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Studies with Primary Tar Distillate from Dakota Lignite

William A. Franta

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STUDIES WITH PRIMARY TAR DISTILLATE
FROM DAKOTA LIGNITE

1. The influence of catalysts on the resinification of the tar acids of the distillate with formaldehyde.
2. The preparation of phenol-formaldehyde resins from primary lignite tar distillate and testing their applicability in insulating varnish.

by

William A. Franta,
B.S. in Chemical Engineering, University of North Dakota,
1933

A thesis submitted to the faculty of the College of Engineering of the University of North Dakota in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering.

May 31, 1934

University of North Dakota

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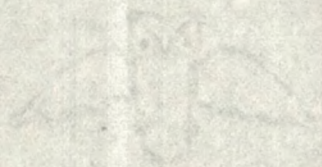
This thesis, presented by William A. Franta as a partial fulfillment of the requirements for the degree of Master of Science in the University of North Dakota, is hereby approved by the Committee in charge of his work.

STUDIES WITH PRIMARY TAR DISTILLATE
FROM DAKOTA LIGNITE

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SHEPHERD BOND



THE PROBLEM.

The problem of this investigation is that of obtaining a satisfactory insulating varnish from a synthetic resin made from North Dakota ^{lignite} tar distillate. This general problem may be subdivided into several sub-groups and this thesis deals particularly with some of these sub-groups.

The making of a satisfactory insulating varnish consists in: (1) resinifying the inherent phenols of the low temperature tar distillate with a suitable aldehyde such as formaldehyde; (2) selecting a suitable solvent for the resin; (3) treating the resin to effect its proper solution and to regulate, in part, the properties of the resulting varnish; and (4) the selection and addition of certain plasticizing, drying, or other agents that may be necessary to impart the desired properties.

Insulating varnishes must be easy to apply, must dry readily, must be able to withstand for long periods of time such temperatures as are likely to be encountered in electrical machines, must be tough and durable and must possess high electrical resistance and dielectric strength under all conditions likely to be encountered.

THIS THESIS

The work performed on the general problem outlined above is described in this report together with the data from this work. The present research covers but part of the general problem and, obviously, definite conclusions in certain directions will have to await further data. However, it is possible now, from results of the present research, to predict rather carefully the effect of acid and basic catalysts on the formaldehyde resinification reaction with lignite tar distillate. This has an important bearing on the general problem.

The experimental data and discussion of this thesis is preceded by a general review of the more important literature pertaining to this subject.

THEORETICAL DISCUSSION

I. PHENOL-FORMALDEHYDE RESINS.

The exact nature of the chemical reactions that can take place between phenols and formaldehyde is not known, nor can the chemical formulae of the resinous products of the various reactions be easily determined. However, detailed studies have been made of the reactions which have led to the recognition of certain definite reactions and the identity of certain reaction products. Authorities generally agree with Baekeland's statement (1) that an immense number of compounds will take part in these phenol resinoid reactions. He states, "In the place of phenol may be used any of the substituted phenols--for instance, even such a sluggish phenol as the phenyl ether of salicylic acid. In place of formaldehyde may be used the aldehydes, the ketones, the dihalides, from both the aldehydes and ketones, and all those compounds which are equivalent in action to aldehydes such as hexamethylenetetramine, acetals, and many others."

Obviously, in the study of reaction between formaldehyde and the phenols of lignite tar distillate, it is proper to consider first of all the course and products of reactions between phenol itself and formaldehyde.

The different resinous products of the reactions fall into two principal classes, those which are permanently soluble and fusible and those which are not. The latter category is generally subdivided into three groups. The types of resins generally recognized are named and described as follows:

Novolak. This resin is soluble in alcohol, acetone, and alkalis and cannot be rendered insoluble in these solvents by ordinary heat treatment. It is usually solid at room temperature, possessing low softening and melting points. Heat treatment may be employed to raise the softening and melting points but will not render the resin infusible. Only by addition of further formaldehyde can the Novolak type of resin be hardened into an insoluble, infusible state.

Bakelite A. The name Bakelite is a registered trade name of the Bakelite Corporation, New York, for its particular commercial product but it is used very widely in plastic literature in conjunction with the letters A, B, or C, as a general designation for resins of the hardening and hardened types. Bakelite A, known also as Resol, may be either liquid, solid, pasty or plastic at room temperature. It is always easily fusible and soluble in alcohol, acetone and alkali. It may be rendered insoluble and infusible by heat treatment.

Bakelite B. This resin, known also as Resitol, is solid at all temperatures and plastic in heat. It is insoluble in alcohol, acetone and alkali, but will swell upon being submerged for a time in acetone. Bakelite B is a product of the heat treatment of Bakelite A and can, in turn, be transformed by mere heating into Bakelite C. There is a tendency on the part of some investigators to disregard the B product as an individual intermediate resin and to consider it only as a mixture of A and C products.

Bakelite C. The chemical and physical properties of this resin have made it technically by far the most important of all

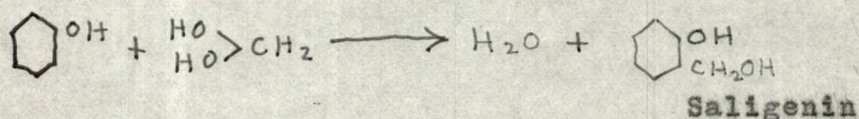
synthetic resins. It is insoluble in alcohol, acetone, alkali, and other similar solvents. It is infusible, carbonizing at a temperature somewhat above 300°C. Resite and Resinite are other names used for resins of this class.

It is generally recognized that the resin forming process consists of a combination of many reactions of various types. Reactions of condensation, rearrangement, dehydration, polymerization, and simple combination have been recognized. When phenol and formaldehyde are allowed to react to form a resin the course of the various reactions, the relation between them, their relative importance, and the nature of the product depends upon: (1) the proportions of phenol to formaldehyde used, (2) the temperature at which the reaction is carried out, (3) the length of time allowed for the reaction to proceed, and (4) the nature of the catalyst or condensing agent used.

Various theories have been advanced to account for the importance of these factors and to explain their influences on the interrelation of various resin forming reactions. The following brief discussion will indicate the lines of reasoning in the theories of three modern schools of investigators.

Baekeland's Theory. In his earlier works (2,3,4,5) Baekeland formulated his theory about the phenol-alcohol, saligenin, formed from the direct combination of phenol and formaldehyde.

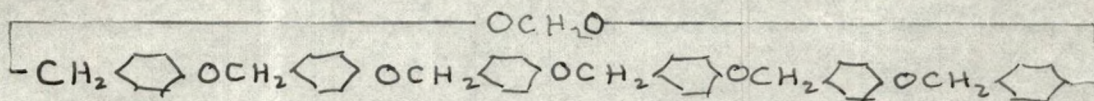
In alkaline solution formaldehyde acts as methylene glycol:



Saligenin dehydrates and polymerizes on heating to form a resin of

the saliretin type. The saliretin resin is soluble and fusible as long as there is an excess of phenol present. Most of this excess phenol is expelled by heat but the last trace is held in the resin very tenaciously and cannot ordinarily be so removed. This trace is sufficient to cause the saliretin product to retain its solubility and fusibility. If saliretin resin is rendered absolutely free of excess phenol it can be hardened into a substance of limited solubility or complete insolubility. This product, however, is not as hard, as strong, or as resistive as the Bakelite C product.

Bakelite resin is obtained by combining the saligenin or saliretin product with a small amount of additional formaldehyde. The addition of one mol of formaldehyde to six of saligenin gives a very satisfactory Bakelite type of resin. Therefore, it seems logical to write the chemical formula of Bakelite C as follows:

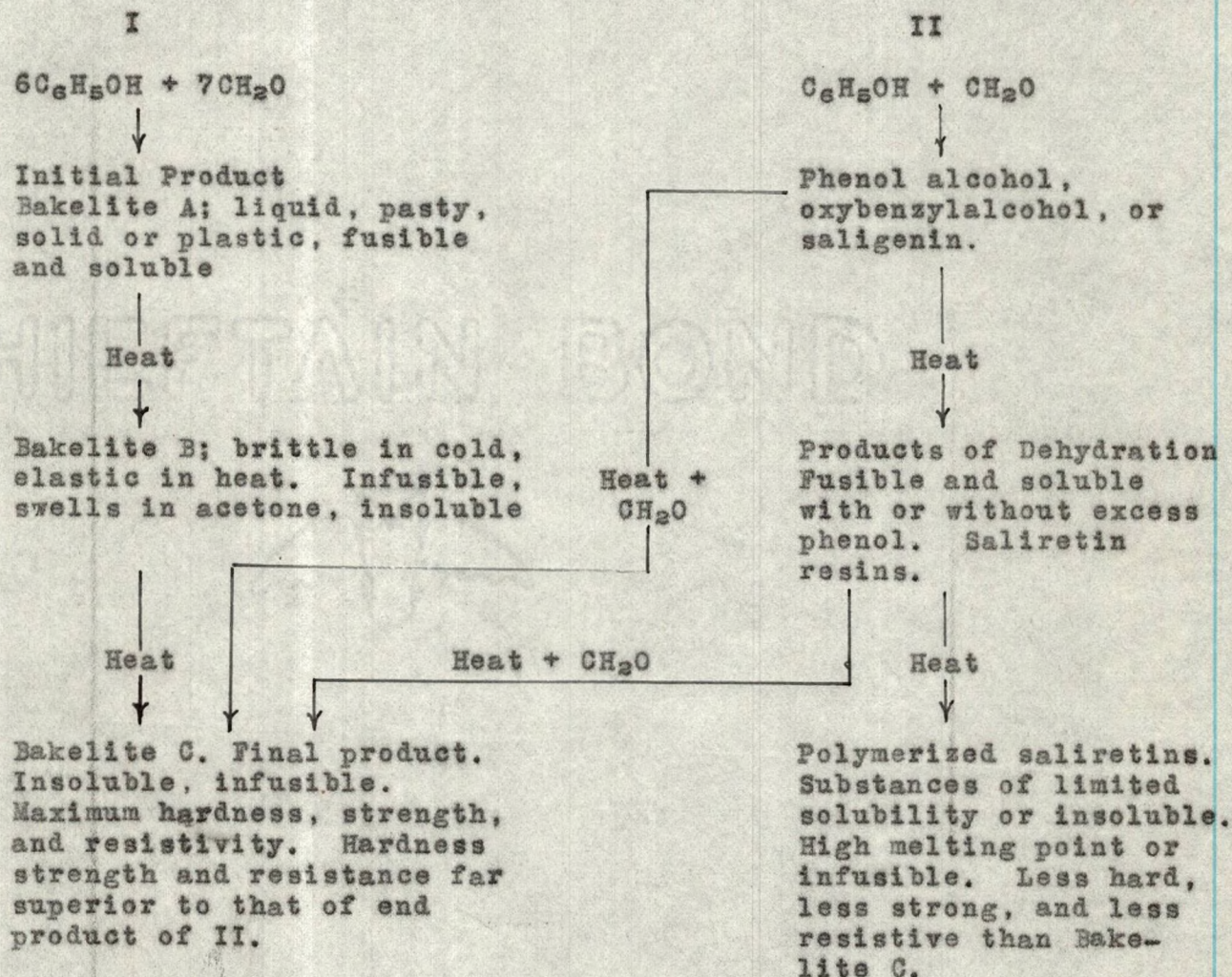


Of course it is possible that more or less than six groups may be combined in each molecule.

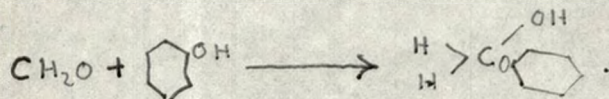
Phenol and formaldehyde react without catalyst but the reaction is too slow to be practicable. Presence of an acid causes, when there is a sufficient excess of phenol, formation of resins of the fusible saliretin type. Small amounts of base prevent the formation of saliretins even in the presence of an excess of phenol. In this latter case the excess phenol is present in solid solution in the infusible product. In other words, Baekeland held that the presence of acids tends to produce

soluble, fusible resins while the presence of bases always produces insoluble, infusible resin.

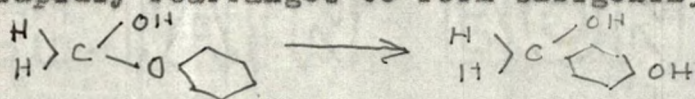
Baekeland's Classification



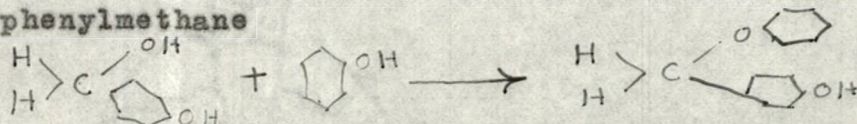
In 1925 Baekeland and Bender (6) published a more detailed theory concerning the resin forming reactions and the chemical make-up of the resins. According to this theory phenol and formaldehyde first unite to form a phenoxy alcohol



which rapidly rearranges to form saligenin.



Saligenin combines with another mol of phenol to form phenol - p-hydroxyphenylmethane

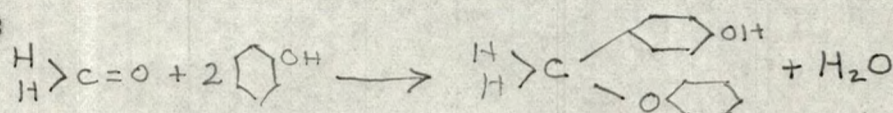


part of which may rearrange slowly to form p-dihydroxydiphenylmethane.

