THE DEVELOPMENT OF A FURFURAL LACQUER

by

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INTRODUCTION

Furfural, applied to the manufacture of plastics on a non-commercial scale, has been the subject of much interesting study and experimentation in the research laboratory. With the aid of these investigations, resulting in the constant improvement of the product obtained, and with the production of large quantities of furfural from agricultural wastes, the manufacture of furfural plastics on a large scale may not be far distant.

The behavior of furfural with various substances is being investigated with the object of finding new uses for it, and to solve the problems involved in its present utilization. While thus engaged, Mr. W. D. Harris, Iowa State College, Ames, Iowa, prepared a resin from furfural and cresol that bore a striking resemblance to lacquers. The substance he prepared, however, cannot be used as such, for it does not possess the necessary qualifications of a good lacquer. It does not harden readily, and it cannot be applied to a smooth metallic surface with good results. The difference in the coefficient of expansion of metals and of this resin is too great, so that the layer eventually cracks and peels.

It is the object of this investigation to determine which ingredients may best be used, and how the variation of physical conditions, or catalysts, affect the preparation and quality of the product. Various solvents for the substance may also be tried, with the aim of producing a lacquer from furfural that may successfully be applied to metallic surfaces.

HISTORICAL

Furfural (10)

Furfural was discovered by Dobereiner in 1830 while preparing formic acid by the action of sulphuric acid and manganese dioxide on sugar. He obtained a small quantity of a yellow "oil" which he called "artificial oil of ants". Shortly after Dobereiner's discovery Emmet obtained some of the same "oil" while preparing formic acid by the treatment of rye and corn with sulphuric acid.

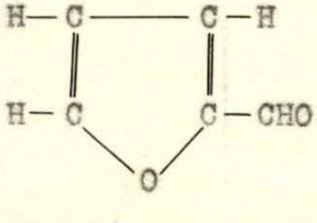
The first man to determine the composition of furfural was Stenhouse, who, in 1840, succeeded in obtaining a yield of one ounce from twelve pounds of oatmeal, from which he determined the composition of the aldehyde as well as some of its physical constants.

The "oil" was given the name of furfurol by Fownes in 1845. However when the compound was later found to be an aldehyde, its name was changed to furfural. Fownes prepared the aldehyde by the distillation of bran with sulphuric acid.

Furfural has been the subject of investigation by many others. It has been prepared from a wide variety of materials such as cane sugar, wood, glucose, and albumen, as well as from such agricultural wastes as corncobs and oat hulls. Although it has been found that the direct sources of furfural are pentoses and pentosans, it has been prepared in small quantities from carbohydrates other than pentoses, particularly from cane sugar and glucose.

When freshly distilled, furfural is a light yellow liquid, which on standing darkens to a reddish brown. It has a boiling point of 161.7°C at standard pressure as determined by Maine of the Bureau of Chemistry and its specific gravity is 1.155. It is soluble in ether, alcohol, and water, and has found considerable use as a high boiling solvent.

Furfural is an aldehyde and chemically resembles both formaldehyde and benzaldehyde, particularly the latter. Its striking similarity to benzaldehyde has led to quite an extensive investigation of the chemical nature of furfural and of its reactions with various organic compounds. Its formula has been found to be



Like many other newly-found compounds, furfural was at first merely a laboratory curiosity, and as such its price was prohibitive. It sold at $6.50 per pound not many years ago, and the first commercially produced furfural, in 1922, sold at $1.00 a pound. However, it is now quoted at 10 cents (1), and has the distinction of being the cheapest of aldehydes. As such it has induced investigators to seek applications of the compound, with the result that it has found a large use in the manufacture of synthetic resins and plastics.

Furfural Resins

The beginning of furfural resins dates back to the beginning of furfural. The early investigators, Stenhouse and Fownes, found that the aldehyde formed resinous materials upon the treatment of furfural with acids and bases. Claisen in 1887 prepared these compounds from furfural and beta-naphthol using hydrochloric acid as the condensing agent. These were not given much attention at first since the products that were obtained consisted of tarry and gummy masses and were of no particular use. Hence no great strides were made during the nineteenth century in the development of these resins. (10)

When the phenol-formaldehyde type of resin gained prominence, investigators turned to furfural as a possible substitute for formaldehyde. Meunier, in 1914, (9) obtained a patent on the manufacture of varnish resins from furfural and bases, which marks the beginning of the period of development of furfural resins.

