THE PRODUCTION OF A CRESOL-CELLULOSE LACQUER

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Introduction

During recent years a large amount of investigation has been carried out in regard to the utilization of agricultural wastes. This is probably, in a large part, due to the realization that increased economies through the use of all farm products are essential to profitable agricultural enterprise even as by-product utilization is to industrial enterprise.

Agricultural wastes form a practically inexhaustible source of cellulose. Straw, corn stalks, cobs, and cane residues are wastes which at present are used but slightly. In fact they are often a nuisance. Cobs are used as a fuel, but there are vast quantities which could be purchased at a very reasonable figure. Oat hulls have been a large waste material, but increasingly large quantities are being used for the production of furfural. Furfural is an interesting substance from a waste utilization standpoint. It shows what is possible in this field. In 1922 it sold in small quantities for one dollar or more a pound. Today it can be purchased in tank car lots for less than ten cents a pound.

Cellulose is one main raw material involved in this investigation. Cresol is another. It may be purchased for less than eleven cents a pound. It will be discussed further in a succeeding chapter.

The basis for this work is the reaction between cresol, and cellulose in the presence of sulfuric acid. When a mixture of these three substances is heated, a reaction visibly takes place. Water is given off, and a thick black fluid is formed which solidifies on cooling. This mass may be dissolved in suitable solvents and used as a lacquer.

The purpose of this investigation is to study the lacquers made from this condensation product, and to determine, as far as possible, whether or not a successful lacquer may be produced. The chemistry of the reaction is complex and will not be considered in this work.

Historical Review

Although the use of lacquers in large quantities is comparatively recent, they have been known and used to a limited extent for a good many years. The early lacquers were not very satisfactory. Nitro-cellulose technology was but poorly developed, and the supply of solvents was very limited. The solvent used in the early lacquers was fusel oil, a by-product of the alcohol industry. The lacquer industry as it exists today is an outgrowth of the World War. The large quantities of nitro-cellulose explosives manufactured during the war and the increased knowledge gained through research advanced cellulose-nitrate technology considerably. Whereas the early lacquers were made from high viscosity nitro-cellulose which is capable of producing only a thin film of lacquer, most of the lacquers of today are made of low viscosity products.

The large amount of solvents needed for the production of smokeless powder forced the solvent industry to develop new methods of producing the old solvents and new ones which were superior. With the end of the war two highly developed industries, the nitro-cellulose and solvent industries, had but little outlet for their products. It was very natural for them to seek a new outlet. It was indeed a propitious moment for the development of a large lacquer industry. The automobile industry was seeking a better surface for their automobile bodies. The old method of finishing took from ten to twelve days and required a large amount of space for drying. When a satisfactory lacquer was developed, it was welcomed by this industry with open arms. In 1923 less than one percent of the automobiles in the United States were finished with lacquer, while by 1927 this had increased to over ninety five percent.

Up to the present time it has been impossible to produce a satisfactory black lacquer using a nitro-cellulose base. As most of the fenders and running boards of automobiles are finished in black, it has been impossible to use a nitro-cellulose base lacquer on them. This has turned the attention to other resins and plastics. The plastic product obtained from the reaction between cellulose, cresol, and sulfuric acid has possibilities in this field. It has a very dark color and looks as if it were black.

But few investigators have studied the products which result from the reaction between phenols or cresols and cellulose. A German patent issued to Gustan Mauthner (3) covers the invention of such a condensation product. The patent states that the properties of the products formed depend upon the temperature at which the reaction is allowed to take place, the relative amounts of the components, and the amount of condensing reagent used. Either sulfuric or hydrochloric acids may be used as condensing reagents. The temperature at which the reaction is carried out depends on the type of product desired and the amount of acid used.