The novolak type of resin consists of varying mixtures of p-hydroxyphenylphenoxy methane, phenoxy methane, phenol, and p-dihydroxydiphenylmethane. The phenol acts as a solvent and determines the melting point of the mixture. The amount of free phenol present in the ordinary Novolak varies from about eight to twelve percent as determined by the action of metallic sodium in xylene. Extraction methods show from one to two percent of crystalline p-dihydroxydiphenylmethane. Prolonged heating converts Novolak into the insoluble, infusible saliretin type of resin described above.

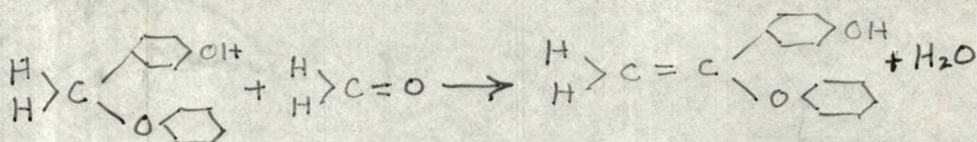
One mol of a methylene yielding substance, as in this case, formaldehyde, converts 1 mol of phenoxy-p-hydroxyphenylmethane into a resin of the bakelite type. The general scheme of resin formation and the relationship between the various kinds of resins then may be outlined as follows:

First Stage:



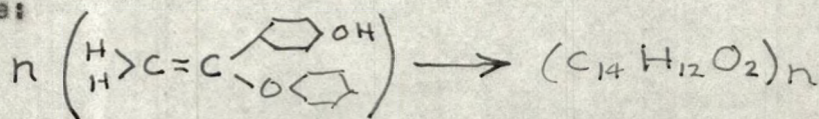
Characterizing Novolak.

Second Stage:



Characterizing Bakelite A.

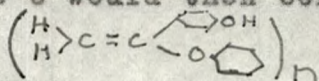
Third Stage:



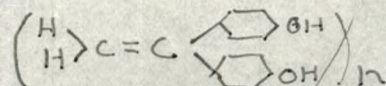
Bakelite C.

Bakelite B is probably a mixture of A and C products.

The Bakelite C would then consist mainly of



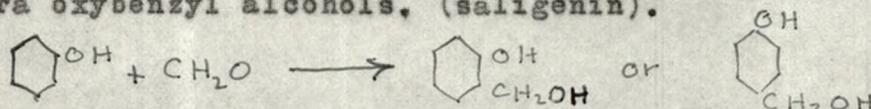
together with some



and traces of unused phenol, unused hardening agent, and some of the intermediate compounds.

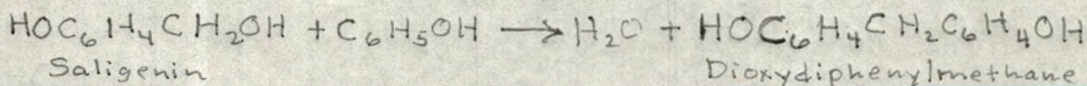
No attempt is made to specifically state the effects of various types of catalysts. The authors simply report, "Practical experience bears out the contention that the differences found in the intermediate bodies from different catalysts may be due to specific action of the catalysts on different reactions in the same series and that the final product may in all cases be much the same."

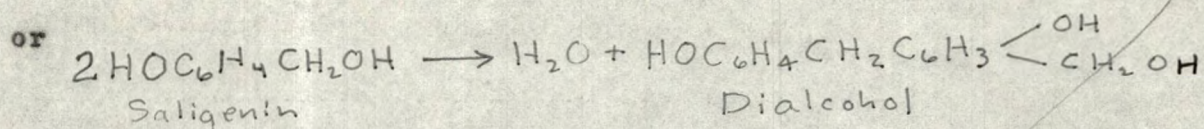
Raschig's Theory. The theory of Raschig (7) as outlined by Ellis (8) postulates the formation, in the first stage, of ortho and para oxybenzyl alcohols, (saligenin).



The oxybenzyl alcohol can react farther in either of two ways, combining with phenol or with additional oxybenzyl alcohol.

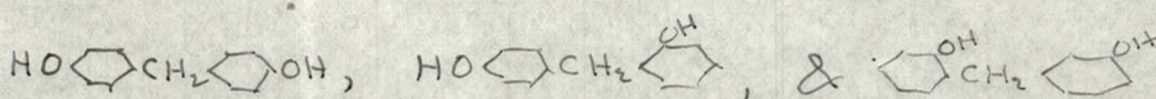
Either





The latter reaction is the more probable. The dialcohol product can react further with phenol or more likely with more alcohol, either mono or di.

Three isomeric forms of dioxydiphenylmethane are possible.

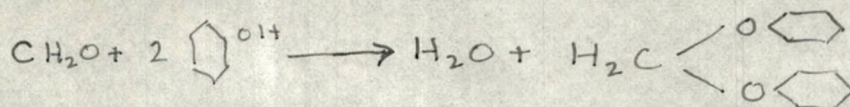


Soluble resins are formed when one mol of phenol reacts with less than one mol of formaldehyde, the reaction generally taking place with only half a mol. Infusible resins arise when one mol, (10 to 20 percent excess is usually used) are used per mol of phenol. Soluble resins (Novolaks) can be converted into the insoluble type (Bakelite) by warming with additional formaldehyde.

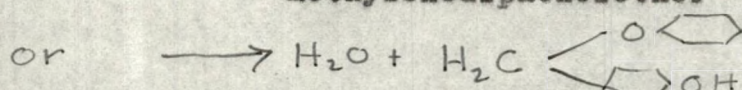
Novolak resin is composed principally of the three isomeric forms of dioxydiphenylmethanes whose relatively low molecular weight accounts for their easily solubility. Larger amounts of formaldehyde lead to formation of dialcohols which react further to form very complex polyalcohols building up a large molecules which tend to be sluggish and insoluble. This accounts for the bakelite types of resin.

No mention is made of the effect of catalysts and condensing agents.

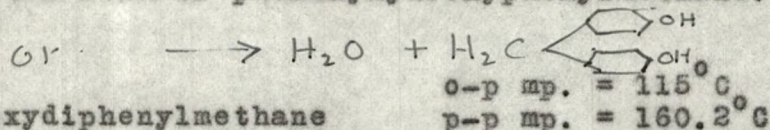
Theory of Sheiber and Sändig. Sheiber and Sändig (9) are of the opinion ^{that} when formaldehyde and phenol condense in molecular proportions one to ten, the reaction forms any or all of three isomers.



methylenediphenolether mp. = 18°C.



semiacetal form or phenoxyhydroxyphenylmethane.



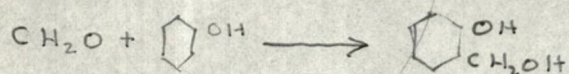
dihydroxydiphenylmethane

o-p mp. = 115°C
p-p mp. = 160.2°C

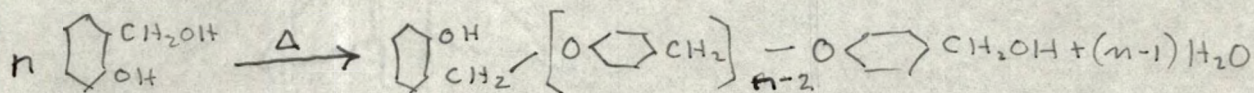
These reactions are promoted by the presence of acids but may take place in the presence of alkalis.

The mixture of the three products is the basis of Novolak.

Equimolal amounts of phenol and formaldehyde combine to form ortho or para hydroxybenzylalcohol (saligenin).



This reaction is catalyzed by bases. Use of more than one mol of formaldehyde per mol of phenol results in the introduction of more than one $-\text{CH}_2\text{OH}$ group per molecule. Such polyvalent alcohols, however, easily liberate formaldehyde on heating while saligenin is rather stable. Saligenin, then, is a fundamental compound of Bakelite A type resins. Bakelite resins of the B and C types are anhydrides of saligenin, the C product being more highly polymerized than the B product.



saligenin
Typifying
Bakelite A.

Saliretin mixture,
typifying Bakelites B and D
MC MB $n_C > n_C$

About the hardening transformation they say: "The conditions (of the hardening transformation) are very complicated as pure

substances are not present. However, sufficient data are available to indicate the main character of the reactions which occur. The following has been established:

"1. Chemically pure *o* and *p*-hydroxybenzyl alcohols can be converted into typical resites (Bakelite C) by sufficiently prolonged heating to a high temperature.

"2. Mixtures of phenol-alcohols undergo the same change much more easily and rapidly.

"3. Dihydroxydiphenylmethanes are not convertible into resites (Bakelite C).

"4. In alkaline condensations, even in the presence of a large amount of alkali (KOH), the reaction between phenol and formaldehyde proceeds as far as resite (Bakelite C) formation even at water bath temperature.

"5. Novolak is converted into resite by treatment with formaldehyde in the absence or presence of contact agents (bases or acids).

"6. Resol (Bakelite A) is spontaneously transformed into resite (Bakelite C) under the influence of acids.

"7. All the indications point definitely to the nature of the transformation as a polymerization process, in the course of which a hemi-colloid is formed. In particular, the intermediate product, resitol (Bakelite B) must be considered to be an analogue of 'vitreous styrol' that is, a solid solution of resite (Bakelite C) in resol (Bakelite A).

"8. In order to achieve maximum hardness, the addition of formaldehyde is necessary or advantageous."

In general, then, acid condensing agents, including acids and acid salts, tend to cause phenol and formaldehyde to react in two to one molecular proportions to give a permanently soluble, fusible resin of the Novolak type, and that basic condensing agents, including bases and basic salts, tend to cause a mol to mol reaction to form a resin of the Bakelite type, soluble and fusible but capable of being rendered insoluble and infusible by heat.

Homologs of Phenol. Sheiber and Sandig (10) have found that the individual isomers, ortho, meta, and para cresol react with varying facility with formaldehyde. The m-cresol reacts with approximately five times ten velocity of o and p-cresol and phenol. The resin obtained from m-cresol and formaldehyde is exceptionally hard and resistant after transformation. Technical cresol (40 per cent m, 30 per cent p and 30 per cent o cresol). showed a reaction velocity almost the same as that of m-cresol but the "time-% resin formed" curve is curvelinear while that of m-cresol, as well as those of o and p-cresol, is rectilinear. This striking fact can be accounted for by attributing catalytic properties to impurities which are invariably present in the commercial cresols mixture.

The cresols are widely used in the commercial production of synthetic resins. Phenolic compounds other than the cresols and phenol itself have not found wide commercial use for this purpose.

Pure xylenol-formaldehyde resins are only slightly soluble in alcohol. They are considered, however, as not particularly undesirable components of ordinary phenol formaldehyde resins.

II. INSULATING VARNISHES.

Monkhouse (11) classifies insulating varnishes as follows:

"(a) Oil varnishes, as a general rule made from boiled and blown linseed oil blended with resins, gums, and driers. Practically all dipping and impregnating baking varnishes belong to this class. China wood (or tung) oil is also used largely in view of its moisture and heat resisting properties.

"(b) Asphaltum varnishes, chiefly made from native asphalts dissolved in benzine (petroleum spirit). Asphalts (both native and pyrogenous residues) are also used dissolved in mineral oils, wax tailings, etc., for impregnating purposes, although in this form the material can hardly be regarded as a varnish.

"(c) Spirit varnishes (including synthetic resin varnishes) are chiefly used as finishing varnishes where stove drying is impracticable, and for mica sticking purposes. The majority of spirit varnishes consist of lacs (shellac, garnet lac, etc.) dissolved in denatured alcohol, acetone, etc.

"(d) Pigmented varnishes, which class includes oil varnishes loaded with lithophone and various pigments to improve the thermal and sometimes the filling characteristics of the varnish."

Drying oils used in varnishes of class (a) include linseed oil, and poppy seed oil. Cotton seed oil and soya bean oil are used as semidrying oils and castor oil, olive oil, almond oil, and rosin oil are used where non-drying oils are required.

Resins used in the manufacture of varnish include copals, succin, sandarac gum, rosin, shellacs, and synthetic resins of all sorts. Solvents used include alcohol (principally ethyl), benzine, spirits of turpentine, and acetone.

The metallic salts usually used as dryers in varnishes are generally objectionable when present in insulating varnishes because of their deleterious effect on electrical properties. For the same reason it is deemed advisable to avoid the formation of metallic salts in a synthetic resin to be used in an insulating

varnish.

Oil Varnishes. Oil varnishes are made by mixing a molten gum or mixture of gums with boiled and blown linseed oil. The resulting varnish is then thinned, filtered, and aged in semi-darkness in order to clarify it. Synthetic resins are just beginning to find application in oil varnishes. They have been found to greatly accelerate the drying of the oils and to provide a very satisfactory film.

Spirit Varnishes. Most synthetic resin varnishes are spirit varnishes, consisting merely of a solution of a resin in one of the solvents named (usually an alcohol-acetone mixture) to which has been added castor oil, glycerine, or some other agent to impart flexibility.