In 1918 Beckman and Dehn (3) developed a phenol-furfural resin, using a variety of phenols and alkalies, acids, and acid salts as condensing agents.

The condensation products were not confined only to the manufacture of synthetic resins, but they also invaded the field of plastics. A number of American patents have been issued covering the preparation of plastics from furfural. These consist chiefly of the phenol-furfural types. The process of making moldable products from these resins was patented by Emil E. Novotny. (11)

The use of accelerators and hardening agents in the preparation of these resins was also investigated by Novotny (13) who was thus able to vary the properties of the products of reaction.

Novotny and Kendall in 1922 (12) obtained a patent covering the preparation of a phenol-furfural resin under heat. They mixed the ingredients in the proper proportions which they heated in the presence of a small amount of a basic catalyst. The effect of this was to remove the water formed in the reaction thereby obtaining a quicker setting resin.

Further advance was made by Webber in 1925. (14) He used either a liquid or solid condensation product of phenol and furfural to which he added a reaction product of a polyhydric alcohol and a polybasic acid such as obtained from glycerol and phthalic anhydride. The advantage of Webber's product is that it may be molded and the product eventually rendered infusible by the use of heat and pressure.

Ellis (5) devised a different process of preparing similar resins. He heated phenol and butyl alcohol to a temperature of about 150°C with hydrochloric acid as the cayalyst. This product he caused to react with furfural in the presence of potassium carbonate, the reaction being carried out at a temperature of about 150°C.

Ellis also produced a plastic by acidulating a mixture of nitrocellulose and furfural. The product is moldable and eventually hardens. (6)

Fleet, Potter, and the Damard Lacquer Co. (7) obtained a British patent covering the use of urea or thiourea in the presence of a reaction mixture composed of phenol, and an aldehyde, such as acetaldehyde, or furfural. The reaction is accelerated by the use of ammonia.

It may be said here that most of the resins described in this paper are infusible if an acid catalyst is used in their preparation. However, the use of a basic catalyst such as ammonia, caustic, or alkali carbonate produces a fusible resin suitable for use in varnishes or lacquers.

It may also be noted that phenol was the favorite substance used in the preparation of the resins, and not until recently was the use of cresol very successful.

Lacquer

Nearly all lacquers now on the market are of the so-called pyroxylin type. A lacquer, therefore, is a blended mixture of a variety of solvents, a dilutent consisting of a volatile liquid which is non-solvent for nitrocellulose, a resin, a plasticizer, and the relatively expensive pyroxylin. (4)

The disadvantages encountered in such a synthetic mixture are at once apparent, and it has long been the aim of investigators to produce a simpler, cheaper lacquer which would have all the good features of the pyroxylin lacquers and none of the bad ones. However, they have not met with any great success.

As early as 1905 Ludwig (8) obtained a patent on the process for preparing a substitute for lacquer in flakes for varnishing furniture. This is prepared by boiling "copal de Manille" or "de Sandaraque" in an aqueous solution of potassium hydroxide until the resin is all dissolved. Linseed oil equal to five percent of the weight of the resins is then added, the mixture is cooled, and the flakes precipitated by the addition of sulphuric acid.

The lacquer produced by the Bakelite Corporation (2) is perhaps the most successful lacquer of simple composition now on the market. This consists of a solution of Bakelite resin in organic solvents. The lacquer may be applied by means of a spray gun or brush or by dipping. The lacquered article is then baked for a period of fifteen to twenty minutes at a temperature of 135°C. This process drives off the solvent, leaving a transparent non-fusible protective film. However, Bakelite lacquer is adapted only to be used as a protective covering for such articles as plumbing fixtures, novelties, vanity cases, hardware, etc. It is amber colored, transparent, and naturally cannot be used as covering where opaque and colored lacquers are required.

It is the object of this investigation to produce a simple lacquer, wherein a furfural-cresol resin is to be used. So far as the literature disclosed, no lacquer of this type has heretofore been produced.

EXPERIMENTAL

A. Materials and Equipment

The essential materials used in the pursuit of this work were cresol, purchased from the Barrett Company of New York; furfural obtained from the Quaker Oats Company of Cedar Rapids, Iowa; and Bakelite solvent, purchased from the Bakelite Corporation, Chicago, Illinois. Ammonium hydroxide containing 29% NH_3 was used as an accelerator, and other reagents used in very small quantities were tricresyl phosphate, dibutyl phthalate, and camphor. The lacquer was applied to galvanized sheet metal, such as is found in any tin shop.

