SURFACING WOODS WITH FURFURAL RESINS

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Signatures have been redacted for privacy

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Introduction

There are produced in the United States annually, millions of tons of agricultural by-products that could well be employed in the production of furfural. This inexhaustible supply of raw material would indicate that furfural should become one of the cheapest industrial chemicals.

Furfural, a five atom ring aldehyde, exhibits the characteristics of aldehydes in general. Much research has been conducted at the Iowa State College investigating possible commercial applications of furfural. This work has shown that furfural has possible extensive commercial applications in production of plastics and resins, lacquers, varnishes, preservatives, paint and varnish removers, fungicides, leather tanning, solvents, etc., and its derivatives have yet wider uses.

One problem that as yet has had little work done upon it, is the development of suitable furfural resins that can be used to surface wood. A resin of this nature would find wide application as a flooring material, (artificial tile or a linoleum substitute), a fast hardening paint, for acid proofing, and for surfacing furniture with a durable glossy finish.

It was the purpose of this project to endeavor to develop a surface resin from furfural.

Historical

Stenhause, in 1840, was probably the first to discover the property of furfural of forming gums and resins when boiled with acids or caustic (2). However, it was not until 1914 when Meunier obtained a patent on the manufacture of varnish resins from furfural (4), that the use of furfural increased to any great degree. Since that date a number of theses have been written and numerous patents granted on the use of furfural in plastics and resins.

In 1921, E. E. Novotny (6) received a patent for impregnating the resinous product of phenol and furfural into fibrous materials which could be made into sheet like form for molding.

Apple and Fillenwarth, in 1930 (1) mention in their thesis an attempt to surface Maizewood and press board with a furfural-sulphuric acid resin. Due to the great absorptive power of these materials, and unequal rates of drying, they did not succeed in producing a satisfactory coating.

In 1937, Albert J. Herberer and Wm. R. Marshall (5) were granted a patent whereby furfural alcohol with or without admixture of furfural, was used with a promotor such as sulphuric acid, to produce a resinous preliminary product. This was dissolved in methyl-iso-butyl-ketone and cellosalve which retards further reaction. Another portion of promoter was added just before application of the coating so that insolubilization was completed after the coating was applied.

The Quaker Oats Company have a process of finishing wood (which they recommend be used for laboratory desk tops) whereby a generous coat of a 50-50 mixture of furfural alcohol and furfural is applied to the surface of the article. It is allowed to soak in for from one to four hours depending upon the degree of impregnation, and then the surface painted with a coat of twenty-five percent aqueous sulphuric acid. The result is a very hard, plossy acid proof surface.

Hall in 1929 (4) is believed to have been the first to use furfurin in plastics or resinous materials. Richard Bruins (3) developed and published in 1934 a method of making a furfurin-furfural mixture and determining the amount of furfurin present by specific gravity means. Because furfurin was made and used extensively in these studies, the author deems it worth while to describe Bruins' method in his own words.

> "The determination of furfurin content of furfurin in furfural solution by means of specific gravity.
>
> The treatment of furfural with anhydrous ammonia results in formation of a solution of furfurin in furfural.
>
> It has been found that the addition of ammonia to furfural raises the specific gravity of the resultant solution sufficiently to enable the determination of the furfurin content by the change in specific gravity. The specific gravity varies of course with the temperature so that the temperature of the solution must be known in order to determine the furfurin content by this method."

Temperature C°	Sp. G. of a 20% furfurin solution
22.5	1.192
32.0	1.184
50.0	1.163
61.5	1.152
70.0	1.144
79.0	1.136
85.0	1.128
91.0	1.120
100	1.111

Experimental

A. Method.

The object of this investigation was to produce a hard, durable, pleasing furface coating that would adhere fast to the wood.

The material used was either commercial grade furfural or a twenty percent solution of furfurin in furfural. Polymerizing agent was hydrochloric or sulphuric acid used either concentrated or in dilute or acetone solutions.

The resins were applied to three inch square blocks of one inch white pine.

All samples were dried at room temperature.

B. Method of Procedure.

Three methods were tried.

1. Successive impregnation.
2. Successive coating.
3. Coating with prepared resinous solutions.

The first method consisted of treating samples of wood in a pressure impregnator first to furfural and then to acid at various pressures, temperatures. concentrations and periods of time. The object was to form a hard resin within the wood as well as on the surface. There was no way to govern the degree and manner of impregnation, and the exact amount of furfural and acid to be used. Therefore, no result worthy of mention were obtained.

The experiments were performed in a cylindrical cast-iron impregnator equipped with electrical heating coil. Air pressure was available up to ninety pounds, per square inch. The furfural was placed in a granite kettle and placed in the impregnator. The wood block was held submerged by a glass rod. The sulphuric acid was contained in a stoneware crock and the furfural treated block held submerged by the same glass rod.