Moisture in Insulating Varnish. The presence of even a low concentration of moisture in a varnish greatly reduces its value for electrical insulating purposes. This is due to the low dielectric strength of the varnish when water is present (12, 13). It is therefore imperative that a varnish for insulating purposes be as moisture free and as impervious to moisture as is possible. Little else is known as to what such a varnish should and should not contain.

Ellis (14) suggests that films forming varnish coatings should be composed of macro-molecules of comparatively large sizes if the utmost in toughness and strength is desired. The formation of such large macromolecules (eucolloids) in synthetic resins is promoted by slow polymerization at a low temperature.

Testing Insulating Varnish. The A.S.T.M. (15) prescribes tests of insulating varnishes for specific gravity, viscosity, flash point, heat endurance, effect of oil, draining (often dipping), non-volatile content by weight, volatile matter by volume, and dielectric strength of varnish in the liquid state.

Arnold and Frost (16) point out the failure of A.S.T.M. tests to indicate to any useful degree the actual applicability of an insulating varnish. They suggest a few "practical" tests for wire enamels which include tests for elongation, heat endurance, pin holes, varnish solvency, dielectric strength, shelf life, power factor, and abrasion resistance.

The purposes for which insulating varnishes must be used are so varied, both as to their electrical and mechanical demands, that no definite minimum "standard of excellence" has been set up stating to just what numerical degree a varnish must possess each of the many qualities desired in order to be an "insulating varnish".

HISTORICAL

The historical background of phenol-formaldehyde condensation from the year 1853 up to the present time is carefully reviewed by Ellis (17). Scheiber and Sändig (18) and Redman, Weith, and Brock (19), present more brief historical sketches of the work. The patent literature is reviewed by Kausch.(20)

All of the work described in the literature involved the use of pure chemical compounds or known mixtures of compounds. When the condensation reaction is applied to phenolic fractions of coal tar, however, much of the detailed information available is of little or no direct value because of the diversity of the compounds at hand. The general principles governing the reaction, however, have been applied with profit.

Gluud and Breuer. In 1919 Gluud and Breuer (21) published an account of a number of experiments they performed with the object of testing the possibility of preparing resins of the Novolak, Bakelite A, and Bakelite C types from the phenols of primary coal tar and formaldehyde.

They used ammonium chloride, ammonia, and benzyl amine as condensing agents to produce Novolak and Bakelites A and C respectively. The condensations were carried out with the entire tar and also with the various lighter phenol fractions of the tar. Novolak types of resins were prepared from the whole tar as well as from the two fractions defined by the temperatures, 150, 250, and 300°C. Bakelite A types of resins were prepared from the three fractions defined by the temperatures 190, 260, and 300°C. Resin of the Bakelite C type was prepared from the tar fraction boiling between 190 and 230°C. The fraction boiling from 230 to 260°C yielded no resin of the C type except when soda was used as a catalyst and then the product was, obviously, of inferior quality. No Bakelite C could be obtained from the fraction above 260°C.

Alcoholic solutions of the soluble resins were painted on wood panels for observation. It was found that resins made so as to contain non-phenolic hydrocarbons (neutral oils of the tar) produced varnishes which were tougher and more flexible when dry than those that did not contain such hydrocarbons. They regarded Bakelite A as more likely suitable substitute for shellac than the Novolak type of resin. However, they probably did not consider the probability of a film of Bakelite A transforming into the very brittle bakelite C state after long exposure to fairly high tem-

perature.

Morgan, Megson, and Holmes. Morgan (22) in 1930 described some experiments made by Pratt on the condensations of the formaldehyde condensations of low temperature tars. Approximately 80 percent of the crystallizable phenols (phenol, the three cresols with m-cresol predominating, and at least five of the xylenols of which the symmetrical is present in the greatest amount) condenses readily with formaldehyde at 70° in the presence of acid to yield a yellow-red resin of the fusible Novolak type.

To effect removal of the unreacted phenols the reaction was carried out in a solvent petroleum (b.p. 60--80°) medium from which the resin separates completely at the end of the reaction. One of the greatest difficulties encountered was to determine the amount of formaldehyde required for the reaction. Use of an excess amount would yield an infusible, insoluble resin even in the case of an acid catalyst. About 75 percent of the viscous tar acids, whose chemical nature is unknown, condenses readily with formaldehyde at 70° when an acid catalyst is used.

"The fraction of low temperature tar of b.p. 170-230° often contains more than 50 percent of petroleum soluble phenols," Morgan states, "and resins of good quality can be obtained from this fraction without the isolation of the phenols. Condensation is carried out at 70° and the neutral oil removed by distillation in steam in the case of a Novolak or by the addition of petroleum in the case of a resin of the Bakelite type."

In 1931 Morgan and Megson (23) prepared hardening resins from the crude phenolic fractions (b.p. 170-230°C) of a typical low

temperature tar and purified them sufficiently to give satisfactory electrical tests. They found that soluble non-hardening resins of the Novolak type accompanied hardening resins in the formaldehyde condensation with pure phenols.

The tar fraction, containing about 50 percent alkali soluble material, was condensed with paraformaldehyde under the catalytic influence of acetone at a temperature of 98° . The reaction was allowed to proceed from eight to seventeen hours after which time the supernatant neutral oils were decanted off. The resin was washed very thoroughly with warm benzene, and distilled repeatedly with methylated spirit finally under reduced pressure. The purified resin was dissolved in acetone to form a varnish. Paper panels dipped in the varnish were dried for two or three hours at 60° and then bakelized at 100° for 24 hours. Films four mils in thickness showed breakdown voltage tests of from 1700-2250 volts per mil.

Holmes and Megson (24) in December 1933 published an account of experiments in which were determined the effects of several different catalysts and the effects of different concentrations of catalyst on the condensation of formaldehyde with the phenols of low temperature tar and with phenol, the cresols and the xylenols.⁺

⁺This work appeared in the issue of Journal of the Society of Chemical Industry (a British periodical) dated December 8, 1933. At this date the work described later in this thesis had already been practically completed.

Chamberlin. Chamberlin (25) in 1933 obtained good molding powders from a low temperature Dakota lignite tar distillate (that from the Lehigh Briquetting Co.). The distillate used in this work had a boiling range of approximately 90° to 300°C, about 50 percent boiling between 170° and 285°C. He found that about 35 percent of the total distillate was dissolved by caustic solution. The work consisted of first separating the phenols from the tar by (1) extracting the phenols from the distillate as phenolates with a 20 percent caustic solution; (2) liberating them from the caustic solution with CO₂; (3) distilling the free phenols, retaining the portion boiling between 150° and 280°C. This portion was then refluxed for three hours with stannous chloride, washed with a ten percent sodium carbonate solution, and resinified with formaldehyde using potassium carbonate as a catalyst. The product was washed with cold water and then ground to a fine powder. This was mixed with a quantity of wood flour and the mixture dried in vacuo. The dried powder was molded by simultaneous application of heat and pressure to form translucent, sharply molded pieces which were of a dark reddish brown color and possessed good gloss.

An impregnating varnish, good in all but electrical qualities, was prepared by dissolving the dried resin in anhydrous ethanol.

THE TAR DISTILLATE

The lignite tar distillate used in this investigation is a representative sample of low temperature lignite distillate obtained by the Lehigh Briquetting Company.¹ The distillate represents the fraction of the primary tar boiling between 210°C and approximately 355°C according to the readings of a thermometer in the ceiling of the still proper (not the still head) at the plant of the company.

The carbonizing plant of the company has a daily capacity of 200 tons of lignite from which are obtained about 4.8 tons of primary tar. From this amount of tar about 600 gallons of distillate are obtained. The distillate has a specific gravity at 20° of about 1.016, varying somewhat from time to time with plant conditions and with the lignite used.

Laboratory fractionations of 250 gram samples of each of two different batches of distillate received from the plant are summarized graphically in Figure I and are tabulated in Table 1.

Table 1.
Fractionations of Lehigh Tar Distillate, 250 g. sample

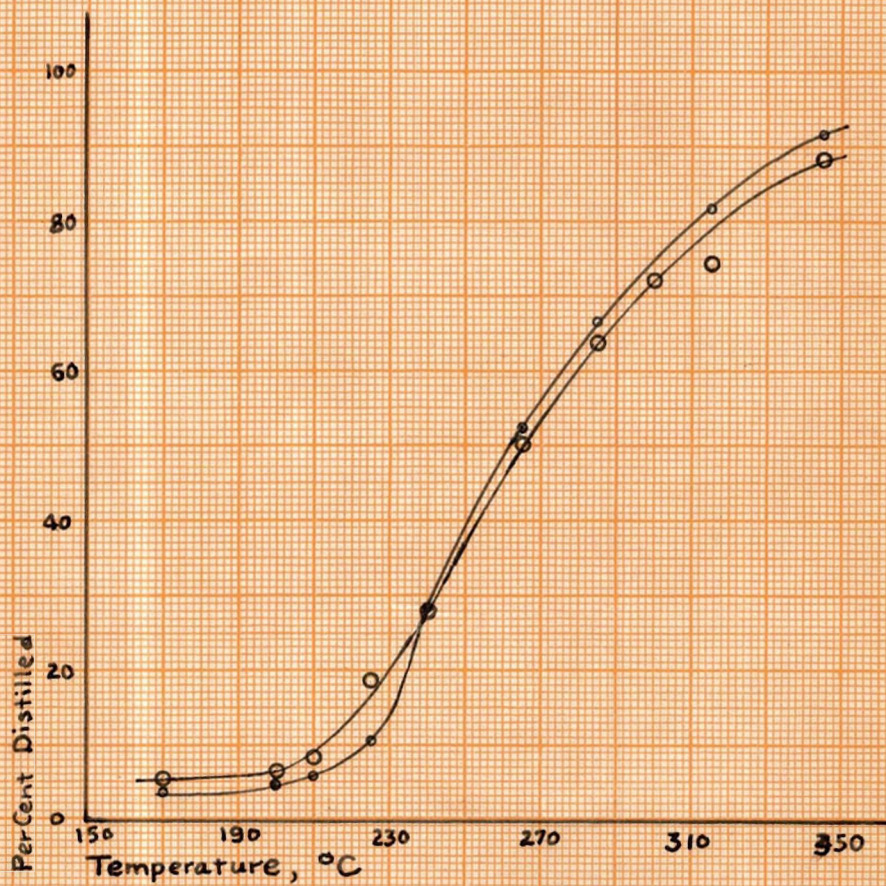
Boiling Range	Wt. of Fraction, grams		Percent of total		Cumulative percent Distilled	
	I	II	I	II	I	II
Under 170	: 8.69	12.4	: 3.49	5.1	: 3.49	5.1
170-200	: 2.85	3.3	: 1.15	1.4	: 4.64	6.5
200-210	: 2.93	4.4	: 1.18	1.8	: 5.82	8.3
210-225	: 12.52	25.3	: 5.03	10.4	: 10.85	18.7
225-240	: 43.93	22.0	: 17.66	9.1	: 28.51	27.8
240-265	: 58.64	54.0	: 23.75	22.2	: 52.26	50.0
265-285	: 34.87	33.2	: 14.02	13.6	: 66.28	63.6
285-315	: 38.37	26.3	: 15.42	10.9	: 81.770	74.5
315-345	: 24.77	33.6	: 9.95	13.8	: 91.65	88.3
Residue	: 20.80	28.4	: 8.35	11.7	:	
	248.37	242.9	: 100.00	100.00		

1. The Lehigh Briquetting Company of Fargo, N. Dak. operates a plant near Dickinson, N. Dak. for carbonizing and briquetting lignite mined in that immediate vicinity. Carbonization is effected

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Laboratory Fractionation Of Lehigh Lignite
Low-Temperature Tar Distillate.

FIGURE 1.



The phenolic content of the distillate varies somewhat from time to time. Samples of the crude distillate extracted with ten percent sodium hydroxide solution showed fifty percent by volume of caustic soluble material.

Allen's Commercial Organic Analysis (31) describes the caustic extraction method of tar acid determination used by the Barrett Company. This method involves distilling the sample to decomposition and determining the percentage of alkali soluble material in the distillate. By a modification of this method Chamberlin (25) working on Lehigh Dakota lignite tar distillate found that the amount of phenol acids available for resin forming condensation constitutes 60.8 of the distillate between 150-275°C or 34.05 percent of the original tar distilling between 210-355°C.

In later work performed in this laboratory Chamberlin (22) made extractions with 10 percent caustic soda solutions on various fractions of the tar distillate. His results are shown in Tables 2 and 3.

Table 2.

Tar Acid Content of Lehigh Low Temperature Tar Distillate			
Fraction of tar distillate	Percent of	Percent	Percent Tar Acids
Boiling between	crude	Distillate	Content
179 - 230 ^o C	17.3		68.65
230 - 241.5	18.1		69.20
241.5 - 255	19.1		67.35
255 - 270	17.0		62.70
270 - 300	17.7		50.00

(1 cont.) by the Lurgi process. (30)

Table 3.