No elaborate equipment was necessary, using such apparatus as is found in any chemistry laboratory--flasks, beakers, test tubes, etc. For the application of the lacquer a small laboratory glass spray gun was used. The samples were baked in a small Freas electrically heated constant temperature oven manufactured by the Thermo Electric Instrument Co., Irvington, N. J.

B. Procedure

Preliminary.

As basis of starting the investigation, the cresol-furfural resin was prepared according to the suggestions of Mr. W. D. Harris. The following mixture was refluxed for the period of one and one-half hours:

Cresol - - - - - - - - - - - - 100 c.c.
Furfural - - - - - - - - - - - 75 c.c.
Ammonia - - - - - - - - - - - 20 c.c.

The reacted misture was then placed in an open dish on a hot plate for a period of 48 hours. The object of this treatment was to complete the reaction, to remove unreacted ingredients, and to drive off any water present. Without this treatment the resin would remain a viscous liquid. After removal from the hot plate, the resin, upon cooling, solidified to a black, shiny, and brittle mass.

This resin was found to be soluble in a number of solvents, such as acetone, benzene, ether, ethyl acetate, ethyl alcohol, Bakelite solvent, and others. Solutions of the condensation product in these solvents were applied to galvanized iron plates by means of a small spray gun, and it was found that the Bakelite solvent gave the best results. The film dried in about an hour, producing on the plate a shiny black surface which was easily marred by scratching with the finger nail or by bending the plate. After drying in the air for several days, the film was found to be very brittle, and it was apparent that the solution thus prepared could not be used as a lacquer.

It was decided that incorporating various plasticizers, or some drying oils, or both and baking would prove beneficial and would produce a lacquer which should yield a harder, more durable film. With this in view several resins were prepared on which these modifications were to be tried.

Preparation of Resins.

Six resins in which certain ingredients were varied as shown in Table I were prepared by refluxing the reagents for a period of ninety minutes. In each case the reacted mixture was allowed to remain in an open dish on a hot plate for a period of 48 hours.

The reagents used in the preparation of the resins are shown in Table I with a summary of the observations on these resins.

Table I

Properties of Resins

Resin	Reagents			Catalyst	Color of Powdered Resin	Remarks
	Cresol c.c.	Furfural c.c.	NH_4OH c.c.			
I	100	75	20	none	Very dark chocolate brown	Hard but brittle
II	100	75		NaOH 10 gms.	Chocolate brown	Very brittle
III	100	60	20	Formalin 15 c.c.	Very dark brown	Very hard but brittle
IV	100	75	20	Camphor 1 gm.	Brownish black	Tenacious. Hard at low temperatures but softens at body heat
V	100	75	20	Di-butyl-phthalate	Very dark chocalate brown	Quite hard but brittle
VI	100	75	20	Tri-cresyl phosphate 0.5 gm.	Brownish black	Rather tenacious but softens at body heat

Note: The color of the solid resin was black in all cases.

Discussion.

It was noted that the resins in the preparation of which plasticizers were used were not so brittle as the others. They did not, however, harden as readily and had a lower fusing temperature; the exception seems to be Resin V, in which dibutyl phthalate was used as a plasticizer; this, however, was quite brittle.

No distinction could be made between Resins I and III. Both set to a brittle shiny, black mass.

All six of these resins were found to be soluble in the solvents mentioned under "Preliminary". The effect of water on these showed all except Resin II to be water insoluble. Part of Resin II went into water solution, leaving an insoluble residue.

Preparation and Application of Lacquers.

Lacquers were prepared by dissolving each of the six resins in Bakelite solvent. It was found that the ratio of resin to solvent which gave the best results with the spray gun was one to two by weight. The lacquer solutions were all of a deep brownish red color, and when applied to a metallic surface in a thin coat, produced a translucent film, of the same color as the solutions. However, a heavier coat yielded more of an opaque black film.

Each of the above lacquer solutions was applied to a plate of galvanized sheet metal by means of a spray gun. The drying time in the air ranged from fifteen minutes to one hour, depending on the thickness of the coat. The lacquers prepared from the plasticized resins took a somewhat longer drying period than the others. The films, although of good appearance, were unsatisfactory because they were quite easily scratched with the finger nail. It was noted, however, that the plasticizers had a beneficial effect, due probably to the fact that they caused the films to retain some of the solvent, thereby making the films less friable.

The Effect of Baking.

