

FURFURAL AS A PAINT AND VARNISH REMOVER

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## INTRODUCTION

The subject of furfural has been of great importance during the last few years in the field of research to find new uses for it which might be applied on a commercial scale. The fact that furfural is easily obtained from agricultural wastes such as corncobs, oat hulls, wood waste, or other pentosan containing material makes it a cheap product for use in industrial manufacture.

Previous research on this subject has dealt mainly with furfural as a plastic. It has been successfully used to make a resin efficient enough to form a good lacquer and has also been tried for other uses in the plastic industry. Mixed with the proper ingredients, furfural forms a sufficiently hard lacquer base which is applicable to metallic surfaces. Further information on this subject may be found in Gottfried's "The Development of a Furfural Lacquer" (2).

The objects of this investigation are to determine what is the best material, if furfural alone is not sufficient, that can be mixed with furfural to form a paint and varnish remover of good efficiency and to find in what proportions these materials should be mixed to obtain the most complete and easiest removal. The approximate time necessary for

removal of a standard paint remover and the products prepared in this research also will be compared.

## HISTORICAL

The discovery (2) of furfural is attributed to Doberseiner who made it accidentally while preparing formic acid by the action of sulphuric acid and manganese dioxide on sugar. The yellow "oil" which he obtained he called "artificial oil of ants". Not long after his discovery, Emmet discovered some of the same "oil" while preparing formic acid by treating rye and corn with sulphuric acid.

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

The name, "furfurol", was given to this so-called oil by Fownes in 1845, but when the compound was later found to be an aldehyde, the name was changed to furfural. Fownes prepared this aldehyde by distilling bran with sulphuric acid.

The great tonnage of waste corncobs in the Middle West offers the country a cheap and steady source of supply of furfural. At the present time the most interesting development seems to be the use of furfural as a paint and

varnish remover. Its odor is rather sweet and, in a manner, resembles the odor of almond oil. Its specific gravity is greater than that of water, being 1.155 and its boiling point, as found by the Bureau of Chemistry, is 161.7°C. at standard pressure. Its effect upon the skin does not appear to be harsh; therefore in that respect and also in consideration of a possible fire hazard it is safer to use than the more volatile liquids. An additional feature is that it has no toxic effect.

In small laboratory tests it has been found to have a very slow evaporation rate due to its low vapor tension, remaining on a horizontal surface for over an hour. Upon a vertical or upright surface it tends to flow like water. This suggests the idea that it should be mixed with some stiffening medium. It may be well to mention some of the liquids to which it might be added (1):

Miscibility of fifty parts of furfural with fifty parts of the common paint liquids by volume.

Tung Oil ..... Completely miscible.

Linseed Oil ..... Partly miscible.

Liquid slightly cloudy, probably about half the oil is miscible with furfural.

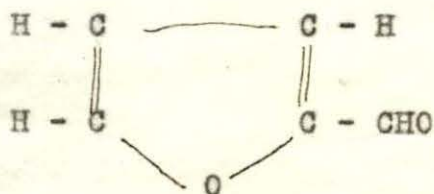
Soya ..... Same as linseed oil.

Turpentine ..... White emulsion,

separating into two layers.

|                           |                      |
|---------------------------|----------------------|
| Converted Pine Spirits .. | Completely miscible. |
| Solvent Naphtha .....     | Completely miscible. |
| Benzol .....              | Completely miscible. |
| Mineral Spirits .....     | Immiscible.          |
| Acetone .....             | Completely miscible. |

Furfural may be described as an aromatic liquid aldehyde which is nearly colorless when first prepared but which darkens upon exposure to air and light. It is completely miscible with the common organic solvents excepting petroleum ether, gasoline, kerosene, and glycerin. The solubility of this substance in water at 20°C. is 8.3 per cent, and that of water in furfural at 20°C. is 4.8 per cent. The empirical formula for furfural is  $C_4H_3O \cdot CHO$ , while its structural formula is



Through research by the Bureau of Chemistry on the production of furfural, a cheap and simple process for its manufacture from corncobs has been developed. The process may be described briefly as follows: The corncobs with some water are placed in an autoclave; steam at about 135 pounds pressure is then fed in. After cooking for

approximately two hours the furfural is blown off with steam, condensed, and collected as a dilute solution of furfural in water. The furfural is then separated from the water by distillation in a specially designed apparatus.

An experimental plant with a capacity of 40-50 pounds of furfural per day was set up at the Color Laboratory, Arlington Farm, Virginia. A yield on the above scale obtained in this plant was about 120 pounds of furfural per ton of cobs.

In 1921 furfural sold for \$30.00 a pound, but early in the year 1923, the Miner Laboratories, Chicago, Illinois, started to manufacture it on a small commercial scale using a process of dilute acid digestion of oat hulls, their capacity being approximately 150 pounds daily and their price being quoted at 50 cents per pound in 100 pound lots. It was estimated from data obtained in the operation of the Bureau experimental plant that by the steam digestion process furfural may be produced in a large scale plant at a cost of about six cents per pound. Today it is known to be the cheapest of aldehydes and sells for around 10 cents or a little less per pound.

To mention the use of furfural as a paint and varnish remover is to mention only one of its various uses. It has been stated before that furfural can be used in the



manufacture of resins somewhat similar to Bakelite. There is a great possibility of employing furfural as a fuel. It has a relatively low flash point and burns with a luminous flame. It has been reported that a few tests made by the General Motors Company in the ordinary type of motor developed pre-ignition trouble. Further experimenting was not pushed because of the high cost of furfural compared to that of gasoline. In the case of countries where the cost of gasoline is high, further research on furfural as a motor fuel seems promising.

Other uses of furfural are as an insecticide and as a solvent in the nitro-cellulose and cellulose-acetate industries. Then, too, furfural can be used in the dye industry, since a series of dyes can be formed from it analogous to those derived from benzaldehyde.

Today the only manufacturer of furfural (3) is The Quaker Oats