The Acid Content of Lehigh Low Temperature Tar Distillate			
Fraction of Tar Distillate	: Percent of	:	Percent Tar Acid
	: crude distillate	:	Content
200-210 ^o C	: 1.8	:	66.5
210-220	: 9.3	:	72.5
220-230	: 11.1	:	72.0
230-240	: 14.4	:	68.0
240-250	: 9.8	:	66.0
250-260	: 15.3	:	62.0
260-270	: 11.4	:	54.0
270-280	: 7.9	:	51.0

In a report from the laboratories of the Universal Oil Products Company (26) it is stated that the original Dakota lignite tar contains 32 percent tar acids, 2.4% bases, and 0.61 percent sulphur. The distillate used in the investigation represents about 53 percent of the total tar produced.

Caplan, Ross, Sevag, and Switz (27) summarize their work on the examination of the phenols of a low temperature tar as follows:

"Low-temperature tar phenols over the range 220^o to 260^oC have been carefully fractionated and examined and the fraction boiling around 220^oC shown to contain mesitol. $(CH_3)_3C_6H_2OH$, 1,3,5,2. The fraction of minimum density, boiling at 234^oC has been shown to consist mainly of 3 methyl 5 ethylphenol.

"Crystalline derivatives, bromides, and phenylurethans of mesitol and methylethylphenol are described.

"Examination of the fractions of tar acids up to 260^oC has indicated that they consist of mixtures of the simple alkylated homologs of phenol.

"A tentative explanation for the uniformly lower densities of fractions of low-temperature tar acids as compared with corresponding fractions of high temperature acids is offered."

Morgan and Soule (28) show the composition of the phenols of a low-temperature tar given in Table 4.

Table 4.

Composition of the Low-Temperature Phenols (Morgan and Soule).

Component	Percentage by Weight		
	Phenols	Basis of Distillate	Crude Tar
Phenol ¹	4.2	1.9	0.6
Cresols ¹	33.4	15.2	4.9
Xylenol fraction	19.0	8.7	2.8
Higher Homologs	34.8	15.9	5.1
Pitch (acid resins)	8.6	3.9	1.3
	100.0	45.6	14.7

The United States Bureau of Mines (29) has published a report of investigations of the nature of xylenols and higher phenols that have been found in primary tars.

¹Ratio: 27 percent ortho-, 19 percent meta-, and 54 percent para-cresols.

EXPERIMENTAL

I. Preliminary Condensations. A few preliminary condensations carried out at atmospheric pressure in porcelain casseroles on a steam bath showed that a resin can be made by using 200 grams of tar distillate and 115 grams of a 37 percent formaldehyde solution without addition of foreign catalyst. Slightly more than five hours was required to form a resin that was solid but plastic at the steam bath temperature. This solid resin was very brittle, easily friable at room temperature and very dark brown, almost black, in color. It was partially soluble in benzene, more so in alcohol. The extent of the solubility of the resin in these solvents was found to depend upon the stage to which the reaction is allowed to proceed.

In each case the solid resin formed in the bottom of the casserole. Over this resin there was found an aqueous layer and upon this, in turn, there floated a layer of neutral oils. It was early noted that the addition of a small amount of pyridine to the reacting mixture accelerated the reaction quite noticeably.

II. Effects of Catalysts. A series of tests was then made to determine the catalytic effect of various substances on the reaction between formaldehyde and the tar distillate. The work consisted of adding a predetermined quantity of the chosen catalyst to a standard mixture of 50 grams of the distillate and 27 grams of 40 percent formalin. These mixtures, in porcelain casseroles, were then placed on a steam bath. They were stirred frequently and the process of resinification was carefully observed. Resin-

ification was carefully observed. Resinification was in each case allowed to proceed to a point where the resin was at a stage of what shall be termed "plastic solidity" at the steam bath temperature. "Plastic solidity" is defined as that degree of hardness of a resin at which it will just support a weight of 23 grams consisting of a glass rod 4 mm. in diameter weighing 3 grams to which is attached a weight of 20 grams. No difficulty was encountered in determining this standard end point within an accuracy of about ± 5 percent. The time required to reach a state of plastic solidity on the steam bath was recorded, in minutes, for each mixture. The resins taken to this stage were all brittle, friable solids at room temperature.

Because of limitations of steam bath space the tests were run in groups of eight or sixteen. For purposes of control and standardization of operating conditions each group included a standard mixture containing five grams of potassium carbonate as the catalyst or, the standard mixture of 50 grams of distillate and 27 grams of 40 percent formalin without added catalyst or both mixtures. Preliminary experiments showed that the former mixture (5 grams K_2CO_3) required only a short time for reaction (25 minutes) while the latter (no catalyst) required a comparatively long time (over 5 hours). Therefore, if rapid reactions were expected in a given group the former was used as a control and if slow reactions were expected the latter was used, and if the speed of the reactions of the mixtures in the group could not be predicted both controls were used.

As indicated above, five grams of potassium carbonate was

taken as the standard catalyst. Chemically equivalent, and in some cases also equimolar, amounts of other compounds were added to the standard mixture of distillate and formaldehyde to test their effects on the resin forming reactions. It should be remembered that the end point described determines the effect of the compound not only as a condensing agent but also as a polymerizing agent because the resin at this end point stage is in a fairly highly polymerized condition.

After the resin had attained a state of plastic solidity on the steam bath the mixture was allowed to cool at room temperature. The supernatant water and neutral oils were then poured off and the resin weighed. The resins were then carefully observed as to gloss hardness, and friability. Judgment of these qualities could be made on a comparative basis only, comparison being limited to other resins in this same series.

A gloss scale of 0 to 10 was arbitrarily chosen. A gloss rating of 10 indicates a very high gloss, one that is very lustrous and, in fact, quite satisfactory. A gloss rating of 0 indicates probably the least gloss possible for a resin. Intermediate degrees of gloss were rated numerically between 0 and 10.

The hardness ratings are mere comparisons of the ease with which the point of a pen knife penetrated lumps of the various resins. Varying degrees of friability tended, of course, to cause errors in judgment, but some useful comparison was made. The hardest resins made in the series were rated "H". They were harder than talc and softer than gypsum (actual standard rating about 1.5).

Softer resins were graded b,c,d,e, and f respectively in order of decreasing hardness.

All of the resins obtained in this work were very brittle at room temperature. A rating of "t" (tough) in table 5 indicates only that the resin is less friable than one marked "b" (brittle). A resin which crumbled under stress rather than breaking into a few small pieces was marked "c" (crumbly).

Table 5 summarizes the results of this series of tests. The various catalysts tried are listed in the order of time required for reaction in their presence.

In general, the organic acids and alcohols retard the reaction; neutral organic compounds and nearly neutral inorganic salts have little catalytic effect; strong acids, bases, acid and basic salts, and strong oxidizing and reducing agents have very pronounced accelerating effects. In general, the organic retarders of the resinification and the neutral compounds exhibiting little or no catalytic effect produced the glossier, tougher, and harder resins. The dull, crumbly resins were all formed with the comparatively violent catalysts.

Table 5.

Effect of Various Compounds on the Reaction at 93°C between 50 grams of Lignite Tar Distillate and 27 grams of 40% formalin.

Catalyst--Name and Formula	Amt. used	Time, Min. to reach plastic solidity	Gloss 10 = highest gloss	Fria-bility t = tough b = brittle c = crumbly	Hard-ness a = hardest f = softest
1. Aniline, $C_6H_5NH_2$	7 cc.	847	10	t	b
2. Citric Acid, $HOOC-CH_2-C(OOH)(OH)-CH_2-COOH$	5.08g.	742	9	t	a
3. Tartaric Acid, $HOOC-CH(OH)COHO-COOH$	5.44g.	658	9	t	a
4. Rosin	5.00g.	643			
5. Methyl Alcohol, CH_3OH	7.0cc.	639	9	t	b
6. Ethyl Alcohol, C_2H_5OH	10.0cc.	606	6	c	b
7. Succinic Acid, $COOHCH_2CH_2COOH$	4.28g.	605	8	t	a
8. Methyl Acetate, CH_3COOCH_3	7 cc.	426	9	t	a
9. Glycerol, $CH_2OHCHOHCH_2OH$	4.5cc.	424	10	b	b
10. Sucrose, $C_{12}H_{22}O_{11}$	5 g.	423	8	t	b
11. Starch, $(C_6H_{10}O_5)_n$	5. g.	421	8	t	b
12. Acetone, $(CH_3)_2C=O$	2.6cc.	386	8	t	b
13. Chloroform, $CHCl_3$	2.9cc.	360	9	b	b
14. Toluene, $C_6H_5CH_3$	7 cc.	348	9	b	b
15. Carbon Tetrachloride, CCl_4	3.5cc.	343	9	t	a
16. Magnesium Nitrate, $Mg(NO_3)_2 \cdot 6H_2O$	9.27g.	332	9	t	b
17. Cobalt Nitrate, $Co(NO_3)_2 \cdot 6H_2O$	10.55g.	331	9	t	b
18. No Catalyst Added Average of 7 tests		330	9	t	b
19. Magnesium Chloride, $MgCl_2 \cdot 6H_2O$	7.35g.	330	8	b	a
20. Aluminum Sulfate, $Al_2(SO_4)_3 \cdot 18H_2O$	12.07g.	316	7	t	b
21. Potassium Chloride, KCl	5.40g.	310	7	t	b
22. Potassium Nitrate, KNO_3	7.32g.	303	9	t	a
23. Sodium Bromide, $NaBr$	7.46g.	298	8	t	b
24. Kerosine, C_nH_{2n+2}	13 cc.	298	10	t	a
25. Sodium Oxalate, $(COONa)_2$	4.85g.	298	2	t	b

Table 5, continued:

Catalysts--Name and Formula	Amt. used	Time, Min. to reach plastic solidity	Gloss 10 = highest gloss	Friability t = tough b = brittle c = crumbly	Hardness a = hardest f = softest
26. Potassium Sulfate, K_2SO_4	6.30g.	292	9	b	b
27. Nickel Sulfate, $NiSO_4 \cdot 6H_2O$	9.53g.	286	8	b	b
28. Strontium Chloride, $SrCl_2 \cdot 6H_2O$	9.67	283	9	t	b
29. Pyridine, C_5H_5N	2.9cc.	283	8	b	b
30. Potassium Bisulfate, $KHSO_4$	4.92g.	267	8	t	a
31. Aluminum Chloride, $AlCl_3$	3.21g.	258	8	t	b
32. Aluminum Chloride, $AlCl_3 \cdot 6H_2O$	8.73g.	257	8	t	b
33. Ammonium Hydroxide, NH_4OH	4.85cc.	228	6	b	b
34. Ammonium Carbonate, $(NH_4)_2CO_3$	4.13g.	211	2	b	c
35. Aluminum Sulfate, $Al_2(SO_4)_3$	4.14g.	205	8	t	a
36. Zinc Nitrate, $Zn(NO_3)_2$	6.84g.	203	10	t	b
37. Zinc Sulfate, $ZnSO_4$	5.83g.	199	9	t	a
38. Ammonium Sulfide, $(NH_4)_2S$	2.5cc.	199	3	t	b
39. Zinc Chloride, $ZnCl_2$	4.92g.	197	10	t	b
40. Pyrogalllic Acid, $C_6H_3(OH)_3$	3.05g.	191	9	t	a
41. Ferric Sulfate, $Fe_2(SO_4)_3$	4.82	187	9	t	b
42. Oxalic Acid, $(COOH)_2 \cdot 2H_2O$	4.57g.	186	7	b	b
43. Calcium Carbonate, $CaCO_3$	3.62g.	185	4	t	b
44. Ferrous Sulfate, $FeSO_4 \cdot 7H_2O$	10.10g.	173	8	t	b
45. Phosphoric Acid, H_3PO_4	4.17cc.	142			
46. Nitric Acid, HNO_3	4.59cc.	140	5	b	b
47. Lead Oxide, PbO	8.08g.	138	8	b	b
48. Lead Nitrate, $Pb(NO_3)_2$	12.00g.	134	7	b	b
49. Potassium Acetate, CH_3COOK	7.10g.	125	8	t	a

Table 5, continued:

Catalysts--Name and Formula	Amt. used	Time, Min. to reach plastic solidity	Gloss 10 = highest gloss	Friability t = tough b = brittle c = crumbly	Hardness a = hardest f = softest
50. Potassium Thiocyanate, KSCN	3.52g.	120	9	b	a
51. Sodium Phosphate, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$	12.98g.	105	8	b	b
52. Sodium Hydroxide, NaOH	2.90g.	49	1	c	f
53. Potassium Hydroxide, KOH	4.06g.	48	2	c	d
54. Calcium Oxide, CaO	2.03	44			
55. Sulfuric Acid, H_2SO_4	2.02cc.	37	9	b	b
56. Potassium Cyanide, KCN	2.36g.	36	2	b	e
57. Sodium Bicarbonate, NaHCO_3	3.05g.	32	2	c	e
58. Potassium Ferrocyanide, $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$	15.30g.	31	3	c	e
59. Lead Peroxide, PbO_2	4.33g.	26	6	b	b
60. Potassium Ferricyanide, $\text{K}_3\text{Fe}(\text{CN})_6$	11.90g.	25	1	c	d
61. Sodium Carbonate, Na_2CO_3	3.84g.	25	2	c	f
62. Potassium Carbonate, K_2CO_3 - Ave. of 10 tests	5.0g.	24	5	b	c
63. Acetic Acid, CH_3COOH	4.17cc.	22	8	t	a
64. Potassium Permanganate, KMnO_4	5.72g.	20	3	c	e
65. Barium Hydroxide, $\text{BaOH} \cdot 8\text{H}_2\text{O}$	11.40g.	17			
66. Hydrochloric Acid, HCl	6.00cc.	14	7	t	a
67. Molybdic Acid, H_2MoO_4	5.87g.	10	4	c	f
68. Potassium Dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$	10.65g.	9	1	c	e
69. Sodium Aluminate, NaAlO_2	2.97g.	7	1	c	f
70. Potassium Chromate, $\text{K}_2\text{Cr}_2\text{O}_4$	7.03g.	6	0	c	e
71. Stannous Chloride, SnCl_2	6.86g.	6	3	c	e
72. Stannic Chloride, $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$	12.68g.	2	4	c	e

III. Effect of Catalyst Concentration. Several tests were made to determine the effect of catalyst concentration on the time required for the resinification process. The work consisted of varying the amounts of potassium carbonate, potassium hydroxide, stannous chloride, hydrochloric acid, sulfuric acid, potassium bisulfate and potassium sulfate used as catalysts in the resinification of the standard tar distillate--formaldehyde mixture. Each of the reactions was carried out under the standardized procedure described in part II. The data obtained in these tests are plotted graphically in Figures 2, 3, 4, 5, and 6.