By mixing the various components in the cold and gradually raising the temperature there is first obtained a fluid product. As the reaction continues, the fluid goes over to a plastic mass, which with further heating goes to a hard resinous body. For the production of a fluid product, take a mixture of one thousand grams of phenol, one hundred grams of sulfuric acid, and three hundred fifty grams of cotton or wood saw dust. When these are heated to seventy five to one hundred degrees C. a distinct reaction occurs, and on pouring the substance into water, it shows a black sheen. This substance is soluble in alkaline solution and may be used as a soap. The solution is precipitated by the salts of the alkaline earths and the heavy metals. The fluid product becomes plastic upon heating at a temperature of one hundred fifty degrees. It becomes hard when heated above this temperature, and prolonged heating at this higher temperature gives an infusible resinous mass.

The fusible bodies have a conchoidal, black glossy fracture, are insoluble in water, hydrocarbons, carbon disulfide, chloroform, and turpentine. They are soluble in alcohol, phenol, ether, acetone, and glacial acetic acid. The solubility of the material depends on the length of time that the products are heated. The longer they are heated the more insoluble they are.

The plastic bodies may be obtained directly, as it is not necessary to go through the fluid state. In order to obtain them directly, the phenol and sulfuric acid are heated and the cellulose gradually added. The product so obtained melts at from seventy to one hundred degrees.

The patent states that these products may be used in the manufacture of lacquers and varnishes, and for the impregnation of porous material; also alone or in mixtures of plastic materials. The claims of the patent are: The invention of the manufacture of a resinous condensation product from cellulose and phenol with a mineral acid as a condensation reagent, and the production of the plastic condensation product through the fluid stage, obtaining the final product by heating.

Another patent issued in Great Britain to Glaessen (2) covers the preparation of a similar material. The holder of this patent used wood or waste in his preparation. His method was to treat the wood pulp or waste in a solution of the phenol in water, alcohol, or benzene. After the reaction had proceeded as far as it would, he separated the excess cellulose. The resin was then separated from the excess liquid which contained any unreacted phenol. His claims were that the product may be substituted for natural resins, pitch, or asphalt. It may also be used as a sizing material. Mention of the work of these men is made in Natural Resins (4).

Method of procedure

The first resins used in this investigation were made in the following manner. One hundred grams of cresol and ten grams of sulfuric acid were placed in a four hundred cc. beaker and well mixed. A small quantity of cellulose was added to the mixture, and the whole was gradually heated until the mixture began to react. This occurred at a temperature of from seventy five to one hundred degrees C. The mass darkened, and water and cresol vapors were given off. The temperature was gradually raised and more cellulose incorporated until thirty five grams had been added. The final temperature was one hundred sixty degrees. The entire reaction took from one hour to one hour and a half. Plastics were made i in this manner from filter paper and sulfite pulp.

This method of making the plastic mass was rather unsatisfactory. The reaction required constant attention, and the cresol vapors evolved were very unpleasant.

It was decided that the plastics might be produced in an autoclave. Plastics were then made in the autoclave at a pressure of eighty pounds of steam. The quantities of materials used were the same as were used in the first method. These products, when taken from the autoclave, had considerable water over their surface and were themselves liquids at room temperatures. However, when they were gradually heated to one hundred fifty degrees, the water was driven off. When they were cooled they could not be distinguished from those produced by the first method. Their properties as lacquers, so far as could be determined, were also identical, This method was then used for the remainder of the plastics produced. HCl and ammonia were tried as condensation feagents, but the reaction did not take place to any appreciable extent. Resins were made from filter paper, sulfite pulp, corn cobs, and corn stalks. Furfural was added to some of the best of the sulfite pulp plastics. The mixtures were heated, and the residual cresol allowed to react with the furfural. The amount of furfural added was ten grams to a batch made from one hundred grams of cresol.

All of the plastics produced were rather hard and brittle. They were ground in a corn mill and dissolved in a solvent for the production of a lacquer. This lacquer was applied with a laboratory glass spray gun. A suitable concentration of plastic in solvent for this method was one part of plastic to five parts of solvent. Bakelite solvent was found to be the most satisfactory one and was esed almost entirely.

