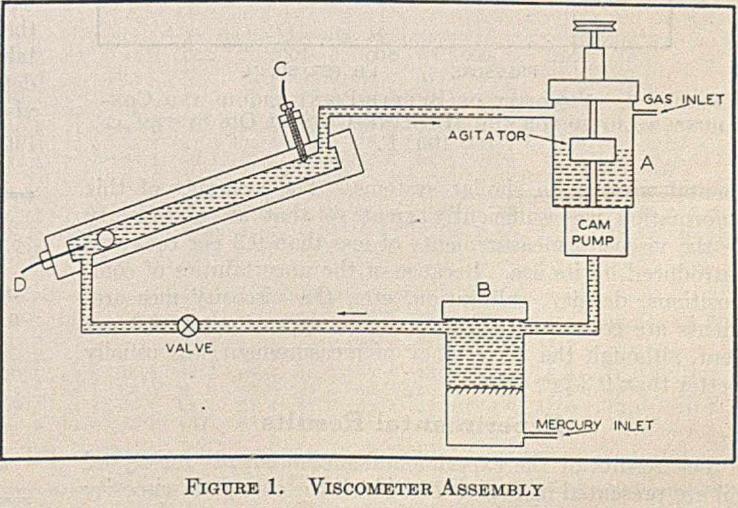

FIGURE 1. VISCOMETER ASSEMBLY

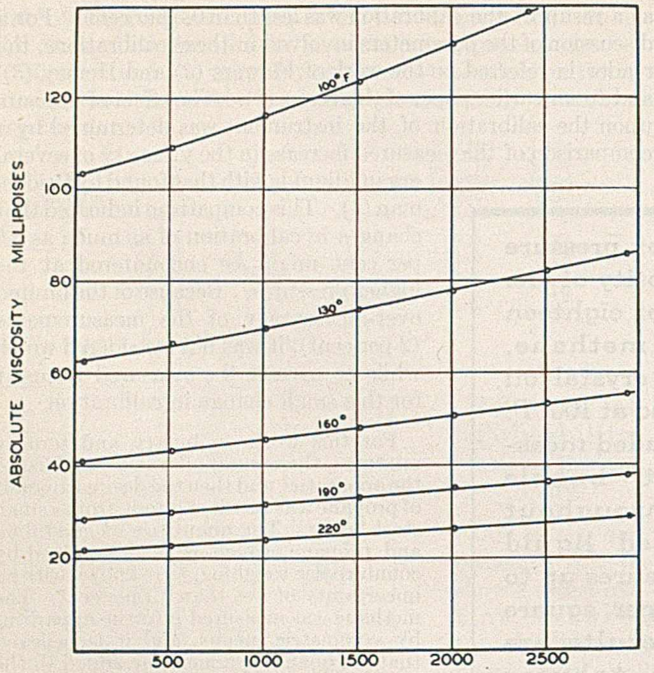

Figure 2. Effect of Pressure and Temperature on Viscosity of Crystal Oil

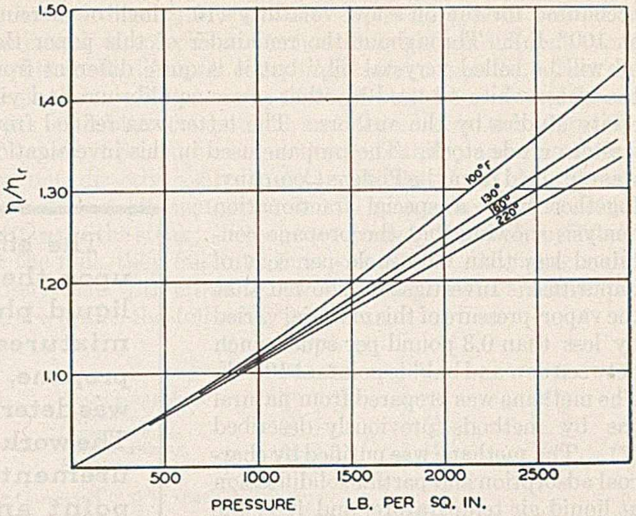

Figure 3. Ratio of Viscosity at a Given Pressure to Viscosity at Vapor Pressure for Crystal Oil

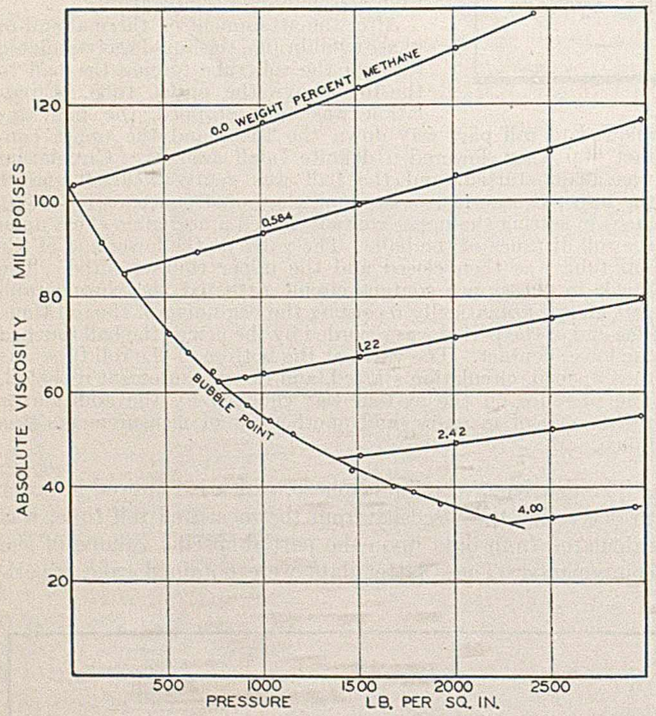

Figure 4. Viscosity of Bubble-Point Liquid and Condensed Liquid for the Methane–Crystal Oil System at 100° F.

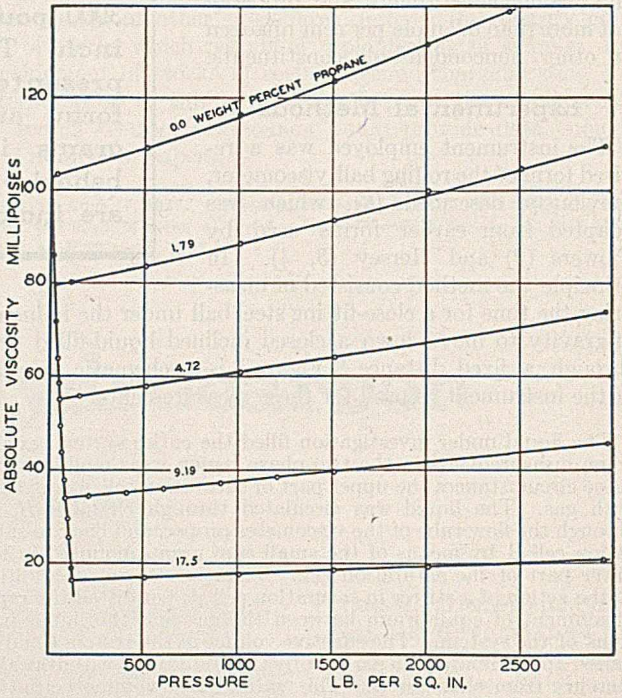

Figure 5. Viscosity of Bubble-Point Liquid and Condensed Liquid for the Propane–Crystal Oil System at 100° F.

mental work upon similar systems. The accuracy of this information was sufficiently great so that an uncertainty in the viscosity measurements of less than 0.3 per cent was introduced by its use. Because of the uncertainties of compositions, density, calibration, etc., the viscosity measurements are considered trustworthy to approximately 2.0 per cent, although the consistency of measurement was usually better than 0.2 per cent.

Experimental Results

The results of the experimental measurements for crystal oil are presented in Figure 2 in which the change in viscosity with pressure is shown for five temperatures. Table I records the results of these measurements. The tabulated values were taken from smooth curves drawn through the experimentally determined viscosities. Figure 3 presents the ratio of the oil viscosity at a given pressure to the viscosity at the vapor pressure for a series of temperatures. Although the per-

Table I. Viscosity of Crystal Oil

Abs. Pressure, Lb./Sq. In.	Abs. Viscosity, Millipoises 100° F.	130° F.	160° F.	190° F.	220° F.
Bubble point[a]	103.0	62.5	40.9	28.2	21.6
500	109.1	66.1	43.2	29.9	22.8
1000	115.8	69.8	45.7	31.5	24.0
1500	123.5	73.8	48.2	33.1	25.2
2000	131.6	77.7	50.6	34.7	26.3
2500	139.9	81.8	53.2	36.4	27.5
3000	148.4	85.9	55.6	38.0	28.6
3500	156.1	90.2	58.0	39.6	29.8

[a] Maximum bubble-point pressure was less than 0.1 inch of mercury.

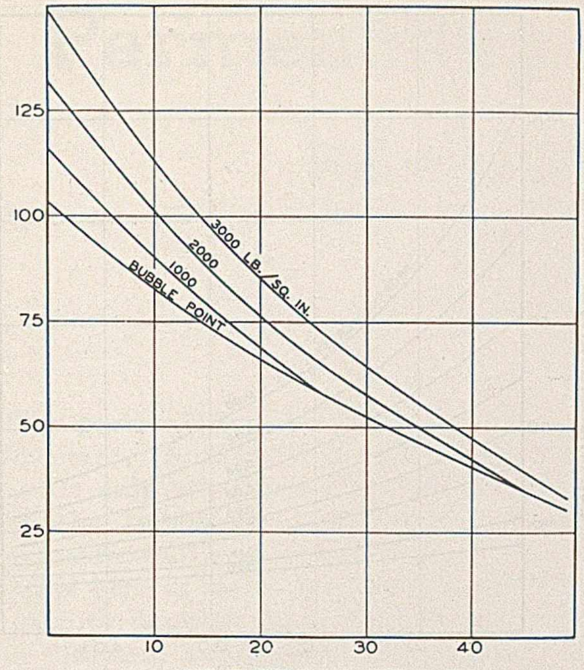

FIGURE 6. EFFECT OF COMPOSITION ON VISCOSITY FOR THE METHANE–CRYSTAL OIL SYSTEM AT 100° F.

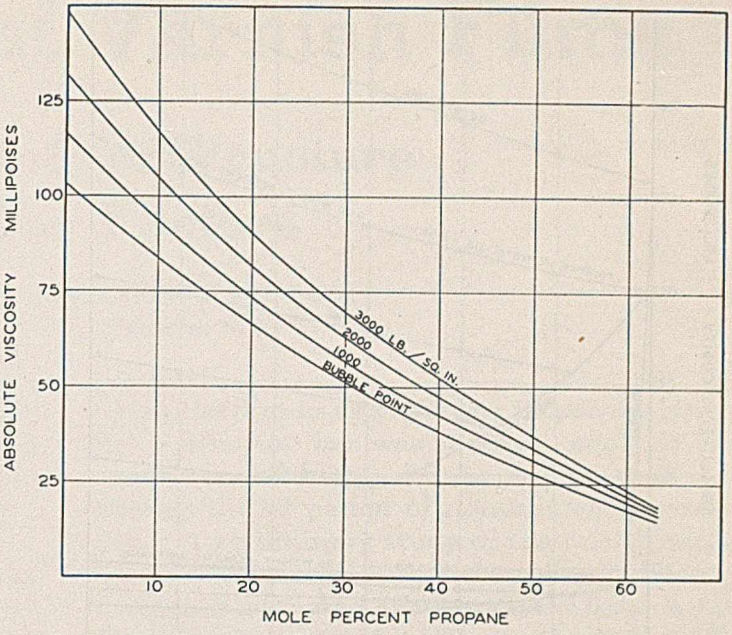

FIGURE 7. EFFECT OF COMPOSITION ON VISCOSITY FOR THE PROPANE–CRYSTAL OIL SYSTEM AT 100° F.

centage increase in viscosity with pressure is not greatly affected by temperature change, there is a much smaller change in viscosity with pressure at the higher temperatures; also the rate of change of viscosity with pressure at a constant temperature increases with an increase in pressure.

Figure 4 presents the experimental results for the methane–crystal oil system at 100° F. The curve at the left represents the variation in the viscosity of bubble-point liquid with bubble-point pressure. The points shown on this curve were taken from measurements made with an appreciable quantity of gas phase in equilibrium with the liquid. Actually there should be a difference between the viscosity of the bubble-point liquid and that in equilibrium with an appreciable amount of gas phase at the same pressure and temperature. However, with the materials involved, this difference was less than the experimental uncertainty. Each of the curves on the right-hand side of Figure 4 represents the change in viscosity with pressure for liquid or constant composition. The liquids containing larger amounts of methane show a smaller isothermal increase in viscosity with pressure. All of the liquids, however, show a greater rate of change of viscosity with pressure at the higher pressures. The results of these measurements are recorded in Table II. These values of bubble-point pressure were determined by the breaks in the viscosity-pressure relations corresponding to that point. Because of the incidental character of the determinations of bubble-point pressure, these values are not considered reliable to better than 5 per cent.

Figure 5 depicts the results of the experimental measurements upon mixtures of propane and crystal oil at 100° F. The general behavior is similar to that found for the mixtures of methane and crystal oil just discussed. All of the experimental points taken in the two-phase region fell on the bubble-point curve within the experimental uncertainty of the measurements, but most of them were omitted from the diagram. Comparison of Figures 4 and 5 shows that propane does not affect the viscosity of the liquid phase as markedly as methane when compared on a weight basis. The results of the experimental measurements upon the propane–crystal oil system are given in Table II.

For some purposes it is interesting to determine the effect of changes in composition upon the viscosity of a two-component liquid. Figure 6 presents the viscosity of the condensed and bubble-point liquid as a function of composition

TABLE II. VISCOSITIES OF LIQUID MIXTURES OF METHANE, PROPANE, AND CRYSTAL OIL AT 100° F.

	Methane and Crystal Oil				Propane and Crystal Oil							
CH_4, wt. %	0.48	1.33	2.42	4.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
C_3H_8, wt. %	0.00	0.00	0.00	0.00	1.79	4.12	4.72	6.52	9.19	10.78	17.54	
Bubble-point pressure	276[a]	775	1390	2270	27	56	62	77	96	99	132	
Abs. Pressure, Lb./Sq. In.	Absolute Viscosity, Millipoises											
Bubble point	85.3	62.3	46.1	32.5	79.5	58.2	55.3	45.3	33.8	29.9	16.2	
500	87.7	..	..	..	83.5	60.9	57.7	47.4	35.2	31.1	16.8	
1000	93.2	63.9	..	..	88.3	64.4	60.7	50.1	37.3	32.7	17.6	
1500	98.9	67.5	46.7	..	93.5	68.1	63.9	52.8	39.4	34.4	18.3	
2000	104.9	71.4	49.3	..	98.9	72.1	67.0	55.6	41.4	36.0	19.1	
2500	110.9	75.5	52.1	33.5	104.5	76.0	70.3	58.3	43.4	37.6	19.8	
3000	117.1	79.6	55.1	36.1	109.9	80.1	73.6	61.1	45.5	39.3	20.6	
	Methane, Propane, and Crystal Oil											
CH_4, wt. %	0.81	1.58	2.76	0.45	1.23	2.56	0.40	1.08	0.41	0.85	2.13	3.93
C_3H_8, wt. %	1.78	1.76	1.74	4.10	4.07	4.02	6.49	6.45	9.65	17.39	17.17	16.85
Bubble-point pressure	415	795	1460	254	600	1165	275	425	245	405	825	1400
Abs. Pressure, Lb./Sq. In.	Absolute Viscosity, Millipoises											
Bubble point	62.4	50.6	36.8	51.1	41.9	31.6	40.1	37.2	28.8	14.4	12.1	9.6
500	63.0	..	..	52.4	..	..	41.2	37.6	29.6	14.5	..	..
1000	66.7	51.8	..	55.3	43.8	..	43.9	40.5	31.2	15.2	12.4	..
1500	70.5	54.8	36.9	58.4	46.3	32.6	46.8	43.5	32.7	15.8	12.9	9.7
2000	74.5	58.1	38.9	61.6	48.9	34.3	49.7	46.5	34.3	16.4	13.4	10.2
2500	78.5	61.4	40.9	64.8	51.4	36.0	52.7	49.6	36.0	17.0	13.9	10.7
3000	82.6	64.5	42.9	68.1	54.0	37.7	55.9	52.7	37.7	17.6	14.4	11.1

[a] Pounds per square inch absolute.

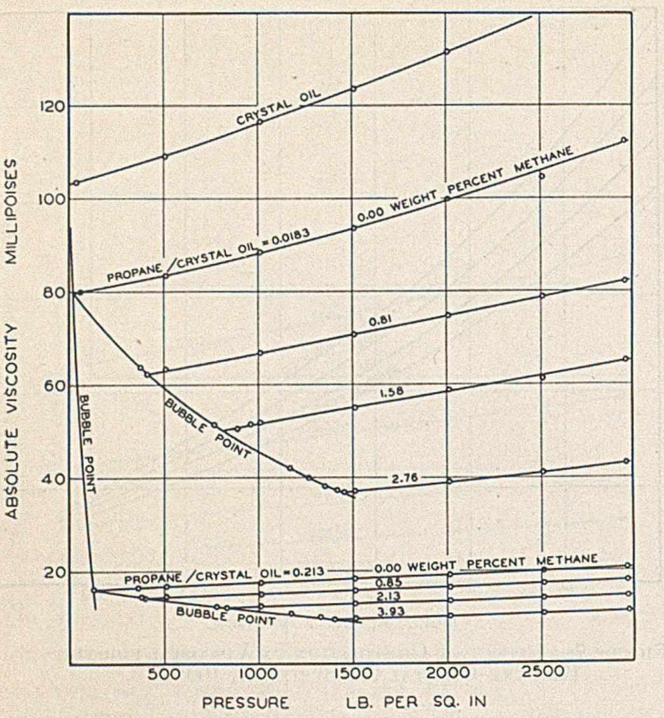

FIGURE 8. VISCOSITY OF BUBBLE-POINT LIQUID AND CONDENSED LIQUID FOR MIXTURES OF METHANE, PROPANE, AND CRYSTAL OIL AT 100° F.

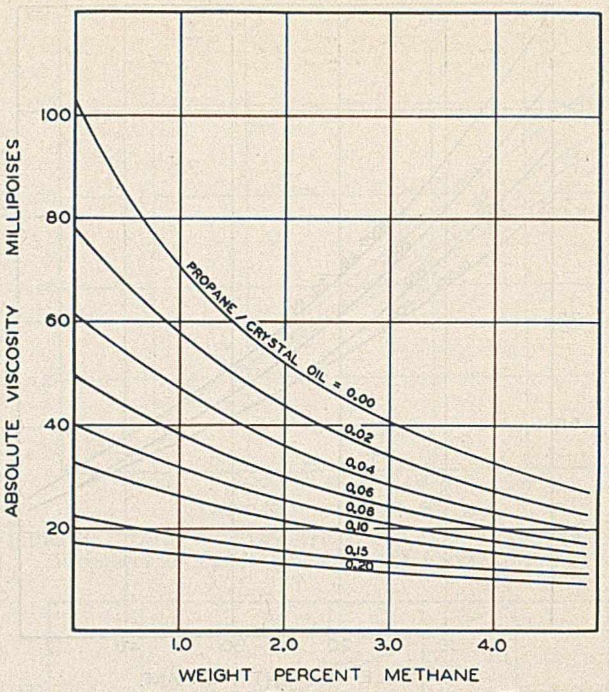

FIGURE 9. EFFECT OF COMPOSITION ON THE VISCOSITY OF BUBBLE-POINT LIQUID FOR THE METHANE–PROPANE–CRYSTAL OIL SYSTEM AT 100° F.

for the methane–crystal oil system. The rate of viscosity change with respect to composition under bubble-point conditions is smaller than the corresponding isobaric change in viscosity. This behavior results from the increase in pressure along the bubble-point curve, tending to increase the viscosity and thus offsetting a part of the decrease caused by the change in composition. A similar diagram for the propane–crystal oil system is presented in Figure 7. Comparison of Figures 6 and 7 shows that under bubble-point conditions the molal effect of methane and propane is similar but that the pressures existing in the two cases are different.

A portion of the experimental work at 100° F. on mixtures of methane, propane, and crystal oil is presented in Figure 8. The general behavior of this system is similar to that found for the methane–crystal oil and the propane–crystal oil systems. The upper family of curves presents the effect of methane upon the viscosity of a mixture composed of a fixed ratio of propane and crystal oil. Throughout all of the measurements for this group of curves, the ratio of the weight of propane to that of crystal oil was 0.0183, while the weight per cent of methane was varied from zero to 2.76 per cent. The lower family of curves represents a similar set of measurements in which the propane–crystal oil ratio was 0.213. The bubble-point curve at the left represents the viscosity of bubble-point liquid as a function of bubble-point pressure for mixtures of propane and crystal oil. The results of the experimental work for this ternary system are reported in Table II. The experimental work on this ternary system was not as complete as might be desired for certain purposes but was sufficient to permit an interpolation on a composition basis. Figure 9 presents the viscosity of the bubble-point liquid as a function of weight per cent methane for a series of propane–crystal oil ratios. The methane has a much smaller absolute effect upon solutions rich in propane than it does upon the crystal oil.

Acknowledgment

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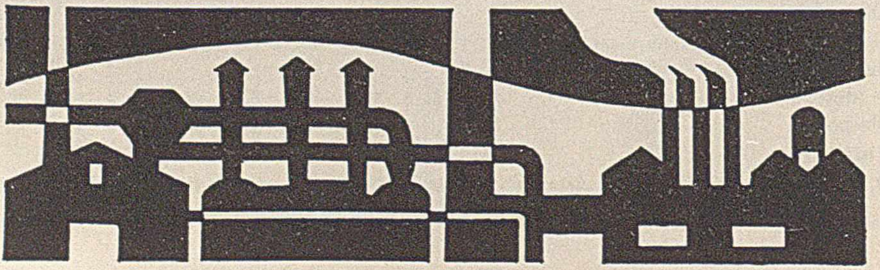

Permeability of Varnish Films

Relative Effect of Structure and Other Factors

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Polytechnic Institute, Brooklyn, N. Y.

The permeability of a material is one of its important, fundamental properties but is specific only when the permeating substance and the permeating conditions are defined. The permeability of a variety of films to four liquids besides water has been studied. Permeability depends upon the solvent power of the diffusing liquid for the film, the relative porosity of the film, and its imbibition capacity. These factors are as important as the physical dimensions and the vapor pressure differential across the film in determining its permeability. Fick's diffusion law was shown to apply to the permeation of both solvents and nonsolvents after an initial period of nonuniform permeation. A preliminary study of the initial stages indicates that structural changes which take place have a marked effect upon the final degree of permeation obtained. The mechanism of diffusion is discussed, relating both the physical and chemical properties of film and liquid to the process.

PERMEABILITY has been a subject of many excellent studies because of its great practical importance. Very little is known, however, concerning the possible mechanism of this phenomenon, since most of the information concerning it has been based upon measurements of permeabilities to water after a constant rate of permeation has been obtained.

Studies of the sorption of moisture by films (*5*, *8*, *17*) and of the reasons why varnish films become opaque (*7*) indicate that the inherent structure of these films (*25*) and the changes which may occur during adsorption of vapors probably have a profound effect on permeability. This has been recognized to some extent by recent investigators (*20*), but the complete picture cannot be obtained from a limited study of a single permeating substance (*15*). This paper will show that structural changes are most pronounced during the early stages when the film is first exposed to the vapors of the liquid. These changes produce a marked effect upon the ultimate permeability of the film, in addition to other physical properties. This is apparent when the usual permeability curves for different liquids are compared for a wide variety of films.

Mechanism of Permeability

The simplest mechanism which has been postulated to account for permeability is based upon the classical theory of diffusion which is supposed to take place through semipermeable membranes. Here it is assumed that the permeating liquid or vapor dissolves in the film and evaporates from the solution so formed. This theory has been used to explain osmosis except in cases of films prepared from glass (*22*) and from brass (*23*). The extension of this hypothesis to various varnish films has been supported by observations of the effect of vapor pressure (*24*) upon permeability and by certain properties of films which would indicate that they have characteristics of semipermeable membranes (*1*). This theory, however, fails to explain the increase in permeability with temperature which Edwards and Pickering (*4*) observed for several gases through thin sheets of rubber, where the solubility of the permeating gases are known to decrease with temperature as would be expected from Henry's law. In like manner it does not take into account many phenomena which unquestionably have a marked effect upon permeability; some of these will be described here.

It is clear moreover from the observations of Sheppard and Newsome (*18*, *19*), that permeability does not take place by simple diffusion through capillary pores as we generally know them except perhaps in certain definite instances where varnish films have deliberately been prepared to contain macropores. They found that the permeability of normal films of cellulose was independent of the hydrostatic head applied at one side of these films. Unquestionably both the purely mechanical structure of the film and its physico-chemical properties and those of the liquid contribute to the ultimate constant rate of permeation which is finally observed.

Similarity to Gels

A careful examination of the properties of free varnish films reveals that substances of this type might well be classified as gels (*2*, *3*, *12*, *14*, *21*). This applies equally well to such diversified substances as oils, resins, rubber, cellulose derivatives, casein, and glue, even though such films are produced by entirely different processes as oxidation, polymerization, thermoplastic setting, or simple evaporation.

Studies of colloids show that, in the formation of gels, molecules are grouped to produce aggregates. These molecular aggregates or micelles are further bound together by cohesive forces into bundles known as fibrils. The nature of these fibrils determines to a large extent the characteristics of the gel. Short fibrils produce brittle gels; long fibrils give the gel elasticity and flexibility. The strength of the gel depends on the cohesive forces between the fibrils. As Van der Waals showed, some of these forces would depend upon the size of the fibrils and the distance between them.

In a nonporous film these fibrils would be packed closely together and held very firmly by the cohesive forces. If some other force were found, however, that would overcome these cohesive forces, then the fibrils would be separated slightly and the interfibrillar spaces might readily become capillary pores. Liquids could then flow through these capillaries and evaporate from the other side at some constant rate, depending upon the adsorptive forces between the film and the liquid.

Gortner (*11*) showed that gels will imbibe liquids and swell considerably against a very great pressure. The pressure required to prevent the imbibition of a liquid by a gel is known as the imbibition pressure. This phenomenon of imbibition is a peculiarity of gels and should not be confused with osmosis which is due to variation in concentration on either side of a semipermeable membrane. Gortner showed that a cactus will draw water from concentrated salt solutions of much higher osmotic pressure than the salt content of the cactus would produce. The gel structure of the cactus makes this possible. Imbibition can thus be regarded as the adsorption of the dispersion medium (*11*). From the heat liberated by this adsorption, it is possible to construct the imbibition curve. These curves are typical adsorption curves represented by the Freundlich equation:

$$x/m = kC^{1}n$$

where x/m = amount of liquid adsorbed per gram of material
C = concentration of liquid in surrounding medium
k, n = constants

Gel imbibition is not limited to hydrogels but has been shown to exist with organogels. Rubber, for example, will imbibe naphtha and swell considerably against a very great pressure, although naphtha is not a solvent for the rubber.

An equilibrium exists in a gel between the adsorptive force toward the liquid and the cohesive forces between the fibrils under a specified set of conditions. This equilibrium determines the amount of liquid imbibed by the film and the extent to which the fibrils can be separated in acting as capillaries for diffusion. A liquid may also penetrate the intra- and the intermolecular spaces of crystalline solids as Lengyel (*13*) showed to be the case from x-ray studies of crystalline silicates. In this case, the imbibition may be greater than that calculated from the porosity of a rigid gel. A true solvent for a film would overcome the cohesive forces between the fibrils completely. It would either disperse the fibrils and produce a colloidal solution, or in some cases would even overcome the forces which maintain the micelles. In this last instance a true solution would be obtained.

Polar liquids are more apt to wet the surfaces of polar solids than are nonpolar liquids (*16*). Similarly, nonpolar liquids are more apt to wet nonpolar solids than are polar liquids. When vapors are in contact with a film, a similar condition should exist, and we should expect condensation of the liquid to take place rapidly following adsorption of the vapors upon the surface of a material.

If the structure of a film is that of a gel, it would be affected also by the orientation of the fibrils at both the air-film interface and the film-solid interface, the surface to which the film is applied. The orientation velocity of a colloid, however, is slower than the velocity with which aggregates form; consequently the interior of a film or gel would have an irregular or "brushheap" fibrillar structure. This irregularity of interior structure can cause relatively large interfibrillar spaces to be scattered throughout the film. These spaces can hold an entrapped nonsolvent liquid phase which may have a marked effect upon the adsorption of various vapors. Syneresis or the squeezing out of the dispersed phase during the drying of a film would also affect its structure.

Materials

The materials used for the preparation of the films were selected for their wide differences in general types, in an attempt to obtain films which would differ in mechanical structure, in solubility, and in dielectric properties. These varnishes, with the possible exception of the glue and the gelatin, are representative of those used in the protective coating industry. Glue and gelatin were included to provide water-soluble materials. Those selected were as follows:

1. Linseed Oil. This was an alkali-refined varnish linseed oil which had been heated to 450° F. (232° C.) to incorporate litharge and manganese linoleate so that it would contain 1 per cent lead and 0.5 per cent manganese for drying purposes. The films were dried for 1 month before testing.
2. Bodied Linseed Oil. In this instance a sample of the same linseed oil had been bodied for 6 hours at 600° F. (316° C.). After cooling, the same proportion of driers was added at 450° F. as with the previous oil. It was then thinned to dipping consistency with Varnolene (mineral spirits), and the films were dried 1 month before testing.
3. Rosin Spar Varnish. This was a 50-gallon China wood oil, rosin spar varnish with lead, manganese, and cobalt driers. The films were air-dried for 1 month before testing.
4. Phenolic Spar Varnish. This was a 50-gallon varnish of the China wood oil but was made with a 100 per cent phenolic resin and with only cobalt as the drier. Films were air-dried for 1 month before testing.
5. Shellac Varnish. This was a spirit varnish of a 2-pound cut of TN orange shellac in specially denatured alcohol. The films were air-dried for 1 month before testing.
6. Rosin Varnish. This was also a spirit varnish, consisting of a 30 per cent solution of WW gum rosin in Varnish Maker's and Painter's naphtha. In this case the films were baked for 2 hours at 160° F. (71° C.) to remove all traces of solvent.
7. Alkyd Resin. This vehicle was composed of an alkyd resin made from phthalic anhydride, glycerol, linseed oil fatty acids, and maleic acid, cooled, and then reduced with toluene. Films were baked for 2 hours at 225° F. (107° C.) for testing.
8. Alkyd Resin. No. 801 Amberol resin was incorporated in resin 7 during the cooking of this product. It was also thinned with toluene, and films were baked for 2 hours at 225° F.
9. Alkyd Resin Varnish. For this varnish, linseed oil and tung oil were incorporated with the alkyd resin 8 and No. 801 Amberol resin during cooking. It was reduced with toluene, and the films were baked for 2 hours at 225° F.
10. Rubber Solution. This was a Heveatex type R. L. rubber solution. Films were air-dried for 3 weeks before testing.
11. Paraffin Wax. Films were prepared by dipping the paper in the molten paraffin wax and allowing them to set for 1 week before testing.
12. Gilsonite. A select grade of gilsonite was melted at 500° F. (260° C.) and reduced with Varnish Maker's and Painter's naphtha. Films were baked for 2 hours to remove the solvent. This, however, did not make a satisfactory film for testing.
13. Glue. A water solution of flake Emery glue was prepared and was heated above the gelling point when dipping the paper. Films were air-dried for 2 weeks.
14. Gelatin. One-half pound of Knox plain gelatin was dissolved in 1 pound of water. The paper was dipped in a hot solution to prevent gelling. Films were air-dried for 2 weeks.
15. "Cotton" Solution. One-half second, R. S. "cotton" was dissolved in a solvent mixture which contained the following parts by weight: 24 butyl acetate, 39 toluene, 5 ethyl acetate, 5 especially denatured alcohol formula No. 5, and 5 butyl alcohol.
16. "Cotton" Solution. This solution consisted of 10 parts by weight of $^{1}/_{2}$-second R. S. "cotton" in the previous solvent mixture to which were added 4 parts of Lindol.
17. Lacquer. This lacquer was prepared by incorporating 8 parts of ester gum in "cotton" solution 16.
18. Lacquer. This lacquer was comprised of 40 parts by weight of R. B. H. aluminum No. 431 lacquer base and 2 parts of Lindol in the above solvent. This was equivalent to 10 parts by weight of aluminum, 30 parts $^{1}/_{2}$-second R. S. "cotton" and 2 parts of Lindol.
19. Lacquer. This was a solution of 40 parts by weight of R. B. H. Celite No. 303 lacquer base, 2 parts of Lindol in the above solvent, or 10 parts Celite, 30 parts $^{1}/_{2}$-second R. S. "cotton," and 2 parts Lindol.

Lacquer 18 was selected because aluminum powder was known to reduce the permeability of a film containing it; lacquer 19 was deliberately overfilled with Celite to provide a film which was known to be porous.

The liquids used were water, methyl alcohol, acetone, ethyl acetate, and benzene. They included a solvent and a nonsolvent for each of the films. These liquids varied in molecular size and in physical and chemical composition. They increased in polarity from the nonpolar benzene to the very polar liquid water. They included an alcohol, an ester, a ketone, and an aromatic hydrocarbon.

Apparatus

Permeability determinations were made in a specially designed cup, similar in principle to the well-known Gardner jar (*6*), where the material to be tested was sealed across the mouth of the cup and the amount of vapor which passed through the coating was measured by the loss in weight. This cup (Figure 1) was made from a metal stamping to which was soldered a brass disk to form a flange at the top. Another brass disk was bolted to the one on the cup with six $^3/_{16}$-inch bolts. The centers of the brass disks were so machined as to give a circular opening exactly 11.34 sq. cm. in area. The contacting surfaces of the disks were carefully ground by hand to optical flatness, so that there was no loss of vapor except directly through the test specimen when it was placed between the disks. Twenty of these cups were employed at the same time to ensure that all films would be tested under the same conditions.

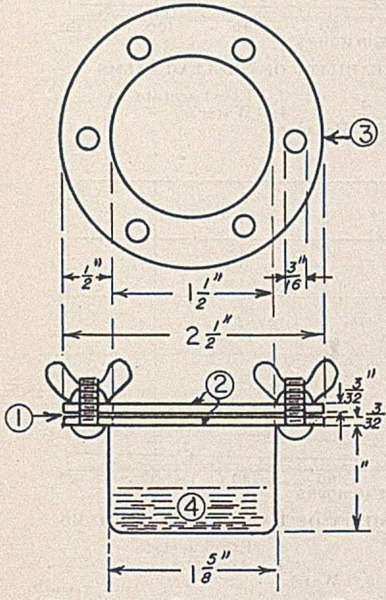

FIGURE 1. PERMEABILITY CUP

1. Film
2, 3. Brass disks
4. Liquid

Preparation of Films

A support was used for films of all of the materials such as had been employed by Gettens (*10*) for similar measurements. This was done because it would have been impossible to produce free films of some of the materials studied without damaging them during the necessary handling.

The support chosen was a pure cellulose paper, which had been calendered to a hard smooth surface. It contained no filler or size. This paper was remarkably uniform, having a thickness of 0.004 inch (0.1 mm.). It can be readily obtained since it is used in the bottle-cap industry where it is impregnated with a resistant varnish. The varnishes completely penetrated this paper except in two instances. Since the purpose of the experiments was to compare the general behavior of the different materials toward the five liquids, this did not prove to be a serious handicap.

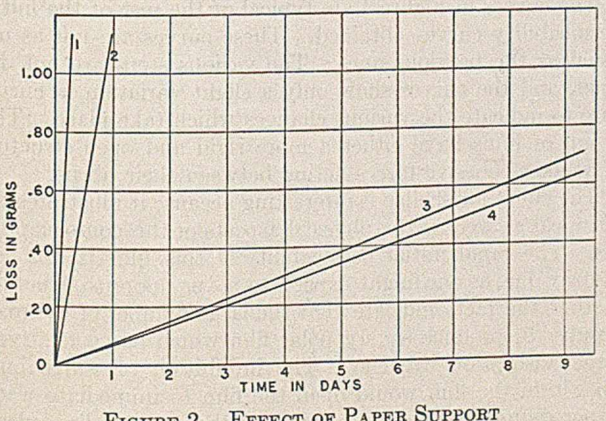

FIGURE 2. EFFECT OF PAPER SUPPORT

1. Open dish
2. Uncoated paper
3. Free varnish film
4. Paper coated with varnish

The varnishes were applied to the paper by dipping strips which were 3 inches (7.6 cm.) wide and 2 feet (61 cm.) long. They were dried as has already been described. Disks were then cut from the coated sheets so that the amount of paper base contained in the disk would not vary in weight more than ±0.0002 gram. Their thickness was calculated from the weight of the disk, its area, and the specific gravity of the dried coating material. It was felt at the time that this was a more precise method than other means for measuring the thickness of the softer materials. The thickness of hard films such as shellac was checked with a sensitive micrometer and was found to agree with the calculated thickness. Figure 2 shows that the paper had a slight impeding effect on the permeability in comparison with that of free films. However, it is unlikely that this base materially affected the general permeability characteristics of any of the films since it was very porous as shown. If it did, the effect would probably be more pronounced during the earlier stages of permeability. That this was not the case can be seen from the similarity in the initial permeability curve for a spar varnish shown in Figure 3, which compares a free film with those having tissue paper and calendered paper for bases.

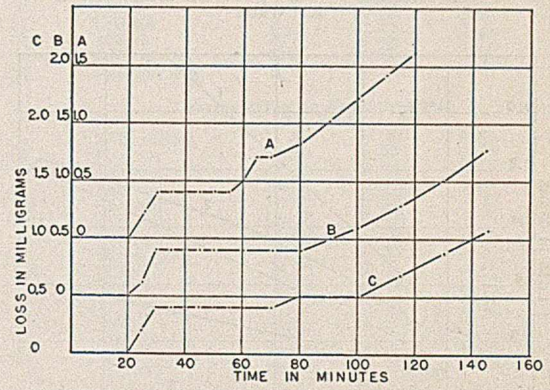

FIGURE 3. EFFECT OF PAPER SUPPORT UPON INITIAL PERMEABILITY

A. Free rosin spar varnish film
B. Same varnish on tissue paper
C. Same varnish on heavy paper

Permeability Measurements

In determining permeability, 10 to 15 ml. of the liquid were placed in the metal cup, and the coated disks were then fastened securely between the brass ring and the flange of the cup under a slight compression. The cups were next placed in an electric oven automatically maintained at 25° C. This oven contained two metal baskets with 5 pounds (2.3 kg.) of anhydrous calcium chloride to remove any traces of moisture not otherwise removed and a circulating fan to remove any escaping vapors. For the initial permeability measurements, the cups were weighed every 5 minutes. A similar period of time elapsed before the first weighing could be obtained. With the other measurements the cups were weighed each morning for 5 days to ascertain the vapor loss through the films.

Initial-Stage Permeability Curves

The stepped-shape curves shown in Figure 3 for the initial permeability of moisture through spar varnish films are un-

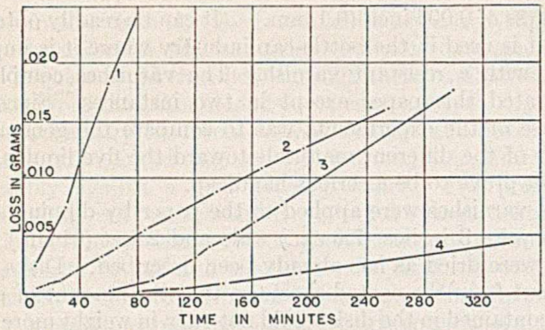

FIGURE 4. INITIAL PERMEABILITY TO WATER

1. Shellac
2. Glue
3. Linseed Oil
4. Rubber

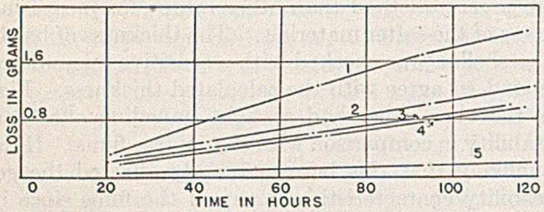

FIGURE 5. PERMEABILITY OF ROSIN SPAR VARNISH FILMS

1. Alcohol
2. Acetone
3. Benzene
4. Ethyl acetate
5. Water

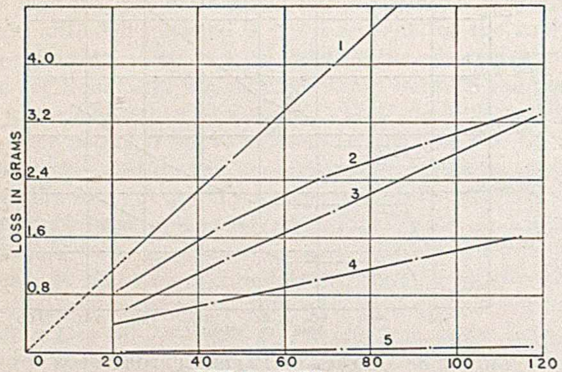

FIGURE 6. PERMEABILITY OF ESTER GUM LACQUER FILMS

1. Acetone
2. Alcohol
3. Ethyl acetate
4. Benzene
5. Water

usual and show clearly what takes place. The curves for free films, for those on tissue paper, and for those on heavy paper have the same characteristic shape, prior to the establishment of the final uniform rate of permeation.

These curves suggest some interesting phenomena during this initial period. The complete lack of permeability for the first 20 minutes would indicate that, if pores exist, they are too small for vapor diffusion through the film, but this does not exclude the possibility of a large vapor adsorption in the interfibrillar spaces which would build up an imbibition pressure sufficient to overcome, by the end of this time, the cohesive forces operating between the fibrils of the elastic gel film structure. The interfibrillar spaces would then be rapidly emptied of water by the vapor pressure differential which exists across the film. This is shown in the curve by the 10-minute period of loss in weight which follows the 20-minute period of imbibition. The loss of water would then allow the cohesive forces again to draw the fibrils sufficiently close together to prevent further immediate diffusion.

The curve shows that the second period of no diffusion was longer than the first one. This would indicate that, although the interfibrillar spaces are too small to permit vapor diffusion

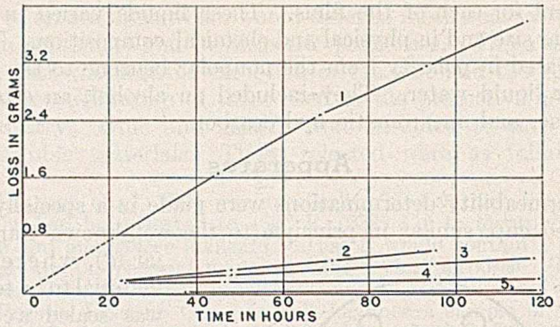

FIGURE 7. PERMEABILITY OF SHELLAC FILMS

1. Alcohol
2. Acetone
3. Ethyl acetate
4. Water
5. Benzene

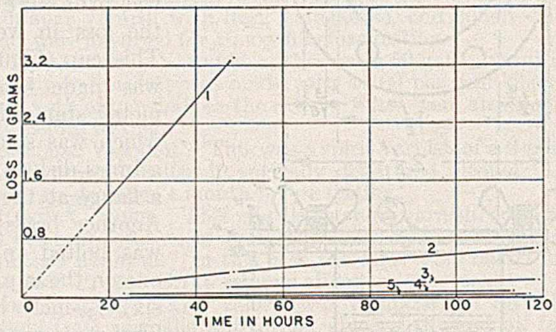

FIGURE 8. PERMEABILITY OF PARAFFIN WAX FILMS

1. Benzene
2. Acetone
3. Ethyl acetate
4. Alcohol
5. Water

during this period, they are larger than they were originally. Consequently a longer adsorption period is required to build up an imbibition pressure which is never as large as that developed during the first impermeable period.

The state ultimately obtained as a result of this swelling and contraction of the film would be one of a constant permeation where an equilibrium would exist between the imbibition and cohesive forces, such as was characteristic of these films and the others studied. This explanation is purely hypothetical. However, it was based upon the physical phenomena which were observed to take place with varnish films in this and previous investigations.

Similar curves were obtained for shellac with acetone and with ethyl acetate. These are not shown, to save space. The effect of adsorption or imbibition was not so evident in these as in the previous graphs, so that only one period of impermeability was clearly defined. This followed rather than preceded a brief period of rapid permeation in the case of these films.

The curves in Figure 4 are typical of the rest of the initial permeability curves obtained. These curves are not as unusual as the previous ones. The various steps are not distinct, and the curves show only a slight variation in curvature to indicate the various changes which take place. This group of films have either a more rigid and open structure or weaker cohesive forces acting between their fibrils.

The curve for shellac is interesting because it illustrates the chemical as well as the physical aspects of this complex process. The rapid initial permeability of this film is not necessarily due, as one might expect, to a very porous structure. Rather the facts indicate that the large number of hydroxyl groups (*9*) produce a very polar film which has a relatively large adsorption capacity. The imbibition pressures built up within the film would open the film to immediate water vapor diffusion, which would not be the case for linseed oil.

It is probable that the adsorbed moisture causes a deaggregation of the shellac agglomerate which would decrease the size of the intermolecular spaces in the film. This would account for the steady decrease in rate of permeability observed. The reverse is true for linseed oil. With films of the latter substance the interfibrillar spaces become progressively larger until an equilibrium is reached.

The permeability curve for shellac and alcohol was similar to that shown for linseed oil and water. Here there can be no question of the imbibition and swelling effects which take place in the former case, since these can be readily observed when shellac is dissolved in alcohol. For example, the resin will completely imbibe the solvent, swelling to form a distinct gel which appears as a single phase, when many samples of shellac are treated with alcohol in proportion to give a 5-pound cut, provided they are not vigorously agitated. These conditions are similar to those in the permeability experiments. In fact, a very slight swelling was also noted for many of the films in carrying out these measurements.

Constant-Rate Permeability

The total weights of the amounts of vapor of each of the five liquids studied which permeated the different films for consecutive 24-hour periods are summarized in Table I. The films are listed in these tables in the order of what is generally taken as permeability—i. e., the rate of permeation after it has become constant. Typical permeability curves are shown in Figures 5 to 8 where it can be seen that in all instances the final rate of permeation would follow Fick's law.

A study of the amount of vapor which passed through films of different thicknesses under these conditions showed that the permeability was not directly proportional to the reciprocal of the thickness of the film. The deviation from the customary proportionality could be neglected, however, in equating results to a single thickness for the film studied in this investigation, since they varied to only a limited extent in their thickness and exceeded in all instances a required minimum of 0.1 gram in weight. Thus, calculated values for a single thickness for comparison are given in Table I. These figures represent the number of milligrams of vapor which would permeate through 0.1 gram of a film 11.34 sq. cm. in area, in 1 hour after a constant rate of permeability had been reached. These values are also shown graphically in Figure 9.

The table and graphs illustrate in a surprising manner the importance which must be attributed to solubility in determining the extent to which the films were permeable to the different vapors. For example, paraffin wax had the greatest impedance to water and alcohol vapors. It was displaced in this respect by the more insoluble material, gelatin, where ethyl acetate and acetone are the liquids; whereas benzene, which is a solvent, causes it to be placed among the most permeable substances.

The permeability was different for each vapor but was not proportional, in general, to the differences in vapor pressures. This was rather striking because it might have been expected that, in the case of soluble films at least, the volatility of the liquid might have been the controlling factor in determining the rate of permeability by true diffusion. Apparently even here the gel structure of the film had not been completely destroyed by the solvent, and its relation to other properties of the liquids still had an important influence upon the rate of permeation. Hence, the effect of vapor pressure differences would be clearly evident only when comparing the permeabilities of liquids of similar properties. Unfortunately, the investigation did not include any films which were soluble in both water and alcohol, but, if comparisons for these two liquids are confined to the insoluble films, it can be seen that alcohol is nearly four times as permeable as water.

Table I. Permeability Data

Film No.	Name	Permeability	Total Weight of Liquid Permeating Film, Grams 24 hr.	96 hr.	120 hr.
		Mg.[a]			
		Permeability to Water			
13[b]	Glue	32.00	0.92	3.08	3.90
19[b]	Lacquer	17.00	4.60	2.72	7.32
14	Gelatin	5.94	0.16	0.57	0.73
15	Lacquer	5.83	0.12	0.56	0.68
1	Linseed	4.90	0.11	0.47	0.58
2	Linseed	2.36	0.06	0.226	0.286
8	Alkyd	2.33	0.03	0.225	0.255
7	Alkyd	2.03	0.045	0.195	0.240
16	Lacquer	2.00	0.050	0.190	0.240
10	Rubber	1.95	0.045	0.187	0.232
3	Rosin spar	1.70	0.036	0.164	0.200
9	Alkyd	1.56	0.045	0.150	0.195
6	WW rosin	0.93	0.070	0.090	0.160
4	Phenolic spar	0.85	0.025	0.082	0.107
17	Lacquer	0.73	0.030	0.070	0.100
5	Shellac	0.42	0.140	0.040	0.180
18	Lacquer	0.31	0.050	0.030	0.080
11	Paraffin wax	0.008	0.000	0.010	0.010
		Permeability to Alcohol			
6	WW rosin	47.0	1.10	4.55	5.65
19[b]	Lacquer	32.8	1.40	3.15	4.55
5	Shellac	31.0	0.70	3.02	3.72
17	Lacquer	26.7	0.84	2.56	3.40
15	Lacquer	24.8	0.80	2.40	3.20
16	Lacquer	24.0	0.85	2.35	3.20
1	Linseed	18.7	0.30	1.72	2.02
3	Rosin spar	18.4	0.30	1.66	1.96
7	Alkyd	16.9	0.30	1.60	1.90
2	Linseed	16.0	0.25	1.54	1.79
13[b]	Glue	16.0	0.42	1.53	1.95
18	Lacquer	13.0	0.45	1.25	1.70
9	Alkyd	11.6	0.24	1.11	1.35
14	Gelatin	9.5	0.21	0.89	1.10
8	Alkyd	8.7	0.15	0.82	0.97
10	Rubber	8.2	0.16	0.79	0.95
11	Paraffin wax	0.01	0.03	0.01	0.04
		Permeability to Ethyl Acetate			
6	WW rosin	41.80	0.95	4.05	5.00
17	Lacquer	23.10	0.60	2.74	3.34
19	Lacquer	21.35	0.61	2.05	2.66
16	Lacquer	19.30	0.45	1.87	2.32
18	Lacquer	14.40	0.40	1.40	1.80
1	Linseed	13.17	0.31	1.27	1.58
15	Lacquer	12.50	0.28	1.20	1.48
3	Rosin spar	7.30	0.20	0.70	0.90
13[b]	Glue	6.31	0.17	0.62	0.79
9	Alkyd	5.70	0.10	0.55	0.66
7	Alkyd	5.42	0.14	0.52	0.66
8	Alkyd	4.70	0.10	0.45	0.56
5	Shellac	3.54	0.14	0.34	0.48
11	Paraffin wax	1.94	0.03	0.19	0.22
14	Gelatin	0.44	0.018	0.042	0.06
		Permeability to Acetone			
6[c]	WW rosin	..	..	..	..
10	Rubber	58.3	1.50	5.60	7.10
17	Lacquer	53.3	1.28	5.12	6.40
19[b]	Lacquer	44.5	1.06	4.28	5.34
15	Lacquer	41.6	0.88	4.00	4.88
16	Lacquer	37.5	0.76	3.60	4.36
1	Linseed	21.4	1.02	2.07	3.09
18	Lacquer	20.4	0.49	1.96	2.45
7	Alkyd	17.3	0.56	1.66	2.22
13[b]	Glue	12.4	0.20	1.28	1.48
9	Alkyd	10.3	0.24	0.99	1.23
3	Rosin spar	10.2	0.24	0.98	1.22
8	Alkyd	9.7	0.27	0.93	1.20
5	Shellac	7.5	0.14	0.54	0.68
11	Paraffin wax	5.0	0.16	0.48	0.64
14	Gelatin	2.2	0.04	0.22	0.26
		Permeability to Benzene			
10	Rubber	285.00	5.7 grams in 20 hours		
11	Paraffin wax	125.00	1.0 gram in 8 hours		
6	WW rosin	29.20	0.65	2.80	3.45
19[b]	Lacquer	29.00	0.80	2.80	3.60
13[b]	Glue	25.00	0.60	2.30	2.90
17	Lacquer	12.50	0.40	1.20	1.60
18	Lacquer	11.56	0.25	1.11	1.36
15	Lacquer	8.70	0.24	0.80	1.04
3	Rosin spar	8.70	0.20	0.80	1.00
4	Phenolic spar	8.44	0.15	0.81	0.96
1	Linseed	8.00	0.26	0.73	1.00
16	Lacquer	7.70	0.16	0.70	0.86
2	Linseed	6.20	0.22	0.595	0.815
9	Alkyd	2.28	0.075	0.210	0.285
8	Alkyd	2.03	0.045	0.195	0.240
14	Gelatin	1.57	0.050	0.150	0.200
7	Alkyd	1.10	0.075	0.105	0.180
5	Shellac	0.288	0.000	0.0028	0.0028

[a] Milligrams of vapor which permeate through 0.1 gram of a film 11.34 sq. cm. in area, 1 hour after a constant rate of permeability is reached.

[b] Porous.

[c] Film dissolved too quickly to obtain any measurements.

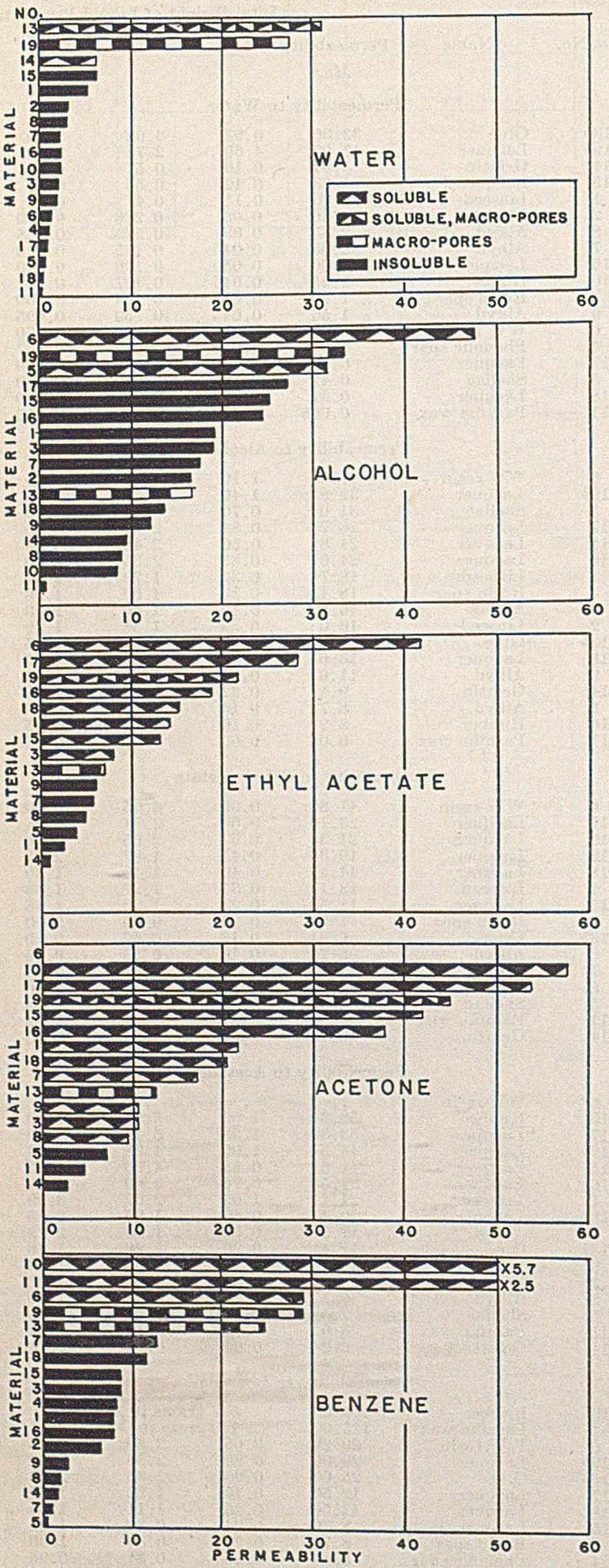

FIGURE 9. COMPARISON OF PERMEABILITIES OF FILMS

1. Raw linseed oil
2. Bodied linseed oil
3. Rosin spar varnish
4. Phenolic varnish
5. Shellac
6. Rosin
7. Alkyd resin
8. Modified alkyd
9. Resin-oil modified alkyd
10. Rubber
11. Paraffin wax
13. Glue
14. Gelatin
15. Cellulose nitrate
16. Plasticized cellulose nitrate
17. Ester gum lacquer
18. Aluminum lacquer
19. Porous lacquer

This ratio is practically the same as that of their vapor pressures at 25° C., where water has a pressure of 23.5 mm. and alcohol has one of 116 mm. This relation does not hold for comparisons between any other two of the liquids studied. The same is true for any relations based upon the molecular size of the vapor molecules.

The graphs also show the effect of porosity. If the pores are large, porosity is secondary in importance only to solubility as a controlling factor. Two sets of films in this investigation had definite macroporous structures—the films from lacquer 19, which was formulated with an excess of fine silica particles, and the glue coatings (*13*), which developed fine cracks during drying. These porous films followed more or less the order of permeability observed for the other films in relation to solubility, except with the two most polar liquids, water and alcohol. The very high permeability of the two liquids through films from lacquer 19 was probably due to the fact that these films were highly polar in addition to being porous. It might be expected that under such experimental conditions, the pores of the film would be the most completely wet of any of those studied.

The films containing the alkyd resins were also of special interest. The order of permeability varied with the liquid, showing that the composition of the resin affects its permeability. Alkyd 7, containing no modifying Amberol resin, showed the least permeability in only one instance—namely, when benzene was the permeating liquid.

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Solvent Balance of a Solvent-Diluent Mixture

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Samples of two mixtures were evaporated 25, 50, and 75 per cent. The rate of evaporation of butyl acetate in terms of itself showed the least variation. The toluene-Troluoil mixture apparently evaporated at a greater rate than toluene alone in such solvent diluent mixtures. Based on the assumption that each ingredient would evaporate from the mixture at the relative rate of evaporation of that ingredient alone, the compositions of the samples were calculated. Fair agreement between the found and calculated values was obtained except for Troluoil. Upon evaporation, the mixture containing Troluoil developed increasing tolerance at a more uniform rate than in the case of the mixture containing only toluene as the diluent. The former also showed correspondingly greater tolerance than the latter. The effect of replacing part of the nitrocellulose with resins was observed by means of dilution ratio, resistance to blush, and viscosity data. The presence of resins appeared to lower the dilution ratio for the mixture containing Troluoil. However, as evaporation progressed, the dilution ratio of this mixture became greater than that of the mixture containing toluene alone as the diluent.

BROWN and Crawford (*3*) pointed out the well-known need of solvent balance during the evaporation of a lacquer thinner from the film. Bent and Wik (*1*) suggested the relative rates of evaporation of the thinner ingredients as a handy tool for estimating solvent balance. The purpose of the present paper is to carry this thought a step further by the experimental study of two mixtures of thinner ingredients. The solvents used were prepared from commercial grades by redistillation. The toluene was of A. C. S. grade. The mixtures, therefore, are not strictly comparable to those found in the lacquer industry.