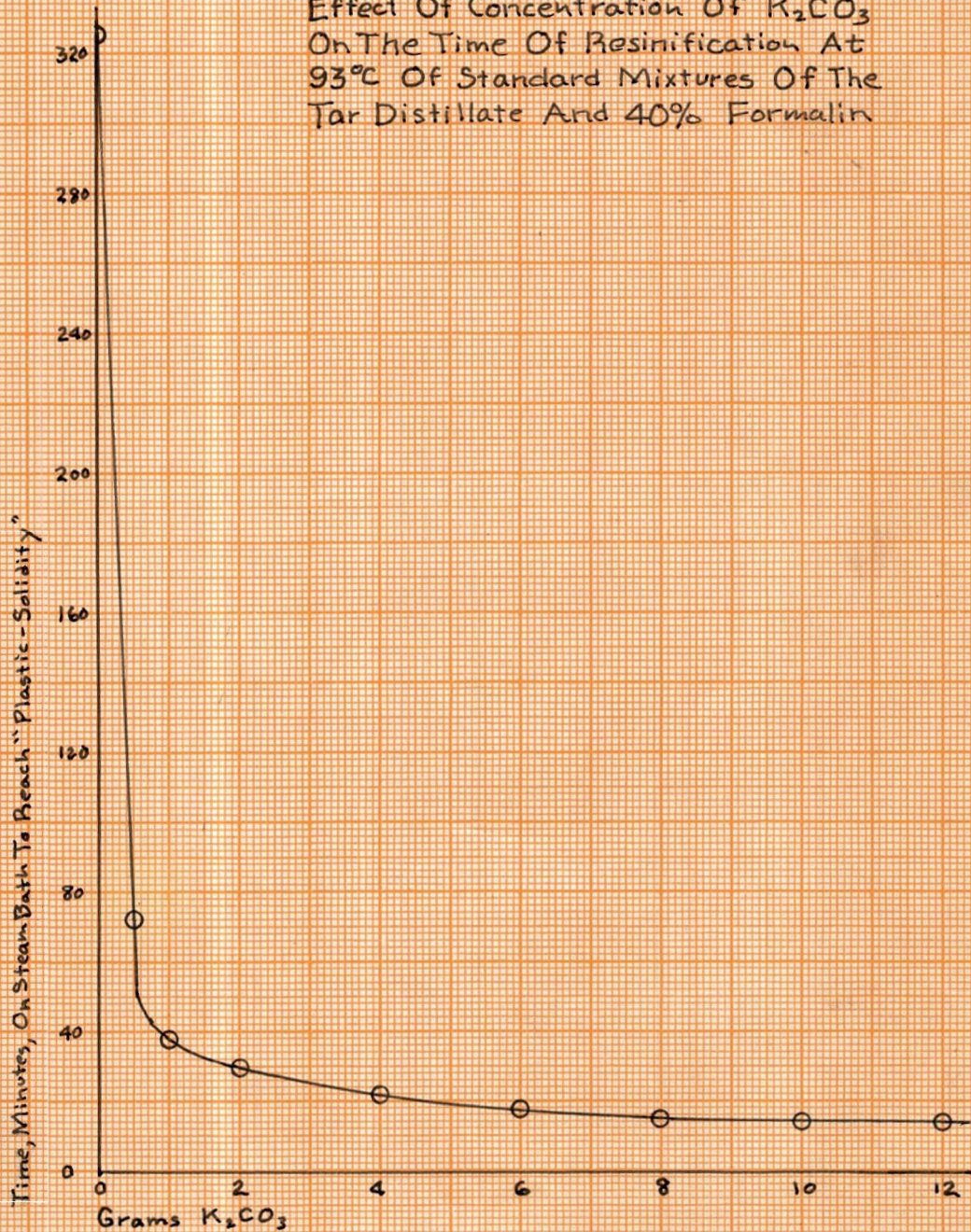
Consideration of Figure 2 shows that the addition of even small quantities of potassium carbonate exerts a marked influence on the rate of reaction. The effect of this agent on the rate of reaction becomes practically constant after a definite concentration of catalyst has been reached.

The potassium hydroxide curve shown in Figure 3 indicates that small additions of this base introduce marked catalytic effects. With increased additions of KOH the time of reaction drops to a minimum, and then increases. It is significant to note in this connection that the work on tar acid determination indicates that between 3.5 and 5.0 grams of potassium hydroxide are required to form phenolate with all of the phenols present in 50 cc. of the distillate. Undoubtedly potassium phenolate is formed when potassium hydroxide is added to the distillate-formalin mixture. It appears, then, since the curve is at its lowest level between points representing the quantities required to form phenolate in 50 cc. of the distillate, that the potassium phenolates and

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FIGURE 2

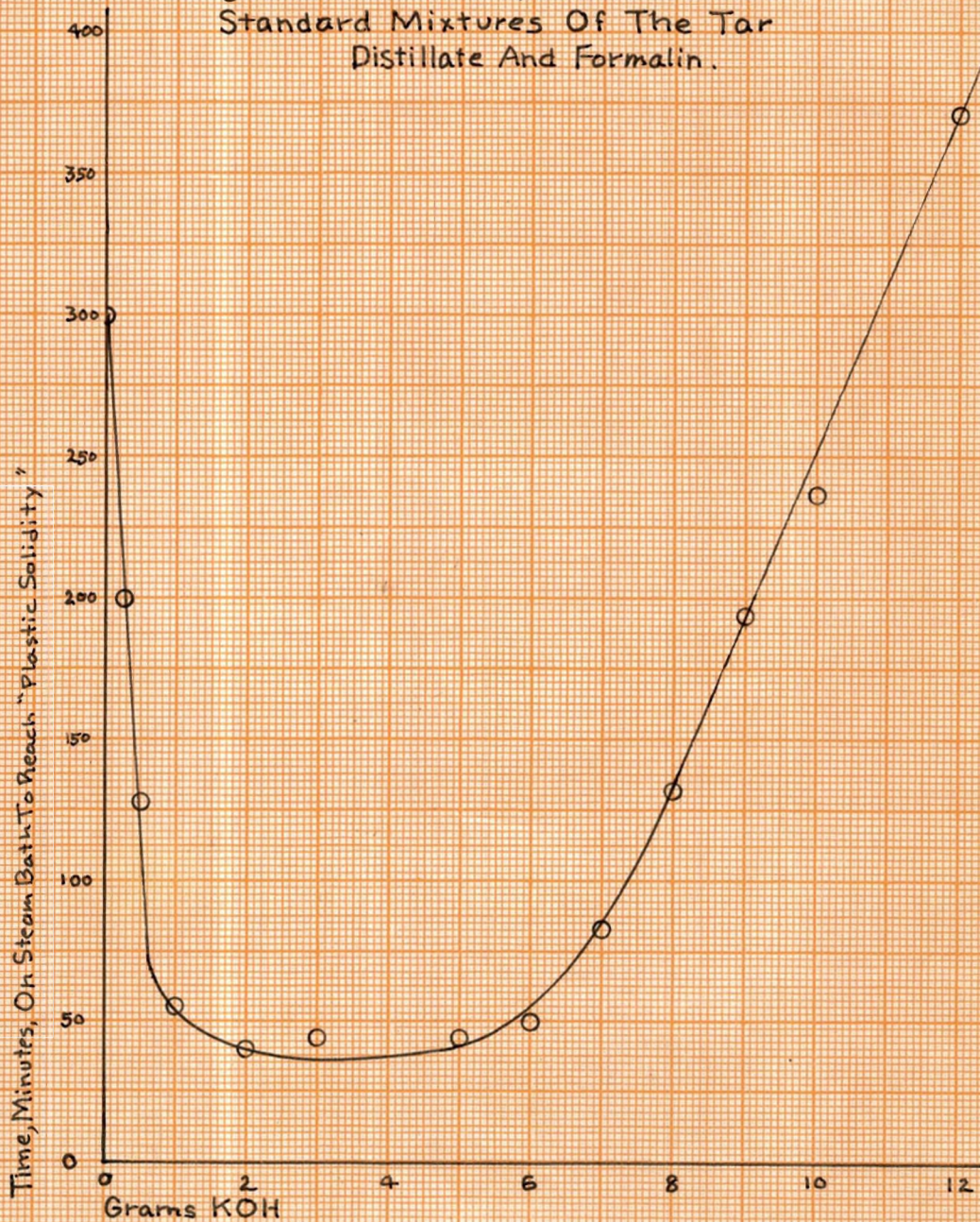
Effect Of Concentration Of K_2CO_3
On The Time Of Resinification At
 $93^\circ C$ Of Standard Mixtures Of The
Tar Distillate And 40% Formalin



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Figure 3.

Effect Of Amount Of KOH Used
On The Time Of Resinification Of
Standard Mixtures Of The Tar
Distillate And Formalin.



formalin react very readily in the presence of whatever catalyst is present in the distillate which may be excess phenol, organic bases, or slight excess of caustic.

The first additions of stannous chloride, as seen from Figure 4, have no catalytic effect on the resinification. This may be due, perhaps, to chemical reaction between the stannous chloride and some constituents of the tar. The further additions of stannous chloride introduce pronounced catalytic effects.

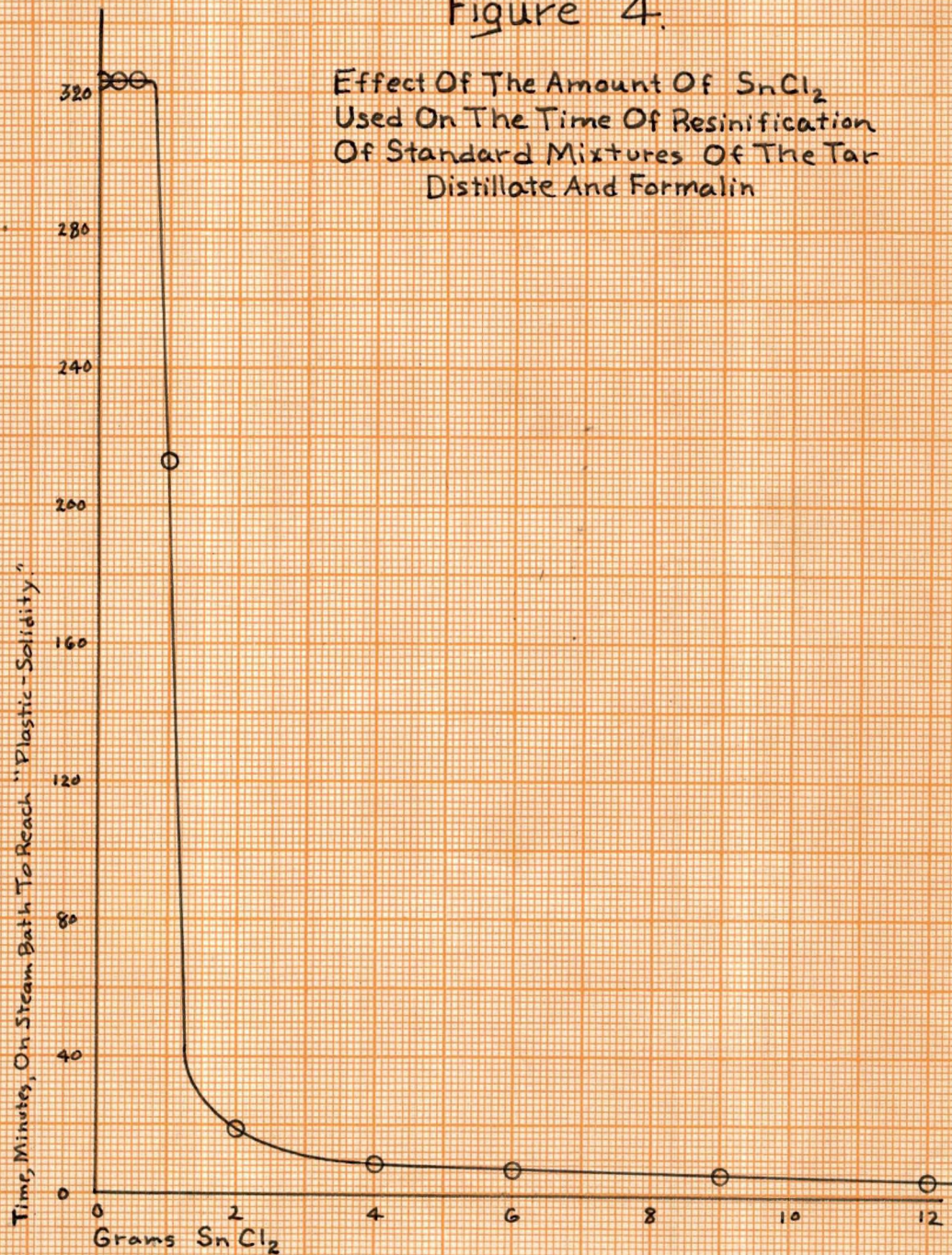
The curve of Figure 5 might indicate that the effect of catalytic substances inherent in the distillate is destroyed by addition of a small amount of hydrochloric acid. This would be due, no doubt, to chemical reaction between the acid and the inherent catalyst of the distillate. Further addition of the acid, it is noted, causes a definite increase in reaction rate.