The spray gun method of application proved to be troublesome and unreliable. Moisture from the air condensed on the surface and ruined it. Water bubbles formed under the surface. These would form craters on weathering. A thicker solution was then used. It consisted of two and o one half parts of solvent to one of plastic. This solution was poured on the surface to be coated and allowed to spread evenly. After it had dried another coat could be applied. Most of the panels were baked when they had dried. They were placed in a cool electric oven and the whole slowly heated to a temperature of 125° C. This took thirty minutes. This temperature was maintained for one hour. At the end of this period, the panels were removed and allowed to cool in the air. Pieces of galvanized iron were used as test panels. They were rubbed down with sandpaper before the lacquer was applied.

It was difficult to determine the exact properties of the surfaces produced. None of the panels would stand much bending. The hardness of the surface was tested by scratching it with the thumb nail. Some of the panels were exposed to the weather to determine how well the surfaces stood up under the action of sunlight and rain..

Data

A series of runs were made wherin the composition of the resins and lacquers were varied by changes in proportions and ingredients; the conditions of the reaction were also varied. These are included in table 1 page 13. The first five runs were made under atmospheric conditions. All of the others were made in the autoclave at a pressure of eighty pounds of steam.

The cresol and acid were heated to one hundred degrees in runs 1, 3, and 5. The cellulose material was gradually added and the temperature raised until the reaction was complete. This took one hour and a half. The cresol and acid were heated to one hundred fifty degrees in runs 2 and 4. Otherwise they were the same as run 1. In the next set of runs, the plastics were heated to one hundred fifty degrees after they had been removed from the autoclave to remove moisture. The water was driven off of plastic 7 by allowing it to stand on the hot plate for twenty four hours. This plastic was softer than no. 6, but the lacquer was the same after baking it. The amount of sulfite pulp and the time of cook were increased in run 8. This run took two hours. Furfural was added to the plastic in run 9. This plastic gave the best lacquer which was obtained. Corn cobs and stalks were used in runs 12 and 13. The time of cook was increased to two hours.

Plastic 11 was tested for solubility in various solvents. A table of solubility follows.

Table 1

Effect of composition on Cresol- Cellulose Lacquers

Run No.	Cresol	Cellulose	Condensing Reagent	Furfural	Solvent	Results
1.	100g.	Filter paper 35g.	H_2SO_4 10g.	none	B.S.*	Poor Decomposed
2.	100g.	Filter paper 35g.	H_2SO_4 10g.	none	B.S.	Same as 1.
3.	100g.	Sulfite pulp 35g.	H_2SO_4 10g.	none	B.S.	Better
4.	100g.	Sulfite p pulp 35g.	H_2SO_4 10g.	none	B.S. B.S.&F.	Same as 3 Better
5.	100g.	Sulfite pulp 35g.	HCl 15g.	none		very little reaction.
6.	100g.	Sulfite pulp 35g.	H_2SO_4 10g.	none	B.S.	same as 3.
7.	100g.	Sulfite pulp 35g.	H_2SO_4 10g.	none	B.S.	Same as 6.
8.	100g.	Sulfite pulp 50g.	H_2SO_4 10g.	none		Incomplete reaction.
9.	100g.	Sulfite pulp 35g.	H_2SO_4 10g.	10g.	B.S. & furfural	Best surface.
10.	100g.	Sulfite pulp 35g.	NH_4OH 20g.	none		No reaction.
11.	100g.	Sulfite pulp 35g.	HCl 15g.	none		Very little reaction More than in 5.
12.	100g.	Corn cobs 35g.	H_2SO_4 10g.	Large residue of unreacted cobs.		
13.	100g.	Corn stalks 35g.	H_2SO_4 10g.	Large residue of unreacted stalks.		
14.	100g.	Sulfite pulp 35g.	H_2SO_4 10g.	0.2 g. Tri-cresyl-phosphate added as plasticizer. Same as 3.		

*B.S. Bakelite solvent #336

Solubility of plastic 11

Petroleum ether	insoluble
Water	insoluble
Sulfuric ether	slightly soluble
Alcohol	soluble
Benzene	insoluble
Ethyl acetate	soluble
Amyl acetate	soluble
Ethylene dichloride	fairly soluble

Test panels: Panels were prepared from various resins and exposed to the sun and rain. A panel made with resin 6 and bakelite solvent did not stand up very well under two weeks exposure. One made with furfural in the solvent from the same resin stood up better. Resin 11 gave good results when the "flow" method was used. It did not give a lasting surface when it was sprayed.