Mixture A was composed of butyl acetate, butyl alcohol, and toluene. Mixture B was composed of butyl acetate, butyl alcohol, toluene, and a petroleum diluent. Mixture B bore a simple relation to mixture A. When both mixtures were used to make nitrocellulose solutions, the latter were found to be similar in three respects. The solutions were equivalent as to nitrocellulose concentration, viscosity, and dilution ratio. The evaporation rates were roughly similar.

The object of this paper was to prepare samples of mixtures A and B which had been partially evaporated and to study them. Liter samples were prepared by removing 25, 50, and 75 per cent of the mixture by evaporation.

Evaporation of Mixtures

A beaker of 4-liter capacity with an inside diameter of 15.2 cm. (6 inches) was used as the container. The beaker was placed 7.6 cm. (3 inches) from a wind tunnel and centered. The wind tunnel consisted of a tin funnel. It was constructed so that its wide end would fit snugly over a 12-inch fan of 110-volt a. c. type. The diameter of the wide end was 34.3 cm. (13.5 inches). The diameter of the narrow end was 23 cm. (9 inches).

As a check on the method of evaporation, liter portions of the same sample were subjected to different conditions. One portion was evaporated to one-fourth of its original volume in a 2-liter beaker by means of a draft of air. One portion was evaporated from a shallow tin pan, 43.5 × 28.2 × 2.1 cm. ($17^1/_8 \times 11^1/_8 \times {}^7/_8$ inch), to one-fourth of its original volume in quiet air. Comparative dilution values of the evaporated samples were 15.6 and 15.3 cc., respectively.

During the evaporation, temperature conditions were kept within relatively narrow limits. The initial temperature of the samples was kept between 19.4° and 20.5° C. (67° and 69° F.). Room temperature was maintained between 20.5° and 26° C. (69° and 79° F.).

Composition

The samples were analyzed by an adaption of the method of Watts (*6*). In the case of simple mixtures the method could be simplified both as to procedure and calculations. The substitution of sulfuric acid of 80 per cent strength by weight (specific gravity 1.727 at 20° C.) for sulfuric acid of 80 per cent strength by volume, apparently improved the procedure. The composition of the samples is indicated in Table I. The change of composition in terms of unevaporated sample is shown in Figure 1 for samples 1 to 4, and 9 to 12.

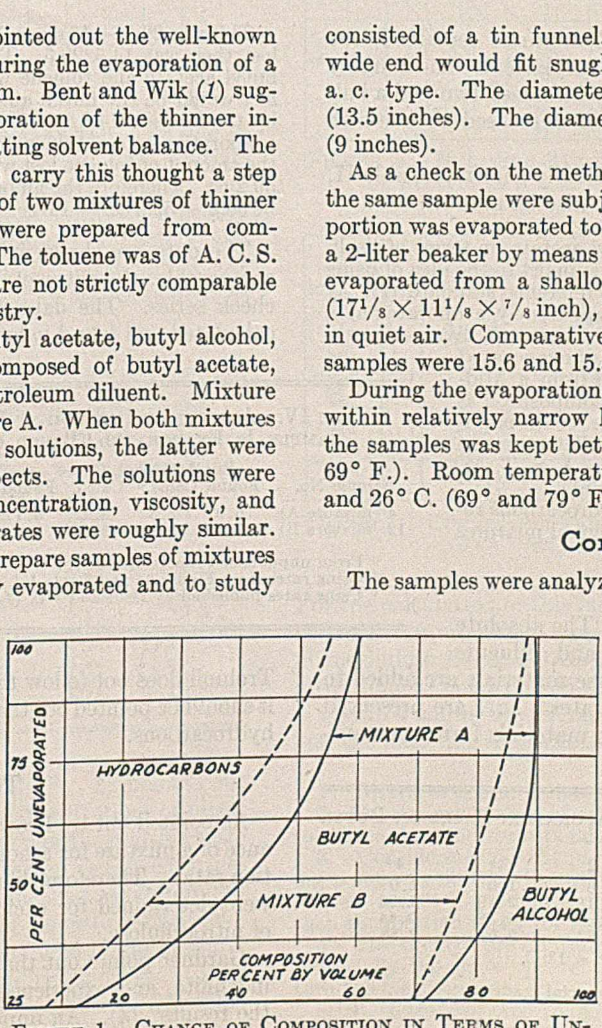

FIGURE 1. CHANGE OF COMPOSITION IN TERMS OF UNEVAPORATED SAMPLE FOR SAMPLES 1 TO 4 AND 9 TO 12

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[1] Present address, Bradley & Vrooman Company, Chicago, Ill.

TABLE I. COMPOSITION OF MIXTURES

% Remaining after Evapn.	Sample No.	Hydrocarbons	Butyl Acetate[a]	Butyl Alcohol
		Per cent by volume		
		Mixture A		
100	1	60.2	29.5[b]	10.3
75	2	54.5	35.14	10.36
49.72	3	41.0	44.11	14.89
25	4	12.55	59.90	27.55
100	5	60.5	30.26	9.24
75	6	54.5	35.80	9.7
50	7	41.4	44.16	14.44
25	8	12.6	60.82	26.58
		Mixture B		
100	9	55.0[b]	33.23	11.77
75	10	45.25	39.23	15.52
47.48	11	28.0	50.21	21.79
25	12	7.15	62.46	30.39
100	13	55.0[b]	33.37	11.63
75	14	45.5	39.28	15.22
49.25	15	29.9	49.50	20.6
25	16	8.45	63.13	28.43

[a] Butyl acetate of 94.5% purity.
[b] A mixture of toluene and Troluoil in the ratio of 20 to 35.

TABLE II. RELATIVE EVAPORATION OF EACH INGREDIENT BASED ON ITS ORIGINAL VOLUME

	Hydrocarbons					Butyl Acetate					Butyl Alcohol				
% Remaining	Sample No.	%	Sample No.	%	Av. %	Sample No.	%	Sample No.	%	Av. %	Sample %	%	Sample No.	%	Av. %
							Mixture A								
100	1	100	5	100	100	1	100	5	100	100	1	100	5	100	100
75	2	67.9	6	67.6	67.8	2	89.2	6	88.6	88.9	2	75.4	6	78.8	77.1
50	3	34.2	7	34.2	34.2	3	74.7	7	72.7	73.7	3	72.3	7	78.2	75.3
25	4	5.2	8	5.2	5.2	4	50.8	8	50.2	50.5	4	68.8	8	71.9	70.4
							Mixture B								
100	9	100	13	100	100	9	100	13	100	100	9	100	13	100	100
75	10	61.8	14	61.9	61.9	10	88.5	14	88.3	88.4	10	98.9	14	98.1	98.5
50	11	25.5	15	27.1	26.3	11	75.4	15	74.2	74.8	11	92.7	15	88.5	90.6
25	12	3.3	16	3.8	3.6	12	46.9	16	47.3	47.1	12	64.6	16	61.6	62.5

When one-fourth of the original mixtures remained, the following changes were indicated: Butyl acetate had roughly doubled. Butyl alcohol had roughly increased two and a half times. Hydrocarbons, however, had decreased to one-fifth or less.

The change in each ingredient is clearly shown in Table II, where the following indications may also be noted:

1. The rate of evaporation of butyl acetate, in terms of itself, shows the least variation. This lends support to the idea of using the evaporation of butyl acetate as a reference standard (*1*).
2. The toluene-Troluoil mixture apparently evaporates at a greater rate than toluene alone. The greatest divergence appears when the original mixtures are half evaporated. Troluoil is a petroleum diluent refined from a Mid-continent crude oil. The estimated composition is roughly as follows: paraffins 58 per cent, naphthenes 39, and aromatics 3. The distillation range of a typical sample, according to the A. S. T. M. method, is 93.3° to 121.7° C. (dry point).
3. Five per cent or less of the hydrocarbons remain when only 25 per cent of the original mixtures are left.

Evaporation

According to Bent and Wik (*1*), "The absolute rates of evaporation of solvents and diluents usually change somewhat when these materials are added to lacquer mixtures, but the relative rates . . . . are preserved during the evaporation unless the materials form constant-evaporating mixtures."

TABLE III. RELATIVE RATES OF EVAPORATION BASED ON BUTYL ACETATE[a]

	1	2	3[b]	4[c]
Butyl acetate[d]	1.0	1.0	1.0	1.0
Toluene[e]	2.21	2.18	2.19	1.96
Butyl alcohol[d]	0.58	..	0.58	0.44
Troluoil	2.71	2.63	2.67	2.88

[a] Usual temperature of evaporation, 21° ± 1° C.
[b] Averages.
[c] Rates of Bent and Wik based on commercial grades.
[d] Redistilled to a boiling range of 1° C.
[e] A. C. S. grade.

Relative evaporation curves were plotted from data obtained by the Rubek-Dahl method as shown in Figure 2*a* (*5*). The relative rates as calculated are shown in Table III. Although not strictly comparable, the rates of Bent and Wik (*1*) are shown. Figure 2*b* indicates approximately the relative evaporation curves of mixtures A and B. Calculations were made to check the hypothesis of Bent and Wik (*1*).

The data of Table I were used to calculate the amounts of each ingredient in the sample when 25 per cent of each mixture remained unevaporated. An example based on sample 4 follows:

> According to Table I, 29.5 cc. of butyl acetate were found in 100 cc. of the original mixture (sample 1). When sample 1 had evaporated to one-fourth of its volume or to 25 cc., only 59.9 per cent or 15 cc. of butyl acetate remained. Therefore the difference between the values represents the volume of butyl acetate that evaporated.
>
> This was 29.5 − 15 cc. = 14.5 cc. The fraction of butyl acetate lost then was 14.5/29.5. Therefore, if the evaporation rates of butyl acetate and toluene were the same, the amount of toluene lost would be the initial amount of toluene (60.2 cc.) multiplied by the fraction 14.5/29.5. However, according to Table III the evaporation rate of toluene is double that of butyl acetate. Then the amount of toluene lost would be 60.2 × (14.5/29.5) × 2.00 = 59.2 cc. Therefore the amount of toluene left in sample 4 would be 60.2 − 59.2 cc. = 1.0 cc. (Found, 3.1 cc.; calculated, 1.0 cc.)

The data are shown in Table IV. Although not strictly comparable, the rates of Bent and Wik (*1*) were used in a check series. The data indicate a fair agreement between calculated and found values with one exception. Apparently Troluoil does not follow the general rule. In this connection it should be pointed out that Troluoil is a mixture of petroleum hydrocarbons.

TABLE IV. AMOUNT OF INGREDIENT WHEN 25 PER CENT OF A 100-CC. SAMPLE IS EVAPORATED (BASED ON LOSS OF BUTYL ACETATE)

	Butyl Alcohol, Cc.			Toluene, Cc.			Troluoil,[a] Cc.		
Sample No.	Found	Calcd.[b]	Calcd.[c]	Found	Calcd.[b]	Calcd.[c]	Found	Calcd.[b]	Calcd.[c]
4 (mixture A)	6.9	7.3	8.1	3.1	−4.7	2.2	...	...	...
12 (mixture B)	7.6	8.2	9.1	0.8	−3.3	−0.8	1.0	−14.3	−18.1

[a] From unpublished report of Dorsch.
[b] Using rates from Figure 2*a* and Table III.
[c] Using rates published by Bent and Wik (*1*).

Tolerance

As pointed out by Brown and Bogin (*2*), the limit of tolerance of a mixture for a nonsolvent has been described as dilution ratio. Therefore, dilution ratios, with respect to Troluoil, were determined for each sample at various concentrations of nitrocellulose.

Gardner points out that "the end points . . . . are rather indefinite, and experience is necessary to be able to check the results" (*4*). An unpublished report of Daley, Johnson, and Wray discussed end points for mixtures A and B. Ac-

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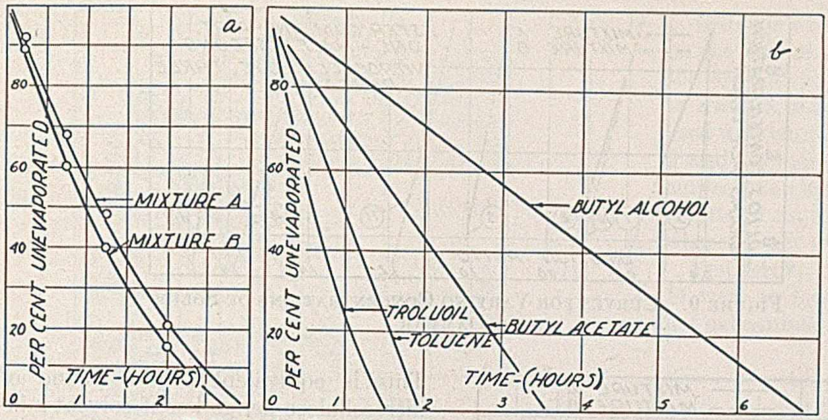

FIGURE 2. RELATIVE EVAPORATION CURVES

a. By Rubek-Dahl Method (5)

b. As calculated

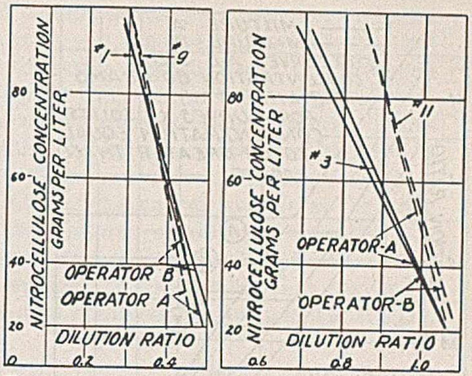

FIGURE 3. DEGREE OF PRECISION OF DILUTION RATIOS

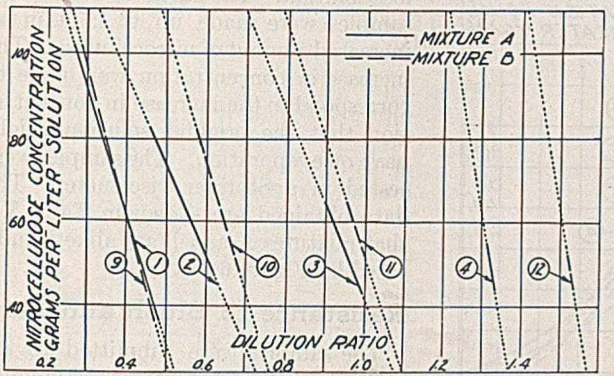

FIGURE 4. AVERAGE DILUTION RATIO CURVES

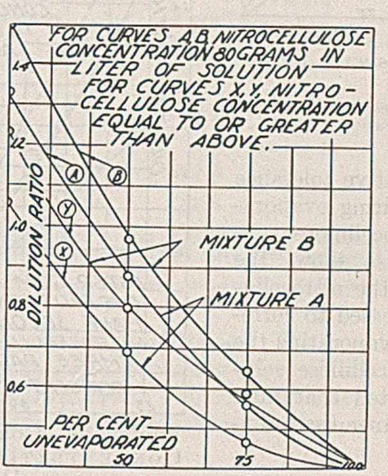

FIGURE 5. RELATIVE TOLERANCE OF MIXTURES A AND B

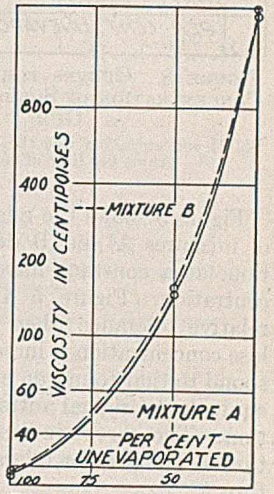

FIGURE 6. VISCOSITY DATA FOR MIXTURES A AND B

cording to them, the end point shall be taken when a film of the solution on the sides of the Erlenmeyer flask appears striated, like the waves of sand at the seashore. In very concentrated solutions the striation may give way to a pebbly effect. The degree of precision is indicated in Table V and Figure 3. Figure 4 shows average dilution ratio curves. As pointed out by Gardner, the curves may be considered as straight lines (*4*).

TABLE V. DILUTION RATIO VALUES FROM THE CURVES

Sample No.	% Thinner Remaining	Operator A	Operator B	Operator C	Average	% Variation
1	100	3.9	4.1	...	4.0	±2.5
2	75	5.45	...	5.60	5.52	±1.5
3	50	0.86	...	0.88	0.87	±1.1
4	25	..	1.35	...	...	...
9	100	4.0	...	4.0	4.0	...
10	75	6.4	6.35	...	6.38	±0.5
11	50	..	0.975	0.963	0.969	±0.6
6	75	5.70	5.67	...	5.69	±0.3
7	50	8.62	8.78	...	8.70	±0.9
8	25	1.31	1.37	...	1.34	±2
14	75	..	6.45	5.84	6.14	±5
15	50	..	9.50	9.70	9.60	±1
16	25	..	1.44	1.46	1.45	±0.7

DILUTION RATIOS OF THINNERS A AND B. As pointed out by Brown and Bogin in 1927 (*2*), the concentrations of nitrocellulose in the samples at the conclusion of the dilution ratio determination should be roughly the same. A concentration of 8 per cent was suggested by them since it was often found in practice. The concentration was apparently defined as 8 grams of nitrocellulose to 100 cc. of the final liquid mixture. The concentration used in this paper differs slightly. It may be defined as 8 grams of nitrocellulose in 100 cc. of the solution found at the end of the determination. This is equivalent to 0.586 pound of nitrocellulose in a gallon of the final solution.

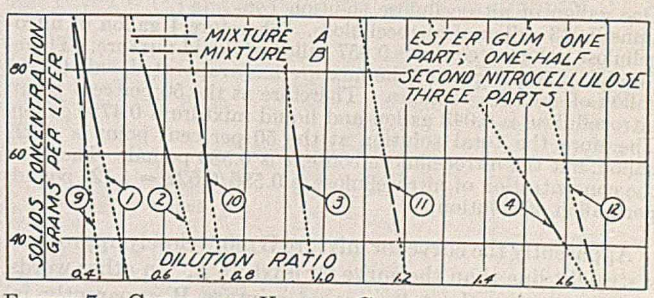

FIGURE 7. CURVES FOR VARYING CONCENTRATIONS OF SOLIDS WITH ESTER GUM

For the calculation of this factor the following bulking values of Hook (unpublished) were used: In mixture A, 1 pound nitrocellulose bulks 0.0739 gallon; in mixture B, 1 pound nitrocellulose bulks 0.0735 gallon.

Figure 4 shows the average dilution ratios for all samples, and the following indications may be pointed out:

1. Mixtures A and B match as formulated.
2. At various stages of evaporation, mixture B has greater tolerance than the corresponding sample of mixture A.
3. Considering only the partly evaporated samples, the following point was noted: The dilution ratios for mixture B samples are less sensitive to changes in the nitrocellulose concentrations than the dilution ratios for mixture A samples.
4. The slope of the dilution ratio curve for mixture B remains practically the same apparently until three-fourths of the mixture has been evaporated.
5. In the case of mixture A, the sample 50 per cent evaporated is apparently more sensitive to changes in the nitrocellulose concentration than are the others.

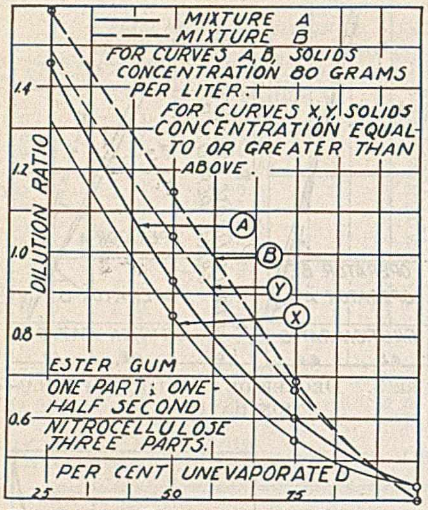

FIGURE 8. CURVES FOR A CONSTANT CONCENTRATION OF SOLIDS WITH ESTER GUM

Solids concentration was the equivalent of 80 grams per liter of solution.

Figure 5 shows the relative tolerance of mixtures A and B during evaporation, at a constant nitrocellulose concentration. Figure 5 also shows the relative tolerance when the nitrocellulose concentration is increased to correspond to that found on evaporating the equivalent original nitrocellulose solution. The curves indicated that mixture B has greater tolerance than mixture A.

EXAMPLE. To determine the nitrocellulose concentration when 50 per cent of the liquid mixture has been evaporated. One gallon of nitrocellulose solution contains 0.043 gallon of nitrocellulose. Therefore 1 gallon of nitrocellulose solution contains 0.957 gallon of liquid mixture. Therefore when 50 per cent of the mixture has evaporated, only 0.4785 gallon of mixture remains. Therefore at the 50 per cent point, nitrocellulose is 0.043 gallon and liquid mixture is 0.4785 gallon. Therefore the total solution at the 50 per cent point is 0.522 gallon, but the nitrocellulose content is 0.586 pound. Therefore the concentration of nitrocellulose is 0.586/0.522 = 1.121 pounds per gallon of solution.

Apparently the curve for mixture B more closely approaches a straight line than the curve for mixture A. In other words, on evaporation the tolerance of mixture B apparently increases more uniformly than the tolerance of mixture A.

Viscosity

Solutions of the original mixtures were made up so as to contain 6 grams of nitrocellulose per 100 cc. of liquid mixture.

TABLE VI. AVERAGE VISCOSITY AT 20° ± 0.2° C.

Liquid Mixture Remaining[a]	Mixture A		Mixture B		Nitrocellulose/100 Cc. Solvent
	Sample No.	Viscosity	Sample No.	Viscosity	
%		*Centipoises*		*Centipoises*	*Grams*
100	1	28.1	9	27.1	6
75	2	47.9	10	51.4	8
49.72	3	147.2	..	....	12
47.48	..	....	11	147.7	12
25	4	2040.0	12	1830.0	24
100	..	....	..	....	..
75	6	50.8	14	50.0	8
50	7	153.4	..	....	12
49.25	..	....	15	145.9	12
25	8	1851.6	16	1765.0	24

[a] Maximum variation is ±0.5%.

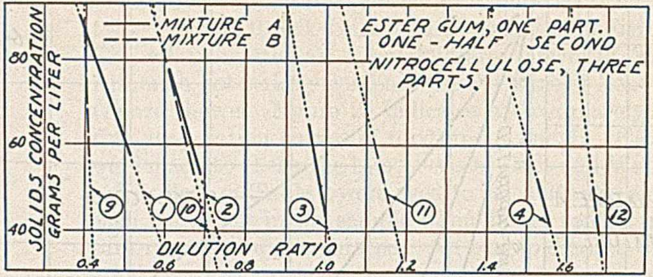

FIGURE 9. CURVES FOR VARYING CONCENTRATIONS OF SOLIDS WITH DAMMAR

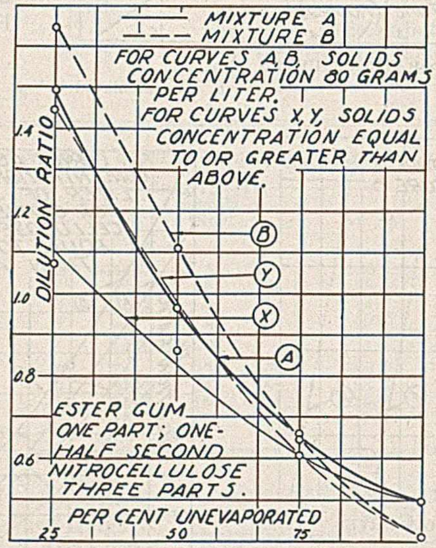

FIGURE 10. CURVES FOR A CONSTANT CONCENTRATION OF SOLIDS WITH DAMMAR

Solids concentration was the equivalent of 80 grams per liter of solution.

This is equivalent to 0.5 pound of nitrocellulose per gallon of solvent mixture and also equivalent to 0.44 pound of nitrocellulose per gallon of nitrocellulose solution. The partially evaporated samples were made up to contain an increased amount of nitrocellulose. The increase in concentration was made to correspond to the increase in concentration that the original solution might have on evaporation. The samples were tested in a Stormer viscometer. The data obtained are shown in Table VI; that mixtures A and B are alike is indicated by Figure 6.

Resistance to Blush and Flow

The samples were submitted to excessively critical conditions of humidity and temperature in order to determine whether a difference in the resistance to blush could be observed under any conditions. Samples in pairs were flowed out side by side on glass plates and placed in a humidity cabinet. The data are shown in Table VII. In all cases where blushing could be observed, the resistance to blush was greater for mixture B samples. No difference in flow was observed.

TABLE VII. RESISTANCE TO BLUSH AT 90° F. (32.2° C.) AND 68 PER CENT RELATIVE HUMIDITY

Liquid Mixture Remaining	Mixture A		Mixture B	
	Sample No.	Blush	Sample No.	Blush
%				
100	1	Slight	9	Very slight
75	2	Slight	10	Very slight
49.72	3	Slight	..	......
49.48	..	...	11	Very slight
25	4	Slight	12	Very slight
100	..	...	..	......
75	6	Slight	14	None
50	7	Medium	..	......
49.25	..	...	15	Slight
25	8	None	16	None

Effect of Natural Resins on Nitrocellulose Solutions of Mixtures

TOLERANCE. The procedure previously described was used. According to Daley, Johnson, and Wray (unpublished report), the end point is more difficult to check than in the case of solutions containing only nitrocellulose. Therefore the precision obtained for curves is less than for nitrocellulose solutions. Further work along this line would be advantageous. In addition, the curves are drawn through points relatively close together. Therefore considerable error could creep in with regard to the slope of the curves. Figure 7 shows the

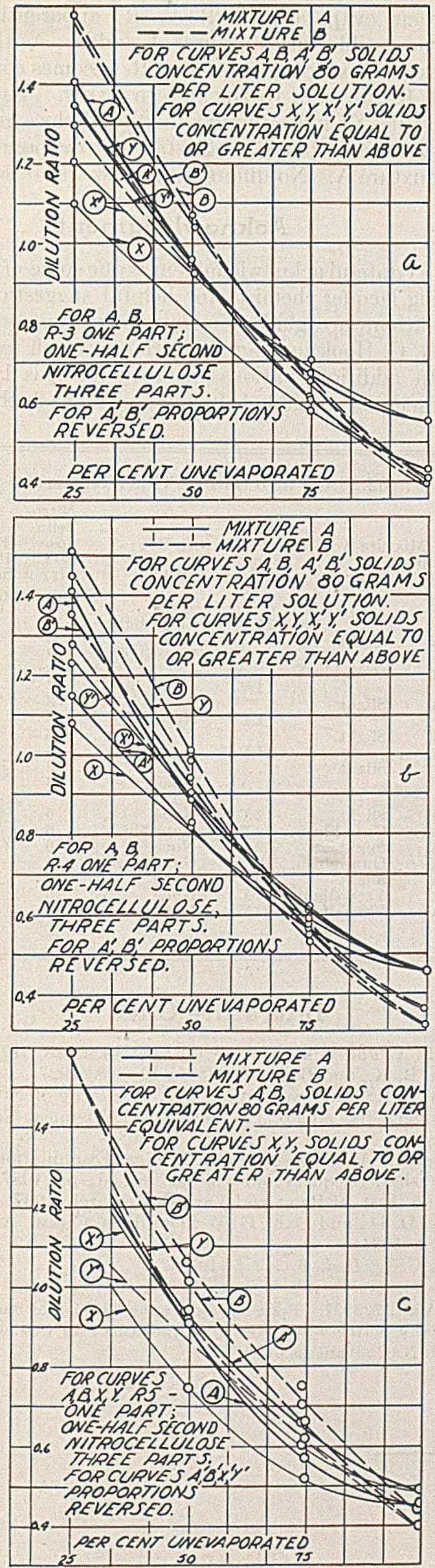

Figure 11. Relative Tolerance of Mixtures with Synthetic Resins

Solids concentration was the equivalent of 80 grams per liter of solution.

average curves of the samples for varying concentrations of solids with ester gum as the resin. Figure 8 shows the curves for a constant solid concentration and for a solid concentration that would correspond to that of an original sample after partial evaporation. Figure 8 therefore corresponds to Figure 5, with the exception of the intersection of the curves found on the former. Comparison of the two figures indicates that the type of curve is the same. Figures 9 and 10 correspond to 7 and 8, respectively. In the case of the former, the resin used was dammar instead of ester gum. Comparison of Figures 5 and 10 indicates that the relative position of mixture B curves has changed with respect to those of mixture A. This results in an intersection of the curves roughly at the stage where 75 per cent of the mixtures remains unevaporated.

Viscosity. The viscosities of samples 1, 2, 9, 10, 6, and 14 were so low and apparently comparable that they were not determined. The data obtained are shown in Table VIII.

Table VIII. Effect of Natural Resins on Average Viscosity at 20° ± 0.02° C.

Liquid Mixture Remaining %	Mixture A[a] Sample No.	Mixture A[a] Viscosity Centipoises	Mixture B[a] Sample No.	Mixture B[a] Viscosity Centipoises	Nitrocellulose/100 Cc. Solvent Grams	Resin/100 Cc. Solvent Grams
			Ester Gum			
49.72	3X	12.6	..	..	3	9
47.48	...	..	11X	12.7	3	9
25	4X	34.7	12X	33.3	6	18
			Dammar			
49.72	3X	12.5	..	..	3	9
47.48	...	..	11X	12.9	3	9
25	4X	33.6	12X	34.0	6	18

[a] Mixtures A and B samples were made up according to composition shown in Table I. These were designated as X samples.

Resistance to Blush. The samples were handled similarly to those containing nitrocellulose as the only solid. The data are shown in Table IX. In all cases where blushing could be observed, the resistance to blush was greater for mixture B samples.

Table IX. Effect of Resins on Resistance to Blush at 90° F. (32.2° C.) and 68 Per Cent Relative Humidity

Liquid Mixture Remaining %	Mixture A Sample No.	Mixture A Blush	Mixture B Sample No.	Mixture B Blush	Nitrocellulose/100 Cc. Solvent Grams	Resin/100 Cc. Solvent Grams
			Ester Gum			
100	1X	Slight	9X	None	1.5	4.5
75	2X	Slight	10X	None	2	6
49.72	3X	Slight	..	....	3	9
47.48	...	....	11X	None	3	9
25	4X	Very slight	12X	None	6	18
			Dammar			
100	1X	Very slight	9X	None	1.5	4.5
75	2X	Very slight	10X	None	2	6
49.72	3X	Slight	..	....	3	9
47.48	...	....	11X	Very slight	3	9
25	4X	Very slight	12X	None	6	18

Effect of Synthetic Resins on Nitrocellulose Solutions of Mixtures

The procedure previously outlined was used. The following typical resins of the lacquer type were chosen:

R_1. Saturated alkyd, soluble in aromatic hydrocarbons and esters, insoluble in aliphatic hydrocarbons and alcohols.

R_3. Modified phenolic, soluble in hydrocarbons and esters, insoluble in alcohols.

R_4. Modified alkyd, soluble in hydrocarbons and esters, insoluble in alcohols.

R_5. Concentrated phenolic, soluble in hydrocarbons and esters, insoluble in alcohols.

R_6. Saturated alkyd, soluble in aromatic hydrocarbons and esters, insoluble in aliphatic hydrocarbons and alcohols.

R_7. Ester gum.

R_8. Dammar.

TABLE X. EFFECT OF SYNTHETIC RESINS ON AVERAGE VISCOSITY AT 20° ± 0.2° C.

Mixture A: Liquid mixture remaining	Mixture A: Sample No.	Mixture A: Viscosity	Mixture B: Liquid mixture remaining	Mixture B: Sample No.	Mixture B: Viscosity	Nitrocellulose/100 Cc. Solvent	Resin/100 Cc. Solvent	Resin No.
%		*Centipoises*			*Centipoises*	*Grams*	*Grams*	
49.72	3X	16.0	47.48	11X	15.4	3	9	R_1
		12.4			12.9	3	9	R_3
		13.8			14.7	3	9	R_4
		12.7			13.0	3	9	R_5
		24.6			24.2	3	9	R_6
		12.6			12.7	3	9	R_7
		12.5			12.9	3	9	R_8
25	4X	47.2	25	12X	55.9	6	18	R_1
		32.2			36.7	6	18	R_3
		45.7			50.2	6	18	R_4
		35.4			40.0	6	18	R_5
		54.2			56.1	6	18	R_6
		34.7			33.3	6	18	R_7
		33.6			34.0	6	18	R_8

TABLE XI. EFFECT OF SYNTHETIC RESINS ON RESISTANCE TO BLUSH AT 90° F. (32.2° C.) AND 68 PER CENT RELATIVE HUMIDITY

Liquid Mixture Remaining	Mixture A: Sample No.	Mixture A: Blush	Mixture B: Sample No.	Mixture B: Blush	Nitrocellulose/100 Cc. Solvent	Resin/100 Cc. Solvent	Resin No.
%					*Grams*	*Grams*	
...	1X	Not dissolved	9X	Not dissolved	1.5	4.5	R_1
100	1X	Heavy	9X	Medium	1.5	4.5	R_3
100	1X	Medium	9X	Slight	1.5	4.5	R_4
100	1X	Medium	9X	Slight	1.5	4.5	R_5
...	...	....	..	....	...	...	R_6
100	1X	Slight	9X	None	1.5	4.5	R_7
100	1X	Slight	9X	None	1.5	4.5	R_8
75	2X	Not dissolved	10X	Not dissolved	2	6	R_1
75	2X	Slight	10X	Very slight	2	6	R_3
75	2X	Slight	10X	Very slight	2	6	R_4
75	2X	Slight	10X	None	2	6	R_5
75	2X	Slight	10X	Very slight	2	6	R_6
75	2X	Slight	10X	None	2	6	R_7
75	2X	Very slight	10X	None	2	6	R_8
49.72	3X	Slight	..	None	3	9	R_1
47.48	...	....	11X	....	3	9	R_1
49.72	3X	Slight	..	....	3	9	R_3
47.48	...	....	11X	Very slight	3	9	R_3
49.72	3X	Slight	..	....	3	9	R_4
47.48	...	....	11X	Very slight	3	9	R_4
49.72	3X	Gum blush	..	....	3	9	R_5
47.48	...	....	11X	Gum blush	3	9	R_5
49.72	3X	Slight	..	....	3	9	R_6
47.48	...	....	11X	None	3	9	R_6
49.72	3X	Slight	..	....	3	9	R_7
47.48	...	....	11X	None	3	9	R_7
49.72	...	Slight	..	....	3	9	R_8
47.48	...	....	..	None	3	9	R_8
25	4X	Slight	12X	None	6	18	R_1
25	4X	Gum blush	12X	Gum blush	6	18	R_3
25	4X	Slight	12X	None	6	18	R_4
25	4X	Gum blush	12X	Gum blush	6	18	R_5
25	4X	Slight	12X	None	6	18	R_6
25	4X	Very slight	12X	None	6	18	R_7
25	4X	Very slight	12X	None	6	18	R_8

TOLERANCE. The procedure as previously described was used. The results are indicated on Figure 11. Apparently the resins gave the same type of curve. They differed as to the values for the original samples. Consequently the curves differ as to the point of intersection. The slopes of the curves lack the degree of precision that was obtained for curves of nitrocellulose solutions.

Indications are that many resins that are less compatible in nitrocellulose solution B than in solution A may become more soluble as evaporation progresses. An exception is noted in the curves of Figure 11*c*.

VISCOSITY. The data of Table X point to the following: When a resin is soluble in nitrocellulose solutions of mixtures A and B, the solutions remain roughly comparable throughout their evaporation. Resin R_1 apparently is not compatible with mixtures A and B. As the evaporated mixtures grow richer, R_1 becomes compatible.

RESISTANCE TO BLUSH AND FLOW. The data of Table XI indicate that mixture B has greater resistance to blush at all stages of evaporation than mixture A. No difference in flow was observed.

Acknowledgment

Grateful acknowledgment is due some of the leading lacquer chemists for helpful suggestions. The authors are glad to acknowledge the assistance of G. C. Hook in the preparation of blush test panels. In addition, various members of this laboratory rendered valuable help and assistance in the work.

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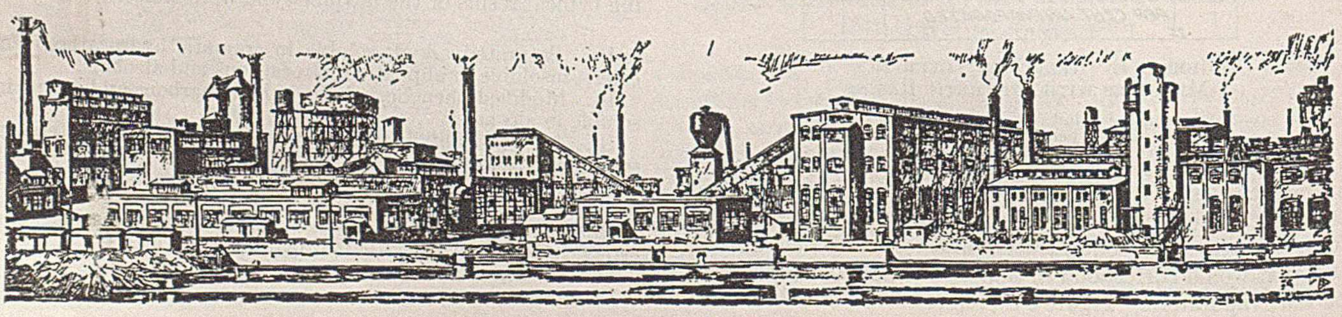

Liquid-Film Heat Transfer Coefficients

For Condensing Dowtherm A Vapors to Petroleum and Linseed Oils in a Vertical-Tube Heater[1]

DONALD S. ULLOCK[2] AND W. L. BADGER
University of Michigan, Ann Arbor, Mich.

A heavy petroleum oil and linseed oil were heated to temperatures up to 600° F. in a tubular heater, using Dowtherm vapor as the heating medium. The film coefficients for heating the petroleum oil agreed reasonably well with the Dittus and Boelter equation. This work is of importance because it confirms the Dittus and Boelter equation up to higher temperatures than have ever been used before (600° F.) and up to higher Reynolds numbers (50,000) than have ever been reached in the heating of oils.

Linseed oil, both raw and bodied, followed the Dittus and Boelter equation with a precision that would ordinarily be considered satisfactory. By trials with different exponents on both the Reynolds and the Prandtl groups, it was found that the equation

$$\frac{hD}{k} = 0.00725 \left(\frac{Du\rho}{\mu}\right)^{0.87} \left(\frac{C\mu}{k}\right)^{0.5}$$

represented the results on linseed oil with a high degree of precision. This work covers a range of the Reynolds group up to 90,000 and of the Prandtl group up to 370.

IN THE turbulent range and for vertical tubes, data are available for the film coefficient of heat transfer from metals to water and oil at moderate temperatures (*14*, *15*). Logan, Fragen, and Badger (*10*) measured liquid-film heat transfer coefficients in a semicommercial vertical-tube forced-circulation evaporator. They boiled sugar solutions of different concentrations, and the data obtained could be correlated by using the Dittus and Boelter type of equation. They obtained the same exponents for the Reynolds and Prandtl groups as did Dittus and Boelter (*13*). The constant for the equation was 0.0205 as compared to 0.0225 obtained by Dittus and Boelter. The range of their Reynolds number was from 7800 to 250,000 and the Prandtl number from 2 to 50.

This investigation involves the study of liquid-film coefficients of heat transfer between condensing vapors of Dowtherm A and petroleum and linseed oils in a vertical-tube heater. Dowtherm A is the eutectic mixture of 73.5 per cent diphenyl oxide and 26.5 per cent diphenyl, and was described by Heindel (*8*). Holser (*9*) presented heat transfer data involving the use of this material. The work on the evaporation of caustic soda by Badger, Monrad, and Diamond (*1*) and the heating of asphalt by Montillon, Rohrbach, and Badger (*18*) was carried out with condensing diphenyl vapors. The advantage of Dowtherm A over either diphenyl oxide or diphenyl is its melting point of 53.6° F. A stable petroleum oil of high grade was used. It was obtained from the Kendall Refining Company and had a viscosity of 140 seconds at 210° F. The thermal properties of Dowtherm A were obtained from calculations and data of Ullock, Gaffert, Konz, and Brown (*25*).

Equipment Flow Sheet

The equipment flow sheet is shown in Figure 1. Its details were dictated primarily by the problem of bodying linseed oil: The oil was pumped from the flash pot to the heater, heated to about 580° F., and then went to a cooler where the temperature immediately dropped 10° or 20° F. From the cooler the oil was returned to the flash pot where an inert atmosphere and a reduced pressure were maintained and where any vapors formed were released; it was then returned to the pump. The heating and cooling were continued until the oil attained the desired characteristics of a bodied linseed oil.

No iron could be used where it would come in contact with the linseed oil because it would produce a dark color in the heated oil. Nickel, brass, and aluminum were used for pipes and fittings. The boiler that supplied the Dowtherm A vapors was a semicommercial type, gas-fired unit (*17*).

The vertical two-tube heater was approximately 12 feet long. The tubes were $^7/_8$ inch o. d., 16 Birmingham wire gage nickel tubes with a heating length of 11 feet 8.5 inches between the tube sheets, and were rolled into nickel-clad tube sheets. The shell of the heater was a 3-inch extra heavy steel pipe. The apparatus was to be subjected to temperatures around 700° F. This would produce stresses between the tubes and the tube sheet due to a difference in the expansion coefficients for the steel pipe and nickel tubes. The tubes were prevented from slipping when under stress by cutting grooves $^1/_{16}$ inch wide and deep in each tube sheet, and in the rolling operation the nickel tubes were expanded into these grooves.

Approximately 18 inches from each end of the heater a 4-inch nipple and a 10-inch flange were welded on opposite sides of the shell to form a cross and allow access to the nickel tubes in the heater (Figure 2). A 2-inch vapor inlet at the top and a 1.25-inch condensate outlet at the bottom were welded to the heater.

Thermocouple Installation

Copper-constantan and copel-X-chromel thermocouples were used for temperature measurements, and the copper-constantan couples were used at the lower temperatures. Liquid tempera-

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[1] Complete tables of data obtained in these experiments will be published in the *Transactions of the American Institute of Chemical Engineers*.

[2] Present address, Carbide and Carbon Chemicals Corporation, South Charleston, W. Va.

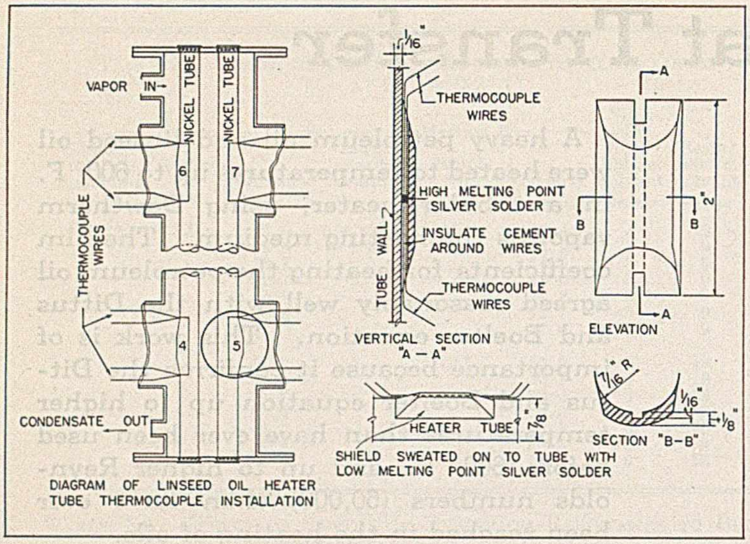

Figure 1. Equipment Flow Sheet for Heat Transfer to Bodying Linseed Oil

tures were measured with bare thermocouples specially installed in tees on the pipe line; the lead wires came through packing glands. The vapor temperatures were measured with couples that had their hot junctions silver-soldered into small blocks of brass. The brass block prevented small fluctuations in temperatures. The couples were installed to meet the conditions outlined by Colburn and Hougen (*4*). Care was taken to have the junction of the couples situated at the center of the stream. Mixing boxes were installed before each thermocouple so that the average temperature of the liquid stream was measured.

The tube temperatures were measured with thermocouples mounted on the tubes at the top and at the bottom of the heater as illustrated in Figure 2. It was not possible to use the method developed by Hebbard and Badger (*7*) but the combined suggestions of Hebbard and McCabe (*6, 16*) were used in the method illustrated in Figure 2. It consisted of a shield made from nickel tubing with an inside diameter equal to the outside diameter of the nickel tubes in the heater. Two-inch lengths of this tubing were cut in half along the axis of the tube. When these pieces were placed on the heater tubes, they fitted snugly. The edges of each shield were beveled off so as to minimize the effect of the shields on the layer of condensate flowing down over the surface of the heater tubes. A groove $^1/_8$ inch wide and $^1/_{16}$ inch deep was cut on the inside of the shield. The junctions of two couples were then soldered at the center of the shield in the groove with a silver solder of high melting point. The excess solder was filed off flush with the inside surface of the shield. An insulating cement was then applied around the thermocouple wires which lay stretched out in the groove of the shield and was allowed to dry. Later the excess cement was filed off flush with the inside surface of the shield until it fitted snugly on the heater tube. The shields were then sweated onto the outside wall of the heater tubes with a silver solder of low melting point.

The most serious objection to this method is the change in the surface of the tubes where the shields are attached. They change the characteristics of the film on the tube wall, which in turn causes a variation in temperature of the tube wall. The shields were beveled so that the condensate may flow down over them without an abrupt change in direction. This precaution helps to give correct tube-wall temperatures. The resistances of the liquid and vapor films are known to be of the same order of magnitude, and the over-all temperature drop will be large. Therefore, it is expected that any variation in the temperature of the tube wall near these shields will not have a critical effect on the calculation of the film coefficients.

Calibrations

The rate of flow of the oil was determined with a sharp-edged orifice. This orifice was calibrated at 212° and 133° F. with a petroleum oil having a viscosity of 79 seconds at 100° F.

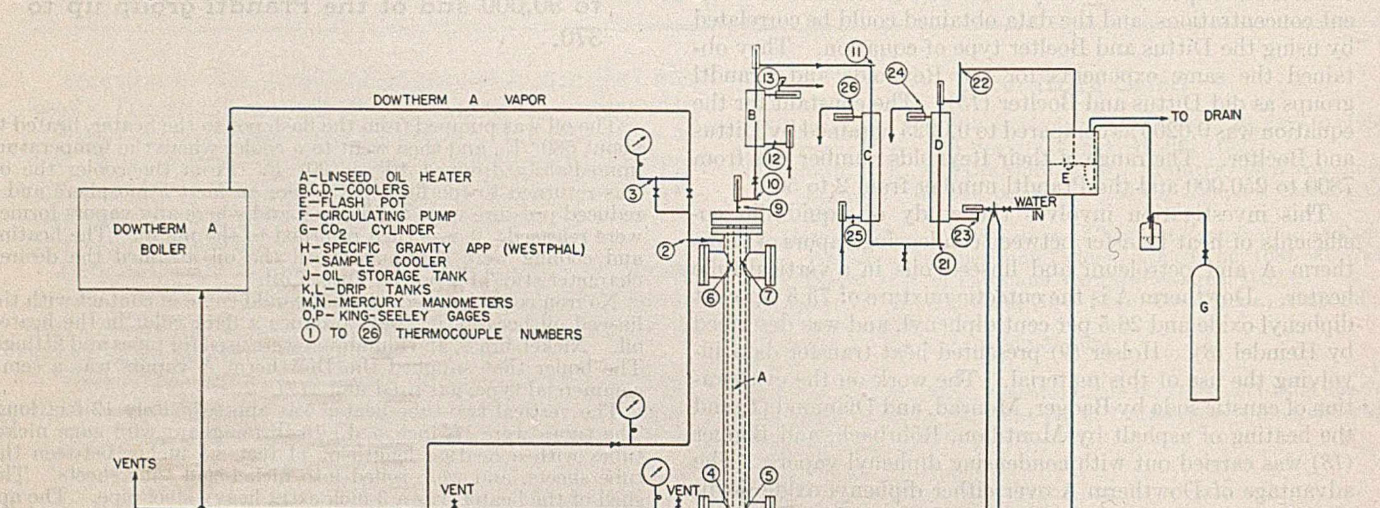

Figure 2. Details of Thermocouple Shield Attachment

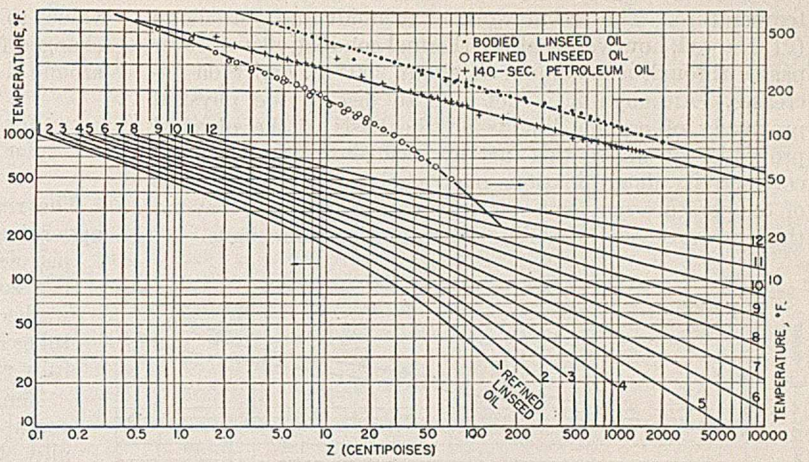

FIGURE 3. VISCOSITY *vs.* TEMPERATURE FOR BODYING LINSEED OIL

This oil had approximately the same specific gravity and viscosity that the linseed oils used in this heat transfer study would have under experimental conditions at the higher temperatures.

The thermocouples used for the measurement of temperatures were calibrated in an oil bath against a calibrated resistance thermometer between the temperatures of 11° and 360° C. The temperature as measured is estimated to be accurate to ±0.5° C. The copel-X-chromel couples were checked with the boiling points of naphthalene and sulfur.

The thermocouples mounted on the linseed oil heater tubes were checked by putting Dowtherm vapor into the heater at known pressures. The inlet vapor for runs 39 to 43, inclusive, was slightly superheated; in runs 44 to 48, inclusive, it came direct from the boiler and had to be slightly wet to ensure saturation conditions of temperature for each pressure. When the pressure became constant, the temperatures of the vapor in, the condensate out, and the tube thermocouples were measured and found to be in excellent agreement.

Heat lost from the linseed oil heater by radiation was determined by putting the heater under pressure with slightly superheated Dowtherm vapor. When the pressure in the heater remained constant, the condensate and time were measured. This procedure was followed at six different pressures.

Physical Properties of Oils

The specific heats of the petroleum oil and the bodied linseed oil were estimated with the use of the Fortsch and Whitman equation (*5*):

$$C = \frac{(t + 670)(2.10 - S)}{2030}$$

This equation was obtained for petroleum oils and should be suitable for the petroleum oil used in these experiments. It is believed that this equation is also suitable for the linseed oil. With this equation the specific heat of the pure linseed oil was calculated to be 0.703 at 550° F. This value agrees to within 6 per cent of the data published by Long, Reynolds, and Napravnik (*11*).

The viscosities of the petroleum oil, refined linseed oil, and a bodied linseed oil were determined with a MacMichael viscometer over a temperature range of 50° to 600° F. The viscometer was calibrated with water, a U. S. Bureau of Standards standard oil sample No. 4, and castor oil. The error introduced on account of the expansion of the disk plunger at 700° F. is less than the experimental error. Several fresh samples of oil were used in covering the 50–600° F. temperature range.

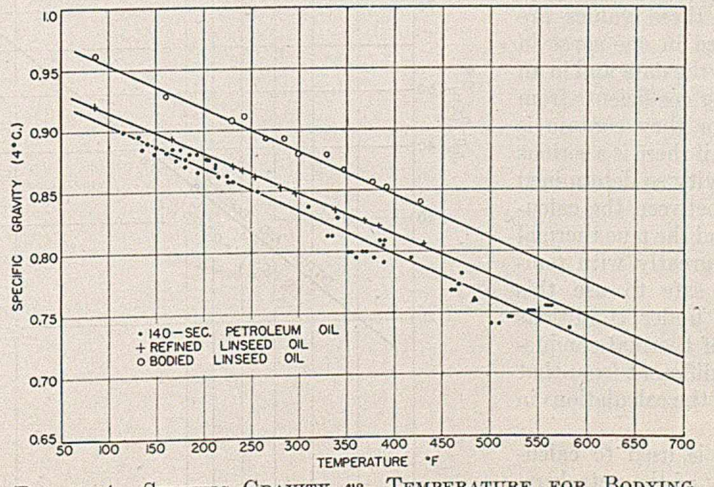

FIGURE 4. SPECIFIC. GRAVITY *vs.* TEMPERATURE FOR BODYING LINSEED AND PETROLEUM OILS

Bodied linseed oil: $ds/dt = -0.000352$
Refined linseed oil: $ds/dt = -0.000334$
$(ds/dt)_{\text{av.}} = -0.000343$

The data are plotted on logarithmic coördinates in Figure 3. Guide lines 1 to 12 represent linseed oil in progressive stages of polymerization or increasing bodying effect. These lines were obtained by dividing the distance between the curves for the refined and bodied linseed oil into eight equal parts. Lines 10 to 12 are extrapolations. If the viscosity of a bodied linseed oil is measured at room temperature, its viscosity can be estimated with Figure 3 at any temperature between 50° and 600° F.

The specific gravities of the petroleum oil, refined linseed oil, and a bodied linseed oil were determined with the Westphal balance equipped with an invar plummet (Figure 4).

The molecular weight was determined in order to estimate thermal conductivity. The freezing point depression method of Beckman was employed for the petroleum oil. Benzene was the solvent, and the molecular weight was found to be 744.

The molecular weight for bodied linseed oil was determined through a correlation of the data of Caldwell and Mattiello (*3*) with viscosity. Figure 5 is a plot of their values of viscosity in poises *vs.* molecular weight on a log-log chart. The curve represents viscosity determinations at 25° C. (77° F.) converted to 15.5° C. (59.9° F.) by Figure 3. The error introduced through the use of these data can have but a minor effect on the calculated value for thermal conductivity for linseed oil. For example, if the molecular weight determined is in error by about 5 per cent, the calculated thermal conductivity will be in error approximately 1 per cent.

Thermal Conductivity

All of the equations that have been commonly used for the correlation of heat transfer coefficients to or from fluids involve the thermal conductivity of the fluid. This offered a particular difficulty in the present case because the temperatures at which the thermal conductivities were to be evaluated were far beyond any range at which thermal conductivities of liquids have ever been measured. Within very narrow ranges the thermal conductivity of most organic liquids is known to decrease with temperature. For a long time it was believed that the thermal conductivity of water increased linearly with temperature. The recent work of Schmidt and Sellschopp (*21*) showed, however, that the thermal conductivity of water passes through a maximum at about 260° F. and then decreases. Although it is not safe to discuss the physical properties of organic liquids on the basis of the physical properties of water, this fact at least shows that thermal conductivity determinations over a relatively narrow range of temperature may not safely be extrapolated far beyond the temperatures at which the determinations were made.

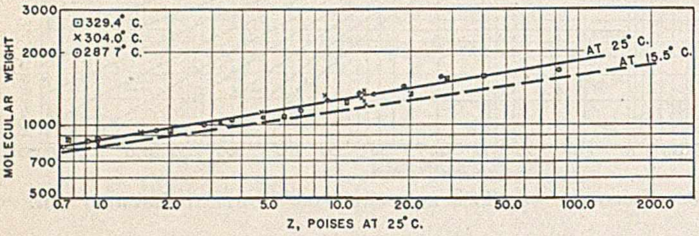

FIGURE 5. MOLECULAR WEIGHT *vs.* VISCOSITY FOR BODYING LINSEED OIL

Weber (*26*), Bridgman (*2*), and Smith (*23, 24*) proposed equations based on various physical constants for the prediction of thermal conductivities. When these equations are applied to linseed oil at 600° F., they give results differing by several hundred per cent. It is doubtful whether the authors of these equations ever expected them to be valid under such conditions. The direct determination of thermal conductivity is a difficult matter in any case and would have been so complicated at the temperatures involved in this work that it was out of the question to consider it.

The only recourse, therefore, was to try one of the above equations to see whether or not the results could be correlated on the basis of the data furnished by it, even though it was unknown whether the values of thermal conductivity so obtained were reliable or not. This does not introduce any fundamental error into the correlation as is shown by the following line of reasoning.

Experimental data, directly determined, are correlated into a single equation by the use of an arbitrary value for the thermal conductivity of the liquid, which may or may not be correct. In using the equation so determined for calculating a desired heat transfer coefficient (i. e., the reverse process from that considered in this paper), the same values of thermal conductivity, determined in the same way, are employed. Consequently, even though these values are purely empirical, they are used in one sense in developing the equation from the data and in an opposite sense in determining coefficients from the equation; thus any error they contain is neutralized. It follows that, if there is a serious error in the thermal conductivity so determined (and especially if the ratio between the calculated thermal conductivity and the true thermal conductivity should change greatly with temperature), it would not be safe to use this method at temperatures or under conditions where the numerical value of thermal conductivity to be used was greatly different from that employed in the range where the calculations in this paper were made.

When the Weber equation is used to calculate the thermal conductivity of the petroleum oil, the correlation of the data gives values which, when checked against the Dittus and Boelter equation, indicate the conductivity values to be high. If the constant in the Weber equation is changed from 0.864 to 0.342, the petroleum oil data will fall around the Dittus and Boelter line. The equations used are:

For bodying linseed oil: $k = 0.864\ (S)(C_p)^3\sqrt{S/M}$
For petroleum oil: $k = 0.342\ (S)(C)^3\sqrt{S/M}$

The runs on petroleum oil were made first, and then the apparatus was cleaned before introducing the linseed oil. The petroleum oil was washed out with kerosene, followed by hot solutions of trisodium phosphate, and was finally washed several times with hot distilled water. The heater tubes had some carbon residue on them. They were carefully wiped clean with cloths.

The bodying of the linseed oil took place over an interval of several hours, and the viscosity was continually changing. The time was divided into 15-minute periods. At the end of the first 15 minutes and every 30 minutes thereafter, a sample of the bodying oil was removed. Three sets of readings for pressures and temperatures, and of the mercury manometer were taken for each 15-minute run. When the viscosity had increased to such an extent that the oil velocity began to decrease, the valve for the Dowtherm vapor was closed and the flow of water to the coolers increased. When the linseed oil had cooled down to about 250° F., it was discharged from the apparatus. Fresh linseed oil was immediately introduced into the apparatus and circulated to wash out the bodied oil. The equipment was then drained, and a new charge of linseed oil pumped in to keep the heater tubes and piping filled with oil.