The curves for sulfuric acid, and potassium bisulfate shown in Figure 6 take a form well in accord with that for hydrochloric acid. The three curves in Figure 6 are so plotted that equal abscissae indicate equimolar amounts of the three compounds represented. Thus, potassium bisulfate appears to exert catalytic effect similar to but less active than that of sulfuric acid. Only a slight catalysis was obtained from additions of potassium sulfate. This effect did not change measurably with wide variation in the quantities of potassium sulfate added.

The curve obtained for ammonium hydroxide as shown in Figure 7 is indeed difficult to explain. It is expected that the ammonium hydroxide will form hexamethylenetetramine with formaldehyde when added to the distillate-formalin mixture. However, rough calcula-

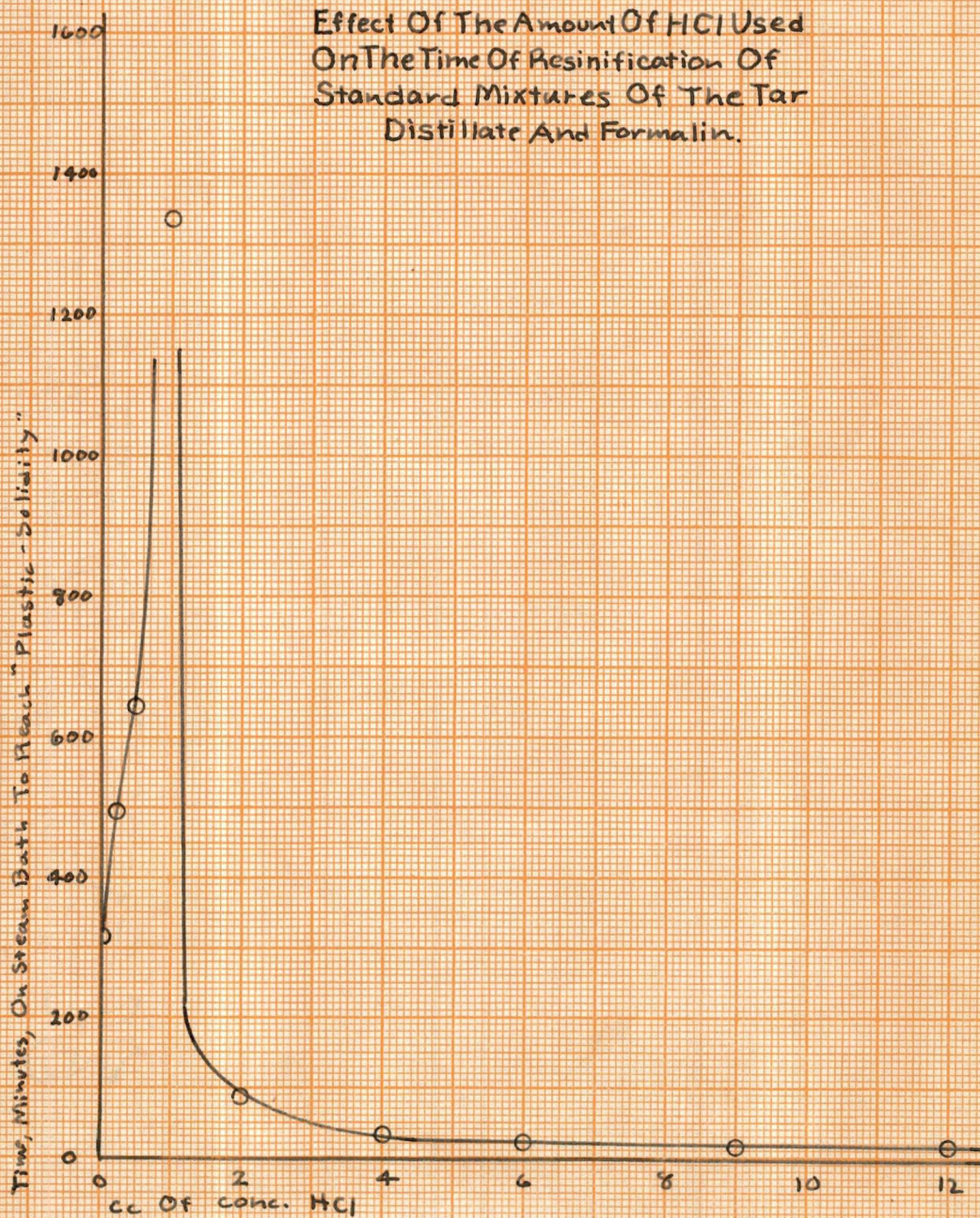
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Figure 4.



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Figure 5.

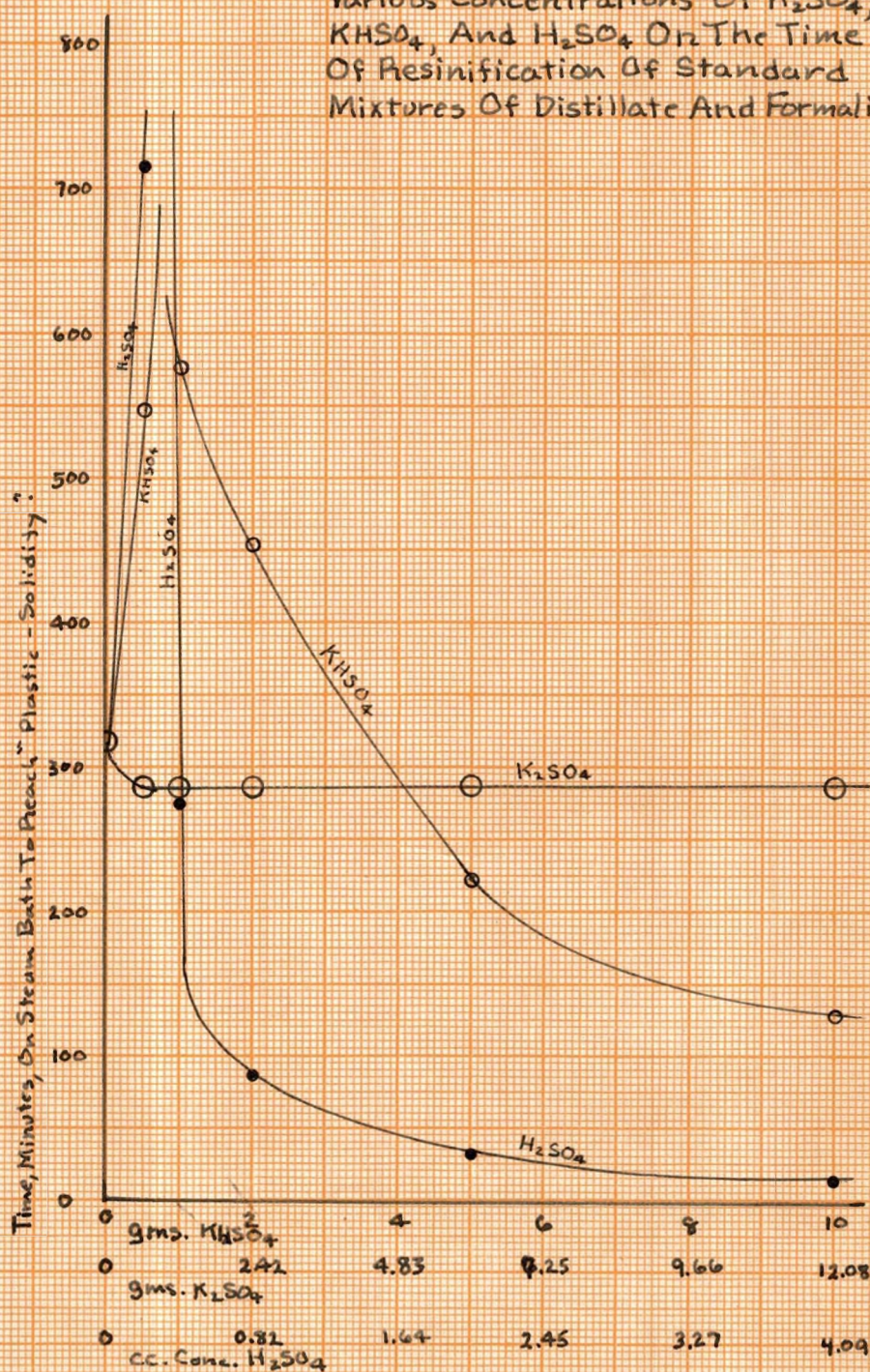


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Figure 6.

Comparison Of The Effects Of Various Concentrations Of K_2SO_4 , $KHSO_4$, And H_2SO_4 On The Time Of Resinification Of Standard Mixtures Of Distillate And Formalin.

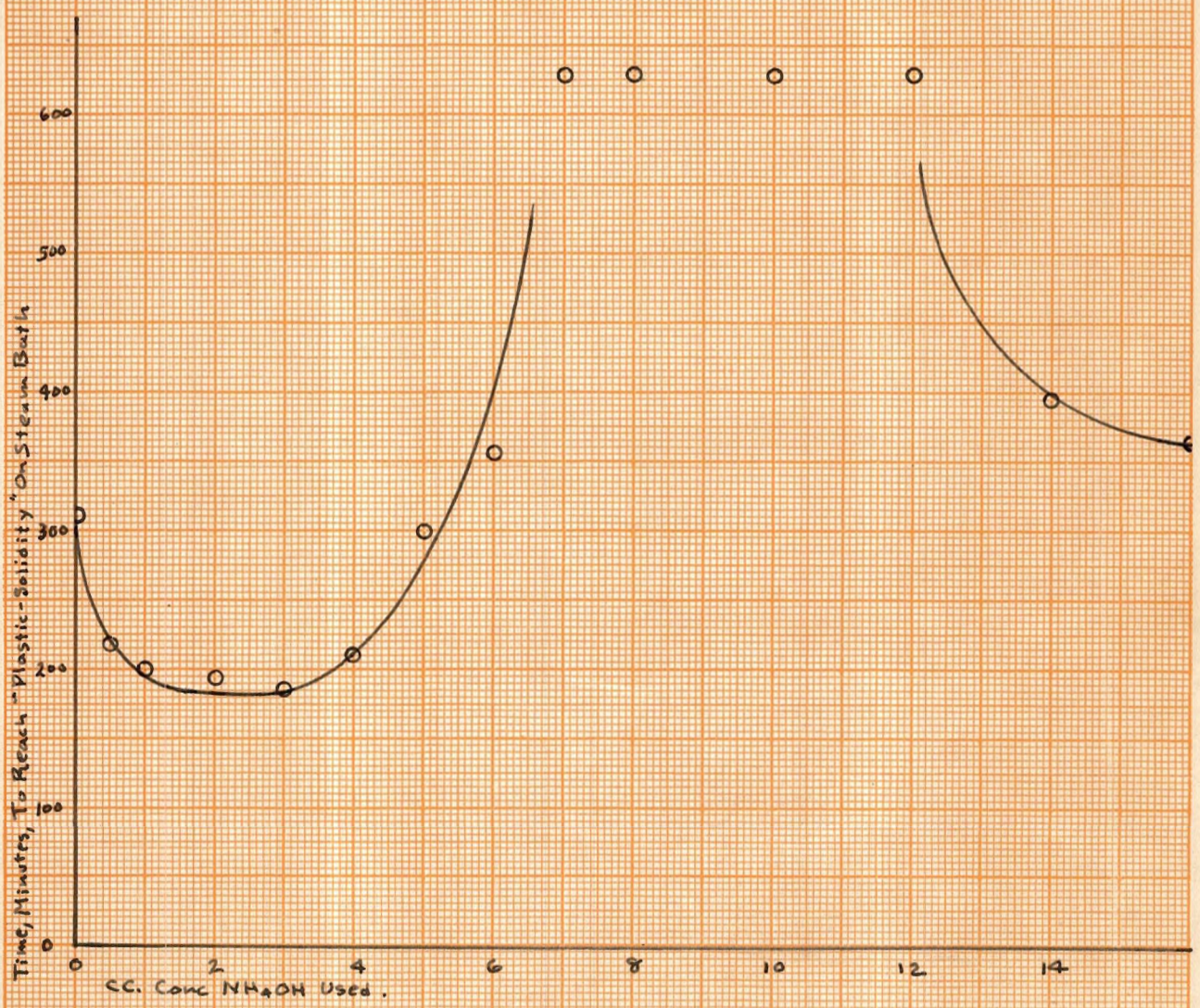


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Figure 7.