Discussion

The plastics made from filter paper gave poor surfaces. On aging it apparently decomposed, and a film of purple dust covered the surface. The plastic, when allowed to age in the atmosphere, showed the same property. However, after having aged for a month, this plastic gave a surface which did not decompose.

The plastics made from sulfite pulp did not show this decomposition. They also gave better surfaces. They were harder and brighter. The hardness of all of the lacquers was increased by baking. Baking also increased the brittleness. Most of the surfaces prepared with the spray gun were unsatisfactory because of the moisture condensation and the unevenness of the surface. The moisture made the surface rough and pitted. Moisture condensation was the main trouble when bakelite solvent was used. When amyl acetate was used, the lacquer dried so slowly that it was also difficult to obtain a good surface. By far the best results were obtained by flooding the panel with the thick lacquer previously described. This method produced a smooth glossy surface free from pits and roughness. The physical properties of the surfaces were further improved by adding from ten to twenty percent of furfural to the bakelite solvent. These surfaces were much harder and more plastic than those obtained with bakelite solvent alone. Many of the latter were so brittle that they chipped easily.

The resin which produced the best lacquer from all standpoints was composed as follows;

Cresol	1oo grams
Sulfite pulp	35 grams
Sulfuric acid	10 grams
Furfural	10 grams

The furfural was added after the reaction with the cellulose was complete.

Gottfried, who was working on a cresol furfural lacquer at the time this work was in progress, noticed that cresol furfural plastics made with acid condensing reagents gave resins which were rather insoluble. This was not the case with the above plastic. It was sufficiently soluble to give a much thicker solution than could be used as a lacquer.

This plastic when applied by the " flow on " method and with a bakelite solvent furfural solvent gave a smooth glossy surface. Two weeks exposure to the sun and rain took the gloss off but did not harm it otherwise. It was possible to polish the surface again with an oil polish. This surface was slightly brittle but not more so than the finish on electrical conduit and outlet boxes.

Lacquers made with plain filter paper or sulfite pulp plastics gave surfaces which crumbled on weathering. They also became brittle on aging. The plastics from corn cobs and stalks were so contaminated with unreacted material that no attempt was made to use them in a lacquer.

All of the surfaces produced appeared to be black. They gave a purple sheen when light was reflected from them. The color of the dilute solution is dark purple.

A long period of time is required to determine the lasting qualities of a lacquer surface. By the time this work had proceeded far enough to get satisfactory surfaces, very little time was left in which to test them. The tests which were carried out did, however, show two things. The "flow on" method is the most suitable method of application, and the quality of the surface is much improved by the addetion of furfural to both the plastic and the solvent.

The lacquer would probably be further improved by the addition of larger quantities of this material. If an excess of furfural were added to the plastic it would react with all of the excess cresol. It would not be necessary to remove the excess furfural, for it could be omitted from the solvent.

The " blush " formed by the water condensation in the spray method of application could probably be eliminatedby a proper blending of solvents. "Blush" is prevented by the use of high boiling solvents in combination with the low boiling ones(1). Furfural in larger quantities might prove to be successful in this connection.

Conclusions

1. It is possible to make a suitable black lacquer from cresol-cellulose plastics.

2. The lacquers are improved by the addition of furfural to the plastics.

3. The lacquer is best applied by the "flow on" or "dip" method.

4. Baking improves the hardness of the surface produced.

5 Corn cobs and stalks are not suitable materials for making the plastics.

Summary

The utilization of agricultural waste products for the production of lacquers to be used in the automobile industry finds an outlet in the possible production of a black lacquer from cresol, cellulose, and sulfuric acid.

The cresol-cellulose plastic was made by heating a mixture of cresol, a cellulose material, and sulfuric acid, either under atmospheric conditions, or under pressure in an autoclave. The lacquer was improved by the addition of furfural to both the plastic and the lacquer solvent. Baking the lacquer after it was dry increased the hardness of the surface.

Further work using larger quantities of furfural in the resin is recommended. It would also be advisable to subject the panels to longer time tests.

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