Rapid baking. Plates of galvanized sheet metal were sprayed with each of the lacquers until a coat of proper thickness was obtained. These were dried in the air for one hour, after which they were placed in a small electrically heated oven. The temperature was rapidly brought up to 125°C which was maintained for a period of 30 minutes. The plates were then removed from the oven.

Slow baking. Plates prepared as above were placed in the oven and baked at a temperature of 70°C for six hours. The temperature was then raised to 125°C at which the plates were further baked for two hours.

A comparison of the results obtained by these two methods of baking is shown in Table II.

Table II

Effect of Baking

Plate with Lacquer	Rapid-baked		Slow-baked	
	Surface	Hardness	Surface	Hardness
I	Good	Can be scratched with fingernail	Good	Easily scratched by fingernail
II	Blistered badly	Crumples to powder	Blistered badly	Crumples to powder
III	Fair	Fairly hard but can be scratched	Fair	Scratched by fingernail with pressure
IV	Good	Can be scratched with fingernail but with difficulty	Fair	Scratched by fingernail with pressure
V	Very good	Fairly hard but scratched with fingernail	Very good	Not readily scratched by fingernail
VI	Good	Scratched by fingernail with some pressure	Very good	Scratched by fingernail only with pressure

Discussion.

Baking of the lacquered plates yielded a harder, though more brittle, film than drying in the air. The general effect was to give the lacquer film a more lustrous and harder surface. Apparently slow baking gives better results than rapid baking. It was found that Lacquer V (in which Resin V was used) gave the best results. Although no state of perfection is reached, this lacquer produces a film which is more durable and more attractive than that made from any of the others.

Lacquer II does not lend itself to baking, since it is apparently decomposed by heat.

Baking of the lacquers prepared from the unplasticized resins merely drove off all the excess solvent, leaving a weak film which was easily disintegrated to a powder by bending the plate.

The Effect of Drying Oils.

In order to determine the effect of oils, two types were chosen--a semi-drying and a drying oil. Chinawood oil was used for the latter, while castor oil was used for the other. It was decided to try the effect of these two oils on Lacquers I and V.

To a portion of these two lacquers was added 5% by volume of each of the above oils. The solutions were heated for a few minutes to insure complete solution of the oils. Plates were then prepared by applying each lacquer solution by means of a spray gun.

It was found that the drying period for these lacquers was prolonged considerably, and even several hours after application the lacquer films were still soft.

The four plates were then subjected to the rapid baking method previously described, and it was found that the films prepared from Lacquer I were still soft, brittle, and not of very good appearance. Lacquer V, however, yielded a hard, smooth, and lustrous black film which could not be scratched by the fingernail. Of the oils tried, the Chinawood oil gave better results than the castor oil. The film prepared from Lacquer V containing the latter oil had greater cohesion than that prepared from the lacquer containing castor oil.

CONCLUSIONS

1. Plasticizers are essential in the preparation of a cresol-furfural resin which is to be used in a lacquer, and of those tried, dibutyl phthalate proved to be most beneficial.
2. The use of sodium hydroxide as an accelerator instead of ammonia in the preparation of cresol-furfural resins gives a partially water soluble resin not suitable for use in lacquer.
3. Baking has the effect of producing a harder lacquer film from the plasticized lacquers than air drying. The unplasticized lacquers give more brittle lacquer films when baked.
4. Slow baking produces a harder and smoother film than rapid baking.
5. The use of Chinawood oil in a plasticized lacquer is more beneficial than castor oil.

SUGGESTIONS

Much is yet to be done in the development of this lacquer to a point where it will be of commercial value, and the writer offers the following suggestions for further work on a furfural lacquer:

The effect of plasticizers other than those mentioned in this paper may be tried--either by introducing them during the synthesis of the resin or by adding them to the lacquer solutions prepared from unplasticized resins.

Baking temperatures higher than 125°C may be tried. Perhaps a rapid baking process at higher temperatures, which is more suitable for commercial practice, can be developed.

Drying oils other than Chinawood oil may be tried, of which linseed and soya bean oil are suggested.

SUMMARY

A baking lacquer applicable to metallic surfaces and yielding a black, lustrous surface was prepared from a mixture of furfural, cresol, and ammonia together with such plasticizers as camphor, di-butyl-phthalate, and tri-cresyl-phosphate, using Bakelite thinner as the solvent, and such oils as Chinawood or castor oil as conditioning agents. Applications to metal panels indicated that the most durable lacquer films were obtained from those lacquers in the preparation of which Chinawood oil and di-butyl-phthalate were used.

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