The Effect Of Various Amounts Of NH_4OH On The Resinification Time Of Standard Mixtures Of Distillate And Formalin.



tions indicate that approximately 16 cubic centimeters of concentrated ammonium hydroxide, (sp.g. 0.90) such as was used in the test, would be required to form "hexa" with all the formaldehyde in the 27 grams of 40 percent formalin of the standard distillate-formalin mixture. Obviously more data is necessary for an intelligent interpretation of the curve.

VI. The Solubilities of "Plastic-Solid" Resins. In order to more clearly define the standard end point used in the work described above a series of tests was made to determine the solubilities in acetone of several resins formed according to the method described.

Standard mixtures of distillate and formalin (50g. to 27g.) were resinified in porcelain casseroles under the influence of various catalysts. The resins were brought to the standard end point of "plastic-solidity" on the steam bath and allowed to cool. When cold they were all brittle, easily friable solids. The cold resins were ground in a mortar to pass a 24 mesh screen, washed once with water, once with kerosine, and twice with petroleum naphtha. Washing was effected by stirring the resin together with the wash liquid in a beaker and then filtering through a cotton towel. The washed resin was air dried, pulverized in a mortar to pass a 150 mesh screen and then a three gram sample was weighed (to nearest 0.01g.) into a weighed beaker. Fifty cc. of acetone was next poured into the beaker to cover the powdered resin and the whole was allowed to stand, with occasional stirring, for an hour. At the end of that time the acetone, which had now leached out most of the soluble portion of the resin, was decanted through

a weighed filter paper. The residue in the beaker was washed repeatedly with acetone until the wash was practically colorless. The bulk of the residue was then transferred with acetone to the filter paper where it was further washed with acetone until the wash liquid was colorless. The residues in the filter paper and in the beaker were air dried until no odor of acetone could be detected and were weighed as insoluble resin. Tests were run in duplicate, and the mean values of the results are reported.

Similar solubility tests were made on several resins which had been made about five months previous to the tests and which had been allowed to stand for that time at room temperature in contact with air. The solubility data obtained in all of these tests is summarized in Table 6.

Table 6.

Solubilities in acetone of Resins at the Standard End-Point Condition.

Catalyst Used	Amt. of catalyst	Time Between Resinification and test	Percentage Insoluble Matter
None		4 days	30.4
Tartaric Acid	5.44 g.	4 days	40.5
Acetic Acid	4.17 cc.	4 days	34.8
Resin	5.00 g.	4 days	33.5
Pyridine	8 cc.	4 days	51.2
Pyridine	.5 cc.	4 days	39.1
None		10 weeks	47.8
None		10 weeks	45.4
Potassium Carbonate	5 g.	10 weeks	84.4
Potassium Carbonate	5 g.	10 weeks	84.2

The solubility figures indicate quite well the exact stage of resinification indicated by the standard end point for each particular resin. As would be expected, the acid catalyzed resins

at the end point condition show lower percentages of insoluble matter than those catalyzed with bases. The resin made without catalyst show some increase in insoluble matter on standing at room temperature for some time. The change in the resins is not rapid enough, however, to cause any serious error during a four day period between resinification and testing.

V. Novolak Resins. An experiment was performed with the view of determining whether a resin made according to the procedure described above (a resin that is plastic-hard on the steam bath and hard at room temperature) would react with additional phenol.

The resin used was made from a mixture of 200 grams of distillate, 80 cc. of 40 percent formaldehyde solution, and 20 grams of tartaric acid. Thirty grams of this resin was powdered and mixed with 43 grams of the fraction of the original tar distillate that boiled between 241° and 255°C . This mixture of resin and tar acids was then slowly heated in an oil bath to 200°C , and then foaming gradually subsided until 135°C . The mixture had by that time become a homogeneous liquid, the resin apparently having gone completely into solution. At about 180° the batch began to evolve inflammable gases (probably cracking) and began to thicken. Thickening continued over a period of about two thousand minutes at the end of which time the solution became a plastic, tarry, sticky mass that did not flow readily even at 200°C . Samples taken during the course of the heating showed that at the point when thickening began the batch was a very viscous liquid at room temperature and completely soluble in alcohol. As thickening progressed samples of the batch became harder and more brittle at room temperature. One

stage was recognized, after a total of 130 minutes of heating, at which point the resin was a brittle glossy solid at room temperature and completely soluble in alcohol. After about 2000 minutes of heating the resin solidified almost as a char and appeared to be only partly soluble in alcohol.

Table 7 shows the general trend of events of this test as related to the temperature at which they occurred.

Tar distillate (total) when mixed with the same original resin and placed on the steam bath form a homogeneous, thick liquid, which, after 15,000 minutes is still a thick liquid showing as yet no sign of solidifying. At room temperature this resin is plastic and soluble in alcohol.

Table 7

Events in Reaction between Resin and Additional Tar Distillate Fraction.

Temperature of Resin-Distillate Mixture °C	Course of the Reaction.
25°	Mixture placed in oil bath at 200°C. Oil bath temperature dropped to Min. of 165°C and began to rise again.
110°	Batch began to foam.
112°	Foaming became violent. Solid resin appeared to be dissolving in the distillate.
125°	Foaming began to subside.
135°	Foaming practically subsided. Batch was now a homogeneous liquid, resin apparently all dissolved. Total time elapsed about 30 minutes. Batch and bath temperatures both rose steadily.
180°	Visible vapor (found to be inflammable) began to be evolved from batch.
190°	Evolution of vapor continued. Total time elapsed, 45 minutes. A sample taken at this point was a plastic-near solid-liquid at room temperature, soluble in alcohol.
200°	Evolution of vapor continued, total time elapsed, 130 minutes. Sample was a glossy, brittle solid at room

Table 7. (cont.)

200°	temperature, completely soluble in alcohol.
200°	Batch continued to evolve vapor thickening as time went on.
200°	After about 2000 minutes total elapsed time, batch was a sticky, viscous, tarry mass at 200°C, a char-like, partly insoluble brittle solid at room temperature.

The resin tends to dissolve in tar distillate even at room temperature.

It appears that the batch heated in the oil bath underwent two reactions, one between 110° and 135° and the other above 180°. The first was probably a violent absorption of phenols by the resin (together with the solution of the resulting new resin in the excess phenols and neutral oils) while the second probably involved breaking down some of the heavier molecules either of the new resin or of the oils mixed with it.

The first reaction can undoubtedly be effected at a steam bath temperature probably even at room temperature. The second requires a higher temperature.

A Novolak resin was prepared by the two step method described above. About 1700 g. of distillate and 900 g. of 40 percent formalin were mixed and heated in an aluminum kettle on a steam bath for seven hours. No foreign catalyst was used. About 1600 g. of resin was obtained which was hard and brittle at room temperature. This resin was crushed to pass a 10⁴ mesh screen and mixed with 2500 grams crude distillate. The mixture was heated in an aluminum kettle on a hot plate. The temperature rose slowly, the

reaction taking the same general course as was recorded in Table 7. At the end of 16 hours at which time the temperature of the batch was 186°C, heating was discontinued and the resin allowed to cool. The resin finally produced, 2230 grams, was hard, brittle and glossy at room temperature. It had a good conchoidal fracture but gloss of the fracture was somewhat reduced by traces of an oily substance invariably present at the fracture. The resin was dissolved in as small a quantity of acetone as practicable (2 parts acetone to 7 of resin). This concentrated acetone solution was thinned with various solvents to form varnishes in which strips of brass and paper could be dipped for the performance of the A.S.T.M. tests. Some of the varnishes did not dry so as to leave films which could be tested. A summary of the experience with solvents encountered here is presented in Table 8.

Table 8.

Characteristics of Novolak Films Obtained from Varnishes Employing Various Solvents.

Starting solution of 7 parts of Novolak in 2 parts of acetone.

Thinner Used	: Parts of : Thinner per : 9 parts of : starting : solution	: Film on Brass	: Film on Paper
Acetone	: 2-1/2	: Badly checked	: Badly checked
Butyl Alcohol	: 3	: Uneven	: Checked and un-
			: even
Butyl Acetate	: 4-1/2	: Very good	: Satisfactory
(1/2 Butyl Alcohol,			
1/2 Butyl Acetate)	: 3	: Uneven	: Checked and
			: very uneven

As is obvious from the table the varnish made using Butyl

Acetate as a thinner was the one used for the tests. No plasticizer or other ingredient of any kind was added to the Novolak solution. Films were made and tested in the manner prescribed by the A.S.T.M. (15).

Five specimens of paper, dipped in the varnish and air dried, averaging about 8 mils in mean thickness showed breakdown voltage per mil thickness for the individual specimens being 805 volts. On a different type of test, one specimen withstood $\times 3500$ volts for one minute followed by 4000 volts for one minute before breaking down. The minimum thickness of this sample in the vicinity of the point of penetration was 6.5 mils.

Baking the paper specimens in an oven with openings for air circulation for 24 hours at $105-110^{\circ}\text{C}$ embrittled them somewhat and caused a marked decrease in their dielectric strength. They showed an average breakdown voltage of only 256 volts per mil thickness.

An air dried film of the resin on brass could be bent to a curvature of $1/8$ inch radius without cracking. The same film, after the 24 hour baking, cracked both inside and outside such a curvature.

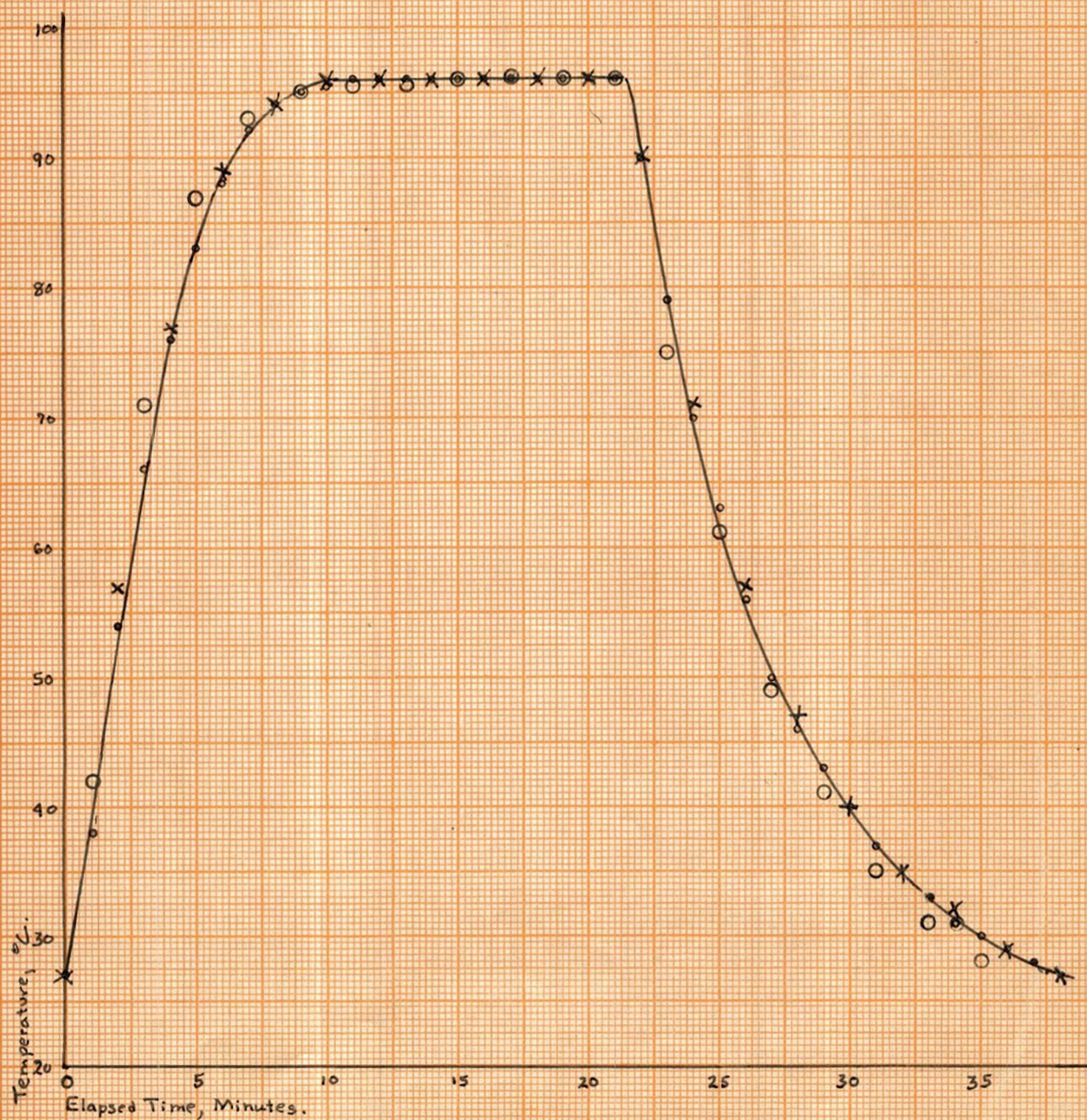
VI. Washed Resins. As has already been pointed out, the literature indicates that a resin for electrical insulating purposes must be of a high degree of purity and dryness. A series of tests was carried out wherein resins produced from the tar distillate and formalin were subjected to various washing processes and then tested for dielectric strength. The experiments each consisted of stopping the resinification at a very early stage, separating the resin liquid at room temperature, from the water and neutral oils, washing the liquid resin with suitable wash solvents, heating the washed resin to convert it to a resin solid at room temperature, dissolving the resin in acetone, and preparing and testing of films obtained from the spirit varnishes so prepared.