The second method consisted of applying to the wood samples, a coat of furfural or a furfurin-furfural mixture. After a period from one-fourth to three hours a coat of the promoter was applied. The main difficulty encountered was that here too there was no way to govern exact proportion used. The surface of all coatings tended to be very acid.

Practically the whole of this thesis concerns the third method. A known value of furfural or furfurin-furfural was measured into a beaker. A known amount of the promoter was added from a burette. The resinous mixture was well mixed and spread on samples of wood. In some cases, the acid had to be added very slowly with much stirring to keep small hard chunks of the resin from forming. Other samples would generate so much heat that the beaker had to be cooled in a water bath to keep from solidifying and firing. This method allowed exact control of composition and the thickness of coat depended only on the amount applied. Sometimes, when the mixture was very thin, the first coat would soak in, in which case a second or a third coat was added. A marked decrease in the acidity of the surface was noted.

C. Results.

($3'' \times 3'' \times 1''$ blocks white pine)

C.C. Furfural	C.C. Con H_2SO_4	Coat			Remarks
		Hard	Glossy	Smooth	
25	2.5	no	mo	no	All spls.crack-
25	7.5	no	mo	no	ed badly.Mix-
25	12.5	yes	yes	yes	tures in beaker
25	17.5	yes	yes	yes	fired and hard-
25	20.0	Powder	yes	yes	ened in a few
					minutes.

C.C. Furfural	C.C. Con HCl	Coat			Remarks
		Hard	Glossy	Smooth	
25	2	no	no	no	Gray, soaked
25	6	no	no	no	" "
25	10	yes	no	no	Black, soaked
25	14	yes	no	no	" "

C.C. Furfural	C.C. $3^{1}H_2SO_4$ 1 Acetone	Coat Hard	Glossy	Smooth	Remarks
10	1	no	no	no	Cracked Non adherence
10	2	Yes	no	no	Cracked
10	4	no	no	no	Cracked, rough
10	6	yes	yes	no	Cracked, curled

C.C. Furfural	C.C. 1.H_2SO_4 1.Acetone	Coat Hard	Glossy	Smooth	Remarks
10	1	yes	no	no	Soaked
10	2	yes	yes	no	Cracked, curled
10	4	yes	no	yes	Ran
10	6	yes	yes	yes	Large cracks
10	8	yes	yes	yes	Cracked

C.C. Furfural	C.C. 1.H_2SO_4 3.Acetone	Coat Hard	Glossy	Smooth	Remarks
10	2	yes	no	no	Ran
10	4	yes	yes	yes	Cracked, curled
10	6	yes	yes	yes	Cracked, curled
10	8	yes	yes	yes	Cracked, curled
10	10	yes	yes	yes	Fired on wood

C.C. 20% Furfurin	C.C. Con H_2SO_4	Coat			Remarks
		Hard	Glossy	Smooth	
10	1	no	yes	no	Fast acting
10	2	yes	yes	no	Beaker fired

C.C. 20% Furfurin	C.C. 3.H_2SO_4 1.H_2O	Coat			Remarks
		Hard	Glossy	Smooth	
10	3	very	very	very	
10	4	very	very	very	
10	5	very	very	very	Cracked

C.C. 20% Furfurin	C.C. 1.H_2SO_4 1.H_2O	Coat			Remarks
		Hard	Glossy	Smooth	
10	1	no	no	no	Soaked
10	2	yes	yes	yes	Thin Ran
10	5	yes	yes	yes	Ran Cracked
10	7	yes	yes	yes	Ran Cracked
10	9	yes	yes	yes	Ran

C.C.20% Furfurin	C.C. 1.H_2SO_4 3.H_2O	Coat			Remarks
		Hard	Glossy	Smooth	
10	4	no	no	no	All spls
10	8	yes	no	no	thin and
10	12	yes	no	no	soaked
10	16	yes	no	no	

C.C.20% Furfurin	C.C. 3 H_2SO_4 1 Acetone	Coat: Hard	Glossy	Smooth	Remarks
10	1	no	no	no	Soaked
10	2	yes	yes	yes	
10	3	yes	yes	yes	Curled
10	4	yes	yes	yes	Curled Cracked
10	5	yes	yes	no	Viscous solution

C.C.20% Furfurin	C.C. 1.H_2SO_4 1.Acetone	Coat: Hard	Glossy	Smooth	Remarks
10	1	no	yes	yes	All very
10	2	yes	yes	yes	excellent
10	4	yes	yes	yes	samples.
10	6	yes	yes	yes	
10	8	yes	yes	yes	Very acid
10	10	yes	yes	yes	Very acid

C.C.20% Furfurin	C.C. 1.H_2SO_4 3.Acetone	Coat: Hard	Glossy	Smooth	Remarks
10	2	yes	no	no	Soaked
10	4	yes	yes	yes	Cracked Curled
10	6	yes	yes	yes	Cracked
10	8	yes	yes	yes	Cracked Curled
10	10	yes	yes	yes	Cracked Curled

C.C.20% Furfurin	C.C. Con.HCl	Coat Hard	Glossy	Smooth	Remarks
10	1	no	no	no	Ran Soaked
10	2	yes	no	no	" "
10	3	yes	yes	yes	" "
10	5	yes	yes	yes	" "
10	7	yes	yes	yes	Cracked
10	9	yes	yes	yes	Cracked

C.C.20% Furfurin	C.C. 3 HCl 1 H_2O	Coat Hard	Glossy	Smooth	Remarks
10	2	no	no	no	Sticky Rough
10	4	yes	yes	yes	Ran
10	6	yes	yes	no	Ran
10	8	no	no	no	
10	10	yes	no	no	
10	12	yes	no	no	

C.C.20% Furfurin	C.C. 1.HCl 1.H_2O	Coat Hard	Glossy	Smooth	Remarks
10	4	yes	no	no	All spls
10	8	yes	no	no	ran badly
10	12	yes	no	no	and
10	16	yes	no	no	soaked in
10	20	yes	no	no	

Discussion of Results

The main problems encountered in the development of these resins were:

1. Cracking
2. Curling
3. Non Adherence
4. Running
5. Soaking

Cracking is probably the largest problem yet to be solved in working with furfural plastics and resins. This fault increases with the size of the object molded. Several substances have been employed as plastizers that have reduced cracking notably. Foremost among these are castor oil, camphor, diethyl or dibutyl or dianyl phthallates, tri cresyl or tri butyl phosphates, butyl stearate and certain arochlars.

There is a difference between curling and non adherence. Sometimes the whole film would loosen from the block and yet not crack, this is called non adherence. The directly opposing example was when the surface would crack a great many times and parts would curl up to give an appearance recembling wood shaving, this is called curling.

Running is a property of thin watery mixtures to seek the lowest portions of the block. Obviously, a thin mixture could not be used as surfacing on any but a very level surface. Usually the watery mixture tended to soak into the block. They would form a resin in the wood to a depth of sometimes an eighth of an inch; however, they did not form a smooth coating on the surface.

It is suggested, in case further work is done upon this problem, that the student develop plastizers and thickeners applicable especially to the hydrochloric acid mixtures. It will be noted that no favorable results were obtained using hydrochloric acid, yet in the past some very good furfural plastics and resins have been made using hydro chloric acid as the polymerizing agent.

A possible method of applying a resin of this nature would be by a two compartment spray gun. In one would be the furfural and in the other the promoter, and by proper adjustment, any desired proportion could be delivered.

Conclusions

Investigation of this problem has led to the following conclusions:

1. A satisfactory resin for use as a wood surfacing material can be produced by polymerizing a twenty percent solution of furfurin in furfural with a sulphuric acid-acetone solution. The resinous mixture is obtained by adding to ten parts of furfurin-furfural from two to ten parts of a fifty percent sulphuric acid solution in acetone. The resulting solution is hard, black, and glossy. At the higher acid concentration it is noticeably acid.
2. Furfural alone with sulphuric acid in acetone, gives a hard, glossy surface but tends to crack badly.
3. A good surface is produced using three parts of seventy-five percent sulphuric acid in aqueous solution, with ten parts of furfurin-furfural. Concentrated acid tends to form a resin that solidifies immediately with evolution of a great deal of heat. A more aqueous solution is too thin.
4. Aqueous hydro chloric mixtures are unsatisfactory and very thin.
5. The furfurin-acetone surfaces are resistant to both concentrated acids and caustic. When exposed to a

flame they do not burn but char and reduce to a black powder.

Summary

Wood is one of the cheapest of construction materials and there is increasing demand for materials to finish and preserve it. In industry there is demand for materials to render it resistant to corrosive substances.

Furfural, because of its inexhaustible sources of raw material and low cost of production is a fitting material to be investigated. Furfural is polymerized to a hard resin by sulphuric and hydro chloric acids, both of which are produced very cheaply.

A satisfactory resin applicable to wood is made of furfurin-furfural and sulphuric acid in acetone. A seventy-five percent aqueous sulphuric acid also yields a good surface but it is more acid. Sulphuric acid, when mixed with acetone, tends to polymerize it and on standing over a period of several days, the mixture becomes very dark and viscous. A little better surface was produced using the older polymerized acid mixture, but because of its viscosity, it is harder to work with.

Furfural alone yields a resin nearly identical to the furfurin-furfural resin but has the bad tendency of cracking.

Most aqueous solutions with both furfural and furfurin-furfural yield resinous solutions that are so thin that they tend to run and soak into the wood leaving the surface of the wood discolored but not covered. Hydro chloric acid pro-

duces a thinner and slower acting solution than does sulphuric acid.

The author feels that he has really just touched upon the fundamentals of this problem and that, although the problem shows good possibilities, much more work is necessary to produce the desired surfacing material.

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