Smoothing and Correlation of Data

The experimental data obtained from heating the petroleum oil were used direct in the usual heat-transfer calculations. Erratic results were recognized only by comparisons among the data or later when they were correlated. The ex-

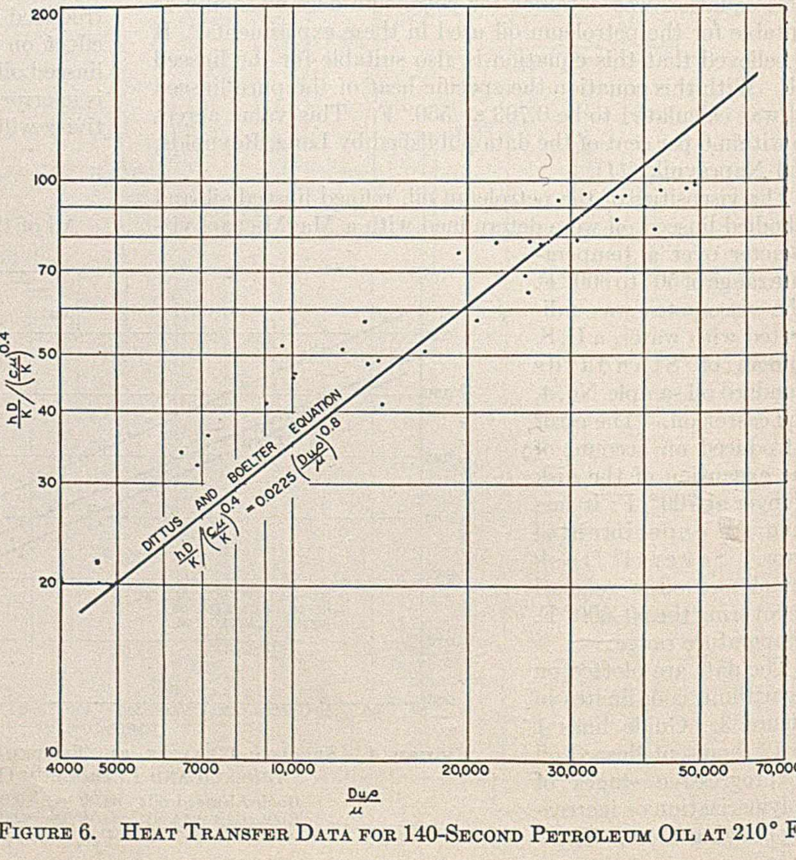

FIGURE 6. HEAT TRANSFER DATA FOR 140-SECOND PETROLEUM OIL AT 210° F.

perimental data obtained from heating the linseed oil, however, can be given a preliminary treatment to improve them. This oil was heated for periods of 2.5 to 4 hours. The readings for each 15-minute run were averaged and plotted against the average time for each interval, and smoothed values obtained from this curve. The B. t. u. transferred, vapor, tube, and oil temperatures, liquid film coefficients, and viscosity were smoothed graphically in this manner. The gross weights of Dowtherm condensate were given a more special treatment by the Running method of graphical smoothing (*20*). This was done because the rate of condensation decreased rapidly with the time of heating.

It was impossible to check the heat input by calculating that absorbed by the oil, since the temperature increase is generally only about 12° F. The accuracy of the temperature measurements was estimated to be about ±1° F., which leaves room for considerable error when the heat absorbed by the oil is calculated.

The data on linseed oil were correlated with the following Dittus and Boelter equation (*13*):

$$\frac{hD}{k} = a\left(\frac{Du\rho}{\mu}\right)^{n}\left(\frac{C\mu}{k}\right)^{m} \qquad (1)$$

The physical properties used in the correlation of the data were based on the arithmetic average of the inlet and outlet temperatures of the oil stream after mixing. This was done in preference to using the film temperature because the correlated data can be compared directly with those presented by McAdams (*12*). In addition, the data are in a more useful form for design purposes. The film temperature of the linseed oil was generally about 30° F. higher than the main body of the oil (which was about 590° F.). A correlation based on the physical properties taken at the film temperature would have given only slightly different results.

The data for the petroleum oil were plotted as $Nu/(Pr)^{0.4}$ against Re and are illustrated in Figure 6. The line representing the Dittus and Boelter equation was drawn through these data. A fairly good correlation resulted.

The values of the exponents for the Prandtl and Reynolds groups for the linseed oil runs were next obtained by trial and error as outlined by Logan, Fragen, and Badger (*10*). This correlation fixed m equal to 0.3 and n equal to 0.64 with the data defining the usual band of points, except that each set of data approximated a straight line (Figure 7).

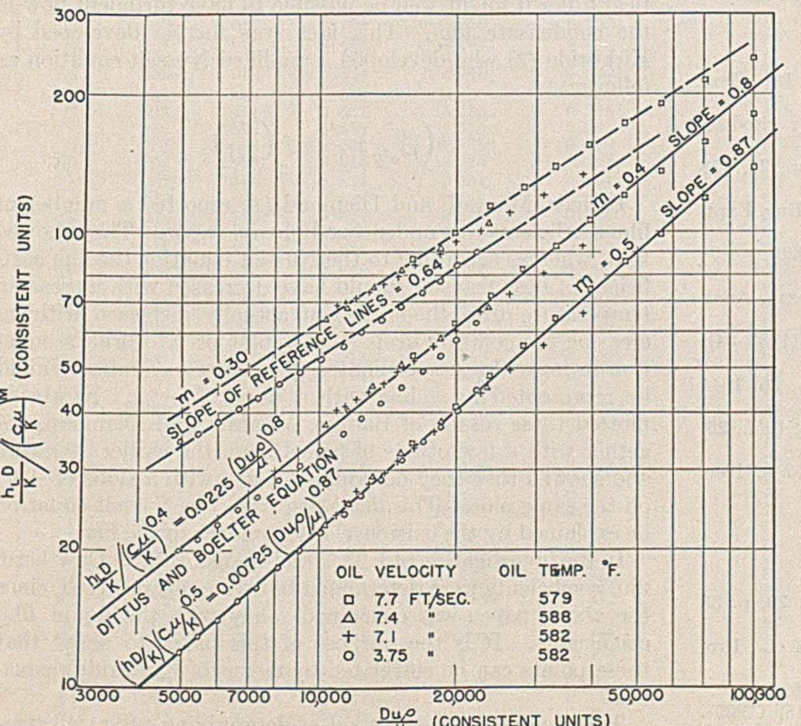

FIGURE 7. HEAT TRANSFER DATA FOR BODYING LINSEED OIL

The values for m and n seem quite low, especially n. The value of m was increased to 0.4 and $Nu/(Pr)^{0.4}$ was plotted against Re. The result was to find the data drawn into a narrow band and is illustrated in Figure 7. If lines were drawn through these data, they would have a slope equal to 0.78. This correlation of the data checks the line of the Dittus and Boelter equation (with a slope of 0.8) very well.

The value of the exponent of the Prandtl group was increased to 0.5 and the $Nu/(Pr)^{0.4}$ plotted against Re. Figure 7 illustrates the result of this operation. All the data are drawn so close together as to approximate a straight line, rather than a band. The slope of this line is 0.87. If the exponent for the Prandtl group is increased further, the correlation becomes poor again with the data falling into a band. Table I illustrates the effect of increasing the value of the exponent of the Prandtl group at a constant Reynolds number of 20,000. The oil velocity is expressed in feet per second, but the Nusselt, Reynolds, and Prandtl groups are in consistent units.

TABLE I. BODYING OF LINSEED OIL

Run No.	Oil Velocity	Nu	Pr	$Nu/(Pr)^{0.3}$	$Nu/(Pr)^{0.4}$	$Nu/(Pr)^{0.5}$	$Nu/(Pr)^{0.8}$
90	7.7	345	70.3	99.6	62.9	41.1	11.5
57	7.1	325	65.3	93.3	60.8	40.2	11.45
66a	3.75	233	31.6	94.3	58.0	41.1	14.72

The data for the bodying of linseed oil, therefore, correlate best with the following empirical equation:

$$\frac{hD}{k}\Big/\left(\frac{C\mu}{k}\right)^{0.5} = 0.00725\left(\frac{Du\rho}{\mu}\right)^{0.87} \qquad (2)$$

Sherwood and Petrie (*22*) have stated that the data on individual fluids can be correlated better with special equations than with the Dittus and Boelter equation. This equation was tried on the data on petroleum oil and some of the data of Morris and Whitman (*19*). A slight improvement was noted, but not enough to warrant its use.

Conclusion

The liquid-film heat transfer coefficients have been determined for a 140-second petroleum oil at 210° F. and for a bodying linseed oil in forced convection at high temperatures. The data on petroleum oil cover a temperature range of 350° to 600° F.; that of the linseed oil, 570° to 600° F. These data were obtained from a vertical heater, equipped with two 10-foot, 0.75-inch i. d. nickel tubes. All the results correlated well with the Dittus and Boelter equation:

$$\frac{hD}{K} = 0.0225\left(\frac{Du\rho}{\mu}\right)^{0.8}\left(\frac{C\mu}{k}\right)^{0.4} \qquad (1A)$$

The degree of correlation is indicated by the following table, which gives the agreement between the calculated and the experimental values of the liquid film coefficients:

Per Cent of Data Correlated to:	Bodying Linseed Oil	Petroleum Oil
	%	%
± 5%	67	15
±10%	98	38
±20%	100	59

Equation 1A was checked between the following limits:

	Bodying Linseed Oil	Petroleum Oil
Nusselt No.	153–520	250–600
Reynolds No.	5,000–90,000	4,500–50,000
Prandtl No.	14–160	50–370
Oil velocity, ft./sec.	3.75–7.7	4–7.8
Viscosity, lb./hr./ft.	1.0–8.5	1.5–10.7

The linseed oil data were even better expressed by the empirical equation. It can be recommended only for bodying linseed oil with the thermal conductivity estimated by Weber's equation. All the physical properties of the oils were taken at the average temperature of the main body of the heated oil:

$$\frac{hD}{k} = 0.00725\left(\frac{Du\rho}{\mu}\right)^{0.87}\left(\frac{C\mu}{k}\right)^{0.5} \quad (2)$$

Nomenclature

Hr. = hours of heating
a = constant in Dittus and Boelter equation
D = diam., ft.
C = sp. heat, B. t. u./(lb.)(° F.)
C_p = sp. heat at constant pressure
k = thermal conductivity, B. t. u./(hr.)(sq. ft.)(° F./ft.)
ρ = density, lb./cu. ft.
M = molecular weight
S = sp. gr. referred to water at 4° C.
Z = viscosity (by MacMichael viscometer), centipoises
Z_{t0} (av.) = av. viscosity at temp. t ° F. (values smoothed graphically), centipoises
μ = viscosity = 2.42 Z_{t0} (av.), lb./(hr.)(ft.)
u = oil velocity, ft./hr.
Nu = Nusselt group h_LD/k
Re = Reynolds group $Du\rho/\mu$
Pr = Prandtl group $C\mu/k$

Acknowledgment

Appreciation is expressed for the assistance and coöperation given by J. Freeman, W. Aldinger, and W. D. Niles. This research is indebted to The Dow Chemical Company for supplying the Dowtherm A and to the Swenson Evaporator Company for the fabrication of the linseed oil heater.

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Heat Transfer Coefficients for Condensing Dowtherm Films

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FILM coefficients for the condensation of vapors are usually calculated from the equations of Nusselt (*4*). It is important to remember, however, that the Nusselt equations were determined by purely theoretical reasoning, and that, in the integration which resulted in the equations usually employed, it was assumed (*a*) that the condensation was true film type condensation and (*b*) that the condensate film was in purely viscous flow.

Monrad and Badger (*3*) pointed out that in the case of vertical tubes it might well be possible to have turbulent flow in the condensate film. This idea was further developed by Kirkbride (*2*) who developed a modified Nusselt equation as follows:

$$h\left(\frac{\mu^2}{k^3\rho^2 g}\right)^{1/3} = f\left(\frac{W}{\mu D}\right)_b$$

Badger, Monrad, and Diamond (*1*) reported a number of film coefficients for condensing diphenyl vapor. They showed that, whereas according to the Nusselt equation the film coefficient of heat transfer should have decreased with increasing temperature drop, the coefficient actually increased with increasing temperature drop. On a plot of Kirkbride's equation in logarithmic coördinates, the Nusselt equation should be represented by a line with a slope of $-1/3$. Kirkbride plotted these results of Badger, Monrad, and Diamond, together with a few others obtained from the earlier literature and showed that they determined a line with a slope of $+1/3$ on the same plot. This deviation from the Nusselt equation he explained by the existence of turbulence in the film.

In the investigation of Ullock and Badger (*5*) the Dowtherm film coefficients were determined but were not reported, since the above paper was concerned solely with the liquid film coefficients. It is the purpose of this paper to show that these points can be correlated by means of Kirkbride's equation.

The apparatus, the method of determining tube wall temperatures, and the method of taking the data are discussed in

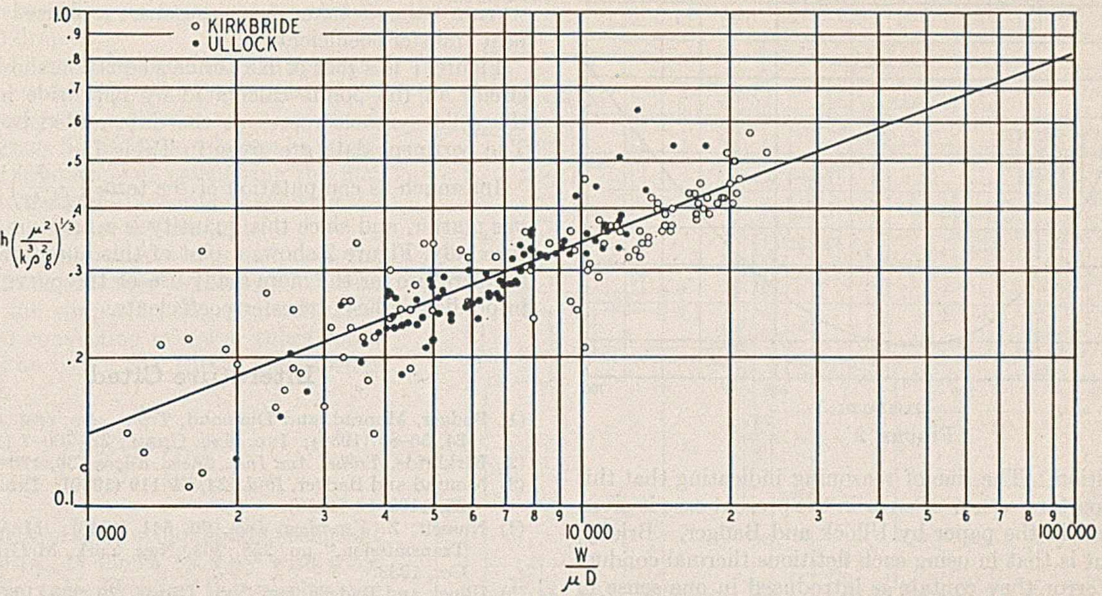

FIGURE 1

the paper by Ullock and Badger. In recalculating these data in terms of Kirkbride's equation, certain constants offered some difficulty.

The viscosity of the liquid in the Dowtherm film must be known at temperatures far above any at which determinations have been made. Determinations made by the Dow Chemical Company up to 400° F. were plotted against temperature to a logarithmic scale and found to determine a straight line with a considerable degree of precision. This straight line was then extrapolated to the temperature range in question. The density of liquid Dowtherm was taken from the tables of constants prepared by the Dow Chemical Company.

No determinations of the thermal conductivity of Dowtherm at any temperature, much less at the temperatures involved in this investigation, were available. The thermal conductivities were therefore calculated by the use of Weber's equation, using values of specific heat and density from the Dow Chemical Company's tables and using a mean molecular weight based on a mixture of 76 per cent diphenyl oxide and 24 per cent diphenyl.

This method of predicting thermal conductivities is open to

TABLE I. RECALCULATION OF ULLOCK'S COEFFICIENTS BY KIRKBRIDE'S METHOD

Run No.	h_v	t_f	μ	$\frac{W}{\mu d}$	$h\left(\frac{\mu^2}{k^3\rho^2 g}\right)^{1/3}$
2	240	552	0.709	3,250	0.255
3	258	546	0.721	5,232	0.274
4	236	647	0.568	4,012	0.268
5	210	650	0.564	5,445	0.239
6	261	650	0.564	6,405	0.297
7	232	651	0.561	5,135	0.265
8	238	620	0.602	4,610	0.263
9	253	618	0.606	4,985	0.279
10	262	616	0.614	4,935	0.288
11	264	616	0.614	5,264	0.291
12	224	596	0.636	4,148	0.243
13	208	596	0.636	3,875	0.226
14	244	594	0.638	4,198	0.264
15	251	596	0.636	4,072	0.272
16	190	574	0.668	2,588	0.204
17	...	...	...	...	...
18	199	573	0.670	3,625	0.213
19	182	572	0.670	3,589	0.195
20	161	547	0.718	2,788	0.171
21	143	547	0.718	2,452	0.152
22	118	549	0.714	1,998	0.125
23	...	...	...	...	...
24	283	543	0.723	5,910	0.300
25	222	545	0.721	4,312	0.235
26	312	592	0.638	7,510	0.338
27	392	592	0.638	9,762	0.424
28	411	590	0.643	10,706	0.444
29	310	626	0.593	9,225	0.344
30	326	619	0.605	11,312	0.360
31	485	626	0.595	15,450	0.538
32	376	668	0.544	13,525	0.437
33	462	667	0.544	17,975	0.537
34	545	670	0.539	13,010	0.635
35	283	677	0.534	7,910	0.332
36	308	679	0.532	7,972	0.363
37	270	678	0.532	7,250	0.318
38	298	703	0.503	7,928	0.353
49	264	669	0.544	7,550	0.307
50	242	670	0.542	7,230	0.282
51	226	671	0.539	6,822	0.264
52	205	672	0.539	6,175	0.240
53	186	673	0.539	5,001	0.218
54	175	674	0.537	4,839	0.210
55	334	670	0.542	12,050	0.389
55a	316	671	0.539	11,175	0.369
56	300	672	0.539	10,288	0.351
56a	284	672	0.539	9,148	0.332
57	274	672	0.539	8,500	0.320
58	263	672	0.539	7,935	0.307
59	256	672	0.539	7,560	0.299
60	243	673	0.539	7,348	0.286
61	239	674	0.537	6,950	0.280
62	231	674	0.537	6,738	0.270
63	227	674	0.537	6,500	0.266
64	220	675	0.537	6,000	0.258
65	220	675	0.537	5,925	0.258
66	283	674	0.537	7,935	0.331
66a	276	672	0.539	7,655	0.323
67	241	676	0.534	7,420	0.283
68	240	676	0.534	7,148	0.282
69	243	677	0.534	6,855	0.286
70	230	677	0.534	6,508	0.271
71	222	678	0.532	6,198	0.261
72	216	678	0.532	5,830	0.254
73	207	679	0.532	5,440	0.244
74	209	679	0.532	5,140	0.246
75	204	680	0.530	4,775	0.241
76	197	681	0.527	4,642	0.233
77	199	681	0.527	4,465	0.235
78	196	682	0.527	4,335	0.232
79	194	682	0.527	4,188	0.230
80	193	682	0.527	4,025	0.229
91	309	656	0.556	12,388	0.354
92	448	648	0.566	11,975	0.509
93	329	658	0.556	11,962	0.378
94	288	664	0.547	11,912	0.333
95	286	665	0.547	11,075	0.331
96	279	669	0.544	10,250	0.325
97	277	670	0.542	9,475	0.323
98	278	672	0.539	8,770	0.325
99	276	672	0.539	8,475	0.322
100	276	675	0.537	8,218	0.323

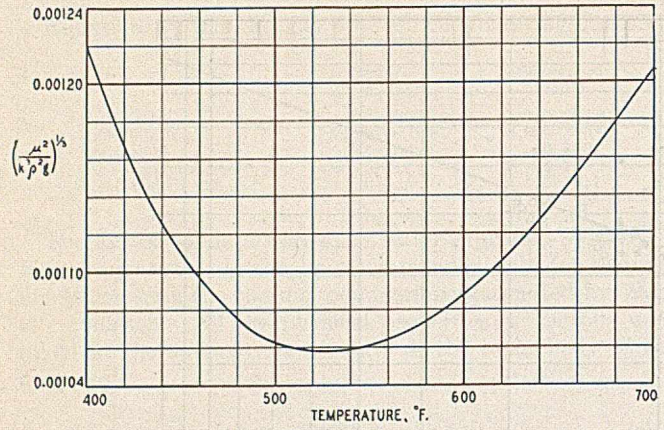

FIGURE 2

serious question. The line of reasoning indicating that this is not an important source of error in the present case is given in some detail in the paper by Ullock and Badger. Briefly, the argument is that in using such fictitious thermal conductivities any error they contain is introduced in one sense in converting the experimental results to the form of Kirkbride's equation and determining the line of Kirkbride's chart. The same error is introduced in the opposite sense when a value is taken from the chart and used to predict a heat transfer coefficient.

Figure 1 is a plot of Kirkbride's equation showing in open circles all the points calculated by Kirkbride in his paper; the solid symbols represent the data added by this paper. The pertinent data are given in Table I.

Inasmuch as computation of the term $\left(\frac{\mu^2}{k^3\rho^2 g}\right)^{1/3}$ is a tedious matter, and since this quantity is a function of temperature only, Figure 2 shows a plot of this quantity in terms of temperature for the more ready use of the curve of Figure 1 in predicting heat transfer coefficients.

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Temperature Drops and Liquid-Film Heat Transfer Coefficients in Vertical Tubes[1]

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THE design of forced-circulation evaporators is at present accomplished by the use of over-all coefficients which are mainly a matter of experience. It has been long realized that the proper approach to this problem is through the use of film coefficients, but there are practical difficulties.

The simplest equation for the design of an evaporator is:

$$Q/\theta = UA\,\Delta T_T \qquad (1)$$

ΔT_T is the true mean temperature drop based on the true mean liquid temperature and the steam temperature and U is the over-all coefficient of heat transfer defined as

$$U = \frac{1}{\frac{1}{h_S} + \frac{k}{L_W} + \frac{1}{h_L}} \qquad (2)$$

This equation holds rigidly only for the case where no thermal resistances are present except the steam film, the wall of the tube, and the liquid film. Where other resistances are present, such as scale and impure steam, they must be included by additional terms in Equation 2. This definition also assumes that the areas of the steam film and the liquid film are appreciably equal.

Equation 1 cannot be used because ΔT_T, the true mean temperature drop, is not known. Most designs are based on the over-all apparent temperature drop because it can be readily determined. The over-all apparent temperature drop, ΔT_A, is defined as the temperature difference between the steam in the steam jacket and vapor in the evaporator body. Coefficients based on this definition are known as over-all apparent coefficients of heat transfer. These coefficients are entirely fictitious because the effect of ignoring boiling point elevation, circulatory system heat losses, temperature changes of the liquid in the tubes, etc., is to show a lower coefficient than the true over-all coefficient of heat transfer. Nevertheless, a large body of data has been built up on this system which has been useful in design. On this basis, design has been a matter of experience. It is desirable to reduce this operation to a logical basis by the use of film coefficients. From the film coefficients can be calculated the over-all coefficient of heat transfer, U, by the use of Equation 2

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[1] Complete tables of data obtained in these experiments will be found in the *Transactions of the American Institute of Chemical Engineers*.

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The temperature drop must be the true mean temperature drop.

Equation 1 cannot be used until the apparent over-all temperature drop from steam to vapor and the average true temperature drop from steam to average liquid in the tube can be reconciled, and until means of calculating the film coefficients without the necessity of knowing the tube wall temperature are available.

Many investigators have reported that the average true liquid film coefficient of heat transfer for the simple heating of fluids moving in forced convection inside of tubes could be predicted by use of the Dittus and Boelter relation (*4*):

$$\frac{hD}{k} = a\left(\frac{Du\rho}{\mu}\right)^{0.8}\left(\frac{c\mu}{k}\right)^{0.4} \qquad (3)$$

Here h, the average true liquid film coefficient of heat transfer, is shown to vary with some function of the tube diameter, the velocity, the physical properties of the fluid evaluated at average bulk temperature, and the constant a.

McAdams (*10*) discussed this equation fully. He concluded that Equation 3 is the best general equation for the simple heating of fluids, with the constant a equal to 0.0225, where all units are consistent.

Logan, Fragen, and Badger (*9*), working on a semicommercial forced circulation evaporator with 8-foot tubes under essentially nonboiling conditions, found that the Dittus and Boelter equation correlated their data. It would appear, then, that the applicability of this equation has been proved in the case where appreciable boiling does not occur.

It is important, therefore, to the problem of the logical design of forced-circulation evaporators that the relation between the over-all apparent temperature drop and the true mean temperature drop be known. Further, the effect of appreciable boiling upon the liquid film coefficient of heat transfer in such a system should be examined. This paper presents the results of such investigations made on a single vertical-tube forced-circulation evaporator. The steam film characteristics of the same runs made on the same apparatus were reported in a previous paper (*11*).

Literature Survey

McAdams (*10*) reviewed the work done on the simple heating of water and other fluids both in horizontal and vertical tubes. The data on the heat transfer to boiling fluids in forced convection are very few. Logan, Fragen, and Badger (*9*) had some boiling when using a sugar solution in a forced-circulation evaporator with twelve 8-foot copper tubes, 0.75 inch inside diameter. Their results followed the Dittus and Boelter equation.

Claasen (*1*), in 1902 in a theoretical discussion, stated that vapor bubbles clinging to the heating surface should reduce the coefficient of heat transfer by blanketing off part of the active area. Jakob and Fritz (*7*) verified this hypothesis, using a horizontal plate evaporator. Cleve (*2*), Linden and Montillon (*8*), and Cryder and Gilliland (*3*) took data on water boiling under natural convection in vertical, inclined, and horizontal tubes, respectively. These investigations, with the exception of that of Logan, Fragen, and Badger, are not significant to the present work.

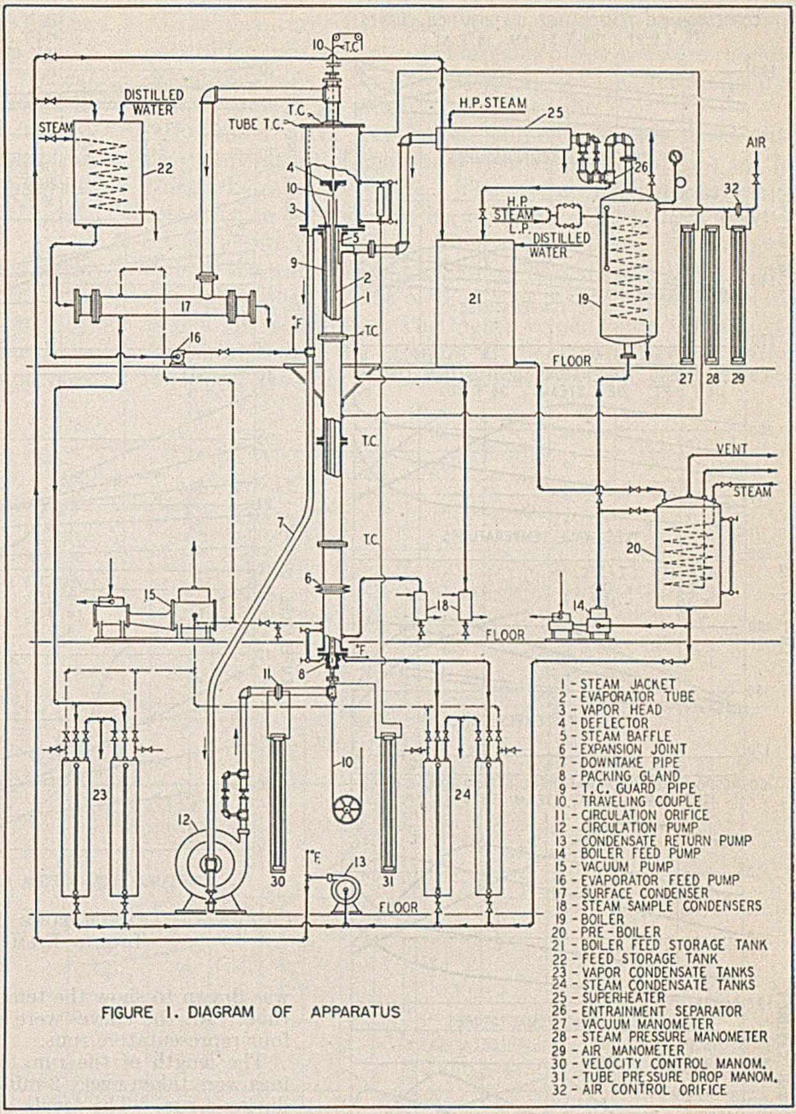

FIGURE 1. DIAGRAM OF APPARATUS

No work on the correlation of the over-all apparent temperature drop with the true mean temperature drop has been reported.

Experimental Apparatus and Procedure

The experimental apparatus was described in a previous paper (*11*):

> It was essentially a single-tube forced-circulation evaporator. The tube was 12 feet long, 0.76 inch inside diameter, with an inside heating surface of 2.367 square feet. The arrangement of the equipment is shown in Figure 1.
>
> All data were obtained on the transfer of heat to distilled water. The variables and the ranges covered by each were: apparent boiling point of the liquid, 140° to 212° F.; condensing steam temperature, 176° to 248° F.; inlet velocity of liquid, 2.5 to 15 feet per second; apparent over-all temperature drop, 18° to 72° F.; and percentage of evaporation, 0.25 to 5.00, approximately.
>
> Condensate from the steam space was measured in closed calibrated receivers. From the weight of this condensate and the known temperature and pressure of the steam, the total heat input was calculated. A semiquantitative check was obtained by measuring the condensate obtained from the vaporization of the liquid in the evaporator tube. Entrainment prevented a close check. The evaporator was completely lagged against heat loss.
>
> Temperatures along the tube were measured by ten copper-constantan thermocouples installed at 15-inch intervals by the method of Hebbard and Badger (*5*). The liquid temperature rise in the tube was followed by means of a traveling copper-

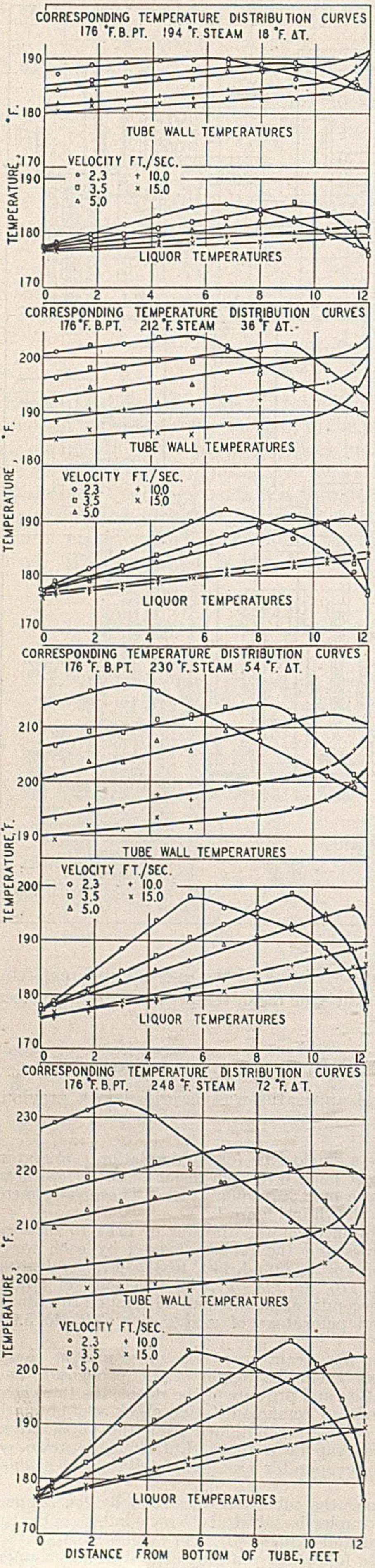

Figure 2. Temperature Distribution of Tube Walls and Liquids

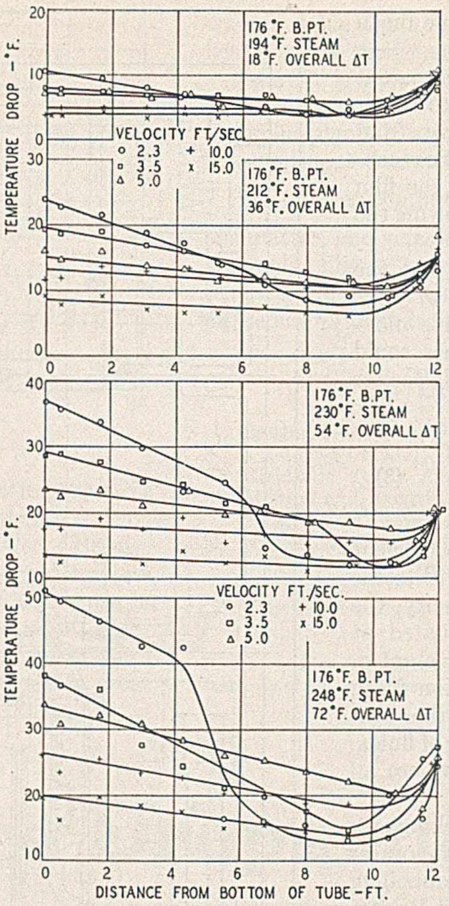

Figure 3. Temperature Drop across Liquid Film

constantan thermocouple. The lead wires were carried out of the evaporator through a $^1/_8$-inch outside diameter brass tube which moved through a packing gland. The junction was soldered direct to the end of the tube, and three brass fins were attached an inch above the hot junction to keep the thermocouple centered in the evaporator tube. A copper wire of approximately the same diameter was soldered to the end of the small tube to act as a tag wire in keeping the brass tube taut in the evaporator tube. By a pulley and take-up system the junction of the thermocouple could be moved to any predetermined point in the evaporator tube. With this arrangement small resistance was offered to the flow of liquid in the tube, and the resistance was constant no matter where the junction was.

Other thermocouples were used to measure the temperature of the steam jacket, vapor space above the tube, liquor inlet at the bottom of the tube, and superheated steam. All readings were made on a Leeds & Northrup type K-2 potentiometer.

The temperature of the liquid side of the tube was calculated from the tube couple readings, the depth to which their junctions were imbedded in the tube wall, and the temperature gradient corresponding to the known rate of heat flow through the tube wall. Typical curves showing the corresponding temperature distributions of tube wall temperatures and liquid temperatures are represented by Figure 2. From these data Figure 3 was drawn to show the temperature drop over the liquid film at any point on the tube. All the curves were similar in their characteristics; those shown were from four representative runs.

The length of the runs was 40 minutes. During that time manometer readings were taken every 2 minutes. All thermocouples were read at least three times during a run. The levels of the condensate in the vapor and steam condensate tanks were read at frequent intervals and plotted to show constancy of operation.

Liquid-Film Coefficients for Long Vertical Tubes

Since Logan, Fragen, and Badger found that they could correlate their data reasonably well by means of a Dittus and Boelter type equation, that was the first step taken in the present work (Equation 3).

The Prandtl group, $c\mu/k$, was not a primary variable in this work. Therefore, the experience of past workers in the general field was drawn upon, and this group was introduced raised to the 0.4 power.

The Reynolds and Nusselt numbers, $Du\rho/\mu$ and hD/k, were calculated from the observed data. In these calculations consistent units were used throughout. The only deviation from past work occurred in the use of the data of Schmidt and Sellschopp (*16*) for the values of the thermal conductivity, k. Their results are lower for water approaching 212° F. than the thermal conductivities based on the work of Jakob (*6*). Since this investigation was on water at temperatures from 140° to higher than 212° F., and since quantity k entered into the Dittus and Boelter equation to the 0.6 power, the calculated values of this work were lower than if Jakob's data had been used. This difference varied from 0 per cent water at 151° F. to 3.5 per cent for water at 212° F.

To check the power function of the Reynolds number, the quantity $\left(\frac{hD}{k}\right)/\left(\frac{c\mu}{k}\right)^{0.4}$ was plotted against ($Du\rho/\mu$). This is shown as Figure 4. A line with a slope of 0.8 on the logarithmic plot adequately correlates the data except at very low velocities where $Du\rho/\mu$ is less than 65,000. The median of the calculated values of constant a for the runs with a Reynolds number higher than 65,000 was 0.0278, and the line on Figure 4 is drawn with a equal to this value.

For water flowing under forced convection in a vertical heated tube with a small degree of boiling, the Dittus and Boelter equation furnishes a satisfactory means of determining the true mean liquid film, h_L. This is a confirmation of the work of Logan, Fragen, and Badger. Equation constant a is, respectively, 0.0205 and 0.0278 for the former and present investigators. This difference is not serious.

For runs with appreciable boiling in the tube (in this work, those with velocities of 2.3 and 3.5 feet per second), the true mean liquid-film coefficient of heat transfer predicted by the Dittus and Boelter equation is much lower than experiment shows. With the data at hand, it was not found possible to give more than semiquantitative demonstrations of this fact.

An attempt was made to break up into two parts the calculations on the runs in which appreciable boiling occurred. Examination of the temperature distribution curves (Figure 2) shows that active boiling in the tube reduces the temperature of the liquid by the conversion of sensible heat to latent heat. If the point where this sudden drop in liquid temperatures occurs is taken as the point of active boiling, then heat transmission in the tube length can be considered in two sections. Simple heating occurs in the part of the tube up to the break in the curve. Thus in Figure 4 it can be assumed that 5.5 feet of the tube are operating under simple heating with 2.3 feet per second velocity; 9.2 feet with 3.5 feet per second; 11.5 feet with 5.0 feet per second; and practically the entire tube with higher velocities. If the heat quantity transmitted over these lengths is calculated on the basis of the pounds of circulation per hour times the sensible heat increase, then the mean true liquid film coefficient can be determined from the Newton equation:

$$Q/\theta = h_L A_L \Delta t_L \qquad (4)$$

The temperature drop over the liquid film, Δt_L, is the integrated temperature difference from liquid to the tube wall thermocouples corrected for the resistance of the portion of the tube wall from the thermocouple junction to the inside surface of the tube.

Inserting this calculated coefficient in the Dittus and Boelter equation, the constant a for the nonboiling section was calculated. The average constant, 0.0293, is much closer to the constant, 0.0278, for runs entirely nonboiling, than would be expected from this procedure.

The value of the Nusselt criterion for the boiling portion is calculated by Newton's equation from the heat transferred over the entire tube, less that assigned to the nonboiling section. The average value of the coefficient to boiling water is approximately twice that of the coefficient to nonboiling water. The temperature drop relations determined by this method exhibit some inconsistencies.

Temperature Distributions Observed

Reference has been made to plots of the temperature distribution and temperature difference between the tube wall and the liquid. These plots have interesting ramifications. A description of the method of attaching the thermocouples to the tube wall has been described by Hebbard and Badger (*5*). The traveling, or liquid, thermocouple is described above. Figure 2 is presented as representative of all the runs. All temperature plots had the same characteristics. The only differences were those of amount of temperature rise and extent of boiling in the tube caused by changes in the effective temperature of the steam outside the tube.

Examination of any liquor temperature plot shows that the temperature of the liquid rises in a straight line to the point where boiling starts. The 10 and 15 foot per second velocities do not show boiling in the tube, and the 5 foot per second shows very little. After boiling starts, the temperature of the water drops in a curved line to a temperature substantially equal to that of the vapor in the evaporator, in the case of low velocities. The higher velocities do not come to equilibrium with the pressure in the vapor space until after the liquid has been ejected from the tube.

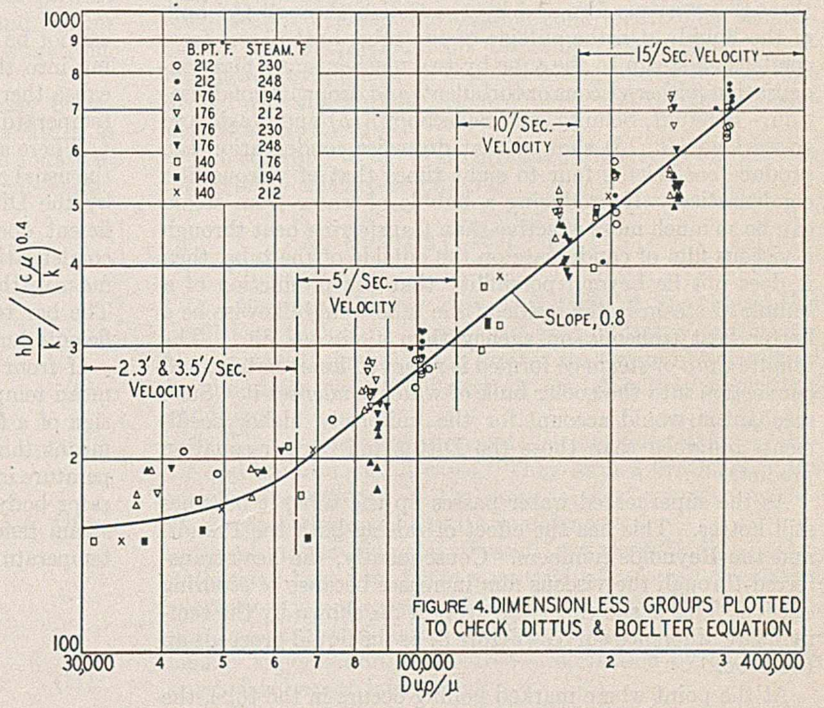

FIGURE 4. DIMENSIONLESS GROUPS PLOTTED TO CHECK DITTUS & BOELTER EQUATION

The plots of the tube wall temperatures show much the same phenomena. The tube wall temperature also rises in a straight line, but the break where boiling starts precedes somewhat the point in the tube where the liquid showed its change in the curve. The tube wall, where boiling occurs, loses temperature in a straight line in contradistinction to the curved line taken by the water. Somewhat surprisingly, the tube wall temperature at the top of the tube in nonboiling runs up sharply.

In the plots of the Δt_L values of these same runs (Figure 3) an interesting similarity is seen. The temperature difference from tube wall to liquid, for the nonboiling runs, drops in a straight line to a minimum and then rises again. The runs in which there is boiling are curved lines, or a mixture of curved and straight lines, to a minimum. This minimum occurs about 2 feet from the top of the tube. Then all curves rise and come approximately together at the top of the tube. That is, Δt_L for the same over-all ΔT but different velocities may be considerably different at the bottom of the tube, but they all go through a minimum about 2 feet from the top and they all rise to a constant value.

The influence of boiling on Δt_L is very marked in the graphs. Based on the temperature data and on the observed coefficients, the following hypothesis of the mechanism of heat transfer to liquids flowing in forced convection in a vertical tube evaporator is suggested.

Mechanism of Heat Transfer to Liquids in a Forced-Circulation Evaporator

The liquid enters the tubes of a forced-circulation evaporator at substantially the equilibrium temperature in the vapor space, although in some cases it may be somewhat cooler than this temperature owing to heat losses in the return line and the use of cold make-up feed. Heat is transferred through the tube wall and superheats the liquid above the equilibrium temperature in the vapor space. The liquid is kept from vaporizing by the hydrostatic and friction heads above it. In this region the Dittus and Boelter equation holds.

The Dittus and Boelter equation is based on the Nusselt theory (*14*) of heat transfer to liquids in pipes, based on conduction and convection. The heat must pass by conduction through a viscous film and by convection through the bulk of the liquid. On the outside of the tube, heat passes from condensing steam to the tube by two mechanisms—film condensation (either viscous or turbulent) and dropwise condensation. Schmidt, Schurig, and Sellschopp (*15*) and Nagle and co-workers (*12*, *13*) showed that dropwise condensation can produce coefficients four to eight times that of viscous film condensation. If producing a bubble of water from steam can be so much more effective than transferring heat through a viscous film of condensate on the outside of the tube, then it does not lie beyond possibility that the production of a bubble of steam in the inside of the tube would likewise be a better heat transmission agency than a viscous film. The minute drop of steam so formed is removed immediately, and convection into the cooler bulk of water condenses it. Such mechanism would account for the uniformly higher coefficients obtained than those the Dittus and Boelter equation predicts.

As the superheated water passes up the tube, it becomes still hotter. This has the effect of raising both the Prandtl and the Reynolds numbers. Consequently, the heat transferred through the viscous film increases because of scouring effects. This is shown by the drop in Δt_L shown by the temperature difference curves (Figure 3) as the liquid proceeds up the tube.

At the point where marked boiling occurs in the tube, the hydrostatic and friction heads are now not sufficient to prevent vaporization of the water. An evolution of stable bubbles occurs which tremendously increases the volume of the mixed liquid and vapor. This induces a large velocity which reduces the thermal resistance of the liquid film over the part of the tube in boiling action. The liquid film coefficient for the boiling sections was approximately twice that of the nonboiling section for these runs.

The lag in the maximum temperature of the liquid as compared to the tube wall loses most of its significance when checked against the corresponding Δt_L. The temperature difference drops smoothly with increasing heat input. This indicates that vaporization in the tube is not sudden but progressive action. The temperature of the tube wall and liquid are not independent variables but are dependent on Δt_L much as the bodies of a multiple-effect evaporator adjust their own temperatures; hence the tube wall and liquor temperature must be in such relationship as to show a smoothly decreasing Δt_L.

Near the top of the tube all temperature drops over the liquid film approach a constant value, no matter what inlet velocity is used. This requires the tube wall temperature of the nonboiling runs to rise. The meaning of this is obscure.

To summarize this hypothesis of the mechanism of heat transfer in a vertical-tube forced-circulation evaporator proposes a three-component action: (1) heat transfer through a viscous liquid film; (2) the formation of incipient bubbles of steam that are reabsorbed in the cooler liquid just the same as those that can be observed by watching a pan of water over a burner; (3) the formation of stable bubbles by flash evaporation of the superheated liquid. If this hypothesis is true, the determination of coefficients to boiling liquids becomes a matter of degree of the relative predominance of the three actions. Possibly the best correlation of this mixed mechanism would be on the basis of the percentage of liquid evaporated.

True and Apparent Temperature Drops in a Forced-Circulation Evaporator

In the logical design of a forced-circulation evaporator, it has been shown that the equation,

$$Q/\theta = UA\Delta T_T \qquad (1)$$

cannot be used at present because of the uncertainties entering into the over-all coefficient of heat transfer, U, and because there was no simple way of determining the true mean temperature drop, ΔT_T.

Where appreciable boiling does not occur in the tubes (i. e., the usual case), the liquid film coefficient, h_L, can be predicted by the Dittus and Boelter equation. The steam film coefficient does not usually control, especially where dropwise condensation occurs. Other thermal resistances which go to make up the over-all coefficient, U, can be predicted or avoided. The bar to use of Equation 1 is not, therefore, one of coefficients but of temperature drops.

If from the over-all apparent temperature drop the true mean temperature drop can be calculated, then a logical design of a forced-circulation evaporator may be made. This means that some relation must be found between the temperature indicated by the pressure of the vapor in the evaporator body and the average temperature of the liquid. The steam temperature is common to both methods of defining temperature drops.

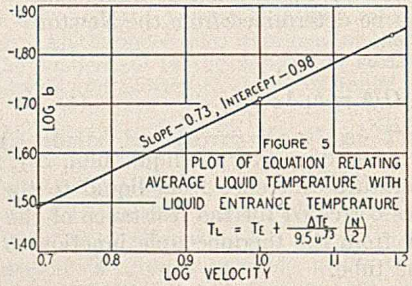

FIGURE 5
PLOT OF EQUATION RELATING AVERAGE LIQUID TEMPERATURE WITH LIQUID ENTRANCE TEMPERATURE

$$T_L = T_E + \frac{\Delta T_E}{9.5u^{.73}}\left(\frac{N}{2}\right)$$

In the simplest case (where there is no elevation of boiling point and no temperature loss in the circulatory system, and where the make-up feed is preheated) the temperature of the vapor is the same as the temperature of the liquid entering the tubes or

$$T_V = T_E \qquad (5)$$

The question of the average liquid temperature when there is no marked boiling in the tubes can be answered by considering the temperature distribution curves.

Figure 2 shows that the temperature of the liquid in the 5, 10, and 15 foot per second velocity runs rises in a straight line as the top of the tube is approached. These lines have increasing slope with increasing ΔT and decreasing slope with increasing velocity.

For each velocity the slopes of the lines were calculated and averaged. By plotting the log of the slopes against the log of the velocities, an equation of the following type was found to fit the data:

$$T_X = T_E + b(u)^s \Delta T_E(X) \qquad (6)$$

where T_X = temp. of liquid at any point, ° F.
T_E = temp. of entering liquid, ° F.
u = velocity, ft./sec.
ΔT_E = temp. drop from steam to entrance temp. of liquid, ° F.
X = distance from bottom of tube, ft.
s, b = constants

On Figure 5 the constants are evaluated. The slope, s, is -0.73 and the intercept, b, is 1/9.5. The average liquid temperature for nonboiling runs lies halfway up the tube; therefore

$$T_L = T_E + \frac{\Delta T_E}{9.5(u)^{0.73}}\left(\frac{N}{2}\right) \qquad (7)$$

where T_L = av. liquid temp. in tube

This is purely an empirical formula that describes the present data. It also fitted the data of Logan, Fragen, and Badger on runs taken at random, even though their liquid was strong sugar solution.

When concentrating a delicate solution that may be injured by high temperatures, the maximum temperature in the system may possibly be checked with the same equation, using the full length of the tube instead of the half-length.

The average true temperature drop is:

$$\Delta T_T = T_S - T_L \qquad (8)$$

where ΔT_T = av. true ΔT
T_S = steam temp.
T_L = av. temp. of liquid in tube

Hence

$$\Delta T_T = T_S - T_E - \frac{\Delta T_E}{9.5(u)^{0.73}}\left(\frac{N}{2}\right) \qquad (9)$$

ΔT_E is equal to the apparent over-all temperature drop, ΔT_A, in this case.

Now

$$\Delta T_A = T_S - T_V \qquad (10)$$

where ΔT_A = apparent over-all temp. drop
T_V = vapor temp.

Therefore, from Equations 5, 9, and 10:

$$\Delta T_T = \Delta T_A - \frac{\Delta T_A}{9.5(u)^{0.73}}\left(\frac{N}{2}\right) \qquad (11)$$

Thus the average true temperature drop is expressed in terms of the over-all temperature drop. This equation gives results about 1° to 2° F. high for ΔT_T in this investigation. No reason for the discrepancy is known.

With a solution having an appreciable elevation in boiling point, the above equation must be changed somewhat. In this case the entrance temperature of liquid to the tubes is the vapor temperature plus the boiling point elevation. The ΔT_E value of Equation 9 is $\Delta T_A - \Delta T_{BPE}$; then

$$\Delta T_T = \Delta T_A - \Delta T_{BPE} - \frac{\Delta T_A - \Delta T_{BPE}}{9.5(u)^{0.73}}\left(\frac{N}{2}\right) \qquad (12)$$

Wherever there is a temperature loss in the circulatory system between the evaporator body and entrance to the tubes, or cold feed is introduced, the proper correction should be made on the temperature of the liquid entering the tubes.

These equations are nothing more than a temperature-drop balance and can be expressed in the general case as

$$\Delta T_A = \Delta T_T + \Delta T_H - \Delta T_F - \Delta T_R + \Delta T_{BPE} \qquad (13)$$

where ΔT_A = apparent over-all ΔT
ΔT_T = av. true ΔT
ΔT_H = av. temp. rise of liquids in tubes, $\frac{\Delta T_E}{9.5(u)^{0.73}}\left(\frac{N}{2}\right)$
ΔT_F = cooling effect of cold make-up feed
ΔT_R = temp. loss through circulatory system
ΔT_{BPE} = boiling point elevation

Therefore, using only those terms which appear in the specific case and which are either known or easily calculated, Equation 1 becomes

$$Q/\theta = UA(\Delta T_A - \Delta T_H + \Delta T_F + \Delta T_R - \Delta T_{BPE} \ldots) \qquad (14)$$

and the rational design of forced-circulation evaporators awaits only a confirmation of the above equations for liquids other than water and sugar solutions.

Summary

1. In investigating the average true liquid-film heat transfer coefficients of a long vertical-tube forced-circulation evaporator operating with velocities and temperature drops that do not cause marked boiling in the tubes, Logan's claim that an equation of the form of the Dittus and Boelter relation adequately correlates the data is confirmed. This demonstrates that the predominant mechanism in the usual forced-circulation evaporator is simple heating and is in complete accord with the work of Logan, Fragen, and Badger who employed a shorter tube.

The equation which best correlated the results on nonboiling water in this investigation is

$$\frac{hD}{k} = 0.0278\left(\frac{Du\rho}{\mu}\right)^{0.8}\left(\frac{c\mu}{k}\right)^{0.4} \qquad (15)$$

2. Semiquantitative determinations of the liquid-film coefficient to boiling water lead to qualitative conclusions that this coefficient is much greater than would be predicted by the above equation based on predominately nonboiling conditions.

3. Film temperature drop and distribution curves are regular and uniform for all cases. They form a firm basis upon which interpretation of the essential heat transfer mechanisms can be approached with confidence.

Based on the temperature and heat transfer data, a hypothesis of heat transfer in a vertical-tube forced-circulation evaporator is presented. This hypothesis visualizes a three-part mechanism of simple heating through viscous films, incipient vaporization, and stable vaporization by conversion of sensible heat to latent heat.

4. Based on the temperature distribution curves, a formula relating the average liquid temperature in evaporator tubes to the entrance temperature is advocated:

$$T_L = T_E + \frac{\Delta T_E}{9.5(u)^{0.73}}\left(\frac{N}{2}\right)$$

This equation should be used in evaluating the physical properties of the liquid for the Dittus and Boelter type equation, especially where a high temperature drop is being used. As is customary in forced-circulation evaporator design, the velocity of the liquid should be sufficient to prevent marked boiling in the tubes.

5. With the means at hand to determine the average temperature increase of the liquid in the evaporator tubes,

$$\Delta T_H = \frac{\Delta T_E}{9.5(u)^{0.73}}\left(\frac{N}{2}\right)$$

The reconciliation of the apparent over-all temperature drop with the average true temperature drop follows very simply. The average true temperature drop is equal to the apparent over-all temperature drop less the average temperature rise of the liquid in the tubes less the boiling point elevation plus the temperature loss in the circulatory system plus the cooling effect of cold make-up feed.

This is an essential step in the development of a method of rational design of forced-circulation evaporators.

Nomenclature

A = area of heating surface, sq. ft.
a = constant in Dittus and Boelter equation
b = constant in liquid temp. rise equation
h = true mean film coefficient of heat transfer
k = thermal conductivity
L_W = tube wall thickness, ft.
N = length of tube, ft.
s = constant in liquid temp. rise equation
u = liquid velocity, ft./sec.
Q/θ = heat transferred, B. t. u./hr.
T = temp., ° F.
Δt = temp. drop across film
$Du\rho/\mu$ = Reynolds criterion, consistent units
$c\mu/k$ = Prandtl criterion, consistent units
hD/k = Nusselt criterion, consistent units

Subscripts:

A = apparent over-all temp. drop
T = true over-all temp. drop
S = steam
V = vapor in evaporator
L = liquid at mean temp.
E = liquid at entrance temp.
H = temp. rise of liquid in tube
BPE = boiling point elevation
F = evaporator make-up feed
R = temperature loss from system

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Heat Transfer Coefficients in the Boiling Section of a Long-Tube, Natural-Circulation Evaporator[1]

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THE long-tube, natural-circulation evaporator falls into the classification of the low-level, climbing-film machines. The most common representative is the so-called Kestner evaporator. This particular type was developed in Europe, beginning about 1900 (*17*). For some reason little interest was shown in this country until recently. Because of the redevelopment of this type of machine in America, entirely independent of the old Kestner evaporator, there is now an inclination to speak of it as the LTV (long-tube vertical) evaporator.

The characteristic feature of this type of evaporator is the length of the vertical tubes, up to 22 feet. In operation, the liquid is fed to the bottom of the tubes so slowly that it does not issue from the top as a solid stream but boils in the tube and is carried to the top as a spray or a climbing film.

Previous Work

A number of papers in the foreign literature extol the virtues of the long-tube, natural-circulation type; among its advantages may be mentioned:

1. Ability to handle heat-sensitive liquids without damage (*2, 15, 23, 24, 27, 28*).
2. Relative freedom from scaling trouble (*3, 24, 27, 28*).
3. Freedom from foaming (*1, 15, 24, 27*).

Within the last few years in this country the LTV evaporator has come into some prominence for the handling of materials such as glue, sugar sirup, sulfate waste liquor, etc., of relatively small unit value but with high viscosities. The latter property makes them difficult to handle in the standard types of natural-circulation evaporators, and the pumping cost is a disadvantage of the forced-circulation evaporator. It has been found that all of these materials, in addition to dilute salt brine, may be handled economically in this type of machine (*26*).

Although many papers have been written about the Kestner evaporator, quantitative data on the subject are lacking. The only two papers that present experimental results (*11, 16*) report them in such a form that they cannot be interpreted.

The other types of natural-circulation evaporators have been more thoroughly investigated (*4, 6, 10, 18, 19, 21*). The coefficients reported, either over-all or film, are based on the entire length of the evaporator tube. They are usually spoken of as boiling coefficients but include the effect of a certain but unknown length of tube in which the liquid is not boiling.

This type of coefficient has been found to be a function of the temperature difference (*6, 19, 21*), the liquid level (*4, 6*), the temperature level (*19, 21*), and the concentration of the solution (*21*). In some cases the velocity of circulation was

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[1] Complete tables of data obtained in these experiments will be published in the *Transactions of the American Institute of Chemical Engineers*.

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determined (*10*, *19*), but its effect on the coefficient could not be determined since the rate of circulation was a function of other variables.

An exhaustive investigation on an evaporator with a single vertical tube is reported by Kirschbaum, Kranz, and Starck (*18*). In this study the rate of circulation, the liquid temperature gradient along and across the tube, and the tube-wall temperature gradient were determined. A correlation of their data is presented. It is entirely empirical and is in no way general.

Kirschbaum and his co-workers, however, did realize that "the way to the development of the final equation probably leads to a division of the heating surface into two parts, one for heating the liquid and one for evaporation."

Considerable study has been made of the individual coefficients of heat transfer between metal surfaces (internally heated) and boiling liquids. In general, the surface has been a flat plate in either a vertical or a horizontal position (*9*, *12*, *13*, *22*). This work is of interest but as yet shows too great inconsistencies to be of any practical significance.

A method, as suggested by Boarts (*8*), has been developed for determining the length of the boiling section in an externally heated tube.

An empirical correlation of over-all coefficients of heat transfer in the boiling section of a 2-inch o. d., No. 10 Birmingham wire gage, copper tube shows that the coefficient is a function of the amount of vapor present, the weight rate of liquid fed to the tube, and the average over-all temperature difference between the steam and the liquid. This correlation is applicable only within the ranges of variables used for experimentation and to water, or to materials with similar physical properties.

The mechanism of boiling in an externally heated tube is exceedingly complicated. Three types of action, froth, slug, and film, have been found, but no definite connection between the types of action and the conditions of operation could be developed.

Experimental Apparatus

The investigation reported in this paper was carried out in a single-tube evaporator of the type known in commercial practice as the long-tube, natural-circulation evaporator. A flowsheet of the equipment is given in Figure 1:

Distilled water for feed was drawn from storage tanks into the feed weigh tanks, 1, from which the feed pump, 2, forced it into the double-pipe feed heater, 3. An equivalent quantity of water was thus forced into the 2.002 inch o. d. × 1.760 inch i. d. copper tube, 6, which was 20.0 feet long between tube sheets. As the water flowed up the tube, it was heated by the condensation of steam in steam chest 7 until it began to boil. The vapor and liquid were separated by the deflector in vapor head 9. The vapor was led through the vapor line, 16, to condenser, 10, where it was condensed. The unevaporated water left the vapor head through the thick liquor line, 17, going to the thick liquor tanks, 11. The steam condensed in steam chest 7 flowed through the condensate U-bend, 14, into steam drip tanks, 8.

The pressure in vapor head 9 was maintained constant within ±1 mm. of mercury by the manual and solenoid vacuum breaks, 23, 22. The steam pressure was maintained within the same limits by means of the steam control valves, 24, and the steam chest vent line, 15.

Measurements and Control Devices

All temperatures were determined by means of copper-constantan thermocouples. With the exception of the traveling thermocouple, the couples were inserted by sealing the wires, with litharge and glycerol cement, into a 6-inch length of $^3/_8$-inch copper tubing which passed through a standard $^3/_8$-inch compression fitting, drilled out with a No. W drill.

Couples of this type were used to determine the temperatures of the inlet to the evaporator tube, the unevaporated water outlet

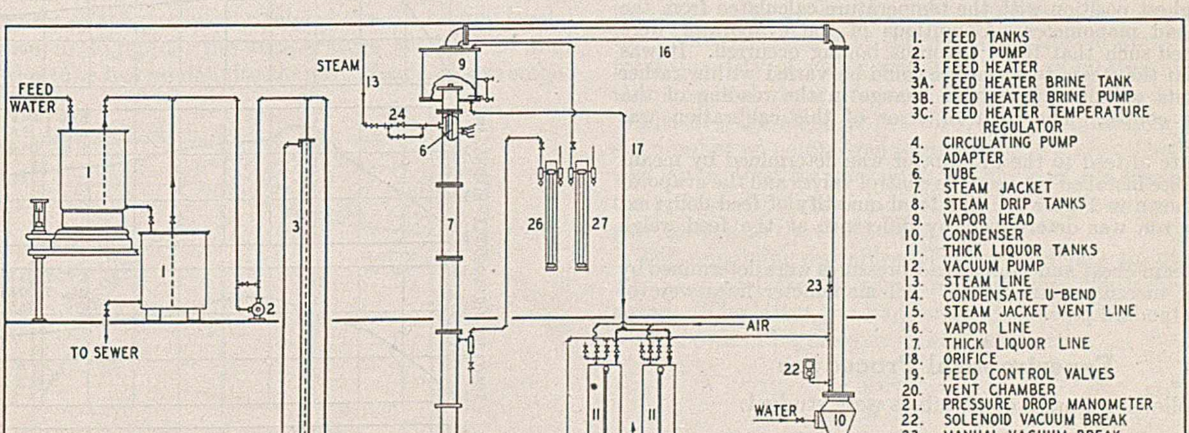

FIG. 1. GENERAL DIAGRAM OF APPARATUS.

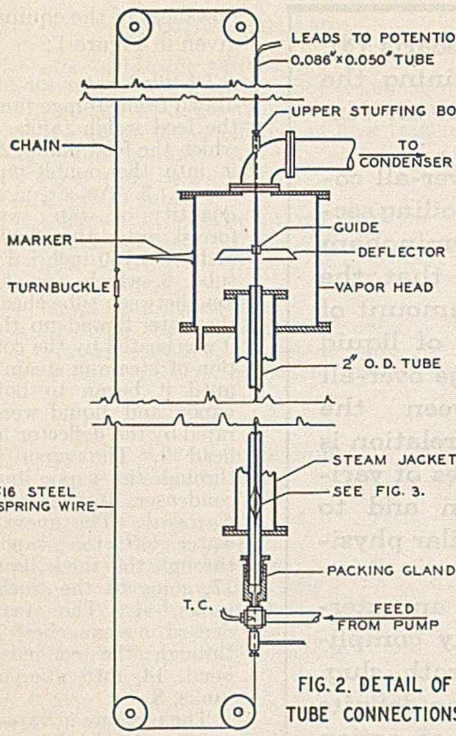

FIG. 2. DETAIL OF TUBE CONNECTIONS

from the vapor head, the vapor in the vapor head, the steam entering the steam chest, the steam in the steam chest (at the top, middle, and bottom), and the condensate leaving the steam chest.

These thermocouples were calibrated in an oil bath against a calibrated platinum resistance thermometer (*5*). The e. m. f. was read with a Leeds & Northrup portable precision potentiometer. The limit of error of the calibration was ±0.04° F.

The traveling couple (Figure 2) for the determination of the liquid temperature along the axis of the tube was of the same general type as that used previously (*8*, *20*). No. 30 Birmingham wire gage, enameled, cotton-covered copper and constantan wires were inserted into an 0.086 inch o. d. × 0.050 inch i. d. tube, 22 feet long. Provision was made for centering the lower end of the tube by vertical fins. The junction extended three-fourths inch beyond the lower end of the brass tube. The leads were withdrawn at the upper end.

The traveling couple was calibrated by comparing the reading in its highest position with the temperature calculated from the vapor head manometer. Conditions in the evaporator were maintained such that fairly vigorous boiling occurred. It was found that the steam temperature could be varied within rather wide limits without appreciable change in the reading of the traveling couple. The limit of error of this calibration was ±0.10° F.

The rate of feed to the evaporator was determined by means of the orifice installed between the control valves and the evaporator, as shown in Figure 1. The total quantity of feed delivered during a run was determined by difference at the feed weigh tanks.

The steam chest and vapor head pressures were determined by means of mercury manometers. All manometer lines were of $^1/_2$-inch standard pipe.

Experimental Procedure

The following ranges of variables were studied:

Variable	Range
Feed rate to the tube, lb./hr.	250, 500, 750, 1000
Feed temp. below vapor head temp., ° F.	10, 25, 30, 50, 60
Boiling point in vapor head, ° F.	150, 175, 200
Steam temp. minus vapor head temp., ° F.	5–50

A run consisted of continuous operation under constant conditions for 20 minutes. All drip tanks and manometers were read at regular intervals, the minimum number of readings being six. Difference readings on the tanks were determined during the run to ensure constancy of heat transfer rate.

Three complete sets of thermocouple readings and three traverses of the tube with the traveling thermocouple were made. The values used for calculation were the average of the three readings in each case.

The total heat input was used as the basis for calculation. Radiation was neglected. Slight superheat was maintained on the inlet steam. The increase in the sensible heat of the feed in being raised from the feed temperature to the maximum liquid temperature was subtracted from the total heat to give the heat transferred through the heating surface in the boiling section, $(Q/\Theta)_B$. This does not include the amount of heat produced by the decrease in the sensible heat content of the unevaporated liquid in cooling from the maximum liquid temperature to the vapor head temperature.

The remaining items in the determination of the over-all heat transfer coefficient in the boiling section are fully discussed below.

In all investigations of this type the condition of the surfaces of the tube is important. An attempt was made in this work to duplicate commercial conditions as closely as possible. Approximately one hundred and fifty runs were made before the data used for this paper were taken. Steam from the University of Michigan powerhouse was used for the heating medium. Hence, the steam side must have closely duplicated the situation present in commercial machines. The condition of the liquid side was controlled by the following procedure: With a given set of feed rate, feed temperature, and boiling point conditions, three runs were made at different values of the apparent temperature difference, spread over the entire range to be covered. Before check runs were made at intermediate values of the temperature difference, the tube was boiled out with a dilute solution of inhibited hydrochloric acid. The results were required to be within ±10 per cent of a smooth curve to be satisfactory.

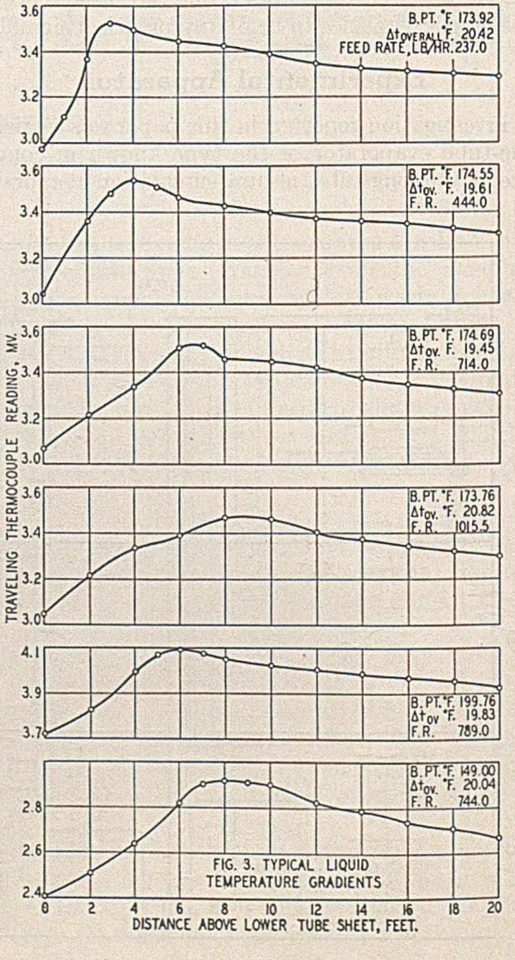

FIG. 3. TYPICAL LIQUID TEMPERATURE GRADIENTS

Determination of Boiling Section

As pointed out above, the liquid temperature distribution along the tube was determined during each run. Several typical curves for temperature *vs.* length are shown in Figure 3. The outstanding characteristic of all of these curves is the maximum which is reached.

The length of the boiling section or the boiling length, L_B, was taken as the length between the point in the tube at which the maximum temperature occurred, and the upper tube sheet. The choice of the maximum liquid temperature as the division point between the section of the tube used for heating and that in which boiling occurs, needs explanation.

The liquid entering the tube, always below the boiling point in the vapor head during this investigation, will be heated as it flows up the tube. At the same time the pressure exerted by the material farther up in the tube (both from static head and friction) will decrease. At some point in the tube, provided boiling occurs, the temperature of the liquid will be such that its vapor pressure will be equal to the pressure existing at that point.

If the liquid comes to equilibrium immediately, boiling should occur when the vapor pressure of the liquid equals the static pressure. There is, however, some doubt that equilibrium is reached at once. Jakob and Fritz (*14*) and Stewart and Hechler (*25*) showed that it is possible to have superheating of the liquid before boiling starts. If this occurs, the liquid will continue up the tube until some temperature is reached, at which point vaporization will occur.

The vapor produced when the liquid boils flows up the tube to the vapor head. Hence, the pressure must decrease as the liquid progresses up the tube. No evidence has been advanced to indicate that superheating of the liquid is possible when boiling has once started. Hence, the temperature of the liquid in the boiling section must decrease as the distance above the boiling level increases.

Thus, the level at which boiling starts is at the point where the maximum temperature occurs. The heat transfer area, A_B, is the area of the evaporator tube above the boiling level.

As shown in Figure 3, the temperature gradient of the liquid in the tube has no definite shape. Hence, the average temperature must be determined graphically. When the average liquid temperature is subtracted from the steam temperature, it permits the calculation of the average over-all temperature difference in the boiling section, $\Delta t_{av.}$.

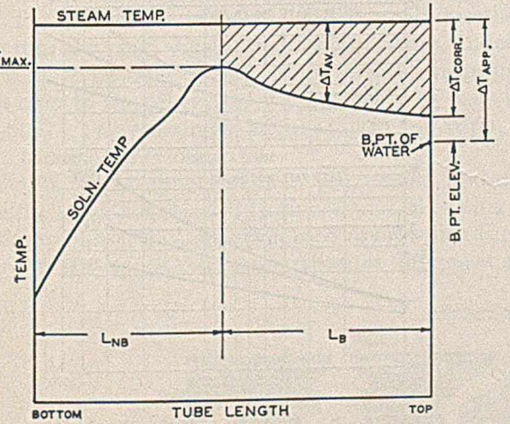

FIG. 4.
DEFINITION OF TERMS USED IN L.T.V. CALCULATIONS

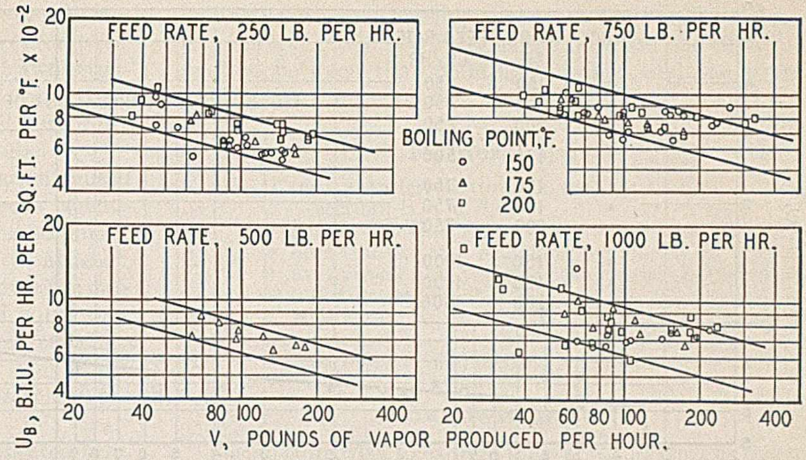

FIGURE 5. U_B vs. V

The terminology developed may be more easily visualized by Figure 4 where temperatures are plotted against tube length. The curve for liquid temperature is for the most general case—namely, a solution with an appreciable elevation in boiling point and a feed temperature below the boiling point in the vapor head. The apparent temperature drop, $\Delta t_{app.}$, and the apparent temperature drop corrected for boiling point elevation, $\Delta t_{corr.}$, are shown as usually defined. The true mean temperature drop in the boiling section, $\Delta t_{av.}$, is the mean height of the shaded portion. The true boiling coefficient, U_B, reported in this paper is calculated on the surface corresponding to the length, L_B, and on the mean temperature drop, $\Delta t_{av.}$.

Correlation of Results

U_B, the average over-all heat transfer coefficient for the boiling section, is mathematically defined as follows:

$$U_B = \frac{(Q/\Theta)_B}{A_B \Delta t_{av.}}$$

It was believed that the most important variable affecting the boiling heat transfer coefficient must be the velocity of the liquid. It was further believed that the controlling factor in this velocity would be the quantity of vapor present in the boiling section. As the most practicable approach, the total quantity of vapor was used. U_B is plotted against V, the pounds of vapor produced per hour, in Figure 5.

The average slope of the three groups containing the largest number of points was found to be −0.27. This average was determined by averaging the slope of the lines through the groups of points at a constant feed temperature and feed rate, as well as the slopes of the bands.

The remaining variables, W_f (the feed rate to the tube), $\Delta t_{av.}$, L_B, and the temperature level were similarly investigated. The latter two had no appreciable effect.

As shown in Figure 6, it was found that:

$$\frac{U_B V^{0.27}}{(W_f)^m} = f\,(\Delta t_{av.})$$

$$m = 0.0557 \log_{10}{}^{-1} \frac{8.28}{\Delta t_{av.}}$$

m is shown graphically as a function of $\Delta t_{av.}$ in Figure 7.

In 81 per cent of the 135 runs the calculated coefficient is within ±20 per cent of the observed.

It is to be emphasized that this correlation is entirely empirical. The information thus far obtained is not sufficient to permit the proposal of any general, theoretical equation for this type of heat transfer. Because of its empirical nature, this correlation should not be used for design purposes

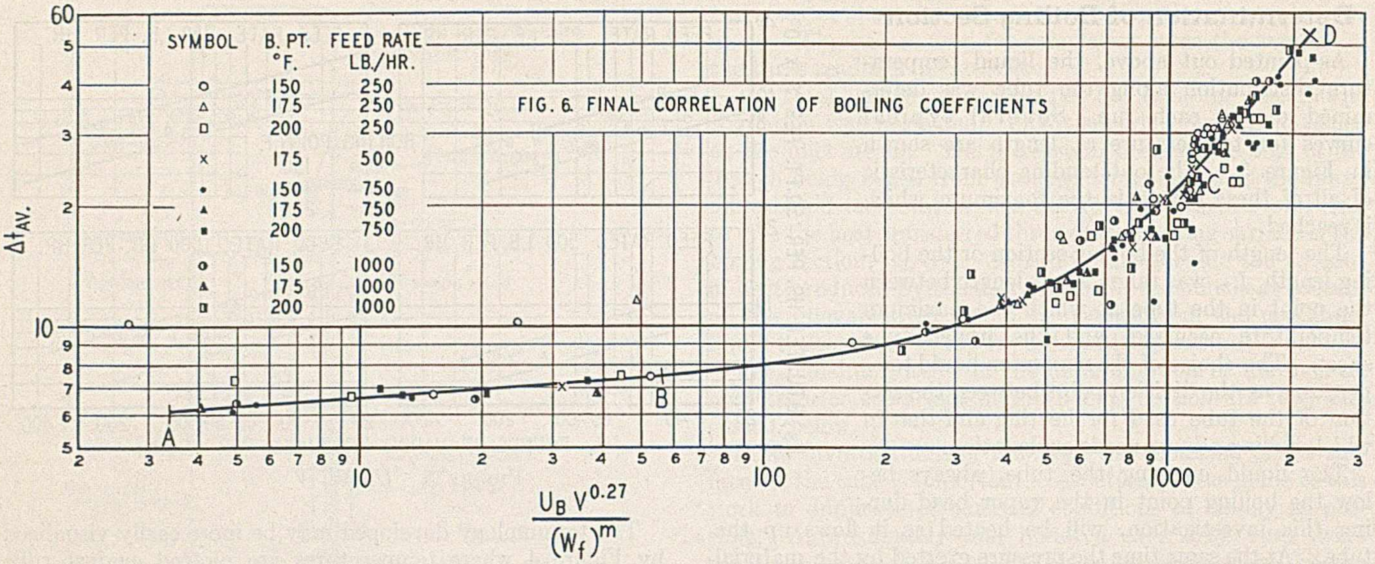

FIG. 6. FINAL CORRELATION OF BOILING COEFFICIENTS

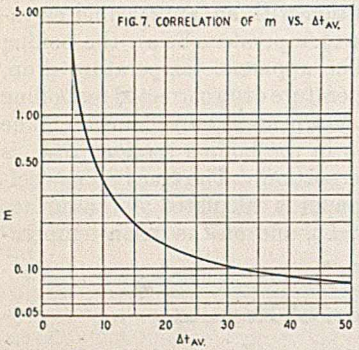

FIG. 7. CORRELATION OF m VS. Δt AV.

where the operating conditions are outside the range of variables used during the experiments upon which it is based.

Owing to the nonuniformity of the liquid temperature distribution curves (Figure 3) it is impossible to predict these curves. In order to predict the value of $\Delta t_{av.}$ from the steam temperature and the vapor head temperature, the curves in Figure 8 were developed. In 85 per cent of the runs the calculated value is within ±0.5° F. of the observed value. This is within the limits with which design data are usually known.

Discussion of Results

This investigation is unique in that the heat transfer coefficients reported apply only to the boiling section. Previously reported results have combined the boiling and nonboiling (or heating) sections; the coefficients reported are a weighted average of the coefficients which apply over the two sections.

The method used to determine the boundary between the two sections is that suggested by Boarts (*8*). However, his results of this type were too few to permit correlation. In addition, they are completely out of the range of the present experiments.

Inasmuch as this investigation was concerned primarily with the section in which boiling occurs, attempts were made to determine the phenomena in this section. The literature is deficient in this respect, yielding only two articles in which any attempt was made to explain the mechanism in the boiling section (*7*, *18*).

Barbet (*7*) describes in detail the appearance of the liquid when boiling occurs. He states that with low inlet velocities of the order of 0.3 foot per second, bubbles form which coalesce, pushing slugs of liquid ahead of them. Because of attrition at the walls of the tube, these slugs become thinner and finally break, allowing the vapor to pass through. If vaporization is sufficient, the liquid on the walls of the tube moves upward. Mention was made that annular rings of liquid appeared on the wall of the tube, above the point where the slugs broke.

These experiments were repeated during this investigation, using a glass tube, approximately 3/8 inch o. d., in a glass steam jacket. Barbet's results were verified; i. e., progressing up the tube the following types of action were encountered:

1. A very short length in which the vapor and liquid were more or less uniformly distributed both transversely and longitudinally in the tube.
2. A section of slug action in which the transverse distribution was uniform but the longitudinal was not; i. e., there were alternate slugs of liquid and vapor.
3. A section in which film action occurred, or the longitudinal distribution was uniform, but the transverse was not; i. e., there was a core of vapor with the liquid in a film of varying thickness on the walls of the tube. The annular rings mentioned by Barbet also appeared in this section.

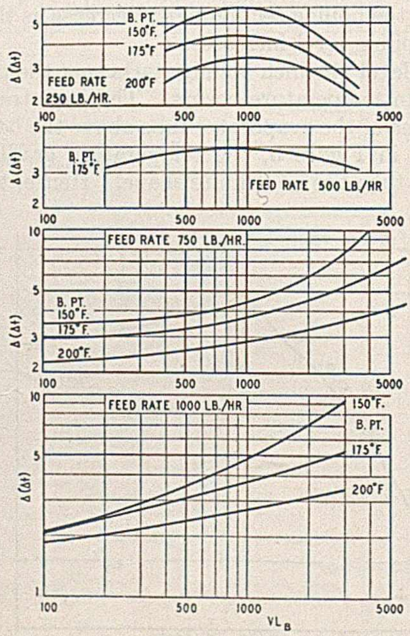

FIGURE 8. CORRELATION OF Δ(Δt) FOR VARIOUS FEED RATES

Correction to over-all temperature difference for the boiling section of 2-inch o. d. tubes. $\Delta(\Delta t) = (\Delta t_{\text{over-all}} - \Delta t_{av.})$ ° F. $\Delta t_{\text{over-all}}$ = (steam temperature − vapor head temperature) ° F. $\Delta t_{av.}$ = (steam temperature − average liquid temperature) °F. L_B = length of boiling section, feet. V = pounds of vapor per hour.

In the apparatus of Kirschbaum et al. (*18*), a special glass plate was installed over the outlet of the evaporator tube. They observed the action mentioned in the first two situations but not that in the third. Instead, the vapor and the liquid, in the form of drops, appeared to be uniformly distributed over the entire cross section of the tube.

It is believed that a faulty method of observation caused Kirschbaum and his co-workers to draw erroneous conclusions concerning conditions in the tube. When a stream of liquid and vapor came out of the tube, some of it, at least, must have impinged on the glass plate installed over the outlet of the tube. The vapor, acting on the film of liquid that would undoubtedly have been present on the glass, certainly would have caused ripples to form in the film. This would not allow the operator to make correct observations of the conditions at the outlet of the tube.

In the apparatus used for the investigation reported here, two sight glasses were installed at the level of the upper tube sheet. These permitted observation of the outlet of the tube.

With boiling lengths of one foot or less, froth appeared, corresponding to situation 1. With small temperature differences the liquid came out in slugs, traveling at high velocity with quiet intervals between the slugs. This corresponds to the second type of action.

As the temperature difference and boiling length increased, two types of spray, coarse and fine, began to appear. The coarse spray seemed to be traveling at a much lower velocity than the fine spray. In addition, the fine spray seemed to be in the center of the tube, whereas the coarse was on the outside. Furthermore, the coarse spray appeared in most cases to be blown outward, but the fine spray traveled up to the deflector in straight lines.

If there were a film on the walls of the tube, it would tend to be blown outward in the form of spray as soon as the retaining walls of the tube were removed. On the other hand, if there were drops of liquid in the vapor stream, they would tend to travel in a straight line for a time, owing to their momentum, even though the line of motion of the vapor changed. Hence, it appears that action according to situation 3 does actually take place with the addition of a phenomenon that has not yet been explained.

In the study made by Kirschbaum and his associates (*18*), it was shown that in the boiling section the temperature distribution across the tube was practically uniform for almost the entire cross section, but that it climbed rapidly at the walls. Since the static pressure at the walls will be the same as that at the center of the tube, boiling should occur at the wall. The formation of a bubble of vapor and its subsequent release into the main vapor stream by bursting, undoubtedly would tend to produce drops. Some of these drops might be thrown over to the other side of the tube—i. e., back into the liquid film. The remainder might stay in the vapor stream to form the fine spray observed.

Hence, it would appear that in progressing upward from the boiling level, a section of froth is found, then slug action, followed by film action, superimposed upon which there may be more or less spray. The temperature difference and the boiling length, and possibly the amount of liquid present, determine the action occurring at the outlet of the tube. The relation between the operating variables and the types of action occurring is not yet known.

Nomenclature

$(Q/\Theta)_B$ = heat transferred through heating surface in boiling section, B. t. u./hr.
L_B = length of boiling section, ft.
A_B = heat transfer area in boiling section, sq. ft.
U_B = av. over-all heat transfer coefficient in boiling section, B. t. u./hr./sq. ft./° F.
$\Delta t_{av.}$ = av. over-all temp. difference in boiling section, ° F.
V = vapor produced, lb./hr.
W_f = feed rate to tube, lb./hr.

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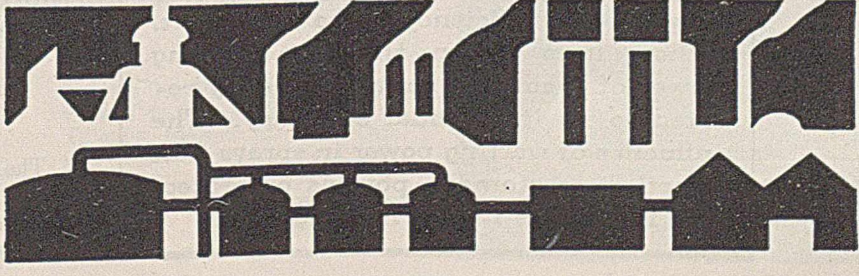

Wetting and Spreading Properties of Aqueous Solutions

Mixtures of Sodium Hydroxide with *n*-Caproic, *n*-Caprylic, *n*-Capric, Lauric, Myristic, and Palmitic Acids[1]

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For aqueous mixtures of sodium hydroxide with a number of fatty acids, at a concentration of 1.0 per cent of fatty acid, it is found that the surface tension, interfacial tension against mineral oil, and spreading coefficient, when plotted as functions of the alkali–fatty acid mole ratio, give curves which are similar in form. The relative positions of the curves correspond approximately with the order of increasing molecular weight of the fatty acids.

The wetting power of a soap solution, as measured by its spreading coefficient on mineral oil, is closely related to its foam-producing power, dirt-suspending power, and efficiency as a detergent. Others have shown that the wetting power of a contact spray is directly related to its insecticidal efficiency. The influence of wetting power in sprays that function as stomach poisons or protective fungicides merits investigation.

THE efficiency of sprays that function as contact insecticides or fungicides is directly related to the ease with which they wet the surfaces to be covered (*4, 6, 7*), and water-soluble "wetters" or "spreaders" are now widely uesd as auxiliary agents to increase their efficiency. The situation is different with stomach poisons and protective fungicides, which function by means of the deposit that remains after evaporation of the liquid medium. In this case the aim is generally to obtain a maximum deposit, evenly distributed over the surfaces to be protected. Solutions with high wetting power will generally produce excessive runoff, thus causing loss of spray material and a lessened deposit of the active material. Maximum efficiency in a spray solution of this type may well be associated with relatively high surface and interfacial tensions against the surface being covered—i. e., with a low wetting power (spreading coefficient). If the wetting power is too low, however, the spray solution will collect in drops instead of evenly covering the surface, and thus leave a spotty deposit. Owing to uncontrollable variations in the surfaces to be protected, it may be difficult to determine and to maintain the particular degree of wetting power that will produce the maximum effectiveness in sprays of this type.

Wetting power is also an important factor in the detergent action of aqueous solutions. The detergent action of such solutions is generally recognized as depending upon such factors as wetting power, solvent action, deflocculating power, and emulsifying power, although under a particular set of conditions one or more of these factors may be more important than the others.

Baker (*1*) found that with solutions of sodium stearate the abundance of foam depended on the hydrogen-ion concentration, and that the foam-producing power of a solution was a good indicator of its dirt-suspending power and efficiency as a detergent. In other words, the foam-producing power, dirt-suspending power, and detergent properties were found to attain a maximum value at a given pH, with lower values accompanying higher or lower pH values. The present writer wishes to emphasize that this correlation may not apply to materials other than the usual fatty acid soaps.

In previous papers (*2*) the author pointed out that the wetting power of certain soap solutions may be substantially decreased by using a slight excess of caustic alkali. This decrease in wetting power is accompanied by a readily apparent decrease in foam-producing power. Excess of carbonate, however, did not produce a similar decrease in wetting power and foam-producing power, and the results as a whole have led to the conclusion that the wetting power of soap solutions depends to a substantial degree upon their hydrogen-ion concentration. It thus appears that the wetting power of a soap solution, as measured by its spreading coefficient on mineral oil, is closely related to its foam-producing power, dirt-suspending power, and efficiency as a detergent.

The present paper extends the previous work to mixtures of sodium hydroxide with six additional fatty acids—namely, *n*-caproic, *n*-caprylic, *n*-capric, lauric, myristic, and palmitic—at the concentration of 1.0 gram of fatty acid per 100 cc. Some of the previously reported measurements with oleic acid mixtures are included for comparative purposes. The measurements include surface tension, interfacial tension, and spreading coefficient on mineral oil, with the alkali–fatty acid mole ratio varying for each acid from 0.80 to 3.0.

Experimental Procedure

The calculated quantities of standard sodium hydroxide, fatty acid, and water were measured into loosely stop-

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[1] For previous articles in this series, see literature citation *2*.

pered Erlenmeyer flasks. Each mixture was heated to the boiling point, shaken well, and allowed to stand at least 1 hour before being tested. The fatty acids were reagent chemicals with alkali equivalents that agreed closely with the theoretical values. The recorded alkali–fatty acid ratios are based on the experimentally determined neutralizing values of the fatty acids.

The surface tension and interfacial tension were measured with a du Noüy interfacial tensiometer, using ring correction factors as determined by Harkins and Jordan (*3*). The oil was a highly refined (medicinal) petroleum oil with surface tensions of 30.5, 28.5, and 27.5 dynes per cm. at 25°, 50°, and 65° C., respectively. To avoid errors due to curvature of the surface or interface, it was desirable to have the diameter of the free surface as large as practicable; for these measurements the containing vessel had an internal diameter of 53 mm. Interfacial tensions were measured 10 minutes after formation of the interface. In measuring both interfacial tension and surface tension, the pull on the platinum ring was increased very gradually to the point of rupture or maximum pull. Myristic and palmitic acids were tested at higher temperatures to avoid the formation of gels, and in the case of palmitic acid only a restricted range could be covered even then.

The results are presented in Table I and Figure 1.

Table I. Variation in Wetting Properties with Sodium Hydroxide–Fatty Acid Ratio, for Mixtures Containing 1.00 Gram of Fatty Acid per 100 Cc.

NaOH–Fatty Acid Ratio	Surface Tension	Interfacial Tension against Oil	Spreading Coefficient on Oil
Moles	*Dynes per centimeter*		
	n-Caproic Acid, 25° C.		
0.80	43.6	27.8	−40.9
0.90	47.1	31.1	−47.7
1.00	47.5	34.1	−51.1
1.10	52.5	31.0	−53.0
1.25	50.4	29.4	−49.3
1.50	49.8	29.4	−48.7
2.00	51.4	29.4	−50.3
	n-Caprylic Acid, 25° C.		
0.80	24.3	16.8	−11.6
0.90	24.3	16.6	−10.4
1.00	41.5	32.1	−41.3
1.10	45.2	28.6	−43.3
1.25	46.6	28.5	−44.6
1.50	45.0	27.9	−42.4
2.00	43.8	26.4	−39.7
3.00	46.4	24.4	−40.3
	n-Capric Acid, 25° C.		
0.80	21.8	13.8	− 5.1
0.90	21.9	13.8	− 5.2
1.00	22.5	14.1	− 6.1
1.10	36.8	17.0	−23.3
1.25	36.6	17.4	−23.5
1.50	35.2	15.7	−20.4
2.00	34.5	15.1	−19.1
3.00	32.2	13.3	−15.0
	Lauric Acid, 25° C.		
0.80	21.8	2.2	+ 6.5
0.90	21.8	2.3	+ 6.4
1.00	27.5	6.4	− 3.4
1.10	34.8	10.8	−15.1
1.25	34.9	10.8	−15.2
1.50	34.4	10.6	−14.5
1.75	34.2	10.2	−13.9
2.00	34.2	10.2	−13.7
3.00	33.4	9.2	−12.1
	Myristic Acid, 50° C.		
0.80	21.0	2.7	+ 4.8
0.90	20.9	1.7	+ 5.9
1.00	24.9	2.6	+ 1.0
1.10	30.4	7.7	− 9.6
1.25	31.9	8.1	−11.5
1.50	30.7	7.5	− 9.7
1.75	30.1	7.1	− 8.7
2.00	30.6	6.5	− 8.6
3.00	29.9	5.9	− 7.3
	Palmitic Acid, 65° C.		
0.80	21.0	0.8	+ 5.7
0.90	20.1	1.2	+ 6.2
1.00	23.1	3.9	+ 0.5
1.10	26.3	4.1	− 2.9
1.25	28.1	5.2	− 5.8
1.50	29.0	4.4	− 5.9
1.75	28.5	4.0	− 5.0

Discussion

The curves show that the surface tension decreases with increase in molecular weight of the fatty acid. The curves for the palmitate, myristate, oleate, laurate, and *n*-caprate are close together and form a rather distinct group from the curves for the *n*-caprylate and *n*-caproate, which are more widely separated from each other and from those of the acids of higher molecular weight.

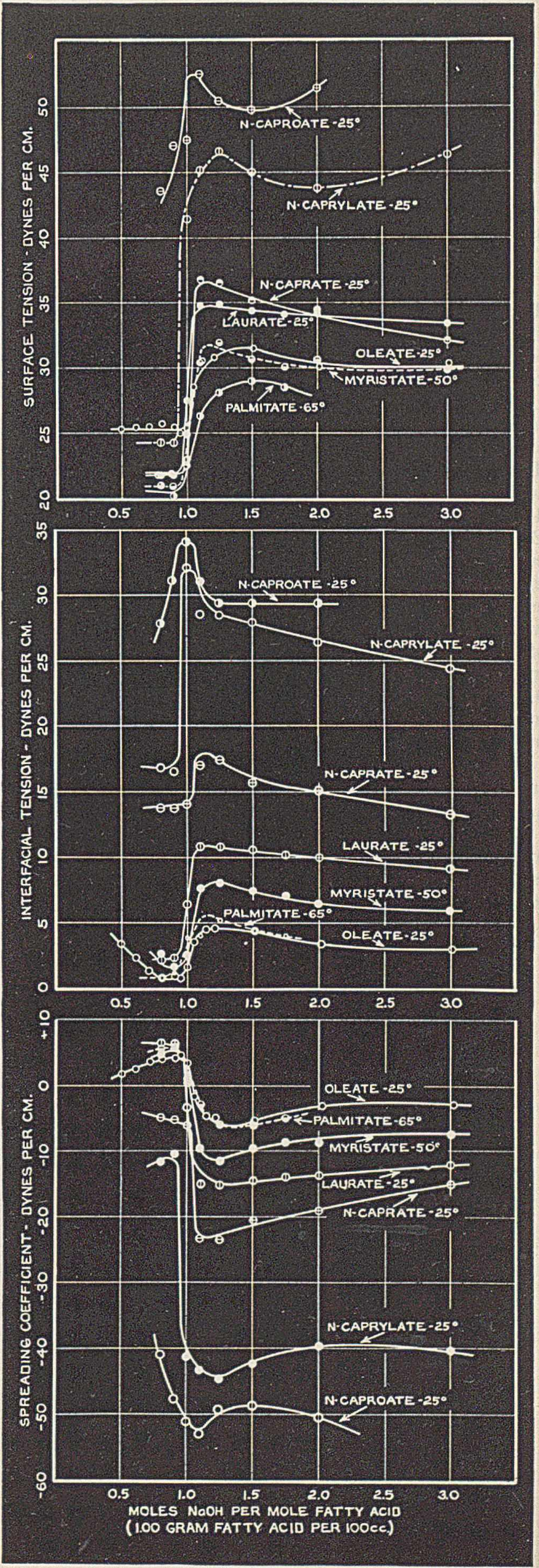

Figure 1. Variation in Surface Tension, in Interfacial Tension against Mineral Oil, and in Spreading Coefficient on Mineral Oil, with Sodium Hydroxide–Fatty Acid Ratio

Table II. Surface Tensions of Fatty Acids

Fatty Acid	Temp.	Surface Tension: Ring method	Surface Tension: Literature values[a]
	° *C.*	*Dynes per cm.*	
n-Caproic	25	27.2	27.1
n-Caprylic	25	28.2	27.9
n-Capric	35	28.4	27.5
Lauric	55	27.8	27.8
Myristic	55	28.5	28.8
Palmitic	65	28.2	28.6
Oleic	25	32.1	32.1

[a] Value for oleic acid from International Critical Tables, obtained by drop-weight method; other values from Landolt-Börnstein, obtained by capillary-rise method. Minor interpolations made to adjust temperatures.

The decrease in surface tension corresponds with the fact that, although the *n*-caproate solutions have substantially no foaming properties, the *n*-caprylate solutions foam a little better and the others are distinctly soapy.

All the curves are similar in form, showing a minimum surface tension below a mole ratio of 1.0, a sharp rise in the vicinity of the ratio 1.0, and a gradual decrease beyond this point. The *n*-caprylate curve shows an especially large increase in surface tension near the point of equivalence, from 24.3 to 45.2 dynes per cm., between the mole ratios 0.90 and 1.10. Between approximately the same two mole ratios the oleate curve increases only from 25.4 to 30.6 dynes per cm. The increase between the mole ratios 0.90 and 1.10 may be taken as a rough measure of the rate of increase of surface tension with increase of the alkali–fatty acid mole ratio in the vicinity of the point of equivalence. These values are, in order of magnitude, oleate 5.2, *n*-caproate 5.4, palmitate 6.2, myristate 9.5, laurate 13.0, *n*-caprate 14.9, *n*-caprylate 20.9. Excluding the *n*-caproate the sequence parallels that of decreasing molecular weight.

The form of the curves might lead one to suspect that the surface tensions in those mixtures containing excess fatty acid are the surface tensions of the respective fatty acids. Table II gives the surface tensions of the fatty acids used in these experiments. It is apparent that the surface tensions of the fatty acids are higher than those of the corresponding aqueous soap solutions containing excess of fatty acid. This accords with the hypothesis, suggested by the writer and by others (*5*), that the lowest surface tensions of the aqueous solutions are due to the presence of an "acid soap" which has a high surface pressure.

The curves representing the interfacial tensions of the same solutions against mineral oil (Figure 1) are similar to the surface tension curves. Minimum interfacial tensions are obtained with an alkali–fatty acid ratio less than 1.0. In the vicinity of the ratio 1.0 a sharp rise occurs, and above this point there is a gradual decrease. In their effectiveness in lowering the interfacial tension the fatty acids follow the same order as their molecular weights, and this relation is more nearly uniform than in the case of surface tension. Whereas the oleate has the lowest interfacial tension curve, its surface tension curve is higher than several of the others. The *n*-caprate curve for interfacial tensions deviates from the curves for the acids of higher molecular weight more widely than does the *n*-caprate curve for surface tension.

As the spreading coefficient is obtained by subtracting the sum of the surface tension plus the interfacial tension from the surface tension of the reference mineral oil, which is a constant value at a given temperature, it is to be expected that the spreading coefficient curves (Figure 1) should show relationships which are similar, but inverse, to those shown by the other two sets of curves. The magnitudes of the spreading coefficients, at least in the range of alkali–fatty acid ratios above 1.0, are in the same order as the corresponding molecular weights.

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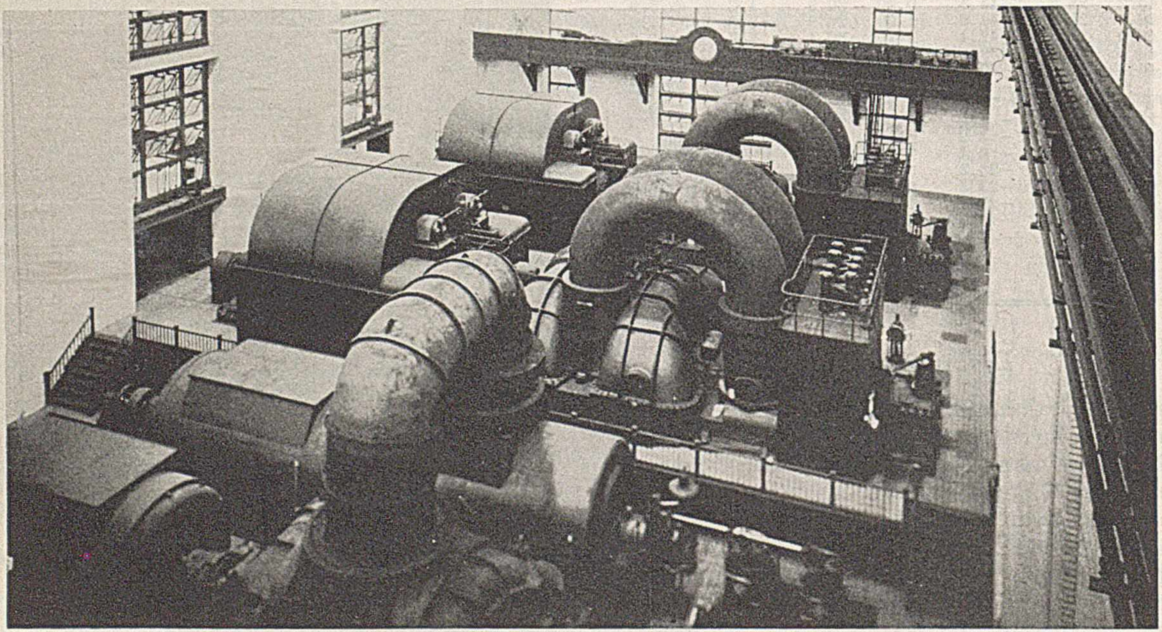

Close-Up View of the Two Giant Turbine Generators in the Most Powerful Steam-Electric Power Plant in the World, the Hudson Avenue Generating Station of the Brooklyn Edison Company. These Two Machines Are of 160,000-Kilowatt Capacity Each, and Their Installation in 1932 Brought the Capacity of the Station Up to 770,000 Kilowatts, or More than 1,000,000 Horsepower. *Courtesy, New York Edison Company.*

Wall Friction in Liquid Agitation Systems

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The laws of fluid motion are studied in cylindrical agitation systems. The logarithmic plot of the friction drag *vs.* the Reynolds number is characteristic and is analogous to the case of a fluid flowing parallel to a flat plate. The relation between power input and stirrer speed, vessel diameter, liquid depth, stirrer depth, stirrer pitch, and fluid properties is given.

THE purpose of this investigation is the application of the laws of fluid flow to the case of an agitation system. Notable advances have recently made the unit operation of agitation better understood. Previous work has been mainly confined to the ability of certain agitation systems to perform some predetermined task (*3*, *4*, *7–13*, *15*, *18*, *20*). The present research was carried out from the standpoint of the fluid motion involved. The fluid motion is obviously very complex, but the effects and thus indirectly the fluid motion may be studied by considering the fluid friction against the walls of the agitation vessel.

The existence of a transition between the two modes of flow has long been recognized, but it is to the credit of Reynolds that a unifying principle was found. He showed that the transition depended on a dimensionless expression known today as the Reynolds number (*14*). The law of similarity, later named after Reynolds, states that two different motions taking place in or around geometrically similar bodies in the absence of free surfaces are also mechanically (dynamically) similar when they have the same value of the Reynolds number.

In the case of the existence of free surfaces, where the effect of gravity must be considered, a second dimensionless quantity, known as the Froude number, must also be satisfied in order to have complete dynamic similarity.

Newton was the first to express an equation for the phenomena of friction drag resulting when relative motion exists between a body and a fluid in contact. Newton's law is:

$$D_f = fA\rho w^2$$

The factor of proportionality, *f*, is as yet undetermined. Newton derived this law from his momentum theorem.

Owing to the difficulty of separating the different types of friction drag, the practice has been to determine only the relation between the total drag and certain other factors. It has become customary to write the drag in the form:

$$D_f = cA\rho w^2$$

The factor of proportionality, *c*, the drag coefficient, is different for various shapes, sizes, and positions of the body.

The simple relations outlined are practically true only when the total drag consists almost entirely of pressure drag and when the geometry of flow is determined by sharp edges. In all other cases the simple relation does not hold because geometrical similarity does not imply dynamic similarity.

The conditions for dynamic similarity as we have seen, where geometrical similarity is ensured, consists in having the Reynolds and Froude numbers the same for the two cases. Only then are the drag coefficients necessarily the same for the two cases. We write, therefore:

$$D_f = cA\rho w^2 = f(Re, F)\rho Aw^2$$

In applying this modified form of Newton's equation to cylindrical agitation vessels, some arbitrary assumptions had to be made in order to analyze the existing conditions. First the Reynolds number was defined as $Nd^2\nu$. The Froude number may be defined as N^2d/g. Newton's equation may be rewritten:

$$D_f = f(Nd^2/\nu,\ N^2d/g)\rho Aw^2$$

In order to have complete dynamic similarity in two cases with both *Re* and *F* defined as above, we must have two liquids of vastly different viscosities. In the case of this research no case exists where complete dynamic similarity exists, based on both *Re* and *F*. It was considered, however, that the surface effects over the range of systems studied would be negligible. In other words, it was assumed that the drag coefficient varied only as *Re*, instead of as both *Re* and *F*. The assumption is substantiated by the agreement of the data over a range of sizes of vessels when analyzed on the basis of *Re* alone. Thus we may write:

$$D_f = c\rho Aw^2 = f(Re)\rho Aw^2$$

In this equation *A* was taken as the internal wetted area of the vessel. Since the depth of the liquid in the geometrically similar series of systems was taken equal to the vessel diameter, the internal wetted area may then be taken as $5/4\pi d^2$ or kd^2 (where $k = 5/4\pi$); *w* was defined as *bNd*. Since the actual velocity at the wall was not measured, the velocity was taken to be a straight-line function of the theoretical velocity at the wall if the whole fluid were rotating at constant angular velocity. The drag coefficient *c* is then defined as

$$c = D_f/\rho Aw^2 = D_f/\rho kd^2(bNd)^2 = D_f/k'\rho d^4N^2$$

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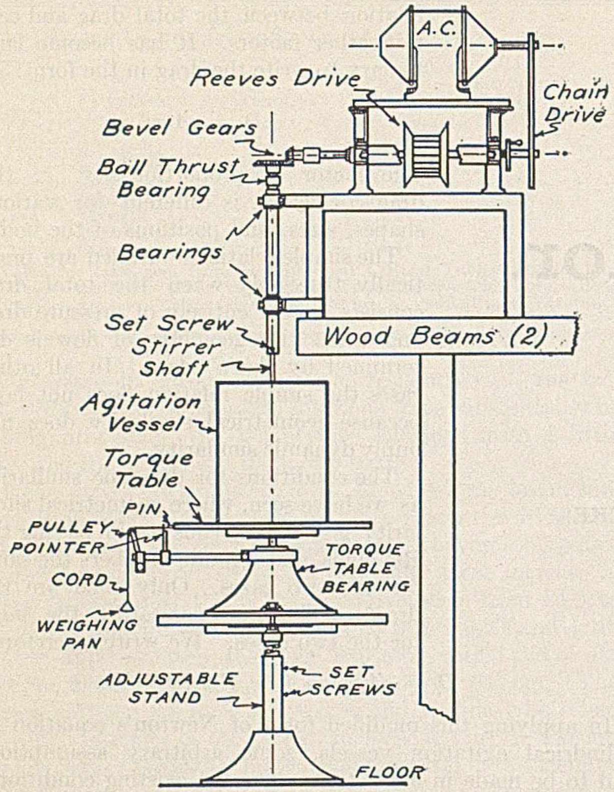


Figure 1. Apparatus Layout

The constant k' was then included in the functional relation between c and Re. The definition of c then is

$$c = D_f/\rho N^2 d^4$$

Apparatus and Materials

As pointed out earlier, it was impossible to extend the study beyond simple liquid agitation systems. The method of measuring the wall friction, which in this work is truly the horizontal component of the friction, was to place the agitation vessel centrally upon the torque table. The details of the apparatus and its setup are shown in Figures 1 and 2. The details of the method of measurement will be given in the ensuing section.

The investigation was first carried out in the vessel of 26.0-cm. (10.25-inch) diameter, using a 45° propeller type of stirrer as described by Hixson and Wilkens (*9*), at the standard depth of liquid and standard stirrer clearance. The liquids used were water, 60 per cent sucrose solution, 27.5 per cent sucrose solution, and 12.5 per cent sucrose solution. The data for the viscosity and density of these solutions were taken from Bingham and Jackson (*1*) as well as from Spencer and Meade (*16*). To vary the viscosity of the 60 per cent sucrose solution over a considerable range, a Nichrome ribbon was wound around the vessel and the temperature of the solution raised. The 60 per cent sucrose solution was made from commercial cane sugar by weight, and the gravity was periodically tested by hydrometer and less frequently by a pycnometer. The solution was preserved by the addition of some sodium fluoride and sodium chloride. The added salts did not affect the viscosity of the solution enough to cause any error in the results.

The investigation was also continued to vessels of larger size as well as one smaller. The agitators used were geometrically similar and fitted their respective vessels to give geometrically similar systems. The specifications are given on Figure 2.

The investigation was extended to a 90° paddle agitator and a 60° propeller agitator, both of the same length and width as the corresponding 45° propeller. These were used in connection with the 26.0-cm. vessel. With the paddle and the 45° propeller, the depth of the stirrer was varied, keeping the liquid depth constant, and then the liquid depth was varied, keeping the stirrer clearance constant.

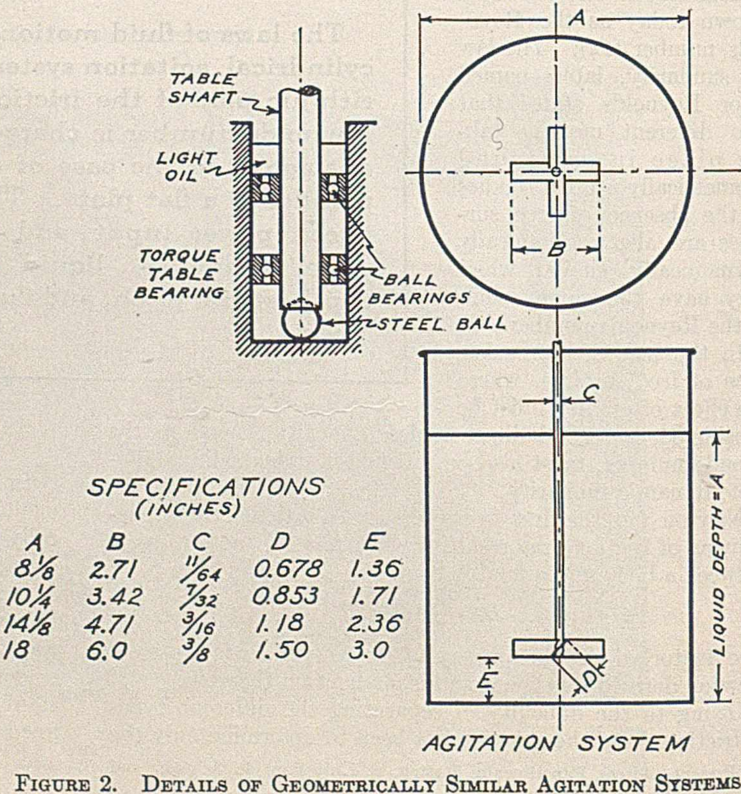
Experimental Method

In this research a special method of balancing the torque produced by the suspended weights against the torque produced by the friction on the vessel walls was developed. The static friction of the table bearing was high enough so that a balance made in the usual way would result in the introduction of very large errors in the relatively small values of the wall friction.

The method used may be briefly described as follows:

With the two torques equal or approximately so, the pointer and the pin on the circumference of the table (Figure 1) are brought together. The table is given a small motion by a tap of the finger so that the pin moves about 5 mm. in the direction of the friction torque away from the pointer. If the torques are balanced, the pin will return to its initial position opposite the pointer. If the pin returns to a position on one or the other side of the pointer, then more or less weight is required on the weight pan. By this method the static friction of the table bearing is partially overcome and the readings of the wall friction are thus more accurate.

In making a run, the procedure was first to check the solution density and liquid level in the vessel as well as the stirrer depth. The friction of the bearing alone was then determined with the stirrer stopped in the manner described. The stirrer was then started and the speeds used were determined by the Reeves drive settings. It was found throughout the research that the revolutions per minute corresponding to any Reeves drive setting did not vary by more than 2 or 3, as determined with the use of a revolution counter and a watch. The temperature of the solution was determined after each reading at each setting. When the Nichrome heating element was used at elevated temperatures, it was found necessary to take a reading of the temperature immediately before and after each reading of the wall friction. Sufficient time was allowed between each change in speed to allow the flow in the vessel to come to equilibrium. The time required was longer in the case of the more viscous



SPECIFICATIONS
(INCHES)

A	B	C	D	E
$8\frac{1}{8}$	2.71	$\frac{11}{64}$	0.678	1.36
$10\frac{1}{4}$	3.42	$\frac{7}{32}$	0.853	1.71
$14\frac{1}{8}$	4.71	$\frac{3}{16}$	1.18	2.36
18	6.0	$\frac{3}{8}$	1.50	3.0

Figure 2. Details of Geometrically Similar Agitation Systems

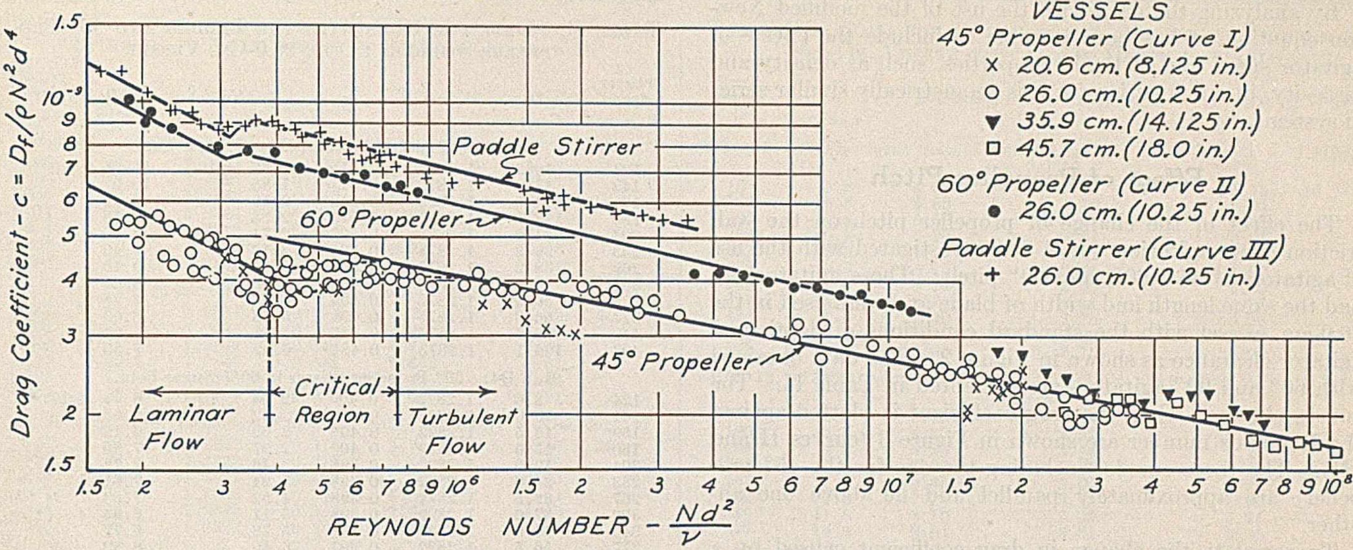


FIGURE 3. PLOT OF DRAG COEFFICIENT *vs.* REYNOLDS NUMBER

sugar solutions. At the completion of a run the density of the solution was again checked.

Wall Friction in Geometrically Similar Systems

According to the theory the drag coefficient should have the same value in two cases where the systems are geometrically similar and the two fluid motions should have the same Reynolds number. In this research a number of geometrically similar systems were investigated. The 45° propeller stirrer was used in these cases. The data for this geometrically similar series of systems are presented in Table I. The values of drag coefficient c, when plotted on double logarithmic paper against the Reynolds number Re (Figure 3, curve I), yield characteristic curves. The concordance of the data to the curves drawn is fairly good, considering the error involved in making the measurement of the relatively small torque involved.

This curve shows definitely the critical range of flow. From the curves for the laminar and turbulent region of flow, the following equations were derived.

for $Re < 4 \times 10^5$: $c = 0.000000258\,(Re)^{-0.5} = 0.0_5258/\sqrt{Re} = 2.58 \times 10^{-7}/\sqrt{Re}$

and $c = 0.00000000625\,(Re)^{-0.196} = 0.0_7625\,(Re)^{-0.196} = 6.25\,(Re)^{-0.196} \times 10^{-9}$

for $Re > 10^6$: $c = 0.0_763/\sqrt[5]{Re} = 6.3 \times 10^{-9}/\sqrt[5]{Re}$

Of particular interest is the functional relation between c and Re for flat plates because of an apparent analogy between the flow of fluid past a flat plate and the flow of fluid in an agitation vessel. The bottom of the vessel is readily seen to belong to the classification of flow against a flat plate. The side walls, although curved, are truly flat plates in relation to the fluid motion, because the stream lines of the fluid are also curved and parallel to the walls. It should be expected, then, that the experiments show an analogy to the flow of fluid along a flat plate. The friction drag against flat plates was studied at Re values below 5×10^5 by the law of Blasius and above 5×10^6 by various investigators. For the laminar flow region the functional relation between c and Re is given by:

$$c = 1.327/\sqrt{Re},\ Re < 5 \times 10^5$$

Investigations by Wieselsberger (*19*), Gebers (*5*), and Gibbons (*6*) show that the relation for the turbulent region can be expressed as

$$c = 0.072/\sqrt[5]{Re},\ Re > 5 \times 10^6$$

The exponents of Re are the same in the case of friction against flat plates and against agitation vessel walls. The difference in numerical coefficients is expected from the geometrical dissimilarity of the two cases.

The line for the laminar region is drawn through the points which were made with the greatest care (run H1) as well as late in the investigation when the full technic of making the readings and operating the apparatus had been developed.

On the basis of an assumption that the liquid velocity outside the stagnant film is a linear function of the theoretical (constant angular) velocity of the liquid at the wall, a relation between the power lost to wall friction and other variables can be formulated. Thus for the turbulent régime of flow,

$$D_f/\rho N^2d^4 = c = 0.0_763/\sqrt[5]{Re} = 0.0_763(Nd^2/\nu)^{-0.2}$$
$$D_f = 0.0_763\rho N^{1.8}d^{3.6}\nu^{0.2} = 0.0_763\rho^{0.8}N^{1.8}d^{3.6}\eta^{0.2}$$
$$P = 0.0_763\rho^{0.8}N^{1.8}d^{3.6}\eta^{0.2}kNd$$
$$P = k'\rho^{0.8}\eta^{0.2}N^{2.8}d^{4.6}$$

where P = power lost to friction

The exponents of ρ, η, and N agree fairly well with those of Buckingham (*2*) who studied power consumption due to windage in turbines. Although the value of k' could not be evaluated at this time, the form of the function which is encountered may be seen.

The exponents of ρ, η, and N also agree with those found by White and his co-workers (*17*), who made a study of the total power requirements of simple agitation systems. By dimensional analysis they found the following relation to hold:

$$P = 0.000129L^{2.72}z^{0.14}N^{2.86}D^{1.1}\rho^{0.86}W^{0.3}H^{0.6}$$

where P = horsepower
L = length of paddles, ft.
Z = absolute viscosity, lb./sec. ft.
N = rotational speed, revolutions/sec.
ρ = density, lb./cu. ft.
D = diameter of agitation vessel, ft.
W = width of paddle, ft.
H = liquid depth, ft.

By analyzing the data with the use of the modified Newton equation, it has been possible to include the effects of agitator speed and of liquid properties, such as density and viscosity, in one function for this geometrically similar series of systems.

Effect of Propeller Pitch

The effect of the change of propeller pitch on the wall friction of an agitation vessel was investigated with the use of agitators of 45°, 60°, and 90° pitch. These agitators all had the same length and width of blade and were used in the 26.0-cm. vessel with the standard conditions of depth and agitator clearance as shown in Figure 2. The data obtained with 60° and 90° agitators are presented in Table II. The curves obtained when the drag coefficient is plotted against the Reynolds number are shown in Figure 3 (curves II and III). The three curves (including the one for the 45° propeller) are approximately parallel and lie above one another.

To correlate the change in drag coefficient caused by a change in the propeller pitch, a plot of the ratio of the drag coefficient for a propeller of one pitch to that of the 90° propeller against the pitch angle at various definite Reynolds numbers is shown in Figure 4. The curves for the three Reynolds numbers chosen do not fall together at the lower pitch angles. This spreading is caused by the fact that the three drag coefficient–Reynolds number curves are not exactly parallel. The curve of $c/c_{\text{max.}} = \sin x$ is also shown on this plot to illustrate that the curves do not follow this simple sine relation. In order to correlate the data with the final purpose of obtaining a composite variable to include the effect of propeller pitch, an average curve was drawn and the equation of this curve was found to be:

$$c/c_{\text{max.}} = \sin(1.13x - 12.0)$$

Table I. Runs with Geometrically Similar Vessels and Agitators with Liquid Depth at Vessel Diameter

Stirrer Speed R. p. m.	D_f Grams	ρ	ν	$Re(Nd^2/\nu)$	$c(D_f/\rho N^2d^4)$
Run B2a: 60% Sugar Soln. in 26.0-Cm. Vessel					
204	8.8	1.2853	0.389	3.53×10^5	3.61×10^{-10}
233	11.4	1.2853	0.389	4.04	3.60
269	15.8	1.2853	0.389	4.66	3.75
302	21.0	1.2853	0.389	5.24	3.96
336	25.5	1.2853	0.389	5.63	3.85
376	32.5	1.2853	0.389	6.52	3.94
425	42.1	1.2853	0.389	7.37	4.00
452	48.3	1.2853	0.389	7.82	4.05
485	54.4	1.2853	0.389	8.40	3.96
Run C1: 60% Sugar Soln. in 26.0-Cm. Vessel (Elevated Temp.)					
124	3.3	1.2810	0.250	3.34×10^5	3.66×10^{-10}
143	4.9	1.2810	0.250	3.85	4.10
160	6.5	1.2812	0.255	4.23	4.36
180	7.7	1.2813	0.257	4.73	4.06
204	9.5	1.2814	0.262	5.25	3.91
376	28.4	1.2820	0.276	9.20	3.46
425	37.2	1.2821	0.278	10.3	3.51
452	46.9	1.2821	0.281	10.85	3.94
485	54.0	1.2821	0.281	11.61	3.92
Run F3: 60% Sugar Soln. in 20.6-Cm. Vessel					
302	8.4	1.2848	0.366	3.50×10^5	4.00×10^{-10}
340	10.0	1.2848	0.366	3.94	3.73
377	12.0	1.2848	0.365	4.38	3.66
421	15.0	1.2848	0.365	4.89	3.66
458	18.0	1.2847	0.364	5.34	3.72
493	20.0	1.2847	0.364	5.75	3.56
Run G1: Water in 35.9-Cm. Vessel					
113	5.1	1.0	0.0089	1.62×10^7	2.4×10^{-10}
124	7.0	1.0	0.0089	1.78	2.75
141	8.9	1.0	0.0089	2.02	2.70
159	10.2	1.0	0.0089	2.28	2.44
180	12.7	1.0	0.0089	2.58	2.38
204	15.3	1.0	0.0089	2.92	2.22
229	19.1	1.0	0.0089	3.29	2.22
267	25.5	1.0	0.0089	3.83	2.17
302	33.1	1.0	0.0089	4.33	2.19
340	42.0	1.0	0.0089	4.87	2.19
377	52.2	1.0	0.0089	5.40	2.22
421	59.8	1.0	0.0089	6.05	2.04
458	68.7	1.0	0.0089	6.58	1.98
493	75.1	1.0	0.0089	7.09	1.87
Run G2: Water in 45.7-Cm. Vessel					
100	11.0	0.996	0.00839	2.49×10^7	2.53×10^{-10}
113	15.0	0.996	0.00839	2.83	2.69
124	20.0	0.996	0.00839	3.10	2.98
141	23.0	0.996	0.00840	3.51	2.66
159	26.5	0.996	0.00843	3.97	2.41
180	30.0	0.996	0.00843	4.48	2.13
204	36.0	0.996	0.00844	5.08	1.99
229	43.0	0.996	0.00844	5.71	1.89
267	54.0	0.996	0.00844	6.65	1.74

Table II. Data for Runs with the Paddle and 60° Propeller Stirrers in the 26.0-Cm. Vessel

Stirrer Speed R. p. m.	D_f Grams	ρ	ν	$Re\ (Nd^2/\nu)$	$c\ (D_f/\rho N^2d^4)$
Run D1: Paddle Stirrer with 60% Sugar Soln.					
124	10.2	1.2879	0.513	1.63×10^5	11.26×10^{-10}
143	11.9	1.2879	0.513	1.88	10.0
160	14.0	1.2879	0.513	2.10	9.45
180	18.1	1.2879	0.510	2.38	9.58
204	21.6	1.2878	0.507	2.71	8.90
233	29.8	1.2878	0.504	3.12	9.40
269	38.2	1.2877	0.501	3.62	9.10
302	47.0	1.2876	0.499	4.08	8.85
336	56.0	1.2876	0.494	4.58	8.28
377	66.3	1.2875	0.490	5.18	8.00
449	79.6	1.2874	0.486	5.88	7.60
493	106.1	1.2873	0.481	6.92	7.50
Run D4: 60° Propeller Stirrer in 60% Sugar Soln.					
124	8.0	1.2822	0.409	2.04×10^5	8.91×10^{-10}
141	10.0	1.2822	0.409	2.32	8.63
159	13.5	1.2822	0.409	2.62	9.15
180	15.0	1.2822	0.409	2.97	7.95
204	19.0	1.2822	0.398	3.46	7.76
233	24.0	1.2822	0.398	3.94	7.61
267	29.5	1.2822	0.398	4.52	7.09
302	37.0	1.2822	0.398	5.11	6.95
340	46.0	1.2822	0.397	5.78	6.77
377	56.5	1.2822	0.397	6.40	6.82
421	67.0	1.2822	0.397	7.15	6.46
458	79.0	1.2822	0.397	7.76	6.46
493	89.0	1.2822	0.394	8.42	6.26

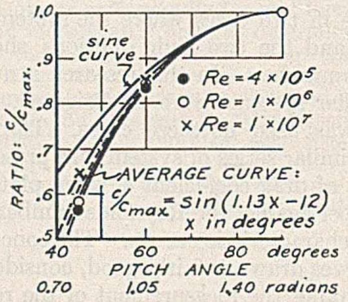


Figure 4. Effect of Propeller Pitch

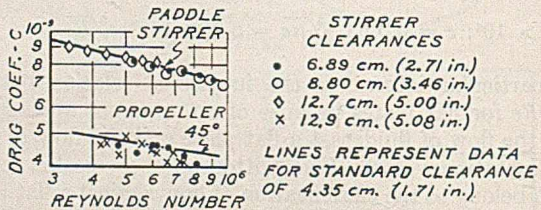


Figure 5. Effect of Stirrer Depth (26.0-Cm. Vessel)

Effect of Agitator Clearance

The effect of the change of propeller clearance—in other words, the agitator depth at constant liquid depth—was investigated with the paddle stirrer and the 45° propeller stirrer in the 26.0-cm. vessel. Clearances of 6.89, 8.80, 12.7, and 12.9 as well as the standard clearance of 4.35 cm. were

TABLE III. DATA FOR RUNS WITH 45° PROPELLER AND PADDLE STIRRERS TO NOTE EFFECT OF STIRRER CLEARANCE

Stirrer Speed R. p. m.	D_f Grams	ρ	ν	$Re(Nd^2/\nu)$	$c(D_f/\rho N^2d^4)$
Run E1: Paddle Stirrer in 60% Sugar Soln.; Clearance = 8.80 Cm.					
267	33.9	1.2842	0.347	5.18×10^5	8.13×10^{-10}
302	42.1	1.2842	0.347	5.85	7.91
340	50.9	1.2842	0.347	6.60	7.51
377	63.2	1.2841	0.344	7.39	7.61
421	77.3	1.2841	0.344	8.25	7.43
458	88.7	1.2841	0.344	8.97	7.23
493	98.4	1.2841	0.342	9.70	6.91
Run E2: Same as E1; Clearance = 6.89 Cm.					
267	34.2	1.2841	0.342	5.26×10^5	8.19×10^{-10}
302	42.1	1.2841	0.342	5.96	7.89
340	51.8	1.2841	0.342	6.71	7.64
377	63.2	1.2841	0.342	7.45	7.61
421	77.3	1.2841	0.342	8.30	7.44
458	88.6	1.2840	0.339	9.05	7.21
Run E3: 45° Propeller, 60% Sugar Soln.; Clearance = 6.89 Cm.					
267	19.0	1.2822	0.378	4.76×10^5	4.55×10^{-10}
302	23.5	1.2822	0.378	5.40	4.30
340	30.4	1.2822	0.382	6.00	4.60
377	37.4	1.2822	0.382	6.66	4.51
421	44.4	1.2822	0.382	7.44	4.28
458	49.6	1.2822	0.382	8.10	4.05
Run E5: 45° Propeller Stirrer, 60% Sugar Soln.; Clearance = 12.9 Cm.					
267	19.0	1.2862	0.426	4.21×10^5	4.55×10^{-10}
302	22.5	1.2862	0.426	4.77	4.22
340	29.5	1.2862	0.426	5.37	4.35
377	36.6	1.2862	0.426	5.95	4.41
421	42.6	1.2862	0.426	6.65	4.09
458	50.1	1.2862	0.422	7.24	4.07
Run E6: 45° Propeller, 60% Sugar Soln.; Clearance = 12.9 Cm.					
267	19.2	1.2860	0.412	4.37×10^5	4.60×10^{-10}
302	25.8	1.2860	0.412	4.95	4.84
340	31.1	1.2859	0.410	5.56	4.58
377	36.4	1.2860	0.412	6.17	4.38
421	45.1	1.2860	0.412	6.90	4.33
458	50.4	1.2860	0.412	7.51	4.10

TABLE IV. DATA FOR RUNS WITH 45° PROPELLER STIRRER IN 26.0-CM. VESSEL WITH LIQUID DEPTH VARIABLE

Stirrer Speed R. p. m.	D_f Grams	$Re(Nd^2/\nu)$	$D_f/\rho N^2d^3h$	$D_f/\rho N^2d^3(d+4h)$
Run I1: 27.0% Sugar Soln.; Liquid Depth = 20.5 Cm.; ρ = 1.1128; ν = 0.0250				
159	3.8	4.29×10^6	3.76×10^{-10}	7.15×10^{-11}
180	6.8	4.85	3.70	7.04
204	5.8	5.50	3.45	6.55
233	6.8	6.29	3.14	5.96
267	8.3	7.20	2.91	5.53
302	9.3	8.15	2.56	4.87
340	12.3	9.24	2.66	5.05
377	14.8	10.20	2.61	4.95
421	19.8	11.40	2.78	5.29
458	23.8	12.40	2.83	5.37
493	26.8	13.30	2.75	5.22
Run I2: 27.0% Sugar Soln.; Liquid Depth = 15.9 Cm.; ρ = 1.1128; ν = 0.0264				
159	2.4	4.06×10^6	3.04×10^{-10}	5.41×10^{-11}
180	3.3	4.60	3.27	5.83
204	4.5	5.20	3.44	6.13
233	5.8	5.95	3.44	6.13
267	7.8	6.85	3.50	6.24
302	9.8	7.74	3.35	5.96
340	11.8	8.70	3.26.	5.81
377	14.8	9.61	3.34	5.95
Run I3: 24.8% Sugar Soln.; Liquid Depth = 29.9 Cm.; ρ = 1.103; ν = 0.0238				
159	3.8	4.5×10^6	2.59×10^{-10}	5.31×10^{-11}
180	5.8	5.10	3.09	6.34
204	7.8	5.77	3.12	6.40
233	9.8	6.60	3.12	6.40
267	11.8	7.55	2.86	5.86
302	13.8	8.58	2.61	5.35
340	15.3	9.65	2.28	4.68
377	19.8	10.70	2.41	4.94
421	23.8	11.90	2.30	4.71
458	27.8	13.00	2.28	4.68
493	30.8	14.00	2.19	4.49

used with the two different agitators. The results of this investigation are shown in Table III and Figure 5. Figure 5 shows particularly that the change in stirrer depth has no effect on the drag coefficient, at least within the error of the experiment. However, it can be safely stated that up to 49 per cent of the liquid depth the change in depth of the stirrer has no effect on the drag coefficient.

Effect of Liquid Depth

The depth of the liquid in the agitation vessel was varied, keeping the agitator clearance constant. The 26.0-cm. vessel was used with the 45° stirrer. Before considering the experimental results, reference to the modified Newton equation at this time will be of value:

$$D_f = c\rho A w^2$$

If the effect of the change of liquid depth can be considered only as a change in the wetted area of the vessel, the term A in this equation will become

$$A = \pi d^2/4 + \pi dh = \pi d(d + 4h)/4$$

As before, the term w can be expressed as kNd so that the quadratic equation of Newton becomes

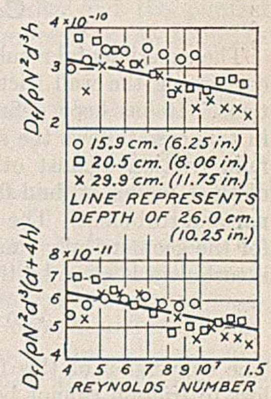
$$D_f = c\rho d(d + 4h)\pi(kNd)^2/4$$

Also as before, the quantity $\pi k^2/4$ can be included in the functional relation between c and Re. A new drag coefficient is then defined, say c', which is not the same as that heretofore discussed; this coefficient is

$$c' = D_f/\rho d^3(d + 4h)N^2$$

The data found for the effect of liquid depth (Table IV) may be plotted as this variable against the Reynolds number as in Figure 7. It is evident that this variable expresses the change of liquid depth fairly well.

If the dimensions of the various factors which enter into the effect of the change of liquid depth were considered, a dimensionally correct variable, $D_f/\rho N^2d^3h$, can be obtained. The use of this variable as a basis of analysis results in the curve shown in Figure 6. The data agree more closely when analyzed on the basis of the first variable. This second, dimensionally correct variable, may be used in those cases where ease of calculation is desired.



FIGURES 6 AND 7. EFFECT OF LIQUID DEPTH

The Composite Variable

Although a great many variables are yet to be considered, time prevented the study of others. However, on the basis of those variables studied, a composite variable can be drawn up to take care of fluid properties (viscosity and density), rate of stirring, vessel size, liquid depth, propeller pitch, and propeller depth. From the foregoing discussion, this composite variable will be

$$c'' = D_f/\rho N^2d^3(d + 4h) \sin (1.13x - 12)$$

When this coefficient c'' is plotted against the Reynolds number, a curve should be obtained which will fit all the data. Such a plot is shown in Figure 8, where it is seen that the data follow this function well in the turbulent region of flow but not very well in the laminar flow region. It may be said that the effect of a number of these variables was considered only for the turbulent region.

The line which fits the data in the turbulent region has a

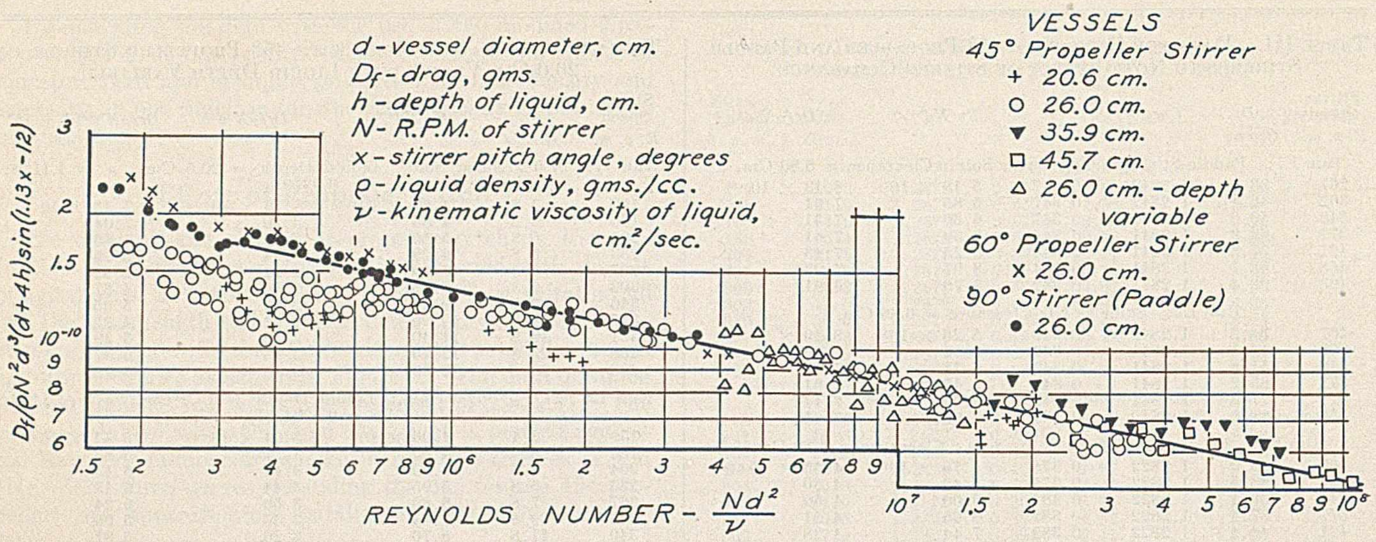


FIGURE 8. PLOT OF THE COMPOSITE VARIABLE $D_f/\rho N^2d^3(d + 4h)\sin(1.13x - 12)$ AGAINST THE REYNOLDS NUMBER Nd^2/ν

slope of −0.21 which is still in fair agreement with the value of −0.2 for flow against flat plates. The equation for the curve was found to be

$$c'' = 2.54\ (Re)^{-0.21} \times 10^{-9}$$

Using this relation the value of D_f is

$$D_f = (2.54 \times 10^{-9})\rho^{0.79}\eta^{0.21}N^{1.79}d^{2.58}\ (d + 4h)\sin\theta$$

where $\theta = 1.13x - 12$

The power lost to wall friction can be derived as before on the basis of this function:

$$P = k\rho^{0.79}\eta^{0.21}N^{2.79}d^{3.58}(d + 4h)\sin\theta$$

Conclusions

The experimental results warrant the following conclusions concerning the wall friction of various liquid agitation systems. It has been definitely shown that the fluid friction in this case follows the same type of laws that exist for the fluid friction against other bodies. The existence of two distinct modes of fluid flow has been shown—namely, laminar and turbulent. The value of the wall friction, in grams, for the geometrically similar series of systems when the flow is turbulent is given by the equation:

$$D_f = 0.0_763\ \rho^{0.3}N^{1.8}d^{3.6}\eta^{0.2}$$

The conversion of this function to one showing the power lost to friction cannot be given at this time. Although the type of function is known, the numerical value of the constant in that function could not be determined. In order to find this power loss accurately, it is necessary to know the fluid velocity immediately outside the stagnant film at the vessel wall.

A number of other variables were considered and these may all be represented in the composite function for the friction drag, in grams:

$$D_f = (2.54 \times 10^{-9})\rho^{0.79}\eta^{0.21}N^{1.79}d^{2.58}(d + 4h)\sin\theta$$

where $\theta = 1.13x - 12$

As before, the actual values of the power lost to friction could not be calculated by the type of function which obtains has been shown.

It is of interest to point out the method by which these results may be used in the future for the purposes of design. Although there is no experimental verification, it is believed that the difference between the power input into an agitation system and the power output to wall friction is a function of the degree or efficiency of mixing. That is, the difference would be a function of the cube-root-law velocity constant for dissolution, or a function of the mixing index of Hixson and Tenney (*8*). The results of this research along with a knowledge of the fluid velocity immediately outside the stagnant boundary fluid layer will give the power lost to friction, overall power measurements such as those of White and his coworkers will give the total power input, and the difference may thus be obtained. With a knowledge of the desired rate of dissolution, the power difference may be calculated and from this the power lost to friction and the total power input may be calculated.

Nomenclature

A = wetted area or area of body projected in the direction of flow, sq. cm.
b = a constant
c = drag coefficient = $D_f/\rho N^2d^4$
c' = modified drag coefficient = $D_f/\rho d^3(d + 4h)N^2$
c'' = composite drag coefficient = $D_f/\rho N^2d^3(d + 4h)\sin(1.13x - 12)$
D_f = drag, grams
d = vessel diameter, cm.
f = factor of proportionality
F = Froude number = N^2d/g
g = acceleration of gravity
h = liquid depth, cm.
k, k' = constants
N = agitator speed, r. p. m.
P = power input, any unit of power
Re = Reynolds number = Nd^2/ν
x = stirrer pitch angle, degrees
w = velocity
η = viscosity, poise
ν = kinematic viscosity, sq. cm./sec.
ρ = liquid density, grams/sq. cm.

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A Polyuronide from Tobacco Stalks

The isolation and partial analysis of a polyuronide from the cured stripped stalk of Havana seed tobacco is described. Upon hydrolysis the polyuronide yields xylose as the chief sugar.

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THE tobacco plant (*Nicotiana tabacum*) is unique in at least two respects. First, few cultivated plants attain as large a growth in as short a time at so great an expense to the soil. Second, few plants of such proportions are as easily decomposed when returned to the soil. These are the chief characteristics which justify the common practice of using the stripped stalks as a fertilizer. This paper represents a portion of a study of the composition of tobacco stalks intended to reveal other possible uses for this material.

In 1932 Hawley and Norman (*5*) differentiated the hemicelluloses on the basis of their association with Cross and Bevan cellulose. On this basis two distinct major groups are recognized—cellulosans and polyuronides. Cellulosans are structural substances found in Cross and Bevan cellulose, which do not contain uronic acids. Polyuronides are incrusting substances not found in Cross and Bevan cellulose, which contain uronic acids. The subject matter of this paper deals with the polyuronides.

Experimental Procedure

The methods of analysis were as follows:

Ash. This determination was made by ignition in a muffle furnace at a dull red heat.

Protein. Nitrogen was determined by the Kjeldahl-Gunning-Arnold method (*1*) and converted to protein by the factor 6.25.

Furfural. The A. O. A. C. phloroglucinol method (*1*) was employed.

Uronic Acid Anhydrides. This group was determined by the method of Dickson, Otterson, and Link (*4*) as modified by Phillips, Goss, and Browne (*9*).

Total Hemicellulose. This group was determined by the method described by Buston (*2*).

The entire stalk of the cured stripped Havana seed tobacco was used for analysis, with the exception of the short woody section at the base. For the most part the portion used represents the material which is returned to the soil. The stalks were dried at 60° C., crushed, and finely ground in a Wiley mill. The ground material was extracted successively with the following solvents: (*a*) 0.5 per cent ammonium oxalate, two 12-hour periods at 70° C.; (*b*) 5.0 per cent sodium hydroxide in 50.0 per cent aqueous alcohol, five 12-hour periods at room temperature; (*c*) 5.0 per cent sodium hydroxide, 48 hours at 70° C.

The method of fractionation of the hemicellulose was essentially that introduced by O'Dwyer (*7*). The hemicellulose precipitate did not appear until after the addition of an equal volume of ethanol. Purification of the precipitate was accomplished by resolution, reprecipitation, and the use of Fehling's solution. After the purified substance was dried in a vacuum oven at 50° C., it was found to have the following general properties: (*a*) tasteless, slightly yellow in color; (*b*) very slightly soluble in cold water; (*c*) soluble in hot water; (*d*) blue color when treated with iodine; (*e*) optically inactive. The production of a blue color with iodine is believed to be due to the presence of anhydroglucose units (*3*, *8*).

Analytical data representing duplicate and triplicate determinations on the percentage furfural and uronic acid anhydrides of the original tobacco stalks and the purified hemicellulose on an ash and moisture-free basis are shown in the following table:

Determinations	Original Stalks	Purified Hemicelluloses
Furfural	10.72	45.20[a]
Uronic acid anhydrides	10.53	11.03
Total hemicellulose	20.13	.....

[a] Corrected for furfural from uronic acid anhydrides (*6*).

A portion of the purified product was hydrolyzed with 4.0 per cent sulfuric acid in a bath of boiling water for 15 hours. The acid-free sugar solution was obtained in the usual manner, and the sugars were allowed to crystallize from alcohol. A second recrystallization yielded a product which gave a positive phloroglucinol test, decomposed at 148° C., and gave an $[\alpha]^{22}_{D}$ value of $+19.42°$. These tests would indicate that the sugar obtained by the hydrolysis of the polyuronide was xylose.

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HYDROGENATION OF NICKEL CARBONYL

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Nickel carbonyl was decomposed and converted into carbon dioxide, methane, and water in a dynamic pressure hydrogenation apparatus. Data, taken from 25° to 400° C. and from 1 to 75 atmospheres pressure, were treated according to the methods employed by Randall and Gerard (*23*), Kelley (*9*), and Chipman (*3*). The resulting equilibrium constants obtained by this treatment showed that the reaction between water and carbon to form carbon dioxide and methane gave constant values over the whole reaction range whereas other possible reactions did not.

NICKEL carbonyl was first recognized by Mond (*12–20*) as an intermediate product in the carbon monoxide reduction of nickel ores. This same compound was believed by Sabatier and Senderens (*27–30*) to exist as an intermediate product in the synthesis of methane by the hydrogenation of both carbon monoxide and carbon dioxide over a finely divided nickel catalyst at temperatures below 400° C. Probable evidence of both the formation and decomposition of carbonyl was observed by Hightower and White (*7*) in the formation of a nickel mirror at the end of their reaction chamber. Later work (*1, 5, 8, 31, 33*) has led to the belief that nickel-gas complexes as well as nickel carbonyl are responsible for the catalytic effect of nickel in hydrogenation reactions.

As a method of determining the hydrogenation reaction mechanism in the methane synthesis, nickel carbonyl was reduced with hydrogen over a temperature range of 25° to 400° C. and a pressure range of 1 to 75 atmospheres. Equilibrium constants determined over this range were compared with those based upon equations and constants given by other investigators. The principal equations are compared in Table I. The equilibrium constants are listed in terms of partial pressures of the reacting gases and also in terms of the constants of Equations 1 to 5.

Experimental Method

The apparatus (Figure 1) was designed for high-temperature, high-pressure, and dynamic operation between liquid and gas reactants:

Hydrogen, taken from a commercial cylinder, *A*, by adjusting a long-handled needle valve, *B*, was passed to a Bourdon pressure gage, *C*, two cylinders, *D*, *E*, a check valve, *F*, and a needle valve, *G*, to a specially constructed Bourdon gage, *H*. Cylinders *D* and *E* acted as cushions for the hydrogen by taking up small surges in pressure. Pressure gage *H*, which had a mirror arm, *I*, welded direct to the extreme tip of the Bourdon ring, reflected a light beam from a source of light, *J*, to a calibrated meter scale, *K*. By this means, pressure was measured within 4 pounds per square inch over the range of 1 to 75 atmospheres. The hydrogen next passed through the orifice flow manometer, *L, L*. This orifice consisted of a small steel disk with two female openings, one on either side, into which were forced two male blocks *L, L*. These blocks were held tightly compressed over the orifice disk by a threaded steel pin in a cast-iron base. By the use of various-sized orifice holes in several steel disks, the size of the orifice was rapidly changed. The difference in head on either side of the orifice was measured by electrical contact with mercury in the manometer well, *N*. The electrical contact points were stationary, and the height of the mercury on either side of the well was measured by forcing the mercury up to the contact points by means of a plunger attached to a graduated micrometer scale. Contact was made on either arm at will by switching a current first through one side arm and then through the other. Thus, the difference in head could be measured directly on the one micrometer scale. A 6-volt battery supplied the current for a small pilot light mounted on the base block of the manometer well and showed when contact between the mercury and insulated contact points was made. Mercury traps *M,M* were installed to prevent mercury from entering the system. The hydrogen passed from the orifice through the needle valve, *O*, into a T-connector, *P*, where it was mixed with nickel carbonyl before entering the reaction chamber.

Nickel carbonyl was taken from a supply container, *Q*, through a needle valve, *R*, and T-connector *S* into the single-acting piston pump, *T*, on the backward stroke of the pump. When the piston chamber was filled with nickel carbonyl, the carbonyl was forced through a T-connector, *S*, and needle valve, *U*, to T-connector *P* where it was mixed with the hydrogen.

The mixed nickel carbonyl and hydrogen then passed into a nickel reaction tube, *AA*. This hollow tube was 2 feet (61 cm.) long, 1.125 inches (2.9 cm.) o. d., and 0.364 inch (0.925 cm.) i. d. Copper cooling coils, *Y*, were wrapped around both ends of the nickel tube to prevent the hydrogen and nickel carbonyl from reacting before they reached the heated tube inside the resistance furnace, *Z*. Over both threaded ends of the reaction tube were screwed two large hexagonal nuts, *BB*, into which were built the iron-constantan couples, *W*, *X*, used in measuring the reaction temperature. These couples extended 9 inches (22.9 cm.) into the bore of the reaction tube or within 6 inches (16.2 cm.) of each other. One element of the couple was a nickel-plated Shelby seamless steel tubing, $^1/_4$ inch (0.635 cm.) o. d., and $^1/_8$ inch (0.318 cm.) i. d. Through this tube was placed a $^1/_8$ inch o. d. quartz tube to insulate the steel element from the constantan wire in the center of the quartz tubing. The steel tube was drawn around the constantan wire, and the two were welded together to make the couple. Thermocouple readings for record were made by a potentiometer, even though a millivoltmeter was also used as a check and guide during the intervals when readings were not taken.

The pipe connecting hexagonal nut *BB* of the reaction tube with the mixing T-connector, *P*, was bent in the shape of a question mark to permit connection to the reaction tube, no matter where the inlet opening in the nut happened to be placed after both hexagonal nuts were drawn tight upon the nickel tube.

The product gases from the reaction tube were expanded through a specially designed needle valve, *CC*, in which any small adjustment could be made, since the needle was exceptionally long and tapered. A 1-foot (30.5-cm.) handle bolted to the metal handle of the valve allowed for even finer adjustment. The reaction products were then run through Pyrex glass condensers, *HH*, *II*, to either a gas holder or a flowmeter. Samples of the gases were taken during the run and analyzed in the direct-connected gas analysis apparatus with explosion pipet *LL*. An aspirator bottle, *NN*, was lowered to draw the gas into the glass sampler, *JJ*, and then raised to force the gas into the gas analysis apparatus.

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TABLE I. PRINCIPAL EQUATIONS IN HYDROGENATION OF NICKEL CARBONYL

Reaction No.	Reaction	Equilibrium Constant[a]
1	$Ni(CO)_4 \longrightarrow Ni + 4CO$	$K_1 = \frac{(CO)^4}{(Ni[CO]_4)} = K_1$
2	$C + {}^1/_2O_2 \longrightarrow CO$	$K_2 = \frac{(CO)}{(O_2)^{1/2}} = K_2$
3	$C + O_2 \longrightarrow CO_2$	$K_3 = \frac{(CO_2)}{(O_2)} = K_3$
4	$C + 2H_2 \longrightarrow CH_4$	$K_4 = \frac{(CH_4)}{(H_2)^2} = K_4$
5	$H_2 + {}^1/_2O_2 \longrightarrow H_2O$	$K_5 = \frac{(H_2O)}{(H_2)\cdot(O_2)^{1/2}} = K_5$
6	$2CO + 2H_2 \longrightarrow CH_4 + CO_2$	$K_6 = \frac{(CH_4)\cdot(CO_2)}{(CO)^2\cdot(H_2)^2} = \frac{K_3K_4}{K_2^2}$
7	$CO + 3H_2 \longrightarrow CH_4 + H_2O$	$K_7 = \frac{(CH_4)\cdot(H_2O)}{(CO)\cdot(H_2)^3} = \frac{K_4K_5}{K_2}$
8	$2C + 2H_2O \longrightarrow CO_2 + CH_4$	$K_8 = \frac{(CO_2)\cdot(CH_4)}{(H_2O)^2} = \frac{K_3K_4}{(K_5)^2}$
9	$2CO \longrightarrow CO_2 + C$	$K_9 = \frac{(CO_2)}{(CO)^2} = \frac{K_3}{(K_2)^2}$
10	$H_2O + CO \longrightarrow CO_2 + H_2$	$K_{10} = \frac{(CO_2)\cdot(H_2)}{(CO)\cdot(H_2O)} = \frac{K_3}{K_2K_5}$
11	$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O$	$K_{11} = \frac{(CH_4)\cdot(H_2O)^2}{(CO_2)\cdot(H_2)^4} = \frac{K_4(K_5)^2}{K_3}$
12	$H_2O + C \longrightarrow CO + H_2$	$K_{12} = \frac{(CO)\cdot(H_2)}{(H_2O)} = \frac{K_2}{K_5}$
13	$CO + CO_2 + 7H_2 \longrightarrow$ $2CH_4 + 3H_2O$	$K_{13} = \frac{(CH_4)^2\cdot(H_2O)^3}{(CO)\cdot(CO_2)\cdot(H_2)^7} = \frac{(K_4)^2\cdot(K_5)^3}{K_2K_3}$

[a] Parentheses indicate partial pressures.

The condensed liquid products were warmed gently by removing the cooling liquids from adjustable platforms. The expanded gas was allowed to bubble through the absorption coils, *RR*, into which were placed 100 cc. of distilled water. Nickel carbonyl, immiscible with water, was drawn out through the petcock, and the water containing any possible reaction products was tested for methyl alcohol and formaldehyde by the methods of Lockemann and Croner (*10*), Dhar and Ram (*4*), and Romijn (*26*). No positive test for either formaldehyde or methyl alcohol was obtained in any run.

Before each run the apparatus was flushed with hydrogen gas, and the combustion tube was activated according to the method of Bone and Wheeler (*2*)—i. e., heating at 350° C. in the presence of hydrogen. During the activation period, the hydrogen was by-passed through the needle valve, *DD*, the T-connector, *FF*, the needle valve, *GG*, to the gas meter. Needle valves *EE* and *PP* were closed.

Data and Results

Table II includes the experimental data obtained under various conditions of temperature and pressure. In all these runs the molecular ratio of hydrogen to nickel carbonyl was maintained at four to one and the molecular ratio of carbon monoxide to hydrogen was one to one. The initial rate of flow for all runs was regulated at 7.26 cc. per minute (standard temperature and pressure, dry basis). From the Orsat analyses of the exit gases were calculated the exit gas mixture percentages, employing the method of Randall and Gerard (*23*).

Numerical values for the equilibrium constants for reactions 1 to 13 were calculated by using the partial pressures of gases obtained from Table II. The resulting $\log_{10}K$ values are given for each reaction in Table III and are compared with corresponding values offered in the literature (*3, 9, 11, 21, 22, 24, 25, 31, 32*). This comparison shows that in the temperature range between 300° and 400° C. the values of the $\log_{10}K$ are constant within experimental error and agree with previous values offered in the literature. A general equilibrium is established within this temperature range.

At 250° C. the $\log_{10}K$ values from experimental data are not constant except for reaction 8. Water, one of the reagents in this system, was formed below 300° C. This was expected both from the results of Bone and Wheeler (*2*) and from the catalytic effect of moisture in speeding up the combustion of coal (*6*).

Figure 2 gives isobaric plots of the equilibrium exit gas mixtures as listed in Table II. These curves show the effect of temperature upon the reaction products, and in each of them smooth lines were drawn through the experimental values.

At 1 atmosphere pressure the nickel carbonyl was relatively stable but decomposed with increasing temperatures. At slightly over 100° C. it was totally decomposed. Above 200° C. reaction began with the formation of water, methane, and carbon dioxide. The quantity of water formed ranged from 58 to 60 per cent of the exit gas volume at 250° C. and gradually decreased in quantity with increasing temperatures. The quantity of methane and carbon dioxide increased to a maximum between 300° and 350° C., and then began to decrease.

At 5 atmospheres pressure nickel carbonyl was more stable and decomposed less with increasing

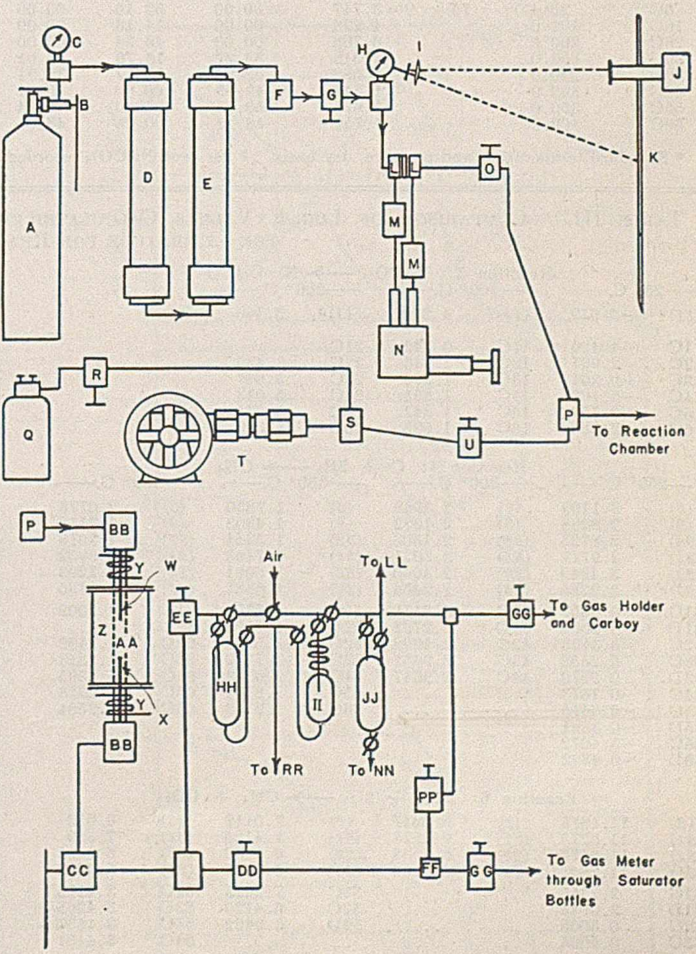

FIGURE 1. DIAGRAM OF APPARATUS

TABLE II. DATA OBTAINED FROM HYDROGENATION OF NICKEL CARBONYL

Expt. No.	Reaction Temp.	Reaction Pressure	Exit Gas Flow[a]	Exit Gas Analysis				Calcd. Exit Gas Mixtures					
				CO_2	CO	CH_4	H_2	CO_2	CO	CH_4	H_2	H_2O	$Ni(CO)_4$[b]
	° C.	Atm.	Cc./min.	Per cent by volume									
1C	27.1	1	4.436	00.00	18.03	00.00	81.97	00.00	10.97	00.00	50.00	00.00	39.03
11C	100.0		7.183	00.00	49.45	00.00	50.55	00.00	48.92	00.00	50.00	00.00	01.08
21C	200.0		7.255	00.00	50.06	00.00	49.94	00.00	50.12	00.00	50.00	00.00	00.00
31C	250.0		1.699	29.10	19.23	25.32	25.74	13.25	08.34	10.71	10.89	57.71	00.00
31D	250.0		1.748	27.56	20.19	24.96	27.27	11.89	08.72	10.78	11.78	56.81	00.00
41C	300.0		1.624	47.88	00.00	45.08	07.02	21.07	00.00	19.85	03.09	55.97	00.00
41D	300.0		1.583	48.41	00.00	44.30	07.39	20.75	00.00	18.98	03.17	57.13	00.00
51C	350.0		1.768	47.09	00.22	40.66	12.01	22.26	00.10	19.22	05.68	52.71	00.00
61C	400.0		2.114	41.46	06.82	32.31	19.39	22.44	03.69	17.48	10.49	45.87	00.00
2C	24.7	5	4.175	00.00	13.04	00.00	86.96	00.00	07.49	00.00	50.00	00.00	42.51
12C	100.0		6.230	00.00	41.72	00.00	58.27	00.00	35.78	00.00	50.00	00.00	14.22
22C	200.0		7.264	00.00	49.87	00.00	50.13	00.00	49.72	00.00	50.00	00.00	00.28
32C	250.0		1.669	28.10	19.65	27.88	25.32	11.75	08.22	11.66	10.59	58.16	00.00
42C	300.0		1.527	47.96	00.00	47.85	04.08	19.99	00.00	19.94	01.70	58.31	00.00
52C	350.0		1.775	45.21	00.17	47.42	07.20	21.85	00.08	22.92	03.48	51.93	00.00
52D	350.0		1.668	46.71	00.10	46.85	06.31	21.15	00.05	21.21	02.85	54.72	00.00
62C	400.0		1.908	43.84	03.39	42.98	09.77	22.27	01.72	21.83	04.96	49.20	00.00
3C	25.2	10	3.979	00.00	08.77	00.00	91.23	00.00	04.81	00.00	50.00	00.00	45.19
13C	100.0		5.533	00.00	34.38	00.00	65.62	00.00	26.19	00.00	50.00	00.00	23.81
23C	200.0		7.204	00.00	49.59	00.00	50.41	00.00	49.17	00.00	50.00	00.00	00.83
33C	250.0		1.617	29.35	19.61	30.27	20.76	11.99	08.01	12.36	08.48	59.13	00.00
33D	250.0		1.579	30.25	17.96	30.54	21.25	12.12	07.20	12.24	08.51	59.92	00.00
33E	250.0		1.628	29.70	18.50	29.68	22.22	12.22	07.63	12.21	09.14	58.85	00.00
43C	300.0		1.489	49.40	00.00	49.30	01.23	20.20	00.00	20.16	00.50	59.10	00.00
53C	350.0		1.646	48.06	00.00	47.71	04.21	21.58	00.00	21.42	01.89	55.10	00.00
63C	400.0		1.787	45.30	02.51	45.16	07.02	21.78	01.21	21.71	03.37	51.92	00.00
4C	26.8	25	3.856	00.00	05.84	00.00	94.16	00.00	03.12	00.00	50.00	00.00	46.88
14C	100.0		4.771	00.00	23.89	00.00	76.11	00.00	15.70	00.00	50.00	00.00	34.30
24C	200.0		7.116	00.00	48.97	00.00	51.03	00.00	47.99	00.00	50.00	00.00	02.01
34C	250.0		1.675	29.84	20.05	29.74	20.36	12.59	08.46	12.55	08.59	57.79	00.00
44C	300.0		1.502	49.69	00.00	49.57	00.72	20.52	00.00	20.47	00.30	58.68	00.00
54C	350.0		1.630	49.00	00.00	48.98	02.02	21.83	00.00	21.81	00.90	55.37	00.00
64C	400.0		1.741	46.73	01.58	46.90	04.78	22.07	00.75	22.15	02.26	52.76	00.00
5C	24.7	50	3.790	00.00	04.16	00.00	95.84	00.00	02.17	00.00	50.00	00.00	47.83
15C	100.0		4.298	00.00	15.58	00.00	84.41	00.00	09.23	00.00	50.00	00.00	40.77
25C	200.0		7.044	00.00	48.35	00.00	51.65	00.00	46.81	00.00	50.00	00.00	03.19
35C	250.0		1.635	30.78	19.14	31.83	18.34	12.78	07.95	13.22	07.62	58.45	00.00
35D	250.0		1.594	31.25	18.45	31.63	18.41	12.66	07.47	12.81	07.45	59.48	00.00
45C	300.0		1.510	49.97	00.00	50.03	00.00	20.78	00.00	20.81	00.00	58.40	00.00
55C	350.0		1.717	49.12	00.00	49.09	01.78	23.14	00.00	23.12	00.84	52.89	00.00
65C	400.0		1.718	47.70	01.20	47.70	03.40	22.34	00.00	22.34	01.59	53.17	00.00
6C	23.4	75	3.747	00.00	03.16	00.00	96.84	00.00	01.59	00.00	50.00	00.00	48.41
16C	100.0		4.226	00.00	14.16	00.00	85.84	00.00	08.25	00.00	50.00	00.00	41.75
26C	200.0		6.768	00.00	46.38	00.00	53.62	00.00	43.25	00.00	50.00	00.00	06.75
36C	250.0		1.516	33.22	16.76	33.01	16.99	12.95	06.54	12.87	06.62	60.98	00.00
36D	250.0		1.582	32.85	17.12	32.94	17.07	13.31	06.95	13.35	06.92	59.45	00.00
46C	300.0		1.543	49.83	00.00	50.17	00.00	21.24	00.00	21.38	00.00	57.37	00.00
56C	350.0		1.675	50.15	00.00	49.84	01.32	23.17	00.00	23.02	00.61	53.79	00.00
66C	400.0		1.751	48.22	00.98	48.07	02.72	23.06	00.00	22.99	01.30	52.17	00.00

[a] Standard temperature and pressure, dry basis. [b] Per cent $Ni(CO)_4$ recorded as volume per cent CO in the molecule.

TABLE III. COMPARISON OF $LOG_{10}K$ VALUES CALCULATED FROM EXPERIMENTAL DATA AND FROM EQUATIONS REPORTED IN THE LITERATURE FOR REACTIONS 1 THROUGH 13

Reaction 1: $Ni(CO)_4 \longrightarrow Ni + 4CO$

25° C.		100° C.		200° C.	
(11)[a]	−2.919	*(11)*[a]	1.272	*(11)*[a]	5.106
1C	−4.426	11C	0.742	21C	...
2C	−2.907	12C	1.146	22C	3.435
3C	+0.261	13C	1.296	23C	3.847
4C	−0.103	14C	1.891	24C	5.013
5C	−2.760	15C	1.347	25C	5.274
6C	−2.750	16C	1.675	26C	5.345

Reaction 4: $C + 2H_2 \longrightarrow CH_4$

250° C.		300° C.		350° C.		400° C.	
(3)	3.1169	*(3)*	2.3963	*(3)*	1.7830	*(3)*[a]	2.0773
(9)	2.8298	*(9)*	2.1022	*(9)*	1.4863	*(9)*	1.7178
(32)	2.8725	*(32)*	2.1503	*(32)*	1.5344	*(32)*	1.7918
(24)	2.9711	*(24)*	2.3071	*(24)*	1.7463	*(24)*	2.0952
(22)	3.4342	*(22)*	2.4040	*(22)*	1.8091	*(22)*	2.1293
(25)	2.9285	*(25)*	2.2434	*(25)*	1.6681	*(25)*	1.1780
31C	0.9557	41C	2.3178	51C	1.7750	61C	1.2009
31D	0.9004	41D	2.2762	52D	1.7178	...	....
32C	0.3193	42C	2.1398	52C	1.5780	62C	1.2492
33C	0.2352	43C	2.9031	53C	1.7779	63C	1.2813
33D	0.2279	44C	2.9647	54C	2.0362	64C	1.2395
34C	−0.1673	..	....	55C	1.8164	65C	1.2528
35C	−0.3475	..	....	56C	1.9172	66C	1.2584
35D	−0.3361						
36C	−0.4072						
36D	−0.4322						

Reaction 6: $2CO + 2H_2 \longrightarrow CH_4 + CO_2$

250° C.		300° C.		350° C.		400° C.	
(3)	11.1075	*(3)*	8.8847	*(3)*	7.0112	*(3)*	6.612
(31)	11.5275	*(31)*	9.2928	*(31)*	7.4105	*(31)*	7.389
(32)	11.0177	*(32)*	8.7538	*(32)*	6.8488	*(32)*	6.3501
(25)	11.2642	*(25)*	8.3163	*(25)*	6.5435	*(25)*	5.0335
31C	2.2355	..	....	51C	7.1225	61C	3.4178
31D	2.0943	..	....	52C	6.4120	62C	3.4268
32C	0.8608	..	....	52D	6.9462	63C	3.4537
33C	0.5068	..	....	..	...	64C	3.4401

Reaction 6: $2CO + 2H_2 \longrightarrow CH_4 + CO_2$ (*Cont'd.*)

250° C.		300° C.		350° C.		400° C.	
33D	0.5967						
33E	0.4865						
34C	−0.3200						
35C	−0.7336						
35D	−0.6770						
36C	−0.8011						
36D	−0.8649						

Reaction 7: $CO + 3H_2 \longrightarrow CH_4 + H_2O$

(3)	8.1608	*(3)*	7.279	*(3)*	5.688	*(29)*	5.5067
(32)	9.03623	*(32)*	7.1273	*(32)*	5.5158	*(32)*	5.1261
(25)	8.6082	*(25)*	6.7996	*(25)*	5.2817	*(25)*	3.9887
31C	2.7588	..	...	51C	4.7426	61C	3.2748
31D	2.6331	..	...	52C	5.1498	62C	3.3109
32C	1.4437	..	...	52D	5.6032	63C	3.3863
33C	1.1747	..	...	..	...	64C	3.3888
33D	1.2177						
33E	1.0909						
34C	+0.3361						
35C	−0.0461						
35D	−0.0006						
36C	−0.1334						
36D	−0.2180						

Reaction 8: $2C + 2H_2O \longrightarrow CO_2 + CH_4$

(3)	−1.1784	*(3)*	−1.0789	*(3)*	−0.9986	*(3)*	−0.9314
(25)	−0.9244	*(25)*	−0.7901	*(25)*	−0.6772	*(25)*	−0.5811
31C	−1.3705	41C	−0.8746	51C	−0.8125	61C	−0.7295
31D	−1.4011	41D	−0.9186	52C	−0.7312	62C	−0.6973
32C	−1.3925	42C	−0.9311	52D	−0.8245	63C	−0.7560
33C	−1.3728	43C	−0.9333	53C	−0.8176	64C	−0.7556
33D	−1.3839	44C	−0.9136	54C	−0.8088	65C	−0.7530
33E	−1.3658	45C	−0.8972	55C	−0.7181	66C	−0.7109
34C	−1.3246	46C	−0.8621	56C	−0.7354	..	...
35C	−1.3057						
35D	−1.3392						
36C	−1.3485						

(Table III continued on page 937.)

Table III (*Continued*)

Reaction 9: $2CO \longrightarrow CO_2 + C$

250° C.		300° C.		350° C.		400° C.	
(*3*)	7.9905	(*3*)	6.4883	(*3*)	5.2881	(*3*)	4.4839
(*21*)	8.1605	(*21*)	6.6184	(*21*)	5.3245	(*21*)	4.5885
(*31*)	8.6562	(*31*)	7.2798	(*31*)	6.1435	(*31*)	5.5190
(*25*)	7.4936	(*25*)	6.0767	(*25*)	4.8691	(*25*)	3.8480
31C	1.2798	..	...	51C	5.3475	61C	2.2169
31D	1.1939	..	...	52C	4.8343	62C	2.1776
32C	0.5413	..	...	52D	5.2284	63C	2.1725
33C	0.2716	..	...	..	...	64C	2.2003
33D	0.3688						
33E	0.3218						
34C	−0.1527						
35C	−0.3921						
35D	−0.3409						
36C	−0.3941						
36D	−0.4327						

Reaction 10: $H_2O + CO = CO_2 + H_2$

250° C.		300° C.		350° C.		400° C.	
(*3*)	1.9467	(*3*)	1.5678	(*3*)	1.3235	(*3*)	1.0546
(*25*)	1.8205	(*25*)	1.5171	(*25*)	1.2625	(*25*)	1.0451
31C	−0.5232	..	...	51C	1.3785	61C	0.1433
31D	−0.5483	..	...	52C	1.2624	62C	0.1156
32C	−0.5245	..	...	52D	1.3653	63C	0.1361
33C	−0.6683	..	...	..	...	64C	0.1024
33D	−0.6216						
33E	−0.5411						
34C	−0.6552						
35C	−0.6780						
35D	−0.6721						
36C	−0.6678						
36D	−0.6500						

Reaction 11: $CO_2 + 4H_2 = CH_4 + 2H_2O$

250° C.		300° C.		350° C.		400° C.	
(*3*)	7.2148	(*3*)	5.6728	(*3*)	4.3650	(*3*)	4.4518
(*22*)	7.0435	(*22*)	5.5228	(*22*)	4.2360	(*22*)	4.0572
(*23*)	6.9380	(*23*)	5.4591	(*23*)	4.2074	(*23*)	4.0783
31C	2.2819	41C	5.5101	51C	4.3643	61C	3.1314
31D	2.1915	41D	5.4708	52C	3.8875	62D	3.1953
32C	2.0298	42C	5.2103	52D	4.2156	63C	3.1816
33C	1.8433	43C	6.7387	53C	4.3733	64C	3.2350
33D	1.8393	44C	6.8430	54C	4.8814	65C	3.2586
34C	0.9903	..	...	55C	4.3516	..	...
35C	0.6226	..	...	56C	4.5717	..	...
35D	0.6670						
36C	0.5344						
36D	0.4347						

Reaction 12: $H_2O + C = CO + H_2$

250° C.		300° C.		350° C.		400° C.	
(*3*)	−6.0336	(*3*)	−3.8825	(*3*)	−3.9420	(*3*)	−3.4294
31C	−1.8030	..	...	51C	−3.9678	61C	−2.0738
31D	−1.7428	..	...	52C	−3.5719	62C	−2.0620
32C	−1.1259	..	...	52D	−3.8630	63C	−2.0362
33C	−0.9401	..	...	..	...	64C	−2.0979
33D	−0.9906						
33E	−0.8630						
34C	−0.5026						
35C	−0.2860						
35D	−0.3312						
36C	−0.2738						
36D	−0.2171						

Reaction 13: $CO + CO_2 + 7H_2 = 2CH_4 + 3H_2O$

250° C.		300° C.		350° C.		400° C.	
(*3*)	16.3756	(*3*)	12.9512	(*3*)	10.0533	(*3*)	9.9585
31C	5.0406	..	...	51C	9.1146	61C	6.4063
31D	4.8150	..	...	52C	9.0374	62C	6.5082
32C	3.4736	..	...	52D	9.8189	63C	6.5880
33C	3.0183	..	...	..	...	64C	6.6238
33D	3.1553						
34C	1.3263						
35C	0.5766						
36C	0.4563						
36D	0.2199						

[a] Literature references are in parentheses; other numbers in these columns refer to experiments.

temperatures. At 200° C. the carbonyl was almost completely decomposed. Reaction at 250° C. yielded water, methane, and carbon dioxide as products. The increased pressure had little effect upon the percentages of these products. Carbon dioxide, which was formed in excess of methane at 1 atmosphere pressure, was produced in almost equal amounts at 5 atmospheres pressure and higher.

With increasing pressures (10 to 75 atmospheres) and the same temperature range, the nickel carbonyl became more and more stable. Upon reaction the same products were formed. In all cases the yield of water was at a

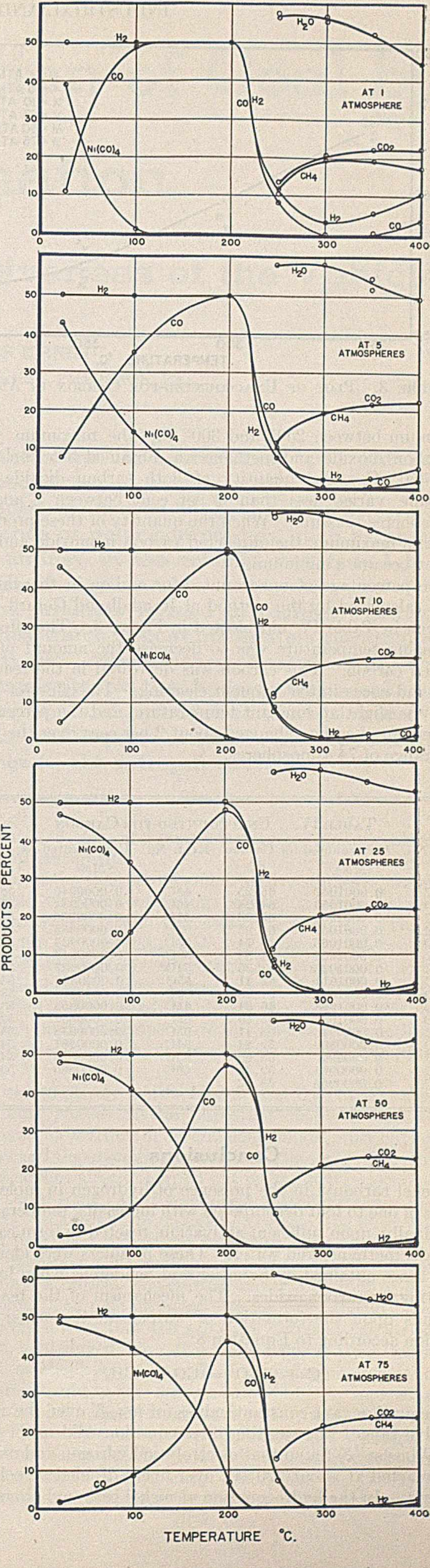

Figure 2. Isobaric Plot of Reaction Products at Various Pressures

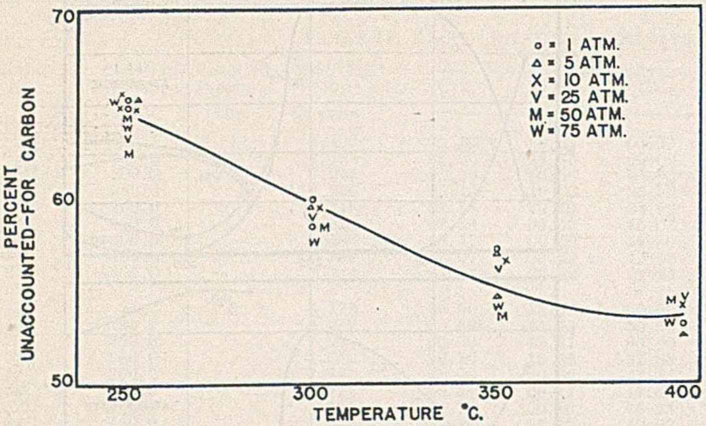

FIGURE 3. PLOT OF UNACCOUNTED-FOR CARBON IN ALL RUNS

maximum between 250° and 300° C.; the maximum yield of carbon dioxide and methane was obtained between 300° and 350° C. The quantity of both carbon dioxide and methane varied less than 4 per cent between 1 and 75 atmospheres pressure. When the quantity of these products was at a maximum, the unreacted carbon monoxide and hydrogen became a minimum.

The percentage of unaccounted-for carbon in the various runs, calculated by the method of Randall and Gerard (*23*), is given in Table IV and plotted in Figure 3. The effect of increasing temperature was to decrease the amount of unreacted carbon. This carbon was deposited in the reaction tube and necessitated frequent cleaning. The effect of pressure was slight at constant temperature, and the percentage conversion of carbon changed about 2 per cent over the pressure range of 74 atmospheres.

TABLE IV. UNACCOUNTED-FOR CARBON

Expt. No.	Unaccounted-for Carbon		Expt. No.	Unaccounted-for Carbon	
	Mole	%		*Mole*	%
31C	0.0001057	65.25	45C	0.0000946	58.40
31D	0.0001053	64.98	46C	0.0000932	57.49
32C	0.0001056	65.23	51C	0.0000926	57.16
33C	0.0001052	64.95	52C	0.0000885	54.62
33D	0.0001065	65.74	52D	0.0000923	56.96
33E	0.0001051	64.88	53C	0.0000917	56.58
34C	0.0001025	63.25	54C	0.0000907	56.00
35C	0.0001011	62.41	55C	0.0000867	53.53
35D	0.0001041	64.28	56C	0.0000873	53.86
36C	0.0001058	65.34	61C	0.0000859	53.03
36D	0.0001035	63.86	62C	0.0000852	52.59
41C	0.0000946	58.41	63C	0.0000878	54.23
41D	0.0000969	59.84	64C	0.0000881	54.33
42C	0.0000967	59.69	65C	0.0000879	54.28
43C	0.0000964	59.51	66C	0.0000860	53.08
44C	0.0000955	58.92			

Conclusions

Nickel carbonyl in the presence of hydrogen in molecular ratios of one to four decomposed with increasing temperatures and finally, upon sufficient activation, reacted to form carbon dioxide, methane, and water. These products were identical with those obtained by Sabatier and Senderens when hydrogenating the carbon oxides. The mechanism of the reaction depends upon the formation of water and the subsequent reaction according to Equation 8:

$$2C + 2H_2O = CO_2 + CH_4$$

This equation gave constant values for $\log_{10}K$ over the whole reactive range, whereas the other equations did not. Bone and Wheeler (*2*) found that electrolytic hydrogen and oxygen first reacted at about 220° C. over finely divided nickel as a catalyst. In the hydrogenation of nickel carbonyl almost 60 per cent water was formed at 250° C. After this water was formed, it reacted with carbon according to Equation 8. The element carbon is quite unreactive to water at 250° C. In the presence of nickel the carbon was activated sufficiently to react with water.

At temperatures above 250° C., general equilibrium prevailed between all the reactions listed in Table III. The $\log_{10}K$ values for these reactions were constant at constant temperature above 250° C. and agreed within experimental error with the results of other investigators.

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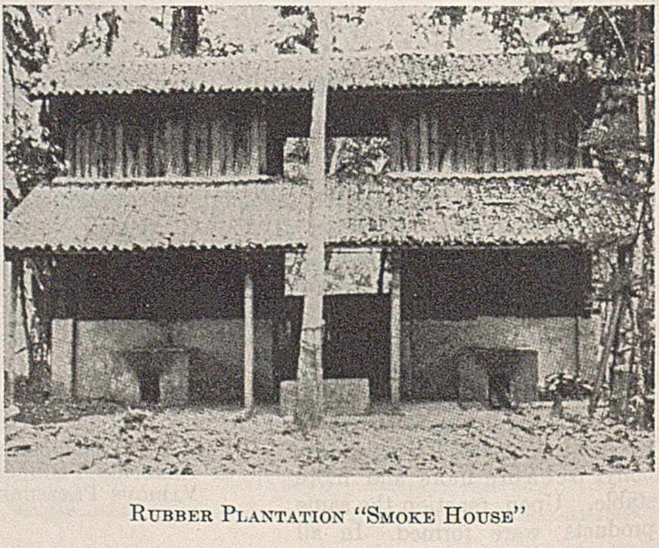

RUBBER PLANTATION "SMOKE HOUSE"

Primary Liquefaction of Coal by Hydrogenation

Chemical Nature and Effectiveness of the Vehicle

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To obtain information on the relative effectiveness of various dispersion media in the primary liquefaction of coal by hydrogenation, Pittsburgh bed coal from the bureau's experimental mine was hydrogenated in over thirty vehicles under comparatively mild conditions (400° C. and 67 atmospheres original hydrogen pressure).

Previous claims that tetrahydronaphthalene is a good dispersion medium were confirmed. Of the other hydrocarbons studied, only methylnaphthalene and diphenyl were of comparable effectiveness. Several completely aromatic (naphthalene and chrysene) and saturated hydrocarbons (decahydronaphthalene and *n*-hexadecane) proved to be poor vehicles. The presence of polar compounds, such as phenols and amines, in the vehicles was found to be beneficial.

The products formed in highest yield were pitches, which melt at moderately elevated temperatures. Elementary analyses of these pitches indicated that hydrogenation had raised the carbon and hydrogen contents, lowered the sulfur and oxygen contents, and caused little change in the nitrogen content.

ALTHOUGH several important variables involved in the liquefaction of coal by hydrogenation have received much attention, little work has been carried out to determine the importance and role of the vehicle. Primarily this is because vehicles other than oils obtained from coal by hydrogenation or carbonization have not been considered interesting from a practical standpoint. The possibility exists, however, that some individual compound, or mixture of several compounds, may be used economically in the initial stages to convert the coal into an ash-free material more suitable for further hydrogenation. A process of this kind, using a mixture of tetrahydronaphthalene and phenols as vehicle, recently received considerable attention and reached the stage of commercial development (*23*). The little evidence now available indicates that the nature of the vehicle is important, especially in the preliminary stages where the main purpose is to get the coal substance into solution. Therefore, a study of the vehicle's influence in coal hydrogenation is of practical as well as theoretical significance.

In laboratory studies a few pure organic compounds have been used as vehicles. Beuschlein, Wright, and Williams (*5*) showed that phenol or anthracene is preferable to diphenyl. Boomer and Saddington (*7*) found that the conversion obtained on hydrogenating various coals in phenol, tetrahydronaphthalene, petrolatum, bitumen, and naphthalene was largely a function of the dispersion agent, tetrahydronaphthalene being the most effective. Pertierra (*21*, *22*) and Pott and Broche (*25*) found that mixtures of tetrahydronaphthalene and tar phenols are better dispersion agents for coal hydrogenation under mild conditions than either tetrahydronaphthalene or phenols alone. Twenty-nine coals ranging in rank from lignite to anthracite were hydrogenated in phenol (*13*, *14*), and unsatisfactory results were obtained only with anthracite.

In one of the most recent and extensive studies of the effect of vehicle, no direct connection between the chemical nature and effectiveness of the vehicle was observed (*10*). The presence of tar acids in the vehicle was shown to be beneficial, and a high-boiling oil from hydrogenated coal was found to be one of the best vehicles; it was surpassed only by a mixture of *m*-cresol and tetrahydronaphthalene. Warren (*30*) found that high- and low-temperature tars, but not lubricating oil, are suitable for the hydrogenation of coal in a continuous system.

To be completely satisfactory in coal liquefaction the vehicle must possess several important characteristics. The compound, or mixture of several compounds, must have high solvent and depolymerizing action on the coal. The numerous researches already carried out on the extraction of coal (*2*, *3*) afford some basis for selecting solvents effective in this respect. In addition to dissolving the coal, the ideal vehicle should be a good solvent for hydrogen under the conditions of the operation. To remain in the liquid phase, the vehicle must have a critical temperature higher than that of the experiment. The melting point and viscosity should be comparatively low so that the solutions obtained can be easily filtered, centrifuged, etc. The boiling point, which must be as high as about 200° C. to afford a satisfactory critical temperature, should be low enough to permit easy separation of the vehicle from the hydrogenated coal by distillation.

The ideal vehicle also should function as a hydrogen carrier. Permanent consumption of hydrogen by the vehicle is objectionable, but temporary absorption and subsequent transference of hydrogen to the coal substance appear to

Table I. Physical Constants of Vehicles

Used in Expt. No.	Compound Used as Vehicle	Reference No.	Melting Point ° C.	Boiling Point ° C.	Critical Temp. ° C.	Surface Tension at 20° C.[a]	Dielectric Constant at 20° C.[a]	Dipole Moment
39	Acetamide	(*16*)	81	222	...	39.3 (85° C.)	60.3 (83° C.)	3.72
9, 20	*m*-Cresol	...	11	203	432	37.4	5.0 (24° C.)	1.60
9, 20	*o*-Cresol	...	31	191	422	39.8 (10° C.)	5.8 (24° C.)	1.44
9, 20	*p*-Cresol	...	35–6	202	426	36.7	5.6 (2.4° C.)	1.64
13	Decalin	(*15, 18*)	...	191–3	384	26.7 (15.5° C.)	2.11	0.0
23	Diphenyl	(*9, 18*)	69–70	255	528	29.5 (129° C.)	2.62[b]	0.0
25	Diphenylamine	...	53	302	...	37.7 (80° C.)	3.3 (52° C.)	1.3
36	Diphenyl ether	(*11*)	27	259	...	...	3.69	1.05
38	Diphenylmethane	(*11*)	25	258	...	37.1 (30° C.)	2.56	0.0
34	Glycol	...	−15	197	...	47.7	41.2	2.2
10	Naphthalene	(*20*)	80	218	...	39.0[b]	...	0.0
26	α-Naphthylamine	(*4, 6*)	50	301	...	51.1[b]	...	1.44
21	Pinene	...	−55	158–61	...	27.0 (10° C.)	2.7	1.10
32	Quinoline	...	−19.5	237	>520	45.0	8.9 (21° C.)	2.25
31	Stearic acid	(*18*)	69–70	291 (100)	...	32.65	2.32 (67° C.)	...
8	Tetrahydronaphthalene	(*29*)	−31	205–7	421	34.25 (18.3° C.)	2.66	0.52
18	*o*-Toluidine	...	−16	200	...	40.0	6.0	1.3

[a] Unless otherwise noted.
[b] Extrapolated.

Table II. Analyses of Bruceton Coal (Per Cent by Weight)

	Moisture	Volatile Matter	Fixed Carbon	Ash						
Proximate	1.6	35.7	56.4	6.3						
Ultimate:	H	C	N	O	S	Ash				
As received	5.3	77.6	1.6	7.6	1.6	6.3				
Moisture-free	5.2	78.8	1.6	6.4	1.6	6.4				
Moisture, ash-free	5.6	84.2	1.7	6.8	1.7	...				
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	P_2O_5	CaO	MgO	SO_3	Na_2O	K_2O
Ash analysis, %	45.4	24.1	19.9	1.0	0.2	3.6	0.6	3.5	0.6	0.9

facilitate the liquefaction. It has been postulated (*7, 8*) that tetrahydronaphthalene acts as a hydrogen carrier or donor in the hydrogenation and extraction of coal under pressure and that its effectiveness as a vehicle is due to this behavior. The possibility of using vehicles that may liberate hydrogen during the experiment (such as decahydronaphthalene, tetrahydronaphthalene, and hydrogenated quinoline) is extremely interesting.

Vehicles for coal liquefaction also should be noncorrosive, nontoxic, and stable to thermal treatment. From a practical standpoint it is desirable that the vehicle be readily available, easily recovered, or produced during the hydrogenation, and it should form with pulverized coal a paste capable of being pumped without settling.

In the present work the vehicles were selected with little regard for practical considerations. Cresol, xylenol, catechol, quinoline, toluidine, naphthylamine, diphenylamine, thiocresol, stearic acid, glycol, and acetamide were studied because of their polar properties. Naphthalene, methylnaphthalene, diphenyl, diphenylmethane, and *n*-hexadecane were used to illustrate the effect of aromaticity or paraffinicity. Decahydronaphthalene, tetrahydronaphthalene, pinene, nicotine, abietic acid, and ethyl dihydroabietate were selected primarily because of the possibility that they would function as sources and carriers of hydrogen. Some of the compounds used as such or as mixtures in the present work for the liquefaction of coal are listed in Table I, together with physical data. Data for which references are missing were taken from International Critical Tables.

Coal and Vehicles

The same coal, obtained at the Bureau of Mines experimental mine at Bruceton, Pa., was used in all the experiments. This Pittsburgh bed coal is classified as a high-volatile A coking coal (*1*) and falls toward the low-rank boundary of this class. Plastic range curves obtained with coal from the experimental mine, which show that the plastic state is first reached at about 388° C., were recently given (*26*). The proximate and ultimate analyses of the coal used in the present work are given in Table II. The sulfur was found to be present mainly in the pyritic and organic forms (0.83 and 0.71 per cent, respectively), sulfate sulfur being present to the extent of only 0.06 per cent. The fusain content of Pittsburgh bed coal generally is 2 to 3 per cent (*12*).

In most cases the vehicles were procured in a satisfactory state of purity and used as such. Decahydronaphthalene (Eastman Kodak Company) was washed with concentrated sulfuric acid and distilled. The cresol (mixture of isomers), tetrahydronaphthalene, and α-methylnaphthalene were redistilled, only the middle fractions being retained. Technical grades of dimethylnaphthalene, chrysene, xylenol, and abietic and stearic acids were used.

Hydrogenation Apparatus and Procedure

The hydrogenation experiments were carried out in a converter (1200-cc. capacity) made of 18–8 stainless steel. The converter rested on rollers which caused rotation (about twenty-three turns per minute) on the horizontal axis. The closure was a modification of the self-sealing Bredtschneider joint recently described (*28*). The seal was effected by means of turned copper rings made from hard drawn tubing. The initial sealing was made by drawing up the head with set screws in a spider web arrangement attached to the head. Heat was provided by an electric furnace, the temperature being indicated by a thermocouple in a well bathed by the converter contents. The difference between the temperature of the converter contents and that indicated by the encased thermocouple was determined and found to be about 4° at 400° C.

A few preliminary experiments were conducted to arrive at the standard conditions to be employed in the subsequent work. Using tetrahydronaphthalene as the vehicle, satisfactory results were obtained at 1000 pounds per square inch (70.3 kg. per sq. cm.) initial hydrogen pressure and 400° C. when either 1 or 0.1 gram of stannous sulfide was present. The liquefaction of the coal was much less satisfactory when the stannous sulfide was omitted; this catalyst was therefore used in the later experiments.

Some of the previous investigators of hydrogenation vehicles have preferred to work without catalysts, and evidence is at hand to indicate that differences in the effectiveness of vehicles are more pronounced in the absence of catalysts (*10*). In spite of this apparent tendency of catalysts to make vehicle effectiveness uniform, a catalyst was used in the present experiments to effect considerable liquefaction under mild conditions and to make the operating conditions similar to those of actual practice.

The following is a description of the procedure adopted:

Table III. Data on Various Vehicles

		A	B	C	D	E	F	G	H
		Products						Conversion of Pure Coal	
No.	Vehicle	Liquids, solids	Gases	Loss	Centrifuged	Oil from Centrifuge	Benzene Insol.	Insol. residue	Ash analysis
		Grams	*Grams*	*Grams*	*Grams*	%	*Grams*	%	%
	Hydrocarbon Vehicles								
2, 8	Tetrahydronaphthalene	193.2	5.8	2.0	171.7	78	14.9	94.5	89.7
16, 44	50% Naphthalene, 50% tetrahydronaphthalene	193.1	4.2	3.7	180.6	61	16.1	93.2	87.8
17	Methylnaphthalene[a]	191.2	6.5	3.3	175.8	79	17.0	92.2	88.1
23	Diphenyl	192.1	...	...	187.0	41	19.2	89.8	88.8
38	Diphenylmethane	195.4	3.6	2.0	182.3	56	25.8	82.4	80.3
46	Chrysene	194.3	...	...	...	..	26.9	81.2	...
10, 27	Naphthalene	191.9	4.6	4.5	181.0	30	29.2	78.7	68.2
13	Decahydronaphthalene	194.6	5.4	1.0	185.3	48	31.0	76.7	...
21	50% Pinene, 50% tetrahydronaphthalene	189.8	6.2	5.0	179.7	55	33.4	74.0	...
30	Cetane	192.7	4.7	3.6	183.9	60	34.9	72.3	...
11	40% Decahydronaphthalene, 60% naphthalene	192.4	3.4	5.2	...	..	36.4	70.7	...
	Hydrocarbon-Phenol Vehicles								
24, 42	50% Diphenyl, 50% cresol	195.7	4.8	0.5	184.8	77	15.7	93.7	91.3
7, 9	50% Tetrahydronaphthalene, 50% cresol	192.8	4.2	4.0	170.8	84	15.7	93.7	88.3
28	50% Methylnaphthalene, 50% xylenol	193.3	6.9	0.8	184.1	79	17.3	91.9	89.0
20, 41	50% Naphthalene, 50% cresol	194.4	5.0	1.6	181.5	74	17.6	91.6	...
29	50% Fluorene, 50% cresol	192.5	3.9	4.6	178.0	42	22.4	86.2	85.0
33	50% Tetrahydronaphthalene, 50% catechol	193.1	5.1	2.8	180.8	66	28.0	80.0	...
	Amine and Hydrocarbon-Amine Vehicles								
19, 32	50% Tetrahydronaphthalene, 50% quinoline	193.9	4.3	2.8	183.1	81	14.8	94.7	91.8
15, 18	50% Tetrahydronaphthalene, 50% toluidine	193.3	4.2	3.5	180.7	78	16.3	93.0	...
37	50% Tetrahydronaphthalene, 50% nicotine	191.5	6.4	3.1	176.1	79	17.8	91.3	...
25	Diphenylamine	192[b]	3.7	...	179.7	49	18.0	91.1	87.3
26	α-Naphthylamine	191.7	3.3	6.0	164.5	57	20.6	88.2	...
	Miscellaneous Vehicles								
22	75% Tetrahydronaphthalene, 25% *p*-thiocresol	187.4	6.7	6.9	179.0	77	16.2	93.1	90.9
39	50% Tetrahydronaphthalene, 50% acetamide	189.3	11.5	0.2	179.7	77	18.8	90.2	...
14	Abietic acid	180.4	17.0	3.6	138.3	..	22.1	86.6	81.9
35	Ethyl dihydroabietate	172.8	20.6	7.6	163.6	30	24.2	84.2	...
34	50% Tetrahydronaphthalene, 50% glycol	175	21.3	...	162.0	63	24.6	83.8	...
31	50% Tetrahydronaphthalene, 50% stearic acid	194.1	7.6	+0.7	188.8	56	29.7	78.1	...
36	Diphenyl ether	196.8	3.4	0.8	186.2	44	30.0	77.8	76.0

[a] 60 per cent alpha- and 40 per cent beta-methylnaphthalene.

[b] Approximate.

A mixture of 1 gram of stannous sulfide (prepared in the usual manner from the chloride) and 100 grams of coal (200-mesh) was placed in the bomb, and 100 grams of the vehicle were added. After the head was attached and the bomb flushed successively with nitrogen and hydrogen, hydrogen was introduced until the pressure was 1000 pounds per square inch. After 0.5 to 1 hour had elapsed, the pressure was again brought to 1000 pounds, replacing the hydrogen which had dissolved in the reactants. The temperature of the converter was then brought to 400° C. at the rate of approximately 2° per minute and maintained at 400° (±3°) for 3 hours. After the converter had cooled overnight to room temperature, the gaseous contents were passed through a wet test meter, and an average sample was collected by mercury displacement. Gas samples were analyzed in the Orsat apparatus, Bureau of Mines type (Table VII).

The liquid and solid contents of the converter were transferred to a weighed bottle and centrifuged for 1 to 2 hours at about 2800 r. p. m. The ash-free oil thus obtained was removed from the bottle, weighed, and distilled. The amount of oil obtained from the centrifuge, calculated as per cent of the material centrifuged, is given in Table III (column E). The products not removed manually from the bomb were washed out with acetone and added to the main residue in the centrifuge bottle. The bomb was weighed before and after the acetone washing on a Troemner bullion balance to determine the amount thus removed. The combined residues were washed several times with acetone at room temperature and dried to obtain the weight of acetone-insoluble material. The acetone residues were washed with benzene for 48 hours in Soxhlet extractors, dried in an oven at about 100° C. for 24 hours (or in a vacuum at 100° for 8 hours), and weighed to ascertain the amount of benzene-insoluble material (column F, Table III).

Since the degree of liquefaction is probably best indicated by the quantity of benzene-insoluble material, a check on the accuracy of the manipulations leading to the isolation of this material was desired. This check was obtained by determining the ash content of the benzene-insoluble residue and calculating the amount of ash recovered. Usually about 6 of the 7.3 grams originally present (6.3 grams of ash and 1 gram of catalyst) was accounted for in the benzene-insoluble residues. The conversion of pure coal was then calculated on the basis of complete ash recovery; these data, which are in satisfactory agreement with the yields (column G) determined in the usual manner, are given in column H.

The centrifuged oil was distilled through a Vigreux column to recover the unchanged vehicle and separate any low-boiling material. The vehicles of moderately low boiling point (naphthalene, Tetralin, cresol, toluidine, etc.) could be easily separated from the high-boiling product in this manner. Great difficulty was experienced in distilling the high-boiling vehicles, either at atmospheric pressure or in vacuum, because of their tendency to foam or run over. The distillation residue, the main product of the liquefaction process, was conveniently poured from the flask while hot.

In a few instances the products were analyzed by a modified procedure. The solid products obtained in experiments 10, 11, and 46 were extracted directly with benzene for 3 to 4 days, the extent of liquefaction being judged by the weight of benzene-insoluble residue. The products obtained in experiments 14, 23, and 27 were converted into viscous oils by warming to 50–60° C., diluted with 30 cc. of benzene or Tetralin, and centrifuged. The centrifuge residues were then washed with acetone and extracted for 48 hours with benzene in the usual manner.

Nature of Products

As obtained from the converter, the products ranged from viscous oils to comparatively firm solids. Products smelling strongly of ammonia were obtained in the α-naphthylamine and acetamide experiments, possibly because of the production of ammonia or aliphatic amines from the vehicles. In most cases the products had the odor of hydrogen sulfide. Centrifuging separated the crude products into:

1. Residues consisting of ash, fusain, stannous sulfide, and other material resistant to hydrogenation, as well as some of the solution containing the vehicle and dissolved products.
2. Small quantity of water and a solution of vehicle and hydrogenated coal. This solution appeared to be homogeneous but exhibited definite colloidal properties upon ultramicroscopic examination.

After being separated from ash and residues by centrifuging and from vehicles by distillation, the products were firm pitches at room temperature. At moderately elevated temperatures (100° to 150° C.) these products were soft or fluid. Although little volatile at reasonable temperatures, distillation of the pitches at 5 mm. to 200° C. produced small yields (8 to 10 cc.) of oil. Ultimate analyses of the pitches are given in Table IV. Since the pitches contained small amounts of ash (about 0.5 per cent) the separation of heavy oil and ash by centrifuging was not complete. As shown in the following table, extraction with benzene in the Soxhlet apparatus caused about 70 per cent of the pitches to dissolve:

Pitch No.	Total Extn. Loss after: 24 hr.	48 hr.	96 hr.	48 hr.[a]	144 hr.
	Weight per cent				
12	63.3	77.3	..	..	..
15	36.4	62.0	..	..	..
17	..	61.3	65.1	..	67.0
22	50.6	69.5	..	..	..
32	..	36.4	53.5	70.7	70.7

[a] Tetrahydronaphthalene.

The two pitches dissolved with greatest difficulty (17 and 32) were obtained by distillation to 245° C.; the other vehicles were removed by distillation to about 215° C. The usual proximate analysis was carried out for pitches 22 and 28 with the results shown below (in per cent):

Pitch No.	Moisture	Volatile Matter	Fixed Carbon	Ash
22	0.7	70.0	29.2	0.1
28	0.5	62.7	36.3	0.5

Several significant conclusions may be drawn from the pitch analyses in Table IV. With certain understandable exceptions, the pitches are rather uniform in composition. The high nitrogen content of the pitches from experiments 18 and 19 are probably due to incomplete separation of the nitrogen-containing vehicles on distillation. As was to be expected, addition of hydrogen and removal of inorganic elements as hydrogen sulfide, etc., increased the hydrogen and carbon contents and lowered the carbon-hydrogen ratio. Both the sulfur analyses and the sulfide-like odor of the products show that the total sulfur content was considerably lowered. The organic sulfur was reduced from 0.713 to about 0.4 per cent. The high sulfur content of pitch 22 probably arose from the incomplete removal of the sulfur added originally as *p*-thiocresol in the vehicle.

TABLE IV. PITCH ANALYSES (PER CENT BY WEIGHT)

Pitch No.	Ash, Moisture-Free: H	C	N	O	S
9	6.3	87.8	1.8	3.6	0.5
16	6.5	88.4	1.6	3.1	0.4
17	6.2	88.6	1.8	3.0	0.4
18	6.8	87.9	2.5	2.5	0.3
19	6.4	87.7	3.2	2.3	0.4
20	6.4	88.2	1.8	3.2	0.4
22	6.5	88.9	1.6	1.4	1.6
28	6.4	89.1	1.8	2.2	0.5
43	6.4	88.5	1.9	2.7	0.5
44	6.6	89.2	1.6	2.2	0.4
Coal analysis	5.6	84.2	1.7	6.8	1.7

The products, excluding the α-naphthylamine and acetamide experiments, had no odor of ammonia. This fact and the nitrogen analyses indicate that the mild conditions used in the present work, although sufficient to eliminate considerable quantities of sulfur and oxygen, failed to remove much nitrogen. Since the recovered hydrocarbon vehicles contained tar bases, some of the coal nitrogen must have been converted into amines.

More than half the oxygen was removed during the hydrogenation (Tables IV and V). The distribution of oxygen among the products of two experiments (hydrocarbon vehicles) is shown in Table V. Unlike the carbonization process which converts most of the oxygen into water, hydrogenation under the conditions of the present experiments gave products which contain a large proportion of the original oxygen in phenols and pitch. Since recovery of all the water formed during hydrogenation is difficult, it is likely that the data for oxygen going into water (Table V) are erroneously low. The carbon dioxide value includes all acidic gases and hence is high. In spite of these errors the data in Table V show clearly that mild hydrogenation gives products whose oxygen distribution is different from that of carbonization products.

TABLE V. DISTRIBUTION OF OXYGEN AMONG PRODUCTS

Appearing in Products as Constituent of:	% Oxygen in Original Coal: Present work: Expt. 16	Expt. 17	Brown coal hydrogenated (*19*)	Bituminous coal carbonized at 520° C. (*27*)
Water (constitution)	7	7	35.6	70.8
Carbon dioxide	7	15	46.0	6.6
Carbon monoxide	2	4	..	2.8
Phenols	5	15	15.5	...
Pitch	42	39	..	1.9
Residue (or coke)	10	12	..	17.9
Total	73	92	97.1	100.0

In no case was it demonstrated that the vehicle could be quantitatively recovered by distillations although good yields were usually obtained. In a number of experiments the recovered vehicles were extracted with alkali and mineral acid to determine the tar acid and base contents (Table VI). The presence of tar acids and bases in the recovered hydrocarbon vehicles indicates that these products were formed from the coal during the liquefaction. Analysis of the recovered phenol and amine vehicles for tar acids and bases showed that these compounds resist hydrogenation under the present experimental conditions. The low tar acid content of the distillate and the high sulfur content of the pitch (Table IV) indicate that the recovery of *p*-thiocresol in experiment 22 was poor. The high yield of water and the high tar acid content of the distillate boiling up to 202° C. (experiment 33, Table III) show that catechol (boiling point 240° C.) was hydrogenated to phenol.

The composition of some of the hydrogenation gases is shown in Table VII. Experiments for which gas analyses are not reported yielded gaseous products similar to those of the first four experiments in Table VII. When the composition of the gas varied much from that of these four experiments (tetrahydronaphthalene, naphthalene, tetrahydronaphthalene-naphthalene, and tetrahydronaphthalene-cresol vehicles) the differences could be traced to reactions of the vehicle. When stable vehicles were used, the gases contained methane and ethane as the chief constituents (excluding hydrogen), the first hydrocarbon predominating. Only negligible amounts of unsaturated hydrocarbons or substances soluble in sulfuric acid were found in the gases.

The presence of large amounts of methane in experiments 34, 35, 37, and 39 indicates that this hydrocarbon was formed by hydrogenation of the vehicle. The high ethane contents of the gases from the glycol and acetamide experiments might be expected. The carbonyl groups in the vehicles [abietic acid (*17*), stearic acid, and ethyl dihydroabietate] were responsible for the high yields of carbon dioxide and monoxide in experiments 14, 31, and 35. It is interesting to note that carbon monoxide, but not carbon dioxide, was obtained in increased yield when acetamide was the vehicle. There is no obvious reason for the high carbon dioxide content of the gas from the glycol experiment. The high yield of acidic gases in experiment 22 was probably due to the conversion of some of the vehicle (*p*-thiocresol) into hydrogen sulfide.

The acetone- and benzene-insoluble residues were brown or black finely divided solids. It was difficult to identify con-

TABLE VI. DISTILLATION OF CENTRIFUGED OIL

Expt. No.	Vehicle	Oil Distilled	Distillation End Point	Distillate Water	Distillate Oil	Vol. % Distillate Tar acids	Vol. % Distillate Tar bases	Gravity at 60° F. (15.6° C.) Distillate	Gravity at 60° F. (15.6° C.) Vehicle
		Grams	*° C.*	*Cc.*	*Cc.*			*°A. P. I.*	*°A. P. I*
2	Tetrahydronaphthalene	127.3	220 200[a]	...	77.5 8	2.9	0.45	...	...
9	Tetrahydronaphthalene-cresol	148.5	214	2.0	80	50.0	...	10.0	10.0
15	Tetrahydronaphthalene-toluidine	135.5	215	1.0	75	...	46.0	12.5	...
19	Tetrahydronaphthalene-quinoline	149.3	245	2.3	71	...	35.6	11.0	...
13	Decahydronaphthalene	88.1	207	...	83	...	...	29.3	27.6
17	Methylnaphthalene	139.2	245	1.3	79	4.8	1.4	11.9	...
22	Tetrahyhronaphthalene thiocresol	137.9	220	0.8	72	9.2	...	13.4	...

[a] At 6 mm.

TABLE VII. ANALYSIS OF HYDROGENATION GASES

Expt. No.	Vehicle	Per Cent by Volume $CO_2 + H_2S$	C_nH_{2n}	O_2	H_2	CO	CH_4	C_2H_6	N_2
2, 8, 12	Tetrahydronaphthalene	1.3	0.1	0.5	88.4	0.3	3.6	3.9	1.8
10, 27	Naphthalene	1.3	0.1	0.3	88.9	0.5	5.3	3.4	0.4
16, 44	Tetrahydronaphthalene-naphthalene	0.7	0.1	0.5	90.1	0.4	4.4	2.8	1.1
7, 9	Tetrahydronaphthalene-cresol	1.0	0.0	0.6	90.0	0.2	4.5	2.0	1.7
14	Abietic acid	11.1	0.0	0.5	77.9	1.0	5.9	3.3	0.3
22	Tetrahydronaphthalene-thiocresol	2.4	0.2	0.4	88.6	0.1	5.5	2.9	0.0
31	Tetrahydronaphthalene-stearic acid	3.6	0.2	0.7	84.4	2.0	6.1	3.3	0.0
34	Tetrahydronaphthalene-glycol	4.4	0.6	0.6	60.6	2.9	10.8	18.2	1.9
35	Ethyl dihydroabietate	10.0	0.0	0.8	67.2	1.9	15.4	4.8	0.0
37	Tetrahydronaphthalene-nicotine	0.5	0.0	0.1	83.5	0.3	10.6	4.3	0.7
39	Tetrahydronaphthalene-acetamide	0.0	0.3	0.3	73.0	3.1	10.2	13.0	0.1

stituents in these residues with the microscope, but their colloidal nature and the excellent distribution of the catalyst were established. The acetone residue from experiment 17 was analyzed with the following results (per cent by weight): hydrogen, 3.3; carbon, 60.3; nitrogen, 1.3; oxygen, 0.8; sulfur, 3.7; ash, 30.6.

The amounts of hydrogen consumed in the liquefaction experiments were calculated and found to vary from 1.5 to 3.5 grams. Since the possibility of slight leakage cannot be completely excluded, great significance cannot be attached to these values. However, in most cases the calculated hydrogen absorption agrees well with the other experimental data. For example, only 1.5 and 1.9 grams of hydrogen were consumed in the diphenyl ether and diphenylmethane experiments, respectively, whereas considerably more hydrogen was absorbed in other experiments in which extensive liquefaction occurred (Table VIII). The vehicles reacted with hydrogen in the naphthalene, tetrahydronaphthalene-quinoline, tetrahydronaphthalene-catechol, tetrahydronaphthalene-glycol, and tetrahydronaphthalene-acetamide experiments (2.7, 3.2, 3.2, 3.5, and 3.4 grams of hydrogen absorbed, respectively). In the diphenyl experiment the outlet tubing became clogged, and a gas sample was not collected. A similar experience with diphenyl was reported by Beuschlein, Wright, and Williams (*5*).

Discussion of Results

Several vehicles were found to be excellent media for the liquefaction of Bruceton coal. These and the other solvents are arranged in Table III approximately in the order of decreasing merit, the degree of liquefaction being judged by the amount of residue insoluble in acetone and benzene. Although considerable differences in effectiveness were observed, it was impossible to make exact comparisons or extensive correlations between constitution of vehicle and effectiveness. The amount of ash-free oil obtained on centrifuging the crude product (column E, Table III) may be taken as a measure of the fluidity of the products at room temperature.

In confirmation of previous claims, tetrahydronaphthalene was found to function excellently as a hydrogenation medium. However, the addition of stable polar compounds (toluidine, cresol, quinoline, etc.) to tetrahydronaphthalene gave vehicles which were equally satisfactory or superior. Because coal hydrogenation proceeds better in the presence of acids (*24*), it is somewhat astonishing that mixtures of amines (*o*-toluidine, quinoline, etc.) with tetrahydronaphthalene gave good results. However, amines (*2*, *3*) such as toluidine and quinoline are known to be effective in dissolving or depolymerizing the coal substance.

Several hydrocarbons (tetrahydronaphthalene, methylnaphthalene, and diphenyl) were found to be good vehicles. Methylnaphthalene is especially interesting because, like tetrahydronaphthalene, it gave a product fluid at room temperature. Why methylnaphthalene is a good dispersion medium is not known. The superiority of methylnaphthalene is in harmony with the observation (*10*) that low-temperature tar (containing alkylated aromatic hydrocarbons) is a better vehicle than high-temperature tar (containing large amounts of naphthalene and other completely aromatic hydrocarbons).

TABLE VIII. MAXIMUM AND FINAL PRESSURES OF HYDROGEN ABSORPTION

Expt. No.	Vehicle	Pressure, Lb./Sq. In. Maximum	Pressure, Lb./Sq. In. Final	Hydrogen Absorbed
				Grams
2, 8	Tetrahydronaphthalene	2458	775	2.4
7, 9	Tetrahydronaphthalene-cresol	2450	765	2.2
10, 27	Naphthalene	2335	658	2.7
16, 44	Tetrahydronaphthalene-naphthalene	2340	705	2.1
19, 32	Tetrahydronaphthalene-quinoline	2125	520	3.2
20, 41	Naphthalene-cresol	2300	640	2.6
24, 42	Diphenyl-cresol	2300	695	2.3
17	Methylnaphthalene	2230	625	2.8
33	Tetrahydronaphthalene-catechol	2440	510	3.2
34	Tetrahydronaphthalene-glycol	2920	630	3.5
39	Tetrahydronaphthalene-acetamide	2910	550	3.4
36	Diphenyl ether	2310	810	1.5
38	Diphenylmethane	2310	750	1.9

Two completely aromatic hydrocarbons, naphthalene and chrysene, were poor vehicles. Diphenylmethane, which is principally aromatic, was also a poor liquefaction medium. Permanent absorption of hydrogen (little or no subsequent dehydrogenation or transference of hydrogen to coal) would explain the failure of these aromatic hydrocarbons to function as good vehicles. It is interesting that, when naphthalene was used with tetrahydronaphthalene or cresol, the liquefaction of coal was better than with naphthalene alone. The saturated hydrocarbons, decahydronaphthalene and *n*-hexadecane, were very unsatisfactory, probably because of their poor solvent action for coal. The poor results obtained with decahydronaphthalene (as well as in the pinene-tetrahydronaphthalene experiment) may be attributed in part to its low critical temperature (384° C.).

The hydrogen-rich compounds (decahydronaphthalene, pinene, abietic acid, and ethyl dihydroabietate), which conceivably might have evolved hydrogen during the experiment, proved very unsatisfactory as vehicles. Perhaps higher temperatures or more suitable catalysts would have converted these compounds into hydrogen and (at least for decahydronaphthalene) good liquefaction media. Another hydrogen-rich compound, nicotine, was very effective, but whether this resulted from hydrogen liberation or from its polar properties is not known.

Although all the other cresol-hydrocarbon mixtures were good vehicles, the cresol-fluorene mixture was only fair. It is interesting to note that fluorene is somewhat similar in structure to diphenylmethane, which is a poor vehicle. Catechol, an interesting compound because of its depolymerizing action on coal derivatives, was an unsatisfactory vehicle, partly because its conversion into phenol and water required a considerable amount of hydrogen. Several other polar vehicles (*p*-thiocresol, acetamide, and glycol) were also hydrogenated during the liquefaction experiments.

TABLE IX. COMPOSITION OF HYDROGENATED COAL DISTILLATE

	Fraction 1	Fraction 2	Fraction 3	Fraction 4
Boiling range, ° C.	To 150	150–225	225–300	300–370
Yield, cc.	37 (0.75 cc. of H_2O)	138.5	275	293
Yield, %	5	18.6	37	39.4
Gravity at 60° F. (15.6° C.) (hydrometer), ° A. P. I.	36.8[a]	23.2	15.8	...
Sp. gr. (pycnometer)	0.822 at 87° F. (30.6° C.)	0.914[a]	0.959[a]	1.029 at 86° F. (30° C.)
Tar acids, %	6.0	21.4	15.9	7.4
Tar bases, %	6.5	3.0	2.1	0.6
Neutral oil constituents, %:				
Olefins	10	0	8	10
Aromatics	33	50.7	70.8	75
Unsulfonated oil (paraffins and naphthenes), %	57	49.3	21.2	15
Paraffin fraction:				
Refractive index at 85° F. (29.4° C.)	1.4115	1.4324	1.4558	1.4678
Sp. gr. (pycnometer) at 85° F.	0.740	0.786	0.835	0.858
Aniline point, ° C.	49.3	56.8	71.6	...

[a] Calculated.

Two fractions (boiling at 185° to 215° and 270° to 399° C.) of a hydrogenated coal distillate furnished by T. E. Warren of the Department of Mines, Ottawa, Canada, were used under the standard conditions of the present work in the liquefaction of Bruceton coal. The analysis of the hydrogenated coal from which these fractions were taken is given in Table IX. The lower boiling fraction (185° to 215° C.) was a poor vehicle (75 per cent conversion of pure coal), partly because of the low critical temperatures of some of its constituents and the hydrogenation of the vehicle (distillation indicated that considerable quantities of lower boiling material had been formed). The product obtained with the higher boiling fraction (270° to 399° C.) was a gummy tar which, although not fluid at room temperature, was almost completely dissolved (excluding ash, fusain, and catalyst) by benzene in a Soxhlet extractor.

Technical dimethylnaphthalene (containing 3.3 per cent tar acids and 8.9 per cent tar bases) was found to be a fair vehicle; 85 per cent of the dry, ash- and fusain-free coal was liquefied. The vehicle recovered by distillation to 260° C. contained 4.3 per cent tar acids and 7.8 per cent tar bases.

Anthracene oil was found to be a good vehicle; over 90 per cent of the pure coal was liquefied. The anthracene oil used contained 3.0 per cent tar acids and 4.6 per cent tar bases; on distillation, 3 per cent came over up to 200° C. and 68 per cent up to 200° C. (9 mm.). The ultimate analysis of the oil follows (per cent by weight): carbon, 90.6; hydrogen, 6.4; nitrogen, 0.8; sulfur, 0.6; oxygen, 1.6. The anthracene oil experiment, as well as the ones employing naphthalene, chrysene, and the two hydrogenated coal distillates, indicates that vehicles of high molecular weight are superior to those of low molecular weight and the same chemical nature.

If a few vehicles are excluded (especially those modified during the experiment), several general correlations can be made between the effectiveness and physical constants. Such generalizations cannot be relied upon completely, for too many variables and unknowns are involved. A satisfactory vehicle should be effective in dissolving the coal substance; the situation is therefore somewhat similar to the extraction of coal, in which polar solvents are known to be superior. However, the extraction of coal in the presence of hydrogen is much more complicated. Other factors, such as resistance to permanent hydrogen absorption, ability to act as hydrogen carrier, etc., are involved. In the following discussion of the relation between effectiveness as a vehicle and physical constants the constants are given for 20° C. unless otherwise stated.

None of the vehicles with low surface tensions (below 30) proved to be effective (Table I). However, the surface tension cannot be taken as a complete measure of the vehicle's merit. For example, diphenylmethane (37.1 at 30° C.) and naphthalene (39.0) were not as good as tetrahydronaphthalene, which has a surface tension of 34. Tetrahydronaphthalene, however, has a dipole moment of 0.52, while the other two hydrocarbons have zero moments. The greater resistance of tetrahydronaphthalene to hydrogenation and its hydrogen-carrying capacity are probably largely responsible for its superiority.

Tetrahydronaphthalene (0.52) was the only vehicle with a dipole moment under 1.3 to function satisfactorily as a vehicle. Some of the worst vehicles (cetane, diphenylmethane, naphthalene, decahydronaphthalene) have zero dipole moments; other vehicles with low moments (diphenyl ether 1.05, pinene 1.10) were also unsatisfactory. However, one hydrocarbon with a zero moment (diphenyl) was a fair vehicle.

None of the good vehicles has dielectric constants below 2.5, and only one (diphenyl, 2.62) has a constant below 3.3. However, one vehicle (diphenyl ether, 3.69) with a constant above 3.3 was a poor dispersion medium. In most cases the best vehicles (cresol 5.5, quinoline 8.9, toluidine 6.0, and xylenol 4.8) have high dielectric constants.

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DER ALCHIMIST

By Martin Johann Schmidt

⁂

Here we see the effect of Shakespeare's witches upon the alchemists' activities. Just what rare element the scorpion contains and its effect upon the elixir of life or love philtre being prepared are, of course, unknown.

Schmidt was born near Krems, Austria, in 1718, and studied in Vienna and Venice. He spent most of his life in Stein on the Danube, where he became a city official, dying here in 1801 after an active career as a painter and etcher.

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Dextrose in the Manufacture of Fruit and Vegetable Products

The physical and chemical properties of refined dextrose are discussed in relation to its suitability in manufactured fruit and vegetable products. Dextrose, as now obtainable on the market, is comparable to sucrose in purity and may be used advantageously in many canned foods, fruit products, and pickles. Because of lower solubility, final dextrose concentrations are limited to less than 50 per cent. Normally, mixtures of sucrose and dextrose must be used unless the amounts are small as in canned vegetables and tomato juice.

Preserves, jams, and jellies containing dextrose should not be "finished" by temperature, because of the higher boiling point of dextrose solutions as compared to those prepared with sucrose. Dextrose alone, or in mixtures with sucrose, does not injure gelation of pectin in jellies and preserves. Similarly there is no effect on yield. A list of products in which dextrose can be used to advantage is given.

The addition of 1 to 2 per cent dextrose to brined cucumbers, peppers, cauliflower, onions, and green tomatoes greatly improves the resulting products by increasing their lactic acid content, preventing spoilage, and enhancing the keeping quality. Preliminary experiments show that dextrose is useful in sweet pickle manufacture by improving the texture and yield without injuring the appearance.

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CRYSTALLINE dextrose manufacture was made commercially possible in 1923 by the granting of the Newkirk patents (*19*, *20*) on corn starch hydrolysis and the economical separation of high-purity dextrose from the converter liquors. Commercial production, which began in 1922, has risen phenomenally. But not until 1926 was chemically pure dextrose accepted by the United States Pharmacopoeia in its Tenth Revision. Industrial applications of refined dextrose and its properties have been pointed out by Cathcart (*4*), Arnold (*1*, *2*), and Krno (*15*), as well as by the manufacturers themselves. Krno, in particular, summed up the information relative to the suitability of various commercial grades of dextrose in the food industries. Bakers and confectioners have always been the largest users of refined dextrose, although large quantities are also used in chocolate, pharmaceutical, and medicinal products. Recently, dextrose has been offered at retail for home use.

Not until 1930, when the Secretary of Agriculture ruled that refined dextrose could be used in the manufacture of food products without label declaration, was the utilization of dextrose by canners, preservers, beverage manufacturers, and allied food industries seriously considered. Although a few states still require the labeling of some manufactured foods containing dextrose, the wisdom of retaining such regulations is questionable. Certainly no fraud is perpetrated and no nutritional or public health aspects are concerned. Dextrose and sucrose have practically equivalent purity and nutritive values. The former contains fewer microörganisms. Since corn is one of our staple agricultural crops and a surplus is often produced, it would seem to be in the public interest to extend, rather than to restrict, the use of refined dextrose.

Physical Properties

Hydrated dextrose contains one molecule of water of crystallization. It is a white crystalline substance resembling sucrose but is only about 75 per cent as sweet. Dextrose is readily soluble in water at ordinary temperatures but not so soluble as sucrose. Thus at 30° C. (86° F.) saturated solutions of dextrose and sucrose contain 54.6 and 68.1 per cent sugar solids, respectively. Mixtures of the two sugars are slightly more soluble than would be indicated by the respective solubilities of the two components. This is of some industrial advantage in that crystallization dangers are decreased. Since jellies and preserves commonly contain from 60 to 70 per cent sugar, it is obvious that these products cannot be manufactured exclusively with dextrose.

Dextrose solutions are somewhat more fluid than sucrose solutions of equal density. This allows the use of higher concentrations of sugar without the product becoming too thick and difficult to handle. This is an advantage in some products, a disadvantage in others. At temperatures between 25° and 50° C. (77° and 122° F.) a 50 per cent dextrose sirup is approximately 22 per cent less viscous than a sugar solution of equal concentration.

The osmotic pressure exerted by dextrose solutions is about twice that exerted by equal concentrations of sucrose. For this reason dextrose sirups are considered somewhat more inhibitive to the growth of microörganisms than sucrose sirups. In this connection Buchanan reported (*3*) that at higher temperatures sucrose solutions destroyed yeasts more effectively than dextrose, but the reverse was true at lower temperatures. He found that dextrose gave carbonated beverages a better "body" than sucrose and also reduced objectionable sweetness. Since dextrose has a higher osmotic pressure, it may be reasoned that fruits packed in dextrose sirups will shrink less than those packed in sucrose sirups of equal concentrations. This is still a moot point. The authors' data show no marked shrinkage reductions in fruits preserved with dextrose.

Extensive data covering the physical and other properties of dextrose have been reported by Jackson and Silsbee (*12*, *13*) and by the Research Committee of the Corn Products Refining Company (*6*). Many of the detailed data not reproduced in the present paper may be found in the theses of Onsdorff (*21*) and Miller (*17*).

Dextrose sirups boil at considerably higher temperatures than sucrose sirups. The respective boiling points for pure dextrose and sucrose sirups are as follows: 20 per cent sirup, 101.4° and 100.6° C. (214.5° and 213° F.); 40 per cent sirup, 102.9° and 101.5° C. (217° and 214.7° F.); 60 per cent sirup, 105.7° and 103.0° C. (222.2° and 217.4° F.). If the finishing point—that is, desired degree of concentration—is determined by a thermometer, the final temperature must be increased when dextrose is used. Thus, if pure dextrose and pure sucrose jellies are cooked to the same temperature and examined with a refractometer, the dextrose jelly will be found to contain 5 to 10 per cent less solids than the sucrose jelly. Other methods are available for the determination of the "finishing point" of preserves, jams, jellies, and sirups, and the differences in boiling point due to the introduction of dextrose into the product are of little consequence in practical food processing. The refractometer gives sufficiently accurate readings with either pure dextrose or dextrose-sucrose mixtures for most purposes.

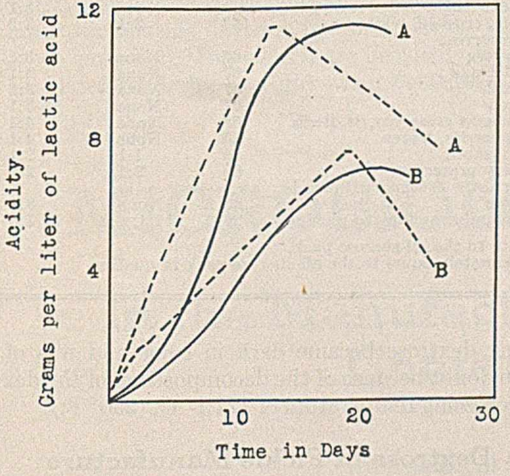

FIGURE 1. EFFECT OF DEXTROSE ON TITRATABLE ACIDITY IN FERMENTING CUCUMBER AND PEPPER BRINES

- - - - Cucumber pickles
——— Sweet green peppers
A. 2 per cent dextrose added to the brine
B. No sugar added

Improvements in manufacturing methods have made possible increased purity of dextrose from year to year. Though pure white in the crystalline form, the regular dextrose hydrate gives a little color when dissolved in water. It depends entirely upon the use to which the sirup is put as to whether its color is an asset or a detriment. In general, the color is insufficient to be of importance in the preserving industry. Recrystallized dextrose hydrate gives clear sparkling solutions.

The subjection of dextrose sirups to high temperatures tends to darken them, though the color change is influenced to a large extent by the pH value of the solution. At pH 4.5 there is no serious change in dextrose when heated to 110° C. (230° F.) for 20 minutes. However, at 121° C. (249.8° F.) considerable darkening takes place. Fruits are never subjected to such high temperatures, although such nonacid vegetables as sweet corn, peas, and beans are normally heat-processed under steam pressure. Alkalies have a marked darkening effect on dextrose solutions although dilute acids are without effect.

Grades of Composition

Several grades of dextrose are available for commercial use. Among these are regular dextrose hydrate, recrystallized dextrose hydrate, and anhydrous dextrose. Since by far the largest output is of regular dextrose hydrate, this is of greatest interest to the food manufacturer. Recrystallized dextrose hydrate, though somewhat more highly refined than regular dextrose hydrate, has given essentially the same results in the food preservation experiments with these sugars.

Market samples of regular dextrose hydrate and recrystallized dextrose hydrate used in the experimental work showed the following values on chemical analysis:

	Regular Dextrose Hydrate	Recrystallized Dextrose Hydrate		Regular Dextrose Hydrate	Recrystallized Dextrose Hydrate
	Per cent	*Per cent*		*Per cent*	*Per cent*
Moisture	7.75	8.00	Fe	0.0001	0.0002
Dextrose	91.4	91.8	Cl	0.016	0.002
Purity of dextrose solids	99.5	99.8	SO_4	0.008	0.008
			SiO_2	0.0035	0.005
Ash	0.05	0.009	Ca	0.0022	0.002

The high purity of dextrose hydrate is of special interest. The ash content is very low. Since dextrose hydrate contains 91.5+ per cent dry substance, it is necessary to use 109.4 pounds in order to obtain the same amount of sugar solids that is present in 100 pounds of sucrose.

Dextrose in Fruit and Vegetable Products

Since dextrose has been available for industrial purposes, it is surprising that so few investigations have been published relative to its use in the food preservation industries. In 1933 Van Arsdale and Eddy (*22*) found that dextrose could successfully replace a part of the sucrose in many fruit and vegetable products. They found dextrose was of particular value in canned tomatoes, peas, beets, carrots, peaches, pears, marmalade, cranberry and currant jellies, and various preserves. The amounts used in the canned vegetables were very small and are not significant. Mrak and Richert (*18*) reported that the swelling of canned prunes was not affected by the sugar used in canning them. Pure commercial dextrose was slightly superior to sucrose or invert sugar, but was inferior to straight prune juice when used as a sirup. Lathrop (*16*) reported in 1926 that "corn sugar" could not be substituted for sucrose in fruit preserves, jellies, maraschino cherries, or even in candy centers without greatly injuring quality and hastening spoilage. Although he gives no data, this investigator apparently refers to fruit products manufactured entirely with "corn sugar" which was a much inferior product to the refined dextrose of today. This is an important point. For example, during the period 1930–1932 Fellers and Mack (*11*) reported that corn sugar was unsatisfactory in frozen fruit because it injured the flavor and color of the fruits. Some of the tests were repeated in 1935 and 1936 with the result that sucrose-dextrose ratios of 3 to 1 were the equal of the all-sucrose packs in the case of strawberries, sour pitted cherries, and red raspberries. Probably the differences obtained were due largely to the purity of the dextrose used. No doubt some of the adverse results obtained several years ago on the suitability of dextrose in food products would have been different had a purer dextrose been available.

Experimental Packs

Experimental packs of canned fruits and vegetables and manufactured food products were made during the past two and one-half years. The procedure was to make small preliminary packs of the various products in glass jars in order to work out details of preparation, preservation, and storage. This was followed by larger semicommercial-scale packs in tin and/or glass containers for careful examination. At least two such packs were made for all products reported in Table I except frozen Morello cherries, Fellenburg plum preserves, apricots, pickled Jerusalem artichokes, yellow clingstone peaches, and loganberries. Several ratios of dextrose and sucrose were used in the several packs, including, in every case, all-sucrose and all-dextrose controls. The usual commercial methods of handling and processing were used, and individual details will not be repeated here.

Quality of the food products was judged after 1 month and again after 4 to 6 months by a qualified group of persons including several women, three men with commercial food packing experience, and from three to five others who were more or less familiar with fruit and vegetable products. Naturally, there was much disagreement among the individuals of this group but the majority opinion was taken after several trials. It was observed that, although some of the judges preferred high-sucrose packs, usually because of their greater sweetness, others preferred more dextrose because the products were less sweet.

In general, there was little to choose between all-sucrose and sucrose-dextrose packs in so far as texture, color, viscosity, and attractiveness were concerned. Hence, the real work of the judges lay in making distinctions of flavor and palatability. Obviously, products showing crystallization of sugars were disqualified. Most of the all-dextrose, and many of the 1 to 1 sucrose-dextrose packs, were disqualified because of crystallization.

The dextrose used in this investigation was from three lots purchased at various times from dealers in Boston and Holyoke. So-called regular dextrose hydrate was used. Although some fruits were also packed in sirups made from recrystallized dextrose hydrate, the results are not sufficiently different to warrant reproduction here. However, recrystallized dextrose hydrate gave whiter sirups and a milder taste with some fruits than regular dextrose hydrate. Products packed with recrystallized dextrose hydrate showed no particular advantages over regular dextrose hydrate.

Pears, berries, and grape products did not lend themselves particularly well to the use of dextrose sirups, although in nearly all products it was possible to use 20 to 30 per cent dextrose in the sugar mixture without adversely affecting quality.

In other products the addition of substantial amounts of dextrose to the sugar mixture brought about an improvement over the all-sucrose packs. Table I shows the results. Gelation or setting of the pectin in fruit jellies, marmalades, and preserves was not affected by dextrose or dextrose-sucrose mixtures. Dextrose had no effect on yield of these products. Cole, Cox, and Joseph (*5*) have also showed that both invert sugar and dextrose give jellies with pectin. Premature gelation may occur if the dextrose used is acid. Ekhard (*8*) reported that "glucose" was a satisfactory sugar for fruit marmalade manufacture. The use of dextrose in the manufacture of sweet pickles is particularly advantageous and a ratio of 1 to 1 sucrose-dextrose mixture seems to be near the optimum.

Sugar is sometimes used in small amounts in canned corn, peas, beets, and tomato juice. Except for sweet corn, dextrose was well adapted for use in canned vegetables and in tomato juice in the amounts shown in Table I. Sweet corn containing dextrose became dark in color and was of poor flavor, no doubt because of the decomposition of the dextrose at the processing temperature of 121.1° C. (250° F.).

TABLE I. SUITABILITY OF DEXTROSE IN VARIOUS PRODUCTS

Product	Total Sugar in Sirup	Ratio of Sucrose to Dextrose	
		Preferred[a]	Acceptable[b]
	%		
Canned Fruit and Vegetables			
Apples, Rhode Island Greening, and Baldwin	20	None	2:1
Apricots	40	None	2:1
Artichokes, Jerusalem, in sweet pickle	17	1:1	All dextrose
Blackberries	40	None	2:1
Beets, diced	4	1:2	All dextrose
Cherries:			
Royal Anne	40	None	2:1
Morello	60	3:2	1:1
Montmorency, pitted	60	3:1	2:1
Grapefruit	10	2:1	1:1
Loganberries	70	None	2:1
Peaches:			
Yellow clingstone	60	2:1, 1:1	1:1
Hale	60	2:1	1:1
Pears, Bartlett and Anjou	40	None	2:1
Peas, Alaska and Alderman	4	1:1	1:2
Pineapple, white Cuban	40	2:1	1:1
Prunes, fresh	40	2:1	1:1, 1:2
Red raspberry:			
Cuthbert	60	None	3:1
St. Regis	60	None	None
Rhubarb, pieces	60	2:1	1:1
Strawberries	60	None	None
Sweet corn:			
Golden Bantam	4	None	None
Evergreen	4	None	None
Tomatoes	3	1:1	All dextrose
Tomato juice	5	1:1	All dextrose
Fruit and Vegetable Products			
Apple jelly, Rhode Island Greening, and Baldwin	68	None	2:1
Apple sauce, Red Astrachan	25	3:1	1:1
Apple butter	20	2:1	1:1
Blackberry preserves	68	4:1	3:1
Cherry preserves, Morello	68	3:1	2:1
Cherries, frozen:			
Morello	33.3	None	3:1
Montmorency	33.3	None	2:1
Cranberry sauce, strained	40	None	2:1
Currant jelly	68	3:1	3:1
Grape jam and butter	67	None	3:2
Grape juice (sugar added to 20%)		None	3:1
Pineapple, crushed, white	66	3:1	3:2
Plum preserves:			
Fellenburg	67	None	3:1
Grand Duke	67	None	3:1
Monarch	67	None	3:1
Damson	67	None	3:1
Red raspberry preserves, St. Regis	68	None	4:1
Red raspberries, frozen	25	None	4:1
Rhubarb, sauce	50	1:1	2:1
Strawberry preserves	69	3:1	2:1
Strawberries, frozen, Howard Supreme	33.3	None	3:1
Sweet cucumber and mixed pickles	36	1:1, 1:2	1:3

[a] Superior to the all-sucrose pack.

[b] Approximately equal to the all-sucrose pack in quality.

Dextrose in Pickle Manufacture

Experiments were conducted for two seasons on the effect of adding dextrose to fermenting cucumber pickles, dill pickles, onions, cauliflower, green tomatoes, and sweet red and green peppers. The dextrose was added to the fruit in the salt brine before fermentation began. In the case of all these products where the sodium chloride concentration varied from 5 to 15 per cent, the addition of dextrose in the ratio of 1 to 2 per cent of the weight of the vegetable materially increased the titratable acid, reduced spoilage, and improved keeping quality and texture. Most striking results were obtained with dill and salt stock cucumber pickles and with red and green peppers. Figure 1 shows graphically how the addition of dextrose increases acidity in fermenting cucumbers and peppers. Similar, though less striking, results were obtained with onions, cauliflower, and green tomatoes.

Vegetables used for brining contain only 2 to 4 per cent sugar, and the added dextrose serves to accelerate the fermentation as well as produces a much greater quantity of lactic acid due to stimulation of lactobacilli by the readily available sugar.

The higher acidity decreases bacterial spoilage and hastens the curing period. Since acidity decreases slowly during storage, a pickle with a high acid content will generally remain firm and sound longer than one of lower acid content. The main factors involved in loss of acidity are surface growths of Mycoderma and scum yeasts which are able to utilize lactic acid as a source of energy.

Although the use of 2 per cent dextrose produced somewhat higher acidities than 1 per cent, the differences in the final products would scarcely warrant the use of 2 per cent dextrose. However, the latter amount ensures a rapid, clean fermentation and improves keeping quality.

Fabian and Bryan (*9*) and Fabian and Wickerham (*10*) recommended the addition of 2 pounds of sugar per 45-gallon barrel of fermenting pickles to accelerate the curing process and increase total acidity. Similarly, Cruess (*7*) found that the addition of dextrose to fermenting green olives resulted in a desirable higher acidity. Joslyn (*14*) showed that the use of 2 to 5 pounds of dextrose per barrel of dill pickles accelerated fermentation and decreased spoilage by producing more lactic acid. Dextrose was superior to lactose in his experiments. The present results are in full accord with those of Fabian and Joslyn.

Dextrose in Sweet Pickles

Sweet pickles are usually prepared from cucumbers, cauliflower, onions, and peppers which have been fermented in salt brine. The vegetables are desalted, cut if desired, and placed in a 2.5 to 3.0 per cent distilled vinegar solution. This solution is gradually sweetened by the addition of sugar until a final concentration of 35 to 50 per cent sugar is reached.

Although only a few experimental packs have been made in these laboratories using dextrose in sweet pickles, the results show much promise. The pickles are decidedly crisper and show an increased drained weight when dextrose is used in place of sucrose. This is true of both sweet cucumber and sweet mixed pickles. A ratio of dextrose to sucrose of 1 to 1 gave good results.

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MICROBIOLOGICAL CONTROL

In the Manufacture of Paper Wraps and Containers for Foods

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CELLULOSE industries have been forced to recognize the profound influence of microörganisms upon manufacturing processes. Uncontrolled development of organisms in pulp and paper mills presents serious obstacles to high operative efficiency and satisfactory quality in finished products. The appearance of discolorations or "slime spots" and the presence of objectionable odors in paper or container board are usually direct evidences of undesirable growth accumulations.

In the case of mills engaged in the manufacture of paper and board which may come in direct contact with foods, it is desirable that methods and practices be consistent with standards of food quality. Rapid developments in the use of paper containers for milk and other foods have brought to the attention of public health authorities and research organizations of food and cellulose products industries, the need for close coöperation with plants manufacturing and handling food container stock in the application of a program of supervision and control. Such a program should start at pulp and paper mills where early contamination of stock takes place.

In a previous paper the author[2] referred to the rich food supply provided by pulp systems, particularly groundwood stock, and to the diversity of types of microörganisms which usually develop there.

Development of Microörganisms in Pulp Systems

The abundance of organisms present in groundwood contributes largely to the excessively high bacterial numbers commonly found in mixed pulp going to paper machines. Inadequate chlorination of fresh water in a sulfite mill may also foster considerable development of microörganisms in

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sulfite stock. Many of the species present throughout the system are slime formers and notorious trouble makers, habitually colonizing on rough surfaces which favor attachment and spread. Figure 1 shows the total bacterial counts of mixed stock in the presence of various proportions of groundwood pulp. Stock consisting of varying amounts of groundwood was obtained directly from mills producing these grades of paper. Temperatures of pulp suspensions during pulp and paper manufacture at the mills included in this investigation were usually between 22° and 35° C. Samples were plated out immediately using standard nutrient agar; plates were incubated at 30° C. for 48 hours.

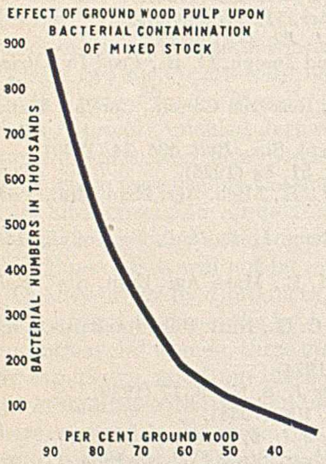

FIGURE 1

Microbiological surveys of pulp and paper mills reveal the growth characteristics of a variety of microorganisms. Examinations of gelatinous coatings, which may readily form on surfaces in contact with pulp suspensions, yield slimy varieties of a number of bacteria which closely resemble the following species:

Isolations from:	Bacteria	
Plant A	*Aerobacter aerogenes*	*Achromobacter pinnatum*[a]
	Aerobacter cloacae	*Achromobacter hartlebii*[a]
	Pseudomonas viscosa	*Achromobacter ambiguum*[a]
	Bacillus vulgatus	*Flavobacterium aurantiacum*[a]
	Bacillus subtilis	*Actinomyces fradii*
Plant B	*Aerobacter cloacae*	*Achromobacter reticularum*[a]
	Alcaligenes faecalis	*Flavobacterium denitrificans*[a]
	Actinomyces fradii	*Flavobacterium turcosum*[a]
Plant C	*Alcaligenes viscosus*	
Plant D	*Didymohelix ferruginea*	
Plant E	*Bacillus peptogenes*	*Micrococcus albus*[b]
	Bacillus albolactis	

[a] Identification somewhat uncertain, since original organism is poorly known.
[b] *M. conglomeratus* and *M. varians* were isolated from the same source.

Detailed study of the isolations reveals which types are intimately concerned in the formation of growth accumulations and those representing only casual contamination. Slime production by pure cultures growing on suitable laboratory media, followed by study and classification of the slime masses produced, yields valuable evidence pertaining to identification and control.

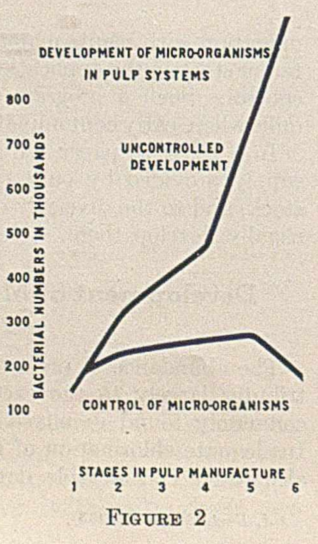

FIGURE 2

In many instances, predominating species are not bacteria but belong with the filamentous or yeastlike fungi. Such organisms often produce leathery or rubbery sheets of fungus growth, characteristic of Oidium, Monilia, Mucor, and Trichoderma. Although sheet formations are usually found in undisturbed or overlooked portions of a mill, fungi of these general types may build up resistant growths in parts of the process involved in regular operation. Typical isolations may include the following groups:

Plant F	*Oidium lactis, Aspergillus fumigatus*
Plant G	*Oidium pullulans, Monilia candida*
Plant H	*Trichoderma lignorum, Mucor racemosus*
Plant I	*Botrytis cinerea, Oidium lactis*
Plant J	*Cladosporium herbarum*
Plant K	*Penicillium guttulosum*

In these cases, too, study and classification of the slime films or membranes produced by pure cultures serve as a basis for determining causal species and recommending remedial measures. It will be obvious that variability in types involved necessitates important differences in methods of eradication and control.

It is significant that an appreciable number of organisms from the above lists have appeared in paper and board off driers and after formation of food containers. These species frequently occur in mills as gelatinous, stringy, or rubbery growth masses and are therefore difficult to eliminate entirely by heat or chemicals. On the other hand, the presence of surfaces and materials contaminated from prolonged contacts, direct and indirect, with organisms from water, pulp, pulpwood, and slime accumulations, may result in recontamination of the newly formed sheet unless immediate steps are taken to remove it, properly protected by suitable wrapping.

Control of Microörganisms

The best method of control may be determined according to the results of a microbiological survey of the plant. The purpose of the survey is threefold: (*a*) to determine predominating types of slime-forming microörganisms, their origin, distribution, and identification; (*b*) to reveal by microbiological tests in terms of numbers or relative contamination per cubic centimeter of white water or stock where focal points of slime contamination occur; and (*c*) to recommend a program of control based upon knowledge of local conditions and specific types of slime involved.

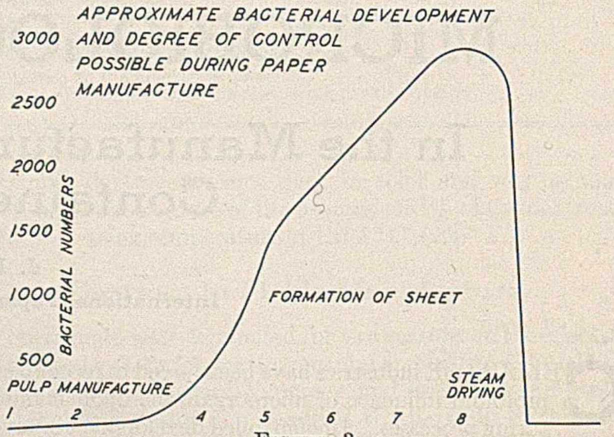

FIGURE 3

Control measures depend upon the utilization of a sterile process water. The system is first cleared of all slime accumulations and contaminated surfaces are periodically hosed out with chlorinated fresh water. Further procedures will vary with local conditions and types of organisms predominating. Forms of fungus contamination, which cannot be economically controlled by chlorination, may be successfully combated by dripping in copper sulfate solution at focal points in the system. Although other chemical treatments are sometimes employed in parts of the country where manufacturing conditions vary, practices in plants of the Northeast do not usually permit the utilization of reagents whose effects are drastic or prolonged. As a matter of fact, no two mills present identical slime problems.

In emergencies the utilization of both chlorine and copper sulfate is a frequent practice. During slime troubles, where bacterial counts are uniformly high, appropriate control measures invariably result in marked reductions of microorganisms.

Figure 2 illustrates the average counts secured under ordinary mill conditions. Results were obtained by the plating method, using standard agar and incubating for 48 hours at 30° C.

Although plant conditions (as shown in Figure 2) may not permit complete control of organisms to a state of practical sterility, it is possible for many mills to manufacture pulp which is relatively free from microörganisms. For example, at bull screens (stage 2, Figure 2) colonies have been reduced to 8 per cc. Counts at groundwood deckers (stage 5) were reduced at the same time from 320,000 to 1,500. Contamination in a sulfite mill was almost completely eliminated; less than twenty colonies per cc. of white water or stock were obtained in this part of the system.

Progress in effective control is reflected in the production of stock which is relatively free from bacteria, offensive odors, and dirt. This is the quality of paper recommended for food wrappers and containers. In cases of contamination of stock by spore-forming bacteria, it should be possible to reduce the number of viable spores in newly made sheets to less than 100 per gram of stock (Figure 3).

Further contacts while paper remains exposed in paper mills tend to recontaminate it with spores, growth fragments, and bacteria-laden dirt. In order to avoid contamination following sheet formation, wrapper and container stock should be immediately encased and sealed in uncontaminated paper wrappers, providing complete protection at ends of rolls or sheeted stock. It is particularly important to eliminate, as far as possible, direct human contacts. Detailed studies of microörganisms present in paper containers for milk suggest that, in order to obtain paper of satisfactory quality for contact with foods, it will be necessary to enlist the aid of sanitary procedures during every step in its fabrication.

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Oat Flour as an Antioxidant

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FINELY ground oat flour, known as Avenex, has been recommended as a suitable inhibitor of rancidity in oil- and fat-containing foodstuffs; it has the advantages of availability, blandness of flavor, absence of color, and acceptance as a food (*2*, *4*, *7*). Experiments are reported here which deal with the dusting of Avenex over the surface of potato chips. Other studies were undertaken to determine the effectiveness of oat flour in reducing the rapid oxidation of fats at the surface of wrapping materials such as parchment paper, wax paper, and cardboard containers. These processes are referred to broadly in certain United States patents (*5*, *6*).

Potato Chips

Potato chips were freshly prepared and dusted with 5 per cent of Avenex. The desirability for the elimination of the proöxygenic actinic rays in the storage of potato chips was previously reported (*1*, *3*). However, because of the fact that exposure of potato chips to ultraviolet light or to direct sunlight does not simulate average commercial conditions, it was considered advisable to store them in the dark and at room temperature.

Peroxide determinations following the Wheeler method (*8*) were made to determine development of rancidity. The following procedure gave consistent results:

> Twenty-five grams of crushed chips were thoroughly extracted by shaking with 50 ml. of chloroform in a tightly stoppered bottle. The contents of the bottle then were transferred to a dry, previously weighed folded filter, and the bottle was washed out with an additional 25 ml. of chloroform which was likewise added to the filter. The filtrate was collected, and the filter plus the extracted chips was thoroughly dried and weighed. By difference the weight of the extracted oil was obtained. Titration of aliquot portions of the total filtrate gave the peroxide number of the oil. Ten-milliliter portions were usually taken for titration. Forty per cent of glacial acetic acid was added together with 1 ml. of saturated potassium iodide solution. After standing for exactly 1 minute, 50 ml. of water and a few drops of starch solution were added, and the solution was immediately titrated with 0.001 *N* sodium thiosulfate.

Table I records the values for treated and untreated chips taken over a period of 42 days. Other series were run with similar results. Slight differences in the peroxide values were observed which could not be correlated with either the length of time the chips remained under test or with organoleptic rancidity. Other unusual variations in the peroxide value were frequently observed, such as the reduction in peroxides of the fat from treated chips between the 10- and 21-day periods.

Food-Packaging Materials

For such products as crackers, potato chips, nuts, etc., the fat of the product is adsorbed at the surface of the packaging material, whereas for butter, lard, oleomargarine, etc., the fat is always in direct continuous contact with the packaging material. Consequently, it was desirable to determine the degree of rancidity protection afforded by the use of oat-flour-treated (Avenized) packaging materials as would be obtained under normal commercial conditions.

Avenized parchment paper was prepared by surface-water sizing with oat flour following the parchmentizing operation; the normal appearance of the paper is not changed by this treatment.

TABLE I. PEROXIDE NUMBERS OF TREATED AND UNTREATED POTATO CHIPS[a] AFTER STORAGE AT ROOM TEMPERATURE IN THE DARK

Treatment of Chips	Peroxide Number after:					
	0 days	3 days	10 days	21 days	32 days	42 days
Untreated	2.1	3.8	4.4	12.6[b]	20.9	35.7
Dusted with 5% Avenex	2.1	2.8	3.8	3.0	10.6	15.3[c]

[a] Cooked in refined cottonseed oil.
[b] Distinct organoleptic rancidity.
[c] Slightly rancid.

Avenized greaseproof wax papers were prepared by mixing 35 per cent Avenex with 65 per cent paraffin in the waxing trough and applying the paraffin-Avenex mixture to the paper in the normal manner. Appearance of the paper was not changed, but moisture resistance was decreased by this procedure.

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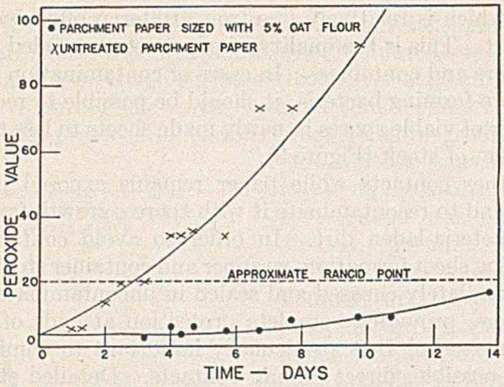

FIGURE 1. PARCHMENT PAPER EXPERIMENT

Avenized cardboard containers were prepared by surface-water sizing or as otherwise described in Figure 3.

That a marked degree of protection was afforded could be simply demonstrated by thinly coating pieces of the Avenized papers and their respective controls with lard, placing them in tightly closed jars, and opening the jars at regular intervals to note any changes in the odor of their contents. The jars containing the controls were found to have a definitely perceptible rancid odor for an appreciable length of time before those containing the Avenized papers.

To demonstrate chemically and quantitatively, however, the exact amount of inhibitory protection afforded, the following method, which was found to be the most convenient for this purpose, was adopted:

> Exactly 1 ml. of molten lard held at 35° to 40° C. was run from a volumetric pipet onto a piece of the paper measuring about 5.5 × 4 inches (14 × 10 cm.). The paper was then tilted up and down until the lard was fairly evenly spread over its surface. The papers thus coated with lard were set aside, and care was taken to place all under exactly identical light and temperature conditions. In these experiments the papers were kept in uniform darkness at room temperature.

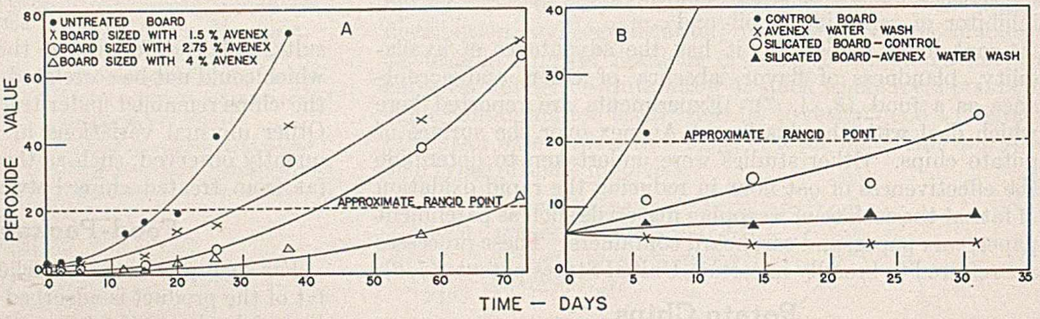

FIGURE 3. CARDBOARD CARTON EXPERIMENT

Substantially the Wheeler peroxide titration method (*8*) was used as before:

> The piece of paper containing the lard to be tested was folded to a convenient size or cut into strips and placed in a 125-ml. Erlenmeyer flask. To the flask containing the paper were added about 10 ml. of a fat solvent, consisting of a mixture of 60 per cent glacial acetic acid and 40 per cent chloroform. The flask was then allowed to stand for about 5 minutes with occasional shaking. At the end of this time, 0.2 ml. of saturated potassium iodide was added, and the solution allowed to stand exactly 1 minute. Ten milliliters of distilled water and a few drops of a 0.2 per cent starch solution were immediately added, and the solution was immediately titrated with 0.01 *N* sodium thiosulfate solution.

The parchment and wax paper experiments were carried out in the Princeton University Chemical Laboratory. Figures 1 and 2 show the degree of rancidity protection obtained with these types of Avenized papers. Since a peroxide number of 20 is generally considered to indicate the approximate rancid point of lard, it is shown in the figures in that manner.

The rapidity of the oxidation of lard spread on the surface of the control papers may be noted; the lard reaches a peroxide value of 20 at the end of 3 days in the case of the parchment paper and at the end of about 5 days in the case of the waxed papers, whereas the oat-flour-treated parchment required 13.75+ days, and the treated wax paper required about 11 and 20 days, depending upon the concentration of oat flour on the paper.

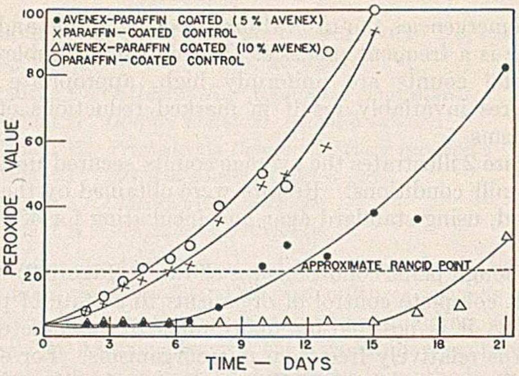

FIGURE 2. GREASE-PROOF WAX PAPER EXPERIMENT

Similar tests were made in the laboratory of Musher Foundation with treated and untreated cardboard packaging materials and are recorded in Figure 3.

The decrease in the initial peroxide number of the lard with increasing concentration of oat flour indicates a destruction of the peroxides initially present by the oat flour. A uniform increase in protection is obtained as the concentration of oat flour is increased. As indicated in Figure 3*A*, 4 per cent of oat flour was sufficient in these experiments to keep the peroxide number below 20 for a period of about 70 days. The control reached this level in 19 days.

These results indicate that it is possible to secure substantial inhibiting effect to formation of peroxides in the fat of (1) potato chips by dusting 5 per cent Avenex over their surfaces, and (2) parchment paper, wax paper, and board materials surface-coated with lard, by treatment of such packaging materials with Avenex.

Acknowledgment

The authors acknowledge the coöperation of the Kalamazoo Vegetable Parchment Company, Paterson Parchment Paper Company, Riegel Paper Corporation, Gair Cartons, Inc., and Chicago Carton Company for the processing of the paper and boards used for these experiments.

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pH Properties of Colloidal Carbon

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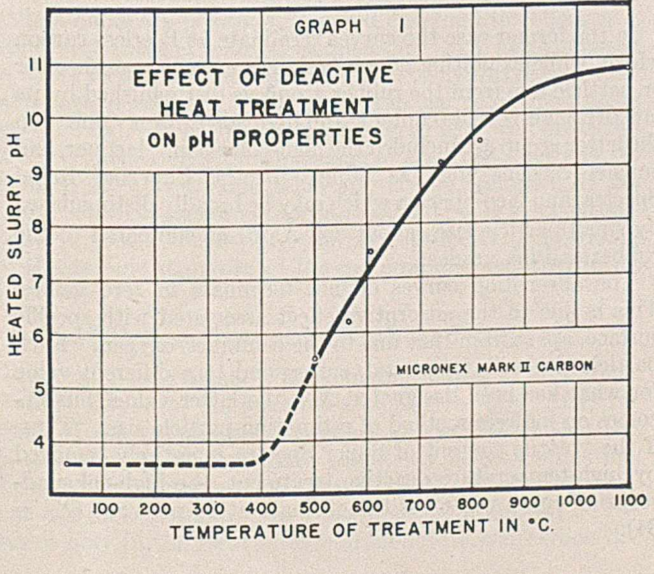
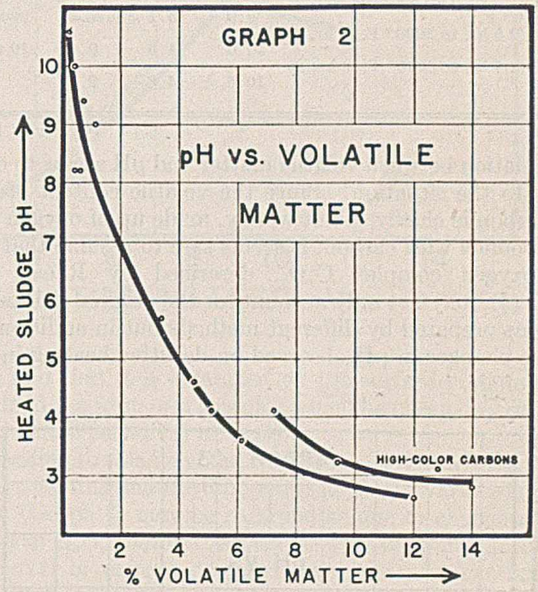
IF ONE part of colloidal carbon pigment[1] is boiled for 15 minutes or more with three to ten parts of distilled water and cooled, the supernatant liquid decanted, and the sludge placed in contact with the glass electrode of a pH electrometer, a reading is obtained which is characteristic of the material. A representative list of the pH values thus obtained is shown in Table I. In this preliminary account some of the factors will be given which influence pH values of particulate carbon, some of the relations between pH and other properties of colloidal carbon, and something of the significance of these pH properties.

Table I. pH Summary of Carbon Sludges

	pH
High-grade impingement carbon blacks:	
Long ink carbon (Peerless)	2.6
Easy-wetting, high-color (Neo-Spectra)	2.8
Highest color (Royal Spectra)	3.1
Medium-color (Superba)	3.2
High-color, general-purpose (Super Spectra)	4.1
Lampblacks:	
High-grade	3.1
Rubber-grade	3.6
Chinese (native) carbon black	4.2
Rubber-grade impingement carbon blacks:	
Slow-vulcanizing (Micronex Mark II)	3.6
Standard vulcanizing (Micronex Standard)	4.1
Fast-vulcanizing (Ultra type)	4.6
Degussa CK 3	5.7
Nonimpingement carbons:	
P-33	8.2
Acetylene black	8.2
Bone black	9.0
Fumonex (or Gastex)	9.3

The results of a great number of experiments are shown in Graphs 1 to 4. It was found: (*a*) The pH value remained unchanged within the experimental error after repeated extraction of the carbon with boiling distilled water; (*b*) organic solvent extraction (acetone, ethyl alcohol, ethyl ether, and toluene) did not change this property of the carbon; (*c*) water-soluble acidity in impingement carbons is less than 0.01 per cent calculated as sulfuric acid, part of which has been shown to be sulfur dioxide, but this does not explain their acid properties; (*d*) carbons produce a greater change in the pH value of neutral salt solutions than they do in distilled water; and (*e*) relations have been found between the pH value, the volatile content, and the adsorption index for diphenylguanidine (D. P. G.).





These results seem to show that the pH change produced by colloidal carbons is an adsorptive phenomenon in which the selective adsorption of the particles of the colloid varies as some function of the volatile matter content; the higher the volatile matter content, the lower (more acid) is the pH. By heating in the absence of air, a carbon (Micronex Mark II) with an original pH of 3.6 has been given a pH value progressively higher (more alkaline) as the temperature of heating is raised above an apparently critical point. The results of this treatment (each carbon sample was held at the temperature noted for one hour) are shown in Graph 1. In Graph 2 the pH values of various types of carbon are given in relation to their volatile content. Volatile matter is determined as follows: Fill a tared platinum crucible completely with the sample. Place the lid tightly in position. Heat for 7 minutes at 950° C. Determine the loss in weight and correct for moisture content.

Graph 3 shows the relation of pH values of the different carbons to their D. P. G. adsorption (*X*) values. Fifty cubic centimeters of a solution of 2 grams of C. P. diphenylguanidine in 1 liter of alcohol are shaken with 1 gram of carbon for 2 hours. After filtering, 25 cc. of the filtrate are titrated with

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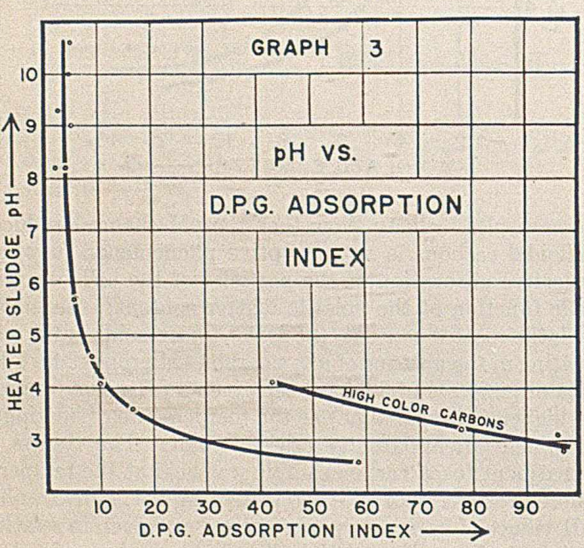
[1] The family of carbon pigments ranges in particle size from approximately 250 to 5000 Å. Impingement carbons range from about 250 to 700 Å. These are estimated values.

0.01 *N* hydrochloric acid using a mixture of bromophenol blue and methyl red as indicator. The result is expressed as percentage of D. P. G. removed. Graphs 2 and 3 were both made up from the carbons listed in Table II, which also shows other properties.

TABLE II. COLLOIDAL CARBON PROPERTIES

Grade	pH	D. P. G. Adsorption Index	Per Cent Volatile Matter	Time of Cure in D. P. G. Type Rubber Compound
High-grade, long-ink carbon (Peerless)	2.6	58.4	12.0	...
High-color carbons:				
Easy-wetting, high-color (Neo-Spectra II)	2.8	97.2	14.0	Several hours
Highest color (Royal Spectra)	3.1	96.0	12.8	
Medium-color (Superba)	3.2	77.7	9.4	
High-color (Super Spectra)	4.1	42.5	7.2	
Rubber-grade carbons:				
Fine-particle, slow-curing (Mark II)	3.6	16.0	6.1	50 min.
Standard-curing (Grade A)	4.1	10.1	5.1	30 min.
Fast-curing	4.6	8.4	4.5	25 min.
Degussa CK 3	5.7	5.3	3.4	17 min.
Nonimpingement carbons:				
P-33	8.2	1.8	0.4	15–18 min.
Acetylene	8.2	4.1	0.6	
Fumonex (or Gastex)	9.3	2.5	0.7	
Deactivated rubber carbons:				
HS-421 (1.5 hr. to 1500° F., 0.5 hr. at 1500° F.)	9.0	5.1	1.1	10 min.
HS-355 (2.5 hr. to 2000° F., 0 hr. at 2000° F.)	10.0	4.6	0.4	
HS-335 (2.5 hr. to 2000° F., 3 hr. at 2000° F.)	10.6	4.8	9.2	

The relation between volatile matter and pH seems to offer the key to the situation. Since the volatile content of colloidal carbon is chiefly, if not wholly, made up of oxygen and its compounds with carbon, it seems safe to assume that the carbon-oxygen complex C_xO_y, described by Rhead and Wheeler (*4*), may not only account for the original pH values of carbons prepared by different methods but in addition explain the changes in pH observed on deactive heating in the absence of air.



The pH values shown in Table I permit the various families of colloidal carbon to be differentiated. The impingement carbons (including CK 3, according to present information) and the lampblacks give low (acid) pH readings. On the other hand, the finely divided thermal decomposition carbons (P-33) and what may be called the furnace type carbons (Fumonex and Gastex) give high (alkaline) pH values. (Fumonex and Gastex are produced in furnaces involving partial combustion, the heat of which causes separation of particulate carbon which is, however, not collected by impingement. The true "thermal" carbons are produced without combustion. Both are "born" in a reducing atmosphere.) By subjecting impingement carbons to deactive heat treatment (*8*), their characteristic pH values can be varied from low to high (acid to alkaline) according to the intensity of the treatment as measured by its time and temperature. The high-color specialty carbons used in inks and paints give low (acid) pH readings, and the rubber carbons fall into an intermediate acid range extending from pH 3.3 to 4.6.

The slow-vulcanizing carbons show lower pH than those which cure rapidly. Most rapid curing of all are the thermal-decomposition and deactivated carbons with the highest pH values. In paints, enamels, and inks the true impingement carbons, which are relatively slow drying, have low pH values. Relatively quick-drying carbons (bone blacks) show high pH.

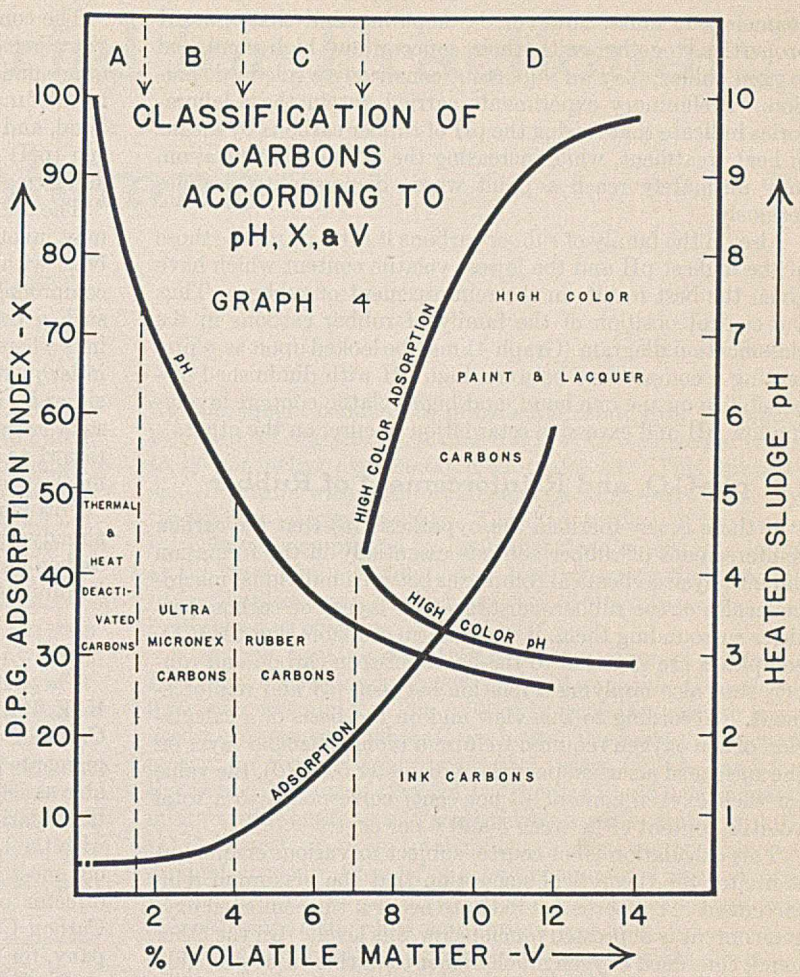
In Graph 4, pH values and adsorption indices (*X*) are plotted as variables dependent on volatile content (*V*). The curves are smoothly drawn from Graphs 2 and 3 and are intended to indicate only broad relations. Four general categories of colloidal carbon may be recognized:

1. Thermal and deactivated carbons, in general, correspond to definitely alkaline reactions ranging from pH 7.5 upwards. The adsorption indices are uniformly below 5, and the volatile contents, in general, are at or below 1 per cent. These carbons include acetylene black, Fumonex, and Gastex, in addition to P-33, and also some forms of graphite, and are markedly quick curing in rubber compounds. This section also includes impingement carbons which have been strongly heat-deactivated to approximately 1.5 per cent volatile, or less. (Thermal carbons of large particle size, such as Thermax and Velvetex, do not appear to have any appreciable pH effect.)
2. The second area may be described as the only blank space in our map. It is populated only by members of the true Ultramicronex series (*8*) which, owing to their high cost, are not in general use at present. The range in pH is from about 4.75 to 7.5, in volatile content from about 1.5 to 4, and in adsorption of *X* from about 4 to 7.5. From the manufacturing point of view this range of carbons represents a middle ground between carbons produced under essentially oxidizing conditions and those under essentially reducing conditions.
3. Next comes the range of commercial impingement carbons used in the rubber industry. The pH ranges from 3.3 to approximately 4.6, the volatile content from 4 to 7, and the adsorption index (*X*) from 8 to 20. This band represents over 85 per cent of all the colloidal carbon now being produced and goes in the main to the reinforcement of tire treads. (Consumption for 1936 is estimated at 363,000,000 pounds.)
4. The specialty carbons are characterized in general by higher volatile content, lower pH, and higher adsorption index. These again are classified according to whether they follow the lower pH and adsorption curves or the upper members which have been designated in the graph as high-color adsorption and high-color pH.

In the former case the curves terminate at Peerless carbon which, while exhibiting no marked difference as regards color or particle size from the rubber group, is distinguished by its low pH, high volatile content, and high adsorption value. In the latter group are included the high-color paint, lacquer, and enamel carbons such as Super Spectra, Superba, Royal Spectra, and Neo-Spectra which may be broadly distinguished by small particle size (about 250 Å., *6*) as compared to the rubber and ink grades.

The adsorption curves do not terminate in zero values. This is due to the adsorptive effect associated with specific surface, apart from that due to the combined oxygen. Each particle size will, in general, correspond to a different value for what has been designated X_0; the latter value thus becomes an indirect method of estimating particle size. Thus, if the volatile content of Super Spectra is entirely removed by high-temperature deactive treatment, the high-color adsorption curve will cross the ordinate at 34 per cent ($X_0 = 34$).

These differences in particle size must be considered in correlating pH with, for example, the retardation in drying of paints and in the vulcanization of rubber. Thus the retarding effect of a rubber carbon with a volatile content of 7 per cent but an adsorption value of only 20 is not so great as that of Super Spectra with almost the same volatile content but with a much higher adsorption index due to its greater specific surface.



Adsorptive Nature of Colloidal Carbon Acidity

The experimental results, especially those dealing with water-extractable acidity, lead to the conclusion that none of the colloidal carbons should be regarded as a true acid nor any of the thermal or highly deactivated carbons as true bases. In pure water the acid carbons tend to adsorb hydroxyl ions, thereupon taking on a negative charge, the corresponding hydrogen ions are more or less loosely associated or bound. With the alkali-reacting carbons the reverse condition holds. In both cases the outer layer or atmosphere of ions is nevertheless capable of affecting the potential of the glass electrode and is perhaps more significantly capable of influencing the behavior of the carbon in the vulcanization of rubber and the drying of paints.

If, however, these carbons are immersed in a neutral salt solution instead of in distilled water, this powerful selective adsorption results in actual chemical decomposition. With an acid carbon immersed in a sodium chloride solution, the selective adsorption toward alkalies will promote hydrolysis, followed by adsorption of caustic soda and the release of free hydrochloric acid. The extent to which such hydrolysis occurs will depend on the pH value of the carbon and on the strength of the acid.

With basic types the reverse condition will obtain. In general, this behavior of carbon is not different from that of other colloids such as fuller's earth. It is believed, however, that the range (pH 2.6 to 10.6), continuity, and amenability to artificial control of the colloidal carbons here described are unique.

pH Properties and Electrical Charge

The incandescent particles of carbon in the luminous hydrocarbon flame are positively charged and tend to collect on a negatively charged plate or channel (*5*, *7*). When immersed in water these particles, by adsorption of hydroxyl ions, take on a negative charge. The reversal in charge of sugar chars reported by Kruyt (*3*) when the material had been heated to 1000° C., together with the change in adsorptive activity towards sodium hydroxide solution, may be regarded, in the light of data presented here, as an isolated point in a continuously varying sequence of adsorptive properties, depending on the surface structure of the material and reflected in its pH values.

pH Properties and Combined Oxygen

The chief ingredient in the volatile matter from carbon black is oxygen in the form of carbon oxides (*2*). After removal of volatile matter, elementary analysis shows that the change in composition consists essentially in the elimination of oxygen and, along with it, of carbon (*10*). The inference is that the bulk of the oxygen content of a carbon can be removed only in the form of carbon monoxide and carbon dioxide, and that it is combined on the surface of the carbon particle in the form of a complex which has been described by Rhead and Wheeler (*4*) as C_xO_y.

According to this view the change in pH which occurs after deactive heating and the differences in pH for various types of carbon (Graph 4) may be regarded as due to changes in the amount of C_xO_y complex associated with the pure carbon.

Removal of oxygen decreases the adsorptive activity of carbon toward alkaline substances and instead induces a selective adsorption towards acidic materials (*10*). This also may now be regarded as a single member of a continuous series, the pH and adsorptive properties of which vary with the combined oxygen content.

In view of the fact that colloidal thermal-decomposition carbons produced under reducing conditions, and heat-deactivated carbons invariably show alkaline pH values, it seems permissible to assume that, in the entire absence of combined oxygen, all members of the colloidal carbon family are characterized by alkaline or high pH values (provided that the particle size is small enough). The progressive addition of combined oxygen may then be regarded as gradually altering the adsorptive characteristics toward the acid side, in accordance with the trend of the pH–volatile matter curve; the latter is a measure of the increasing oxygen content. The flattening of the pH curve at a minimum value of approximately 2.6 suggests complete saturation of the carbon surface with C_xO_y radicals.

pH Properties, Combined Oxygen, and Dispersibility

Reference has been made to the fact that the low-pH carbons retard vulcanization of rubber and drying of paints and enamels. It must, however, be kept in mind that low pH properties, together with their concomitant high combined oxygen values, play an important constructive role in dispersion. Preliminary experiments carried out in these laboratories indicate that raising the pH of rubber carbons by means of heat treatment, while increasing the rate of vulcanization, may ultimately reach a point where dispersibility declines seriously.

Also, in the family of rubber carbons it is by no means those of the highest pH and the lowest volatile content which have given the best results in the reinforcement of rubber. Thus the central position of the family of rubber carbons in the classification diagram (Graph 4) may be looked upon as representing a compromise between high pH with diminished dispersibility on the one hand, and high volatile content involving low pH and excessive retardation of cure, on the other.

pH–C_xO_y and Reinforcement of Rubber

If there is any merit in the hypothesis (*6*) that the carbon reinforcement of rubber consists essentially in the formation of new physico-chemical complexes between individual macromolecules of the rubber substance and layers of carbon particles surrounding them, it would seem probable that the C_xO_y complexes are essential to the bond between carbon and rubber, thus also implying a relation between pH and reinforcement. According to this view and on the basis of a calculation of the oxygen required to form a monomolecular layer on the surface of a carbon particle of diameter 50μ (*10*), the value for such oxygen content (3 per cent) corresponds to a total volatile content of between 5 and 6 per cent.

This calculation is, of course, subject to various errors, but it invites the theoretical suggestion that the maximum reinforcement of rubber is not likely to occur if the combined oxygen content is depressed much below this level. On the other hand, combined oxygen much higher than this value probably plays no useful role in the development of what may be termed the "reinforcement bond."

The role of fatty acids in the dispersion of carbon in rubber is now recognized as important (*1, 6, 9*). The higher the C_xO_y content (with progressively lower pH), the higher appears to be the dosage of fatty acid required to bring out the full reinforcing properties of the carbon (*6*). It would thus seem that the C_xO_y contribution to the carbon-rubber bond can reach its highest effectiveness only if the rubber units (macromolecules) are, as it were, activated by the presence of long-chain polar bodies.

On the other hand, the optimum pH (or combined oxygen content) for a rubber carbon is in all likelihood influenced by the available content of fatty acid or its equivalent, in the mixing.

pH–C_xO_y and Paint Vehicles

The considerations respecting rubber apply with added force to many paint and ink vehicles. This derives from the fact that here mechanical work plays a relatively minor role, with the result that the attainment of complete colloidal dispersion necessitates the highest degree of compatibility between carbon and vehicle.

The heat bodying of linseed oil *in vacuo* leaves the dispersing characteristics of this widely used vehicle in a comparatively low state, whereas heat bodying under oxidizing conditions results in a varnish highly responsive, or activated, to colloidal carbon pigments of the proper chemical structure. The presence in considerable proportions of the oxygen-containing and generally acidic, highly polymerized substances in open-kettle-bodied linseed oils permits and indeed requires a correspondingly higher C_xO_y, or low pH, in the carbon with which it is ground.

The conclusion is inescapable that ease of dispersion, high "flow" characteristics, freedom from thixotropy, seeding, and other undesirable characteristics depend upon the development of maximum carbon vehicle as opposed to carbon-carbon bond, and that this in turn is governed by the combined oxygen (pH) of the carbon in conjunction with the presence of activating bodies in the vehicle.

The use of very low pH (2.6 to 3.0) carbons in ink and paint may involve retardation in drying, just as those rubber carbons with lower pH values retard vulcanization, so that a compromise may be preferable in this case as well. Often such a compromise need not influence the selection, as in inks where quick surface drying (skinning) is undesirable and in lacquers and some synthetic enamels where drying occurs either by evaporation or by a nonoxidizing mechanism. In such cases the pH of the carbon may be selected with sole regard to dispersion behavior, color, tone, and gloss of the finished product.

Fortunately carbons with a wide range of pH values are already available, so that a selection of the most compatible carbon for any given vehicle can now be made in a systematic, if empirical, manner.

Acknowledgment

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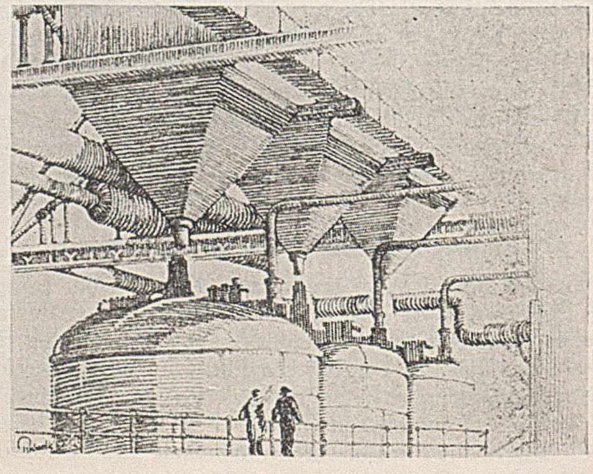

Packing Material for Fractional Distillation Columns

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A SINGLE-TURN helix packing material for distillation and extraction work was developed in this laboratory and found to have excellent efficiency and throughput (*2*, *3*, *4*, *6*). The helixes were usually made of No. 26 B. & S. gage wire in sizes from $^{1}/_{8}$ to $^{1}/_{4}$ inch (3.2 to 6.4 mm.) i. d. The efficiency increased and the throughput decreased as the inside diameter of the helix was decreased. Helixes made of No. 30 B. & S. gage wire, with an inside diameter of $^{3}/_{32}$ inch (2.4 mm.), have now been tested. The results show this packing material to be more efficient than any other used in this laboratory and yet to have a good throughput.

These $^{3}/_{32}$-inch diameter helixes exhibit to a marked degree a peculiarity found previously in other packings (*5*)—namely, a relation between efficiency and dryness of the packing prior to testing. The number of theoretical plates realized is much greater if the test is started with the packing thoroughly wet rather than dry. Apparently when the packing is first wet, the subsequent condensate spreads uniformly over the entire wet surface; on a dry packing the flow of condensate tends to be somewhat agglomerated or coalesced. This effect is usually greater with the more efficient packings but is probably true of all packing materials. Thorough wetting of the packing is best accomplished by deliberate flooding of the column at the start of the distillation or test. Pouring the material to be distilled down through the top of the column has not been found as effective.

This new packing was tested in two different columns. Each column was made of glass and had an inside diameter of 0.79 inch (20 mm.). The stillheads were the regular type used in the research laboratories here. The height of packed section for the first column was 23.5 inches (60 cm.) and for the second 111 inches (282 cm.). The test liquid was a binary mixture of *n*-heptane and methylcyclohexane; alpha = 1.07 (*1*). All tests were at total reflux. Whenever possible the original concentrations of the two components were chosen so that neither the distillate nor the still would be too rich in one component when equilibrium was established. Because of the difficulty of analysis, errors of considerable magnitude may develop if the still is too rich in methylcyclohexane or the distillate too lean. The rate of distillation was measured by opening the take-off stopcock and timing the condensate

TABLE I. EFFICIENCIES OF $^{3}/_{32}$-INCH SINGLE HELIXES IN A COLUMN WITH 0.79 INCH INSIDE DIAMETER AND 23.5 INCHES OF PACKED SECTION

Test No.	Time between Tests	Rate of Boiling	*n*-Heptane Distillate	*n*-Heptane Still	No. of Theoretical Plates in Column	H. E. T. P.[b]	H. E. T. P.[b]
	Hours	*Cc./hr.*[a]	*Mole per cent*	*Mole per cent*		*In.*	*Cm.*
Column Started with Packing Dry							
1	4	430	54.2	31.2	14.0	1.7	4.3
2	1	430	51.4	32.3	11.5	2.0	5.1
3	2	690	50.5	31.2	12.0	1.95	5.0
4	2	780	51.4	31.0	12.5	1.9	4.8
5	2.5	750	53.0	29.5	14.5	1.6	4.1
Column Deliberately Flooded							
6	2.5	785	55.5	27.3	18.0	1.3	3.3
7	2	720	56.0	27.0	18.5	1.25	3.2
8	2.5	340	60.3	25.5	22.0	1.05	2.7
Column Shut Down and Let Stand Overnight to Dry Packing; Restarted and Deliberately Flooded							
9	3.5	1350[c]	54.7	29.0	16.0	1.45	3.7
10	4	800	54.9	27.3	17.5	1.35	3.4
11	2	300	62.3	27.0	22.0	1.05	2.7
12	2	360	61.7	26.2	22.5	1.05	2.7
13	5	1140	53.6	24.9	18.5	1.25	3.2
Column Shut Down and Let Stand Overnight to Dry Packing; Column Restarted and Packing Wet by Pouring Liquid in from Top							
14	4	600	55.5	29.5	16.0	1.45	3.7
15	1.5	780	56.8	28.7	17.5	1.35	3.4
Column Shut Down and Let Stand Several Days; Restarted and Deliberately Flooded							
16	3.5	750	55.2	29.2	16.0	1.45	3.7
17	2	750	58.7	29.0	18.5	1.25	3.2
Column Shut Down and Let Stand Overnight to Dry Packing; Restarted and Deliberately Flooded							
18	2.5	800	60.6	27.6	20.5	1.15	2.9
19	5.5	880	60.6	27.6	20.5	1.15	2.9
Column Shut Down and Let Stand Overnight to Dry Packing; Restarted with Packing Dry							
20	4	940	50.0	27.6	14.5	1.6	4.1

[a] The actual measured rate.
[b] Height equivalent to a theoretical plate.
[c] At higher rates the column flooded.

TABLE II. EFFICIENCIES OF $^{3}/_{32}$-INCH SINGLE HELIXES IN A COLUMN WITH 0.79 INCH INSIDE DIAMETER AND 111 INCHES OF PACKED SECTION

Test No.	Time between Tests	Rate of Boiling	*n*-Heptane Distillate	*n*-Heptane Still	No. of Theoretical Plates in Column	H. E. T. P.	H. E. T. P.
	Hours	*Cc./hr.*[a]	*Mole per cent*	*Mole per cent*		*In.*	*Cm.*
Column Started with Packing Dry							
1	4	1200	90.3	15.5	58	1.9	4.9
2	5	120	89.6	15.5	57	1.9	4.9
Column Shut Down and Left Overnight to Dry Packing; Restarted and Deliberately Flooded							
3	6	1260	95.8	7.4	84	1.3	3.4
4	2	1260	97.4	5.0	97	1.1	2.9
5	5	660	97.2	3.7	100	1.1	2.8
6	5	280	96.9	3.4	100	1.1	2.8
Column Shut Down to Allow Packing to Dry; Restarted with Packing Dry							
7	6	770	60.9	4.8	51	2.2	5.5
Column Shut Down to Allow Packing to Dry; Restarted with Fresh Binary Solution and Packing Dry							
8	8	880	70.4	14.0	39	2.8	7.2
9	10	900	68.6	10.5	43	2.6	6.6
10	5	900	67.4	10.5	42	2.6	6.7
11	6	1020	63.0	6.6	47	2.4	6.0
12	7	1000	58.0	6.6	44	2.5	6.4
Column Deliberately Flooded							
13	9	920	79.9	2.2	77	1.4	3.7
Column Shut Down to Allow Packing to Dry; Restarted and Deliberately Flooded							
14	9	960	99.9	8.8	...	...	...
15	2	900	98.8	6.9	103	1.1	2.7
16	7	860	98.8	3.8	113	1.0	2.5
17	3	1080	95.4	2.2	101	1.1	2.8
18	5	1260	89.0	0.8	102	1.1	2.8

[a] Actual measured rate.

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[1] Present address, Standard Oil Development Company, Elizabeth, N. J.

TABLE III. PRESSURE DROP FOR 3/32-INCH SINGLE HELIXES IN A COLUMN WITH 0.79 INCH INSIDE DIAMETER AND 111 INCHES OF PACKED SECTION

Rate of Boiling[a] *Cc./hr.*	Pressure Drop *Mm. Hg.*	Rate of Boiling[a] *Cc./hr.*	Pressure Drop *Mm. Hg*
580	11	900	18
624	14	1000	22
780	21	1120[b]	28
810	19		

[a] Actual measured rate for *n*-heptane–methylcyclohexane mixtures at total reflux.
[b] This rate is approaching flooding.

for one minute. This is a minimum value, since the take-off tube did not catch all the condensate and some condensation took place below this tube.

The results (Tables I to III) are given in some detail so that the effect of preliminary wetting and other variables may be observed. To ensure constancy of operation, certain of the tests were conducted for as long as 36 hours. The wetting of the packing by flooding was accomplished by raising the still heat so that the rate of distillation was too great for the capacity of the column. As soon as the flood had subsided, by momentarily shutting off the still heat, the latter was set for the desired rate of distillation. The data in the tables represent consecutive time intervals of continuous operation except where otherwise noted.

These results show high efficiency combined with reasonable throughput and low-pressure drop per theoretical plate (approximately 0.3 mm. of mercury). The maximum measured rate of condensation in the 23.5-inch column was 1350 cc. per hour, and in the 111-inch column, 1260 cc. with *n*-heptane–methylcyclohexane mixtures. These figures correspond to 0.86 and 0.80 feet per second vapor velocity, respectively. The actual condensation rate is estimated to be 8 to 23 per cent greater.

With this packing, columns of the order of 100 theoretical plates can be built in a laboratory of average height. Such columns have the advantages of simple packed columns, including cheapness, ease of operation, simplicity of operation, ruggedness, and low pressure drop per theoretical plate.

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RECEIVED May 28, 1937.

Isoöctane Production by Simultaneous Polymerization and Hydrogenation

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Universal Oil Products Company, Riverside, Ill.

RECENTLY a new simultaneous reaction, hydropolymerization, of olefinic hydrocarbons was described (*3*). This reaction takes place in the presence of mixed catalysts consisting of a combination of polymerizing and hydrogenating agents. In the presence of such mixed catalysts and hydrogen the simultaneous polymerization and hydrogenation of olefinic hydrocarbons take place, resulting in the formation of hydrogenated polymers; this reaction was therefore called "hydropolymerization." In the study of different catalysts adaptable for this reaction particular attention was given to phosphoric acid, because of its successful use in the polymerization of olefins (*2*) and the development of the industrial process of catalytic polymerization of cracked gases (*1*). The most interesting and important hydrocarbon submitted to hydropolymerization was isobutylene.

By hydropolymerizing isobutylene in the presence of a solid phosphoric acid–nickel oxide–iron catalyst under hydrogen pressure, it was possible to obtain direct a mixture of isomeric octanes.

The experiments were conducted in a steel rotating autoclave, 1 liter in capacity. The catalyst and the liquid isobutylene were weighed in a steel liner which was afterwards placed in the autoclave.

In each experiment 80 kg. per sq. cm. of hydrogen were used. The liquid products of the experiment were fractionated through a Podbielniak column. The gases were analyzed by a combined Göckel and Podbielniak method.

Isobutylene was obtained by catalytic dehydration of isobutyl alcohol over an alumina catalyst at 350° C. The catalyst was prepared by mixing 1.5 parts of solid phosphoric acid catalyst (*1*) with 1 part of reduced iron and 0.5 part of nickel-oxide. Twenty grams of this mixed catalyst were used in each experiment. The following table represents the results of two experiments:

	Expt. 1	Expt. 2
Temperature, ° C.	250	300
Reaction time, hours	12	6
Isobutylene taken, grams	108.7	117.0
Liquid product obtained, grams	100.0	112.5
Isobutylene conversion, %	92	96
Pressure drop during expt., kg./sq. cm.	36	35

The results of the investigation of the product of each experiment are as follows:

	Expt. 1	Expt. 2
Unsatd. content of product, %[a]	10	9
Octane fraction (b. p., 100–125° C.), % of total liquid product	46	56
Octane No. of octane fraction	83[b]	84
Gases from the reaction, %:		
Hydrogen	95.8	95
Butane	4.2	5.0

[a] Determined by sulfuric acid method.
[b] The fraction of this product boiling at 100–110° C. had an octane number of 100. The comparatively low octane number (83) of the total octane cut is probably due to the formation of isomeric octanes other than 2,2,4-trimethylpentane.

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RECEIVED May 10, 1937. Presented under the title of "Hydropolymerization" before the Division of Organic Chemistry at the 92nd Meeting of the American Chemical Society, Pittsburgh, Pa., September 7 to 11, 1937.

ELECTRODE POTENTIALS

Relation to Corrosion of Alloys and Metals in Lubricating Oils

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AND JOHN K. ANTHONY
The Cleveland Graphite Bronze Company,
Cleveland, Ohio

Data are presented on the electrode potentials of various bearing metals and alloys in several lubricating oils. Potentials were found to start at about 110° C. in unstirred cells and at about 70° C. in stirred cells. Voltage as high as 1.1 volts at 170° C. was found. Potentials varied considerably with temperature. A reversal of polarity was found in several instances. The possibilities of correlating these potentials and their variations with the problem of bearing corrosion are discussed. It is pointed out that much work is yet to be done before any definite conclusions may be drawn.

CORROSION of metals dates from the time when man first prepared and used them. It is not the purpose of this paper to discuss the various prevailing theories of corrosion but rather to point out a possible factor which appears to have been thus far overlooked by workers in this field—namely, the electrode potential of metals and alloys in contact with oils and the resulting electromotive force of the various connected parts.[1] The purpose of this work is to determine (*a*) whether a measurable electromotive force exists, and (*b*) if it does exist, to measure it, using several metals and alloys in different oils at various temperatures. For example, in the automobile engine much work has been done to explain and eliminate corrosion. However, work thus far has not taken into consideration that each part is made up of various alloys or metals, and all of these parts are connected in such a way as to form a network of electrodes in contact with oil. Each metallic part has a definite potential against its surroundings, which ordinarily is oil. This potential may be large or it may be so small that it is immeasurable by the best potential measuring instruments. However, whichever it may be, the final result is the presence of a large number of cells, each contributing its electromotive force caused by various chemical reactions which may prove destructive to the surfaces of the various metallic parts.

For example, let us take a bearing made of metal *X* and a crankshaft composed of metal *Y*. These two are contacted by some oil, and the whole setup acts as a galvanic cell. The following results may be expected as the cell works: (1) *X* or *Y* may, because of its electrolytic solution pressure, dissolve and form a conducting solution. (2) *X* or *Y* may serve as electrodes at which some of the components of the oil are oxidized, and then these oxidation products may chemically attack the metals in contact. (3) The oxidation products may cause further chemical reactions in the oil which may result in corrosive substances. Thus it may be possible that the electrode potential is either directly or indirectly responsible for some of the corrosion in the case illustrated.

Experimental Procedure

TEMPERATURE CONTROL. A regular 4-liter Dewar vessel fitted with a stirrer and knife-edge type of heater was filled with mineral oil. This served as an outside temperature controlling bath. It was possible when desired to hold the temperature even at 170° C. to ±0.2° C.

THE CELL. A Pyrex glass beaker served as a container for the cell. It was held in place by suspending it from a Bakelite board that was securely fastened to the top of the wooden frame holding the Dewar vessel (Figure 1). In order to avoid any stray electromotive forces, the oil in the cell was heated entirely by conduction of heat from the outside temperature bath. A stirrer in the cell assured uniform temperature throughout. The electrodes were approximately 5 cm. long, 0.9 cm. wide, and 1 mm. thick, and were held tightly about 1 cm. apart. At first it was thought desirable to hold the electrodes quite close together in order to approximate the actual working conditions in an automobile engine. After numerous runs when the electrodes were held 0.007 to 0.015 cm. apart, it was found almost impossible to obtain any reproducible and therefore trustworthy results owing to poor oil circulation. In future work a cell will be constructed with moving electrodes, making it possible to reproduce the actual working conditions of an engine. Only

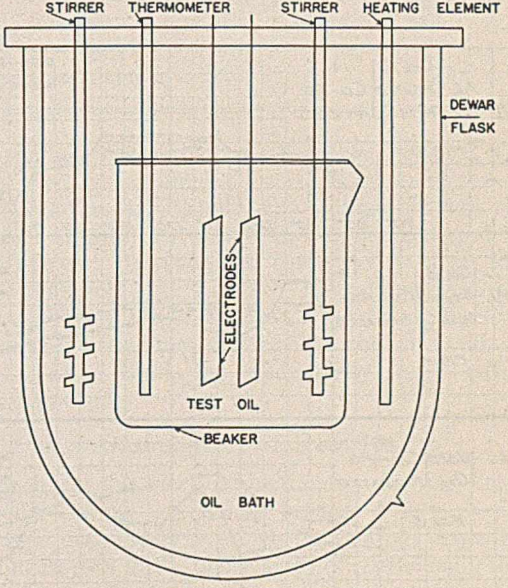

FIGURE 1. DIAGRAM OF CELL ASSEMBLY

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[1] A suggestion of this possibility was first made about two years ago during a conference by Zay Jeffries, General Electric Company, Cleveland, Ohio.

TABLE I. EFFECT OF TEMPERATURE ON RELATIVE CONDUCTIVITY OF OILS IN VARIOUS CELLS

Cell	T °C. (First Cycle)					T °C. (Second Cycle)				
	140	155	170	155	140	140	155	170	155	140
Al$^-$–used oil–Cd-Ag$^+$ annealed	1.3	3.0	3.6	1.6	1.1	1.3	2.1	3.4	3.1	2.7
Al$^-$–oil B–Cd-Ag$^+$ annealed	1.3	1.6	2.7	2.3	1.6	1.2	1.6	2.1	1.7	1.1
Al$^-$–oil A–Cd-Ag$^+$ annealed	1.1	2.4	3.9	2.4	1.6	1.1	3.1	4.1	3.9	1.6
Steel$^+$–oil B–Cd-Ag$^-$ annealed	1.1	1.2	2.9	1.9	1.2	1.3	2.2	2.8	2.3	1.4
Steel$^+$–oil B–Cd-Ag$^-$ annealed	1.2	2.4	3.8	2.8	2.0	2.2	2.8	4.0	3.4	2.2
Steel$^+$–used oil–Cd-Ag$^-$ unannealed	2.0	4.1	6.1	3.9	3.0	3.3	4.7	8.5	6.7	5.2
Steel$^+$–used oil–babbitt metal$^-$	1.5	1.5	3.0	2.1	1.7	1.1	1.7	3.6	3.4	1.9
Cu$^+$–used oil–Cd-Ag$^-$ unannealed	2.5	3.3	6.0	5.0	5.0	5.8	8.5	11.3	8.9	7.2
Steel$^+$–used oil–Al$^-$	1.4	2.1	3.9	2.8	2.2	2.1	3.1	5.0	3.3	2.3

about half of the electrodes were allowed to dip into the oil, in order to eliminate any electromotive force that might be due to connecting metals. Heavy copper leads, attached to the electrodes, passed through a cork which was held in position by fitting it tightly in the Bakelite board.

THE POTENTIOMETER. Since oils exhibit very high resistance, it was necessary to use a sensitive galvanometer in order to cope with the low microamperage of the cell. A type H. S. Leeds & Northrup reflecting galvanometer was available, and, although not the most adaptable one Leeds & Northrup make, it gave sufficiently qualitative results to justify its use. In future work a galvanometer will be used which will have specifications to meet the requirements of the new cell in which the metals serving as electrodes will be as close as they are in their natural working conditions. The galvanometer was mounted on a solid wall and was used with a lamp and scale at 1 meter distance. The potentiometer used was the Leeds & Northrup type K_2.

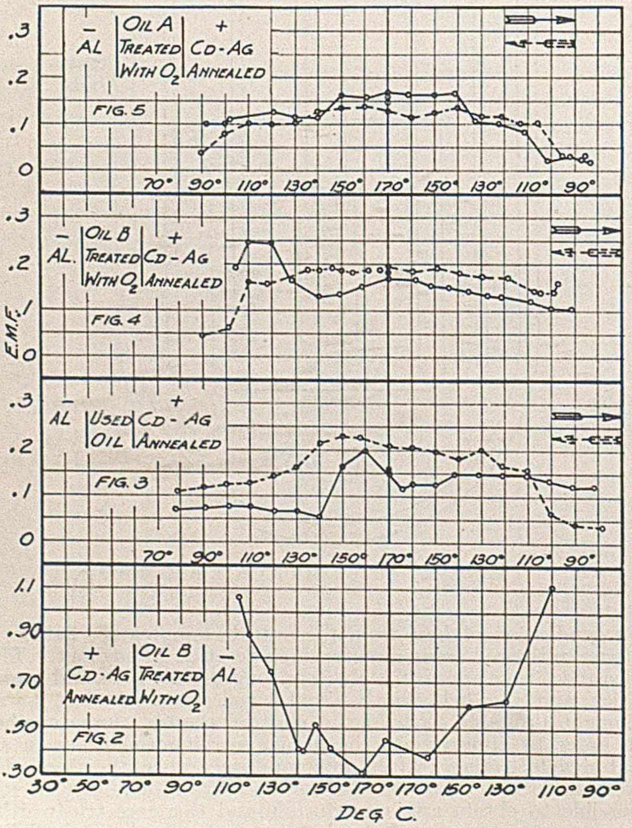
CONDUCTIVITY. The conductivity was determined at various times in order to obtain a few comparative values. Two methods were employed: (*a*) A direct current of 120 volts was passed through a conductivity cell, and the resulting amperage was determined. (*b*) A regular Leeds & Northrup Kohlrausch bridge using two-stage amplification was used. However, since only qualitative results were obtained at this time, it was thought desirable to report only in relative terms the effect of temperature on conductivity. This was done separately for each cell by using the term I/E as determined from the total deflection of the galvanometer and the electromotive force. For simplicity the conductivity at 120° C. was made unity (Table I).

MATERIALS. The oils used in this investigation consisted chiefly of new oils A and B and used oil. The used oil was obtained by pipetting the oil out of 40 V-8 Fords in which the oil was used for at least 500 miles, but less than 1000 miles. All of the forty fractions were mixed in order to give a better average used oil. No attempts were made to re-refine or to dry the oils. For a great many of the experiments the A and B oils were treated with oxygen. This was accomplished by bubbling oxygen through the oil for 24 hours at about 170° C. A definite darkening of the oil occurred in each case due to the oxidation. The constants of these oils are given in Table II. For some of the work, new oils C and D were also used.

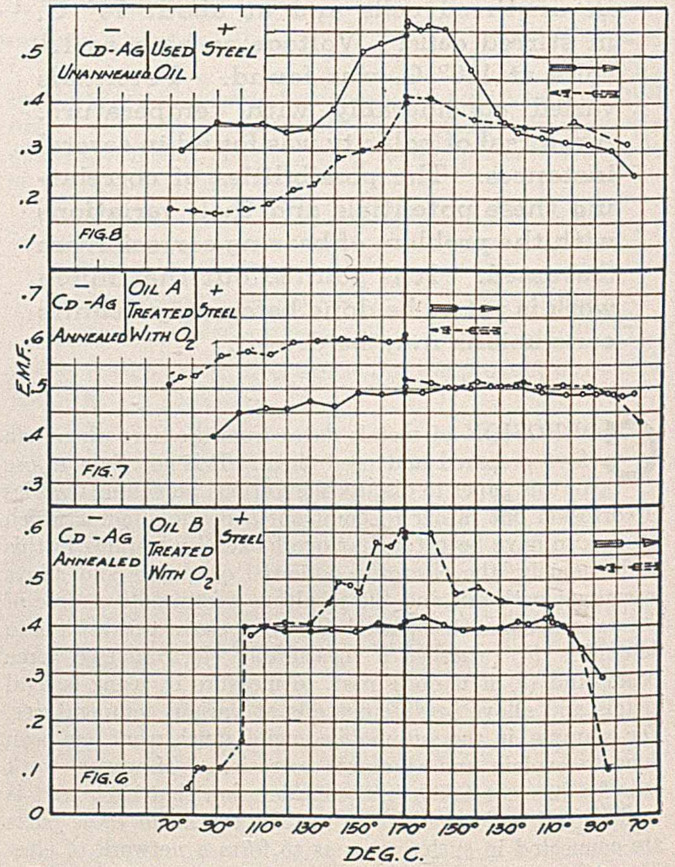
TABLE II. OIL CONSTANTS

	Oil A	Oil A (Oxidized)	Oil B	Oil B (Oxidized)	Used Oil
Gravity at 60° F., °A. P. I.	27.7	27.3	29.4	28.1	26.8
Flash point, ° F.	440	445	435	440	240
Fire point, ° F.	505	500	495	500	360
Saybolt Universal viscosity, sec.:					
100° F.	439	547	445	605	431
210° F.	65	67	66	73	64
Viscosity index	116	106	116	109	115
Carbon residue, %	0.50	0.60	0.20	0.30	0.91
Sediment, %	....	....	....	....	0.24

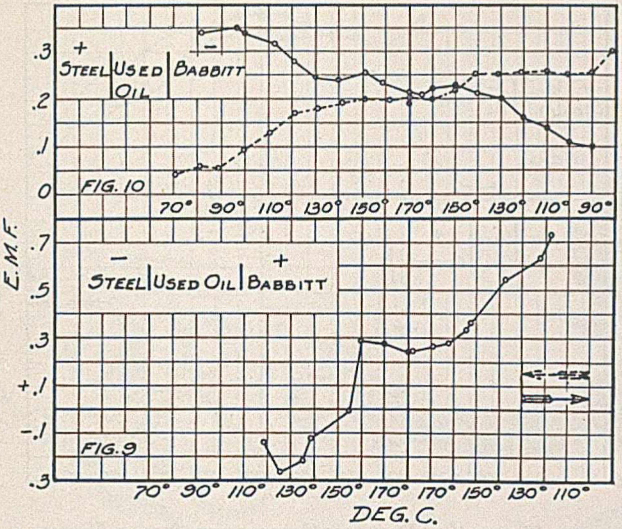
Three types of regular production bearing alloys were furnished by The Cleveland Graphite Bronze Company. These



FIGURES 2 TO 5. DATA ON ALUMINUM-OIL-CADMIUM-SILVER CELLS



FIGURES 6 TO 8. DATA ON CADMIUM-SILVER-OIL-STEEL CELLS



FIGURES 9 AND 10. DATA ON STEEL–OIL–BABBITT METAL CELLS

alloys were babbitt metal, cadmium-silver, and copper-lead. The annealing of some of the cadmium alloys was carried on at about 175° C. The steel and aluminum electrodes were made of steel and aluminum automobile parts. Pure copper served as a copper electrode.

PROCEDURE. The speed of the stirrer and the amperage of the heaters were controlled manually by rheostats. No readings of the electromotive force were taken until the temperature of the cells became constant. At first each cell was heated without regular stirring from room temperature to 170° C. or above and then cooled down to room temperature. Readings of the electromotive force were taken every 10° C., both when increasing and decreasing the temperature. Later, to learn the effect of efficient and regular stirring and also the effect of heating and cooling on the recovery of the system, it was decided to run continuously through two complete cycles; that is, the oil was (*a*) heated from room temperature to 170° C. or above, (*b*) cooled to room temperature, (*c*) again heated to 170° C., and (*d*) cooled to room temperature. As before, the recordings were taken for every 10° C. change in temperature, and check readings were taken at the highest temperatures. Efficient stirring was used for both of the cycles. A complete run required 12 to 20 hours.

Results

To simplify the discussion, the more important data were graphed using only the electromotive force and temperature. In each single-cycle run the electromotive force obtained on heating up to 180° C. appears on the left of the voltage axis; the electromotive force obtained on cooling appears on the right of the axis. The graphs of the two-cycle runs are plotted as follows: The first cycle is identical with a single-cycle run, but the second cycle is designated by a broken line; its electromotive force on heating appears on the right and that of the cooling appears on the left of the voltage axis. In each graph the original polarity of the electrodes is indicated. Data for one of the two-cycle runs appear in Table III.

The results of this work may be expressed in several ways. For convenience, various electrode systems will be taken individually at 170° C. Equilibrium conditions are probably most easily attained, at this temperature, partly because of low viscosity and partly because of higher conductivity conditions prevailing.

The cell aluminum–oil–cadmium-silver (Figures 2 to 5) gave about 0.2 volt. The electromotive force of the two-cycle runs reproduced itself almost exactly. Figure 2 shows the irregularities when stirring is not employed.

In the cell cadmium-silver–oil–steel (Figures 6 to 8) the cadmium-silver was negative; in the cell used for Figures 2 to 5 it was positive. Since the unannealed electrodes were heated to 170° C. during the first cycle, they should be considered as annealed during the second cycle. The conductivity during the second cycle was from 20 to 40 per cent greater than during the first cycle. This was the experience with all the following cells.

During both of the cycles the steel–oil–babbitt metal cell (Figure 10) exhibited a decrease in the electromotive force on cooling. When no stirring was employed, the opposite effect was found (Figure 9). This cell also had a strong tendency to reverse itself in polarity.

As would be expected, a relatively flat curve was obtained for the cadmium-silver–oil–cadmium-silver annealed cell (Figures 11 to 14) for the two-cycle run; very irregular curves with frequent changes in polarity were obtained for the single runs.

Figures 15 and 16 illustrate cells with other metals.

TABLE III. ELECTROMOTIVE FORCE OF UNANNEALED CADMIUM-SILVER ALLOYS AGAINST STEEL IN USED OIL AT VARIOUS TEMPERATURES

Time	Temp., ° C.	E. M. F.	Time	Temp., ° C.[a]	E. M. F.
7:40 A. M.	20	...	2:00 P. M.	29	...
7:50	60	...	2:08	59	...
8:02	75	0.30	2:13	76	0.314
8:13	90	0.359	2:17	89	0.372
8:19	100	0.356	2:24	99	0.366
8:24	109	0.357	2:29	109	0.347
8:29	120	0.337	2:35	120	0.347
8:35	129	0.336	2:40	129	0.356
8:43	139	0.385	2:47	139	0.364
8:50	150	0.505	2:55	150	0.507
8:58	159	0.526	3:07	160	0.408
9:05	169	0.547	3:15	170	0.407
9:10	170	0.567	3:19	170	0.408
9:11	170	0.566	3:22	170	0.407
9:18	165	0.556	3:35	159	0.314
9:23	161	0.566	3:50	151	0.304
9:29	153	0.554	4:00	141	0.289
9:40	143	0.468	4:11	131	0.232
9:53	132	0.381	4:22	122	0.217
10:04	123	0.342	4:37	112	0.191
10:17	113	0.331	4:54	102	0.181
10:34	103	0.322	5:10	91	0.170
10:51	93	0.313	5:24	80	0.175
11:10	83	0.300	5:34	71	0.18
11:21	73	0.249	5:50	61	0.18
11:31	64	0.22	6:04	55	
11:40	58	0.23	6:14	51	
11:50	53				
11:58	49				

[a] Allowed to cool slowly to 29° C.

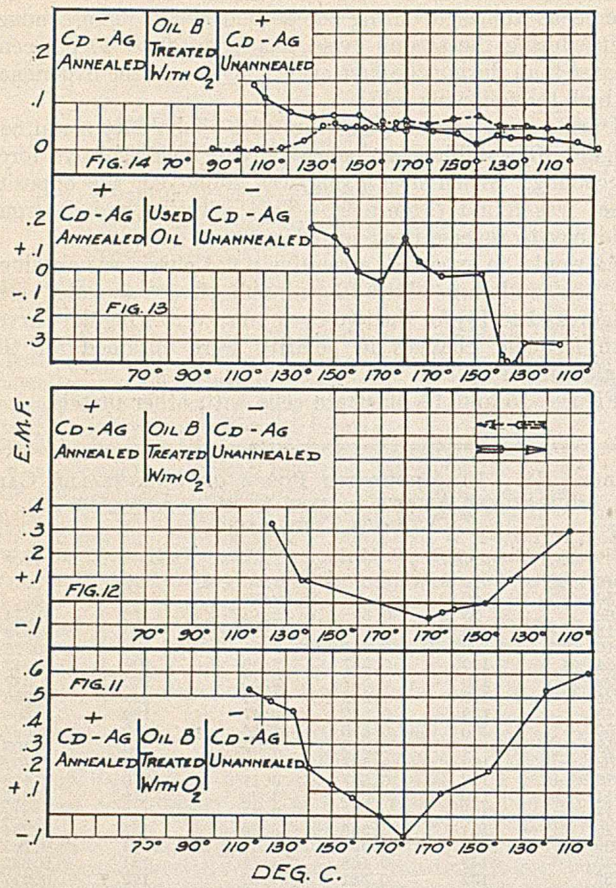
When various new untreated oils, including A, B, C, and D, were tried with different electrode systems, they gave electromotive forces. Usually, the voltage did not appear until a temperature above 100° C. was reached, and it was of small extent. However, the conductivity of all the oils was very different. For instance, the voltage in C and D oils was less than 0.1 volt at 170° C., but the conductivity in C oil was about ten times greater than that in D oil. In A oil, on the other hand, the conductivity was about twice as great as in C oil.

Discussion of Results

Inasmuch as this work is preliminary in this field, one cannot offer definite conclusions because it is impossible as yet to reproduce every step in the various experiments. This is due in part to the uncertainty of reproducing the oils, particularly the used oil. The following general observations, however, seem to be warranted by the experimental data:

All of the various combinations of metals and alloys gave rise to an electromotive force in the oils thus far used.

In almost all of the single runs where there was a change of temperature but no stirring, the electromotive force was greater at lower than at higher temperatures. At correspondingly high temperatures the electromotive force of a single-cycle run agreed usually well with that of a two-cycle run. This is probably due to high diffusion when the viscosity is low at high temperature.

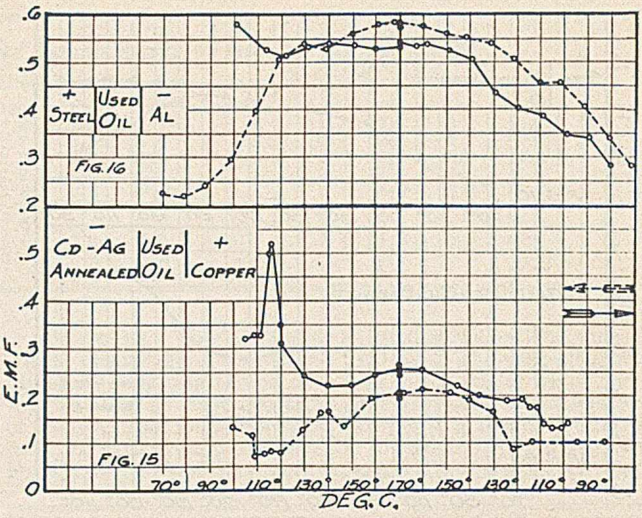


Figures 11 to 14. Data on Cadmium-Silver-Oil-Cadmium-Silver Cells

In almost all of the single-cycle runs the electromotive force started and stopped approximately at 115° to 120° C. However, in the case of two-cycle runs the electromotive force appeared at a much lower temperature and usually persisted on cooling to an even lower temperature. The presence of water in all of the oils used may be a factor in explaining this behavior.

Steel in different combinations with annealed and unannealed cadmium alloys exhibited a positive potential. However, steel against aluminum showed a normal behavior as in water. Steel in combination with babbitt metal exhibited a greater electrolytic solution pressure under certain conditions. This may explain why in some cases a steel crankshaft becomes pitted when a motor has been idle for a long time.

In order to relate corrosion and electromotive force, it is necessary to know the conductivity of the oils used. It was found that the conductivity of the oils increased considerably with temperature. This is due to many factors. Some of the more important are decrease in viscosity, presence of water, increase in the oxidation products which may yield ionized substances, etc. Since the amount of chemical reaction is proportional to the amperage it is possible to have (*a*) a high electromotive force and low amperage and (*b*) low electromotive force and much higher amperage than in case *a*. Both of these cases have been demonstrated during this work. In used oil the amperage was always much higher than for the same voltage with A and B oils. When two-cycle runs were made, the amperage was always greater during the second cycle by 20 to as much as 100 per cent in spite of the fact that the electromotive forces were nearly equal. This means a decrease in resistance which results in higher conductivity (Table I). This property ought to be of importance to the oil chemist because with each heating the oil may become more and more conductive, which may result in greater and greater corrosion, regardless of whether the corrosion is due to galvanic action or to straight chemical reaction or to both. To inquire into the cause of what contributes to the conductivity of oil is to inquire into the physical and chemical make-up of the oil itself. (In the case of used oil the colloidal particles no doubt contribute a great deal to the high conductivity through cataphoresis, and this effect would probably be more evident during the second cycle.)



Figures 15 and 16. Data on Cells with Other Metals

No doubt many substances added to oils for various reasons may prove detrimental if they are conductive by themselves, or if they are easily converted into good conductors. This fact is shown by the work on entirely new and untreated oils. For example, if such an oil as C starts with ten times the conductivity of oil D, there is apt to be great corrosion immediately, and such an oil may prove to be almost useless in a short time. However, it is also quite possible to have a new oil with a very high resistance, which will contain substances that are easily converted into conductive solutions; the final result will be the same as the example just given.

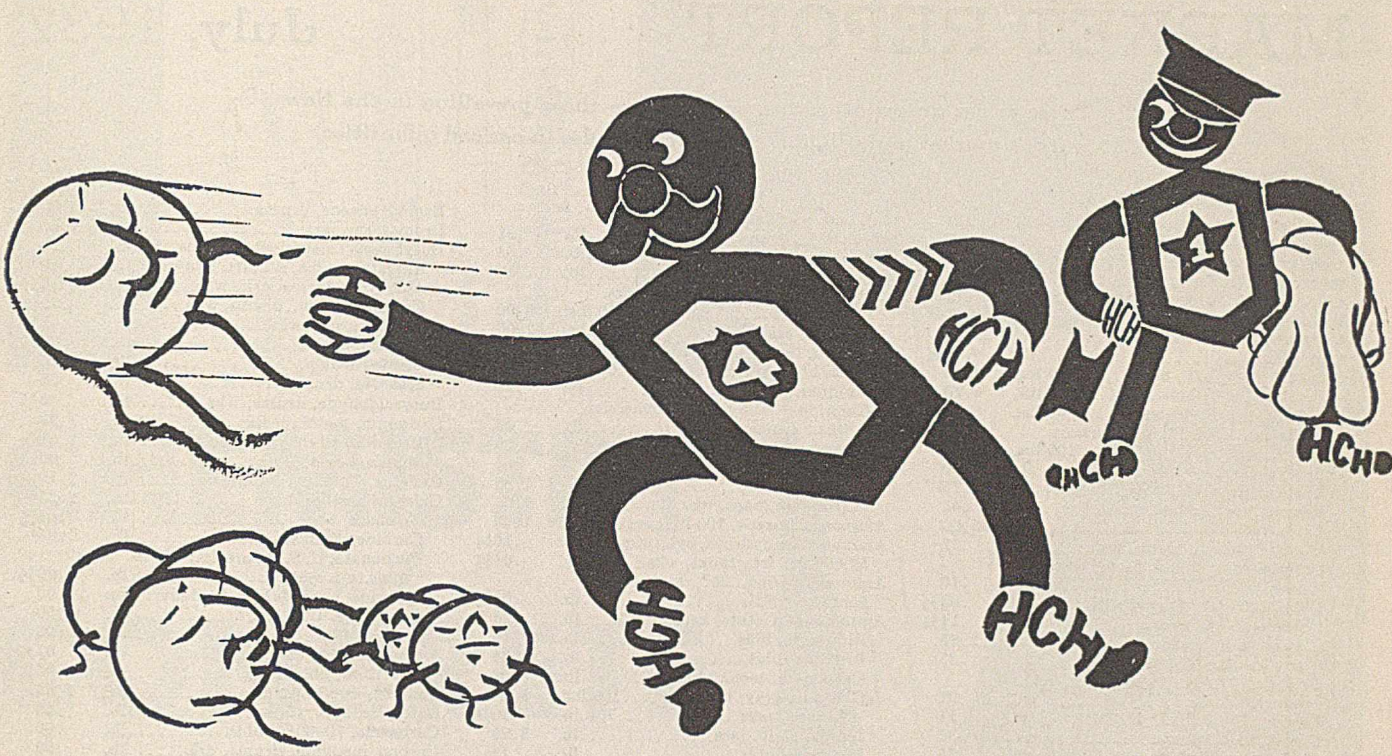
Much work needs to be done to correlate corrosion in oils (with and without the various agents commonly added to them) with such factors as conductivity and electrode potentials of metals and alloys in contact with them, and further to correlate these factors with actual service conditions. Undoubtedly some of these properties will be used eventually to characterize oils just as much as viscosity is today.

For the present these experimental data do not permit the discussion of the effects of such factors as polarization and oxygen gas electrodes. The presence of either one of them or both would help to explain some of the results.

A. P. Anderson of the Shell Petroleum Corporation called the writers' attention to the fact that Wawrziniok [*Automobiltech. Z.*, 35, 428–30, 600–1 (1932); *Chem. Abstracts*, 27, 407, 1153–4 (1933)] published some work on "Corrosion of Automobile Engine Parts Caused by Lubricating Oils," in which it is claimed that "corrosion of motor parts may be due to galvanic currents generated between different metal parts, the oil serving as electrolyte."

The summary of Wawrziniok's data in *Chemical Abstracts* reveals that his results are of the same order as the present ones.

Received November 18, 1936.



DON'T KILL 'EM - STUN 'EM

You can poison the u h m* in cracked gasoline with sulfuric acid and drag them out feet first but some of the gasoline and a lot of its anti-knock value go to the morgue with them

That's mighty expensive It's better just to stun them

That's what the chemical sergeant does He marches in when the job is too tough for the chemical cop He paralyzes the u h m and the o m** in the air so they can't get together and form gumbugs The molecules come to later and do their proper work in the engine

The chemical sergeant saves the cost of acid, saves loss of gasoline, preserves anti-knock value

Saves you money

*u h m Unsaturated hydrocarbon molecules
**o m Oxygen molecules

Universal Oil Products Co
Chicago, Illinois

Dubbs Cracking Process
Owner and Licensor

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MARKET REPORT

July, 1937

These prices unless otherwise specified are those prevailing in the New York market, July 15, for commercial grades in carload quantities.

Acetaldehyde, drums, c/l., wks.	lb.	.14
Acetaldol, 50-gal. drums	lb.	.27
Acetamide, tech., c/l., drums	lb.	.32
Acetanilide, U. S. P., powd., bbls.	lb.	.25
Acetic anhydride, drums, frt. allowed	lb.	.13
Acetone, drums, wks., c/l., frt. allowed	lb.	.06
Acetphenetidin, bbls.	lb.	1.30
Acid, abietic	lb.	.09¾
Acetic, 28%, c/l., bbls.	100 lbs.	2.53
56%, c/l., bbls.	100 lbs.	4.75
Glacial, c/l., drums	100 lbs.	8.70
Glacial, U. S. P., c/l., carboys	100 lbs.	13.75
Acetylsalicylic, U. S. P., bbls.	lb.	.50
Anthranilic, tech., bbls.	lb.	.75
Benzoic, tech., bbls.	lb.	.43
Boric, tech., bbls.	ton	95.00
Butyric (99%), drums, wks.	lb.	.22
Chloroacetic, mono-, tech., bbls., wks.	lb.	.16
Chlorosulfonic, drums, wks.	lb.	.03½
Chromic, 99%, drums	lb.	.14¾
Cinnamic, bottles	lb.	2.85
Citric, U. S. P., cryst., bbls.	lb.	.25
Cresylic, H. B., c/l., wks., frt. equal, drums	gal.	.91
Formic, 90%, cbys., N. Y.	lb.	.11
Furoic, tech., drums	lb.	.35
Gallic, tech., bbls.	lb.	.65
H, bbls., wks.	lb.	.50
Hydriodic, 57%, 5-lb. bot.	lb.	2.65
Hydrobromic, 10%, U. S. P., cbys., wks.	lb.	.18
Hydrochloric, 20°, tanks, wks.	100 lbs.	1.10
Hydrofluoric, 30%, bbls., wks.	lb.	.07
60%, bbls., wks.	lb.	.15
Hydrofluosilic, 35%, bbls., wks.	lb.	.10½
Hypophosphorus, 30%, U. S. P., 5-gal. demis	lb.	.75
Koch, bbls.	lb.	.36
Lactic, 22%, dark, bbls.	100 lbs.	2.50
44%, light, bbls., wks.	100 lbs.	6.50
Linoleic, drums	lb.	.16
Maleic, powd., drums	lb.	.30
Mixed, tanks, wks.	N unit	.06½
	S unit	.0085
Naphthenic, S. V. 120–200, drums	lb.	.07
Naphthionic, tech., bbls.	lb.	nom.
Nitric, C. P., cbys.	lb.	.10½
Nitric, 36°, c/l., cbys., wks.	100 lbs.	5.00
Oxalic, bbls., wks.	lb.	.10¾
Phosphoric, 50%, U. S. P.	lb.	.12
Picramic, kegs	lb.	.65
Picric, bbls., c/l.	lb.	.35
Pyrogallic, tech., bbls.	lb.	.90
Salicylic, tech., bbls.	lb.	.33
Sebacic, tech., drums	lb.	.37
Stearic, d. p., bbls., c/l.	lb.	.12½
Sulfanilic, tech., 250-lb. bbls.	lb.	.17
Sulfuric, 66°, c/l., cbys., wks.	100 lbs.	1.25
66°, tanks, wks.	ton	15.50
60°, tanks, wks.	ton	12.00
Oleum, 20%, tanks, wks.	ton	18.50
Tannic, tech., bbls.	lb.	.26
Tartaric, U. S. P., cryst., bbls.	lb.	.24¾
Tungstic, tech., kegs	lb.	2.75
Valeric, C. P., 10-lb. bot.	lb.	2.50
Alcohol, ethyl from molasses, 190 proof, bbls.	gal.	4.13
Amyl, from pentane, tanks	lb.	.123
Secondary, tanks	lb.	.08½
Butyl, drums, c/l., wks., frt. allowed	lb.	.10
Cinnamic	lb.	2.50
Denatured, No. 11, comp. denat., c/l., drums	gal.	.35
Diacetone, tech., c. l., drums	lb.	.12½
Furfuryl, tech., 500-lb. drums, c/l.	lb.	.30
Isoamyl, drums	lb.	.27
Isobutyl, ref., drums	lb.	.09½
Isopropyl, ref., 91%, drums, frt. allowed	gal.	.39½
Wood, *see* Methanol		
Aldol, 95%, drums, c/l.	lb.	.21
Alpha-naphthol, bbls.	lb.	.52
Alpha-naphthylamine, bbls.	lb.	.32
Alum, ammonia, lump, bbls., wks.	100 lbs.	3.00
Chrome, casks, wks.	100 lbs.	7.00
Potash, lump, bbls., wks.	100 lbs.	3.00
Soda, bbls., wks.	100 lbs.	3.25
Aluminum, metal, N. Y.	lb.	.20
Chloride, anhyd., commercial, wks., drums extra, c/l.	lb.	.05
Stearate, 100-lb. bbl.	lb.	.19
Sulfate, comm'l, bags, wks., frt. equal	100 lbs.	1.80
Iron-free, bags, wks.	100 lbs.	2.00
Aminoazobenzene, 100-lb. kegs	lb.	1.15
Ammonia, anhydrous, cyl., wks.	lb.	.15½
50,000-lb., frt., tanks, wks.	lb.	.04½
Ammonia, aqua, 26°, tanks, wks., contained NH_3	lb.	.04½
Ammonium acetate, kegs	lb.	.26
Bifluoride, bbls.	lb.	.16
Bromide, bbls.	lb.	.35
Carbonate, tech., bbls.	lb.	.08
Chloride, gray, bbls.	100 lbs.	5.50
Lump, casks	lb.	.10½
Iodide, 25-lb. jars	lb.	3.25
Linoleate, bbls.	lb.	.11
Nitrate, tech., cryst., bbls.	lb.	.04
Oleate, bbls.	lb.	.10
Oxalate, kegs	lb.	.22½
Persulfate, cases	lb.	.21
Phosphate, dibasic, tech., bbls.	lb.	.07½
Stearate, anhyd., drums	lb.	.26
Sulfate, bulk, wks.	ton	26.50
Amylene, tanks, wks.	lb.	.09
Amyl acetate, tech., from pentane, tanks, frt. allowed	lb.	.11½
Chloride, normal, drums, wks.	lb.	.56
Chlorides, mixed, tanks, wks.	lb.	.06
Mercaptan, drums, wks.	lb.	1.10
Oleate, l. c. l., drs., wks.	lb.	.25
Stearate, l. c. l., drs., wks.	lb.	.26
Aniline oil, drums	lb.	.15
Anthracene, 80–85%, casks, wks.	lb.	.75
Anthraquinone, subl., bbls.	lb.	.65
Antimony, metal	lb.	.14⅛
Chloride, cbys.	lb.	.17
Oxide, bbls., c/l.	lb.	.15½
Salt, dom., kegs	lb.	.23¾
Sulfide, golden, bbls.	lb.	.22
Arsenic, metal, kegs	lb.	.42
Red, kegs, cases	lb.	.15¾
White, c/l., kegs	lb.	.03
Barium carbonate, bbls., bags, wks.	ton	44.00
Chloride, bbls., wks.	ton	72.00
Dioxide, drs., wks.	lb.	.11
Hydroxide, bbls.	lb.	.04¾
Nitrate, casks	lb.	.07
Thiocyanate, 400-lb. bbls.	lb.	.27
Barytes, floated, 350-lb. bbls., wks.	ton	23.65
Benzaldehyde, tech., drums	lb.	.60
Benzidine base, bbls.	lb.	.70
Benzol, tanks, wks.	gal.	.16
Benzoyl chloride, drums	lb.	.40
Benzyl acetate, F. F. C., bottles	lb.	.55
Chloride, tech., drums	lb.	.30
Beta-naphthol, bbls.	lb.	.23
Beta-naphthylamine, bbls.	lb.	.51
Bismuth, metal, cases	lb.	1.00
Bismuth, nitrate, cases	lb.	1.20
Oxychloride, kegs	lb.	2.95
Subnitrate, 25-lb. jars	lb.	1.22
Blanc fixe, dry, bags, c/l.	ton	60.00
Bleaching powder, drums, wks.	100 lbs.	2.00
Bone ash, kegs	lb.	.06
Bone black, bbls.	lb.	.08¼
Borax, bags	ton	42.00
Bordeaux mixture, drums	lb.	.10
Bromine, cases	lb.	.30
Bromobenzene, drums	lb.	.50
Bromoform, jars	lb.	1.40
Butyl acetyl ricinoleate, drums	lb.	.24
Acetate, drums, c/l., frt. allowed	lb.	.10
Aldehyde, drums, c/l., wks.	lb.	.16½
Carbinol, norm., drums, wks.	lb.	.60
Carbinol, sec., wks.	lb.	.60
Lactate, drums	lb.	.22½
Oleate, drums	lb.	.25
Stearate, drums	lb.	.26
Butyraldehyde, drums, wks.	lb.	.35½
Cadmium, metal, cases	lb.	1.20
Bromide, 50-lb. jars	lb.	1.61
Sulfide, boxes	lb.	.90
Caffeine, U. S. P., 5-lb. cans	lb.	2.10
Calcium acetate, bags	100 lbs.	2.25
Arsenate, bbls.	lb.	.06¾
Carbide, drums	lb.	.05
Carbonate, U. S. P., precip., 175-lb. bbls.	lb.	.06½
Chloride, bags, flake, c/l., deliv.	ton	22.00
Gluconate, U. S. P.	lb.	.50
Tech.	lb.	.28
Phosphate, monobas., bbls.	lb.	.07½
Tribas., bbls.	lb.	.06½
Calomel, 100-lb. drums	lb.	1.59
Camphor, Jap., slabs	lb.	.55
Carbazole, 70–80%, bbls.	lb.	.60
Carbon bisulfide, drums, c/l.	lb.	.05
Carbon black, bags, c/l.	lb.	.05
Carbon dioxide, liq., cyl.	lb.	.06
Carbon tetrachloride, drums	lb.	.05¼
Casein, stand. gr., bbls.	lb.	.13
Cellulose acetate, bbls.	lb.	.08½
Cerium oxalate, kegs	lb.	.28
Charcoal, willow, powd., bbls.	lb.	.06
China clay, bulk	ton	8.00
Chloral hydrate, drums	lb.	.80
Chlorine, liq., c/l., cyl.*	lb.	.055
Chlorine, tanks	100 lbs.	2.15
Chlorobenzene, mono-, drums	lb.	.06
Chloroform, tech., drums	lb.	.20
Chromium acetate, 20° soln., bbls.	lb.	.05
Coal tar, bbls., wks.	bbl.	7.50
Cobalt oxide, bbls.	lb.	1.67
Copperas, c/l., bulk	ton	12.00
Copper, metal, elec.	100 lbs.	14.00
Copper carbonate, bbls., 52/54%	lb.	.18
Chloride, bbls.	lb.	.15
Cyanide, drums	lb.	.37
Oxide, black, bbls.	lb.	nom.
Sulfate, c/l., bbls.	100 lbs.	5.15
Cotton, soluble, bbls.	lb.	.40
Cream of tartar, bbls.	lb.	.18¾
Crotonaldehyde, drums, c/l.	lb.	.26
Cyanamide, bulk, Atlantic ports	Ammonia unit	1.15
Diaminophenol, kegs	lb.	3.80
Diamylamine, drums, c. l., wks.	lb.	.47
Diamylene, tanks, wks.	lb.	.08½
Diamyl ether, drums, wks.	lb.	.08½
Diamyl oxalate, lc-l., drs., wks.	lb.	.30
Diamyl phthalate, tanks	lb.	.20½
Diamyl sulfide, drums, wks.	lb.	1.10
Dianisidine, bbls.	lb.	2.25
Dibutoxyethylphthalate, wks., drums	lb.	.35
Dibutyl ether, drums, wks.	lb.	.30
Dibutyl phthalate, drums, wks., frt. allowed	lb.	.21
Dibutyl tartrate, drums	lb.	.35
Dichlorethyl ether, drums, c/l., wks.	lb.	.15
Dichloropentanes, tanks, wks.	lb.	no prices
Diethanolamine, drums, wks.	lb.	.31
Diethylaniline, drums	lb.	.50
Diethylene glycol, drums, wks.	lb.	.22
Monobutyl ether, drums, wks.	lb.	.26
Monoethyl ether, drums, wks.	lb.	.16
Diethylene oxide, drums, wks.	lb.	.20
Diethyl carbinol, drums, wks.	lb.	.60
Diethyl phthalate, drums	lb.	.19

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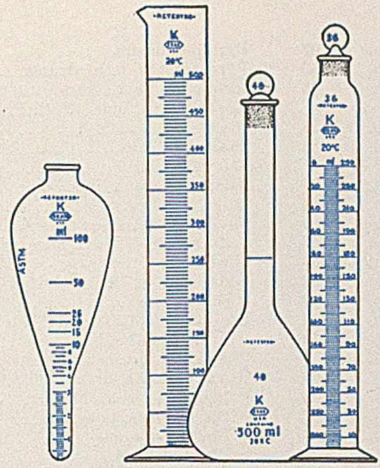
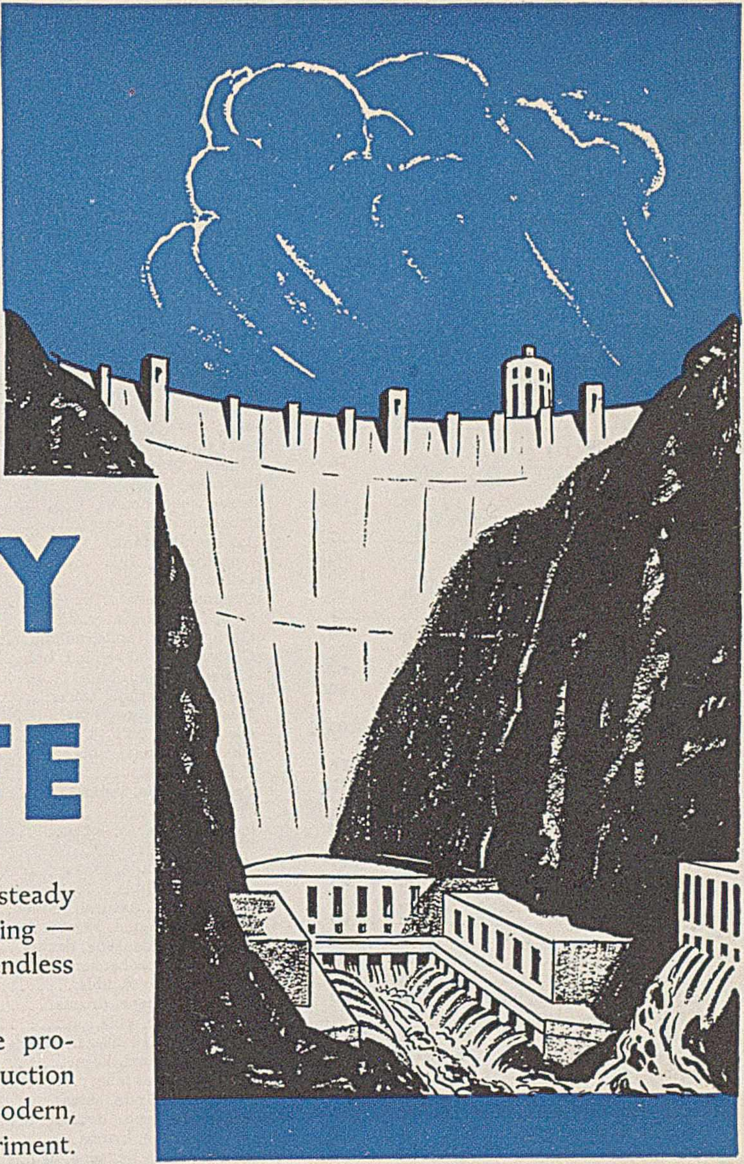
* F. O. B. destination.

(Continued on page 44)





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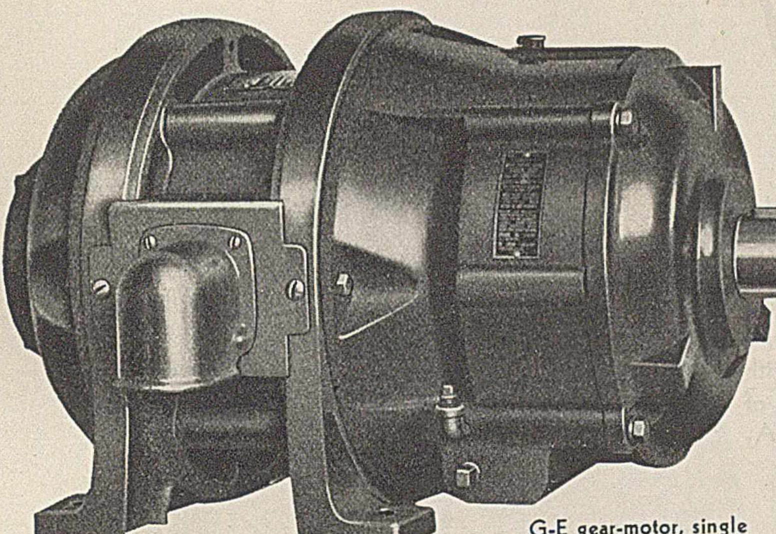
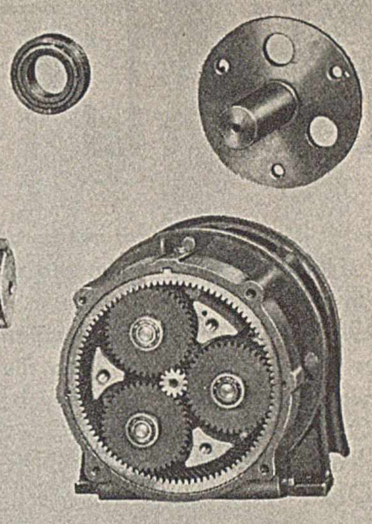
MARKET REPORT (continued from page 42)

Diethyl sulfate, tech., drums, wks.	lb.	.13
Diglycol oleate, light, bbls.	lb.	.24
Dimethylamine, pure 25.40% sol.—100% basis, drums	lb.	.95
Dimethylamine, frt. allowed E. Miss., drs., c. l.	lb.	1.00
Dimethylaniline, drums	lb.	.26
Dimethyl ethyl carbinol, drums, wks.	lb.	.60
Dimethylsulfate, drums	lb.	.45
Dimethyl phthalate, drums, wks., frt. allowed	lb.	.21
Dinitrobenzene, tech., drums	lb.	.16
Dinitrochlorobenzene, bbls.	lb.	.16½
Dinitronaphthalene, bbls.	lb.	.35
Dinitrophenol, bbls.	lb.	.23
Diphenyl	lb.	.15
Diphenylamine, bbls.	lb.	.31
Diphenylguanidine, bbls.	lb.	.35
Epsom salt, tech., bbls., c/l., N. Y.	100 lbs.	1.90
Ether, conc., drums	lb.	.09
Ether, nitrous, bot.	lb.	.75
Ethyl acetate, 85–88%, tanks, c/l., wks., frt. allowed	lb.	.06½
Acetoacetate, 110-gal. drums, wks., frt. allowed	lb.	.27½
Bromide, drums	lb.	.50
Carbonate, 90%, 50-gal. drums	gal.	1.85
Chlorcarbonate, carboys	lb.	.30
Chloride, drums	lb.	.22
Ether, absolute, 50-gal. drums	lb.	.50
Formate, l. c. l., drs., frt. allowed	lb.	.31
Methyl ketone, drums	lb.	.07
Ethylbenzylaniline, 300-lb. drums	lb.	.86
Ethylene dichloride, drums, wks., frt. allowed	lb.	.05½
Ethylenechlorohydrin, anhyd., drums, wks.	lb.	.75
Glycol, c/l., wks.	lb.	.17
Monobutyl ether, drums, wks.	lb.	.20
Monoethyl ether, drums, wks.	lb.	.16
Monoethyl ether acetate, drums, wks.	lb.	.14
Monomethyl ether, drums, wks.	lb.	.18
Oxide, cylinders, wks.	lb.	.50
Feldspar, bulk	ton	11.00
Fluorspar, 98%, bags	ton	nom.
Formaldehyde, bbls.	lb.	.05¾
Formaniline, drums	lb.	.37½
Fuller's earth, bags, c/l., mines	ton	10.00
Furfural, drums, tech., contract, works	lb.	.10
Glauber's salt, bbls.	100 lbs.	1.05
Glycerine, c. p., drums	lb.	.22
Glyceryl phthalate, drums	lb.	.30
Glycol phthalate, drums	lb.	.29
Stearate, drums	lb.	.23
G salt, bbls.	lb.	.45
Hexamethylenetetramine, tech., drums	lb.	.35
Hydrogen peroxide, 100 vol., cbys.	lb.	.20
Hydroquinone, kegs	lb.	.90
Indigo, synth., liq., bbls.	lb.	.16½
Iodine, resubl., jars	lb.	1.50
Iron acetate, liq., 17°, bbls., c/l.	lb.	.03
Iron chloride, cryst., bbls.	lb.	.05
Isobutyl carbinol (128–132° C.), tanks	lb.	.32
Kieselguhr, bags, Pac. Coast, wks.	ton	22.00
Lead, metal, N. Y.	100 lbs.	6.00
Lead acetate, drs., white	lb.	.13½
Arsenate, drs.	lb.	.11½
Oxide, litharge, bbls., 20-ton lots	lb.	.07½
Peroxide, drums	lb.	.46
Red, bbls., 20-ton lots	lb.	.08½
Sulfate, bbls.	lb.	.07
White, basic carb., bbls.	lb.	.07½
Lime, hydrated, bbls.	100 lbs.	.85
Lime, live, chemical, bbls., wks.	280 lbs.	1.70
Lithopone, bbls.	lb.	.04½
Magnesite, calcined, 500-lb. bbls., wks.	ton	60.00
Magnesium, metal, wks.	lb.	.30
Magnesium carbonate, bags	lb.	.06¼
Chloride, drums	ton	39.00
Fluosilicate, cryst., bbls.	lb.	.10
Oxide, U. S. P., light, bbls.	lb.	.36
Manganese chloride, bbls.	lb.	.09
Dioxide, 85–90%, bbls.	ton	51.50
Sulfate, casks	lb.	.07
Manitol, pure, cryst., cs., wks.	lb.	1.48
Mercury bichloride, cryst., 100 lbs.	lb.	1.22
Mercury, flasks, 76 lbs.	flask	95.00
Meta-nitroaniline, bbls.	lb.	.67
Meta-phenylenediamine, kegs	lb.	.80
Meta-tolylenediamine, bbls.	lb.	.65
Methanol, pure, synthetic, drums, wks., frt. allowed, c/l.	gal.	.38
Tanks, wks., frt. allowed	gal.	.33
Methyl acetone, tanks, wks., frt. allowed	gal.	.36
Chloride, cylinders	lb.	.36
Formate, l. c. l., drs., frt. allowed	lb.	.39
Hexyl ketone, drs., tech., wks.	lb.	.60
Lactate, l. c. l., drs., frt. allowed	lb.	.30
Propyl carbinol, drums, wks.	lb.	.60
Salicylate, cases	lb.	.42
Michler's ketone, kegs	lb.	2.50
Monoamylamine, drums, c. l., wks.	lb.	.52
Monoethanolamine, drums, wks.	lb.	.31
Monomethylamine, drums	lb.	.65
Naphthalene, crude	100 lbs.	2.50
Nickel, metal	lb.	.35
Nickel salt, single, bbls.	lb.	.13
Double, bbls.	lb.	.13
Niter cake, bulk	ton	nom.
Nitrobenzene, drums	lb.	.08
Nitrogen solution unit	unit	1.04
Octyl acetate, tanks, wks.	lb.	.15
Oil, castor, No. 1	lb.	.10¾
China wood, bbls.	lb.	.12¾
Coconut, tanks	lb.	.05½
Cod, N. F., bbls.	gal.	.52
Corn, crude, tanks, mills	lb.	.08¼
Cottonseed, oil refined, bbls.	lb.	.10½
Linseed, boiled, bbls.	lb.	.116
Menhaden, crude, tanks	gal.	.40
Neat's-foot, pure, bbls.	lb.	.13½
Oleo, No. 1, bbls.	lb.	.13
Olive oil, denat., bbls.	gal.	1.50
Foots, bbls.	lb.	.11¼
Peanut, crude, tanks	lb.	.08¼
Perilla, drums	lb.	.11¾
Rapeseed, denat., bbls.	gal.	.95
Red, bbls.	lb.	.11⅝
Soy bean, crude, tanks	lb.	.095
Sperm, 38°, bbls.	lb.	.10
Whale, bbls., natural, refined	lb.	.105
Ortho-aminophenol, kegs	lb.	2.15
Ortho-dichlorobenzene, drums	lb.	.06
Ortho-nitrochlorobenzene, drums	lb.	.28
Ortho-nitrophenol, bbls.	lb.	.85
Ortho-nitrotoluene, drums	lb.	.07
Ortho-toluidine, bbls.	lb.	.14
Paraldehyde, 110–50-gal. drums	lb.	.16
Para-aminophenol, kegs	lb.	1.05
Para-dichlorobenzene	lb.	.16
Para-formaldehyde, cases	lb.	.34
Paraldehyde, tech., drums	lb.	.16
Para-nitraniline, drums	lb.	.45
Para-nitrochlorobenzene, drums	lb.	.23½
Para-nitrophenol, bbls.	lb.	.35
Para-nitrosodimethylaniline, bbls.	lb.	.92
Para-nitrotoluene, bbls.	lb.	.35
Para-phenylenediamine, bbls.	lb.	1.25
Para-tertiary amyl phenol, drums, c/l., wks.	lb.	.26
Para-toluidine, bbls.	lb.	.56
Paris Green, 250-lb. kegs	lb.	.22
Perchlorethylene, drs., frt. allowed	lb.	.10½
Phenol, drums	lb.	.13¼
Phenolphthalein, yellow, drums	lb.	.85
Phenylethyl alcohol, 1-lb. bot.	lb.	3.75
Phloroglucinol, tech., drums	lb.	15.00
c. p., drums	lb.	20.00
Phosphorus, red, cases	lb.	.40
Oxychloride, 175-lb. cylinders	lb.	.16
Trichloride, cyl.	lb.	.16
Phthalic anhydride, bbls.	lb.	.14½
Platinum, metal, solid	oz.	48.00
Potash, caustic, drums	lb.	.06¼
Potassium abietate	lb.	.06
Acetate, kegs	lb.	.26
Bicarbonate, gran., bbls.	lb.	.10
Bichromate, casks	lb.	.08⅝
Binoxalate, bbls.	lb.	.23
Bromide	lb.	.31
Carbonate, 80–85%, calc., casks	lb.	.05½
Chlorate, cryst., kegs	lb.	.09¼
Chloride, crystals, bbls.	lb.	.04
Cyanide, cases	lb.	.55
Meta-bisulfite, bbls.	lb.	.15
Muriate, fert., bulk, per K_2O unit		.53½
Permanganate, drums	lb.	.18½
Prussiate, red, casks	lb.	.35
Yellow, casks	lb.	.15
Titanium oxalate, bbls.	lb.	.32
Pyridine, drums	gal.	1.30
Pyrocatechin, c. p., drums	lb.	2.15
Resorcinol, tech., kegs	lb.	.75
Rochelle salt, bbls., U. S. P.	lb.	.15½
R salt, bbls.	lb.	.52
Saccharin, cans	lb.	1.70
Salt cake, bulk	ton	12.00
Saltpeter, gran., bbls.	lb.	.06
Silica, ref., bags	ton	22.00
Silver nitrate, 16-oz. bot.	oz.	.32¼
Soda, ash, 58%, light, bags, contract, wks.	100 lbs.	1.23
Soda, caustic, 76%, solid, drums, contract, wks.	100 lbs.	2.60
Sodium abietate, drums	lb.	.08
Acetate, flake, bbls.	lb.	.04¼
Alginate, drums	lb.	.69
Antimoniate, drs.	lb.	.15¼
Benzoate, tech., bbls.	lb.	.40
Bicarbonate, bbls.	100 lbs.	1.75
Bichromate, casks	lb.	.06⅝
Bisulfite, bbls.	lb.	.03¼
Bromide, bbls., U. S. P.	lb.	.31
Chlorate, cryst., bags	lb.	.06¼
Chloride, bags	ton	14.80
Cyanide, cases	lb.	.16½
Fluoride, bbls.	lb.	.07¼
Metallic, drums, 12¼-lb. bricks	lb.	.19
Metasilicate, cryst.	100 lbs.	2.75
Metasilicate, gran., bbls.	100 lbs.	2.15
Naphthenate, drums	lb.	.12
Naphthionate, bbls.	lb.	.52
Nitrate, crude, bulk, N. Y.	ton	26.50
Nitrite, bbls.	lb.	.07
Perborate, bbls.	lb.	.14¾
Phosphate, disodium, bags	100 lbs.	1.70
Phosphate, trisodium, bbls.	100 lbs.	2.05
Picramate, kegs	lb.	.65
Prussiate, bbls.	lb.	.10
Silicate, drums, tanks, 40°	100 lbs.	.80
Silicofluoride, bbls.	lb.	.05¾
Stannate, drums	lb.	.38
Sulfate, anhyd., bags	100 lbs.	1.45
Sulfide, cryst., bbls.	lb.	.02¼
Solid, 60%	lb.	.03
Sulfocyanide, bbls.	lb.	.28
Thiosulfate, reg., cryst., bbls.	lb.	.024
Tungstate, tech., kegs	lb.	no prices
Strontium carbonate, pure, bbls.	lb.	.30
Nitrate, bbls.	lb.	.07¾
Peroxide, 100-lb. drums	lb.	1.25
Sulfur, bulk, mines, wks.	ton	18.00
Sulfur chloride, drums	lb.	.03
Sulfur dioxide, commercial, cyl.	lb.	.07
Sulfuryl chloride, drums	lb.	.10
Tetrachlorethane, 50-gal. drums	lb.	.08
Thiocarbanilid, bbls.	lb.	.20
Tin	lb.	.60⅛
Tin tetrachloride, anhydrous, drums, bbls.	lb.	.30¼
Oxide, bbls.	lb.	.58
Titanium dioxide, bbls., wks.	lb.	.16¼
Toluene, tanks	gal.	.30
Triamylamine, drums, c. l., wks.	lb.	.77
Triamyl borate, l. c. l., drs., wks.	lb.	.27
Tribromophenol, cases	lb.	1.10
Tributyl citrate, l. c. l., drs., frt. allowed	lb.	.45
Phosphate, l. c. l., drs., frt. allowed	lb.	.50
Trichloroethylene, drums, wks., frt. allowed	lb.	.089
Tricresyl phosphate, tech., drs.	lb.	.24½
Triethanolamine, drums, wks., frt. allowed	lb.	.26
Trihydroxyethylamine oleate, drums	lb.	.40
Stearate	lb.	.35
Trimethylamine, drs., frt. allowed E. Miss., c. l.	lb.	1.00
Triphenylguanidine, drums	lb.	.58
Triphenyl phosphate, drums	lb.	.34
Tungsten, tech., powder	lb.	nom.
Urea, crystals	lb.	.0475
Vinyl chloride, 16-lb. cylinders	lb.	1.00
Whiting, bags	ton	7.00
Xylene, 10°, tanks, wks.	gal.	.30
Xylidine, drums	lb.	.36
Zinc, metal, E. St. Louis	100 lbs.	7.00
Zinc ammonium chloride, bbls.	lb.	.0465
Chloride, granulated, drums	lb.	.05
Oxide, Amer., bbls.	lb.	.06¼
Perborate, 100-lb. drums	lb.	1.25
Peroxide, 100-lb. drums	lb.	1.25
Stearate, bbls.	lb.	.20
Zinc dust, bbls., c/l.	lb.	.0890



G-E gear-motor, single reduction unit



Above is shown the planetary-type of transmission in G-E gear-motors. The even distribution of gear-tooth pressure made possible by this design assures long, trouble-free operation.

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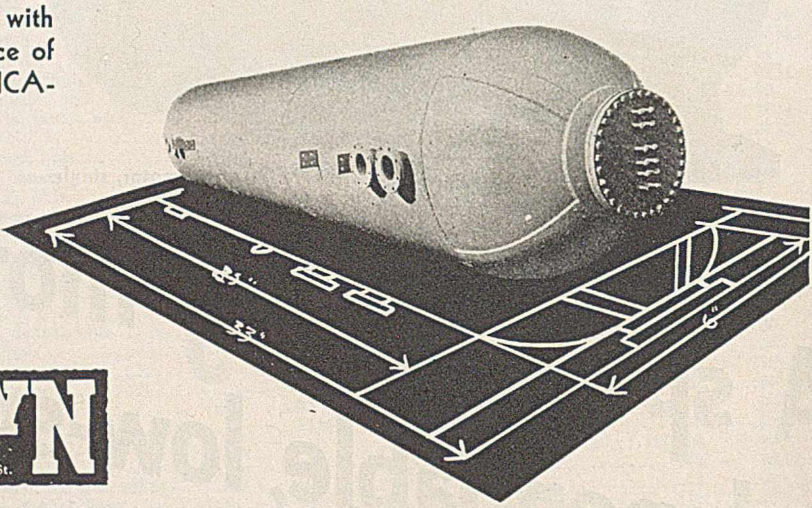

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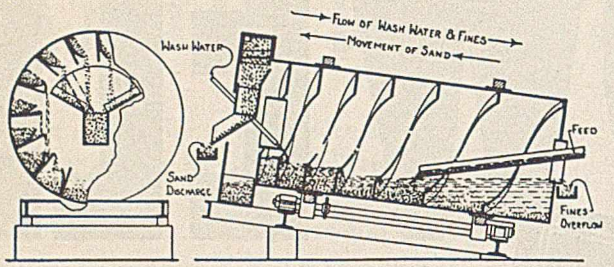

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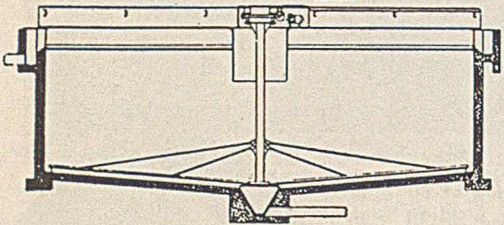

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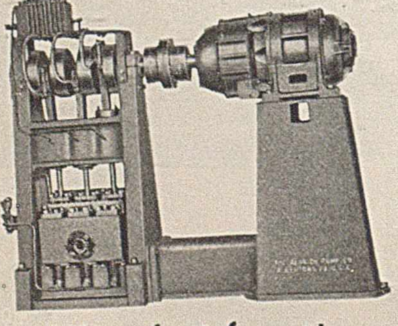

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