Each test was conducted by the following general method: 2000 grams of distillate and 1075 grams (1000 cc.) of 40 percent formalin were heated together with constant stirring in an aluminum kettle in a steam bath. No foreign catalyst was used and the reaction proceeded at atmospheric pressure. Heating and stirring were continued for a total time, including heating up period, of twenty minutes. Heating up to the maximum temperature attained required about ten minutes; during the second ten minutes the temperature remained at the maximum value of $96^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$. At the end of the twenty minutes the batch was water cooled to room temperature in from 15 to 20 minutes, stirring being continued throughout the cooling period. Temperature readings were made every minute during both heating and cooling periods to check uniformity of procedure. Three typical curves plotted in Figure 8 indicate the degree of

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Figure 8

Time-Temperature Curves
For First Heating Period In
The Preparation Of Three
Resins To Be Washed.



uniformity that was maintained between tests.

When the resinified mixture had been cooled to room temperature it was weighed (the loss during the resinification ranged from 15 to 35 grams). The entire batch was then poured into two separation jars where it was left to form three layers, oil, water, and resin. The separation jars were cyanidation jars of two liter capacity whose necks were fitted with large stop cocks. The separation of the three layers was effected by merely draining the resin out through the stopcock at the bottom of the jar, the water next, and the oil last. Eleven tests show an average of 1172 grams of resin recovered, 941 grams of water, and 868 grams of oil per test.

The resin layer was a viscous liquid at room temperature. Viscosity and specific gravity measurements were made to check the uniformity between tests of the resin at this stage. The specific gravities at room temperature, taken with a hydrometer- picnometer ranged from 1.092 to 1.099. The viscosities were measured by pouring a 100cc. sample of the resin into a Scott viscosimeter and measuring the time required for efflux through the orifice at room temperature of 25 cc. The resin time ranged from 129 to 155 seconds; the time required for the efflux of 25cc. of distilled water under the same conditions was 7.5 seconds.

The liquid resin was then washed several times, using petroleum naphtha, kerosine, and water individually and in various combinations different wash liquids being used in different tests. Washing was carried out by shaking the resin together with 500 cc. of the wash liquid together in a 2-1/2 liter glass stoppered bottle. When the

resin had been thoroughly dispersed in the wash liquid it was allowed to settle out in the bottle, then shaken up again, allowed to settle and this procedure repeated for several times. Finally the mixture was thoroughly mixed and poured into a separation jar for separation of the resin from the dirty wash liquid. The resin would settle to the bottom of the jar whence it was drawn off and washed again using more of the same or of a different wash liquid as the case might be.

After the final wash the resin was drained into an aluminum pan of 2 liters capacity for the second heat treatment. This second heating was performed on an electric hot plate, with occasional stirring. Temperature readings were taken frequently. The resin would heat up uniformly to the boiling point of the wash liquids used. The temperature rise would then be retarded while the wash liquid which had remained entrained in the resin boiled off. At about 125°C the resin began to thicken with violent foaming usually accompanying the thickening process. The thickening continued as the temperature rose until about 135°C . Then foaming gradually ceased and the resin would heat up uniformly with only a slow evolution of gases resembling in odor those evolved in the last stage of Novolak preparation as described above. Heating was continued to 185 or 200°C after which the resin was cooled in air and chopped out of the pan in which it was formed.

The resins washed with only kerosine or petroleum naphtha thickened so much in the period 125 to 135°C that it was practically impossible to stir them. They were heated to the cessation of excessive foaming, 140°C and cooled from that temperature.

The resins formed were very hard, brittle, and glossy at room temperature. They were dark brown in color, clear and translucent in very thin layers, and had a fine, glossy conchoidal fracture. They had but a slight phenolic odor. The resins which had been repeatedly washed with water, however, were decidedly different from the others. They were darker in color, far less translucent, had a strong odor and taste exactly resembling that of ordinary tar pitch. They were not so hard, more plastic, but no less glossy than the others.

In an attempt to remove every trace of water that might be present, washed resins in the liquid state prior to the second heating were subjected to alcohol distillation which were repeated five times. Ethyl alcohol dehydrated by distilling over lime, specific gravity 0.792, was used. 300 grams of the resin was dissolved in 100cc. of the alcohol, the alcohol distilled off, 100cc. more alcohol added, that distilled off, and so on. After the fifth 100cc. of alcohol was distilled off the heating was continued to harden the resin. As the temperature rose a distillate of unknown nature was collected as indicated in Table 9. At 125°C this distillate was water white. It darkened gradually until it was a distinct yellow at 200°C and further to an orange-red color at 320°C when the heating was discontinued. The resin at 320°C was a thin liquid.

The successive alcohol distillates showed decreasing specific gravities, which approached a constant value for the last two in each case. The kerosine washed resin was distilled with great difficulty due to very excessive foaming. This resin converted

over into the insoluble infusible state during the final heating period. Heating of this sample was discontinued at 185°C. The distillates collected between 200° and 320°C were tested for phenolic bodies by measuring the percent soluble in ten percent caustic solution.

Table 9.

Alcohol Distillations of Three Resins

Resin No.	Washes in : Receiv- ed	Wt. of Resin taken	Temp. range of al- cohol distil- lations:	Sp. Grav. range of alcohol distillate	Wt. Dis- tilled 125-200°C	Dis- tilled Weight:	200- 320°C % Phen- ols by vol.	Wt. Final Resin
3	Kerosine	362.6	85-105	0.890-0.807	Heating at 185°C	Discontinued	204.3	
3	Water	294.2	85-125	0.838-0.809	26.0	80.0	70	184.0
3	Water	351.9	84-125	0.870-0.799	27.2	106.6	60	197.6

The resins which had been water washed as liquids formed, after alcohol distillation and subsequent heating, resins which were solid but plastic at room temperature. They were completely soluble in acetone.

Acetone solutions were made of all the washed resins and alcohol distilled resins. Films for observation and dielectric tests were made by dipping brass sheets and paper into the varnish in the manner prescribed by the A.S.T.M. (15). In some cases the acetone solutions of the resins did not give satisfactory films and butyl alcohol or butyl acetate were added as thinners rather than additional acetone. In most of these cases the films were somewhat improved but did remain unsatisfactory. The brass and paper used were of the A.S.T.M. specifications.

Ten specimens on paper were prepared of each varnish. Five of these were subjected to breakdown tests after air drying while five were heated in an oven at 105-110°C for 24 hours before testing. Sheets of brass were dipped and observed before and after baking. Table 10 summarizes the data in a series of preliminary tests. In cases where two sets of data are given for a resin the first applies to the film before baking, the second, after baking.

Table 10
Results of Preliminary Tests of Washed Resin Films

Resin Number	Wash liquid used K=Kerosine N=Petroleum Nap- the W=Water Ad=Alcohol Distill- late	Solvent used, Acetone + BAc# Butyl Acetate BAlc=Butyl Alcohol	Description of the twice dipped paper specimen	Average thickness of specimens, mils	Mean Breakdown vol- tage. Volts per mil thickness of specimen	Description of film on brass
1.	None	BAc + BAlc	Checked badly Segregation Red Translucent Embrittled and Darkened	7.2 7.0	324 126	Red_Brown Checked some Bends O.K. On A 1/8" Radius. Darkened. Very brittle
2.	K-N-W	-----	Even film, not smooth. Red Translucent High Gloss Em- brittled and Darkened. Pin- point Indenta- tions	6.5 6.3	617 260	Red_Brown Bends OK on 1/4" Radius Darkened. Very brittle
3.	N-N-N	-----	Same as 2.	10.4	548	Same as 2.
4.	N-N-W	-----	Same as 2.	10.3	132	Same as 2.
			Same as 2.	6.5	519	Same as 2.
			Same as 2.	5.8	158	Same as 2.
5.	W-W-W-W-W	BAlc + BAc	Very Uneven, not smooth Red, translucent Glossy	4.5	633	Brown, Uneven Bends on 1/8" Radius Black. Some-

Table 10 (cont.)

Resin Number	Wash liquid used	Solvent used, =	Description of the twice dipped paper specimen	Average thickness of specimens, mils	Mean Breakdown, volts per mil thickness of specimens	Description of film on brass
5.	K-Kerosine N-Petroleum Napthas W-Water AD-Alcohol Distillate	BAlc + BAc	Black Opaque. Low Gloss. Even, Not <u>Smooth</u> Embriittled	4.2	617	Dark Brown. Bends OK on 1/16 inch Radius
6.	K-K-W	----	Same as 2.	6.7	376	Same as 2.
7.	K-K-K	----	Same as 2.	8.1	335	Same as 2.
8.	W-W-W AD	BAc + BAlc.	Same as 8	3.9	403	Same as 8
9.	W-W-W-W-W AD	BAc + BAlc.	Same as 8	4.0	200	Same as 8

As noted in the table, none of the film tested was smooth, that is, there were irregularities and tiny indentations in them that made the electrical measurements highly questionable. However, this data points out quite conclusively that the resins do have fairly high dielectric strengths and that this property is increased by washing the resin while it is in the liquid stage. This conclusion is further substantiated by tests in which high voltages were applied through some of the film over short periods of time. For instance, the film made from the unwashed resin, (Resin number 1 in Table 10 having a total breakdown value of 2700 volts) withstood the applica-

tion of 1500 volts for 30 seconds followed by the application of 2000 volts for 30 seconds followed in turn by 2500 volts for 15 seconds before breaking down. The film made from the resin which had been washed once each with kerosine, petroleum naphtha, and water in the order named (Resin number 2 in Table 10) withstood the application of 3000 volts for 30 seconds followed by 3500 volts for 30 seconds followed in turn by 4000 volts for 5 seconds before breaking down. The two specimens tested were of comparable thickness, measuring 7.9 and 7.8 mils respectively.

The data given in the table indicates too that petroleum naphtha is superior to kerosine as a wash liquid for producing resins of high dielectric strength. The water washed resin seems to be of a type distinctly different from those washed with other solvents.

The baking process to which most of the resins were subjected invariably caused a marked reduction in dielectric strength. This can be accounted for by two facts. Upon baking the resins evolve a gas, which evolution leaves innumerable pin point indentations on the entire surface of the specimen. These indentations cause an immeasurable, though very significant, decrease in the actual thickness of the specimen and can, therefore, be expected to cause a decrease in dielectric strength. Then also, the baking causes the resin to transform into a very brittle condition. The examination of a baked specimen under a magnifying glass showed a complete network of fine cracks in the whole surface of the specimen. These cracks are formed audibly when the specimen is removed from the baking oven into the cold atmosphere of the room. These cracks can

be expected to cause a marked decrease in breakdown voltage for the specimen.

The resins as used for the preparation of these films might be expected to be of the Bakelite A type, which would be converted into the C stage by the 24 hour baking period. This assumption, however, is belied by the following facts:

(1) That the resins before being dissolved to form the varnish, were maintained at temperatures near 200°C for comparatively long periods of time, during the last stage of their preparation, and

(2) the resins of the baked specimens are apparently completely soluble in acetone. It is possible that the resins are neither of the Bakelite nor Novolak types but of the type described by Baekeland in his earlier writings (see Theoretical Discussion) as saliretin resins.

SUMMARY OF RESULTS

The data of this thesis indicates that, in general, the resinification of the tar acids with formaldehyde is retarded by the presence of organic acids and alcohols; is accelerated by acids, bases, acid and basic salts, oxidizing and reducing agents; and is little affected by neutral inorganic salts and neutral organic compounds. This data is in good accord with the general statements in the literature concerning catalysts.

The solubility data, however, shows that insoluble resins can be and are formed regardless of the nature of the catalyst used. This is somewhat in conflict with Baekeland's original statements which quite definitely pointed out that acid catalysts caused the formation of fusible resins and basic catalysts, the infusible type. Sheiber and Sandig, however, recognize the possibility of forming resin of either sort from either type of catalyst. They regard the function of the catalyst as merely that of tending to influence the reactions in one direction or the other, the tendencies in either direction being stronger with some catalysts than with others. This latter view is strikingly corroborated by all the data obtained in this study.

The general forms of the catalyst concentration vs. time of reaction curves are well in accord with the data recently reported by Holmes and Megson(24) for pure phenols and English coal tar fractions. The curves of this study are, however, somewhat complicated by the presence of inherent catalyst in the tar distillate used.

A Novolak resin giving films of some dielectric strength can be prepared by first making a Bakelite type of resin and then reacting this with additional tar distillate. The resin so formed obviously contains some impurities, as evidenced by the oily appearance of its fraction.

Tar Acid-formaldehyde resins can be washed to advantage while they are in a liquid state at room temperature. Washing with petroleum naphtha, or water, or both causes a marked increase in dielectric strength of the films produced. The resins will not stand baking, however, because of embrittlement and distortion of the surface due to evolution of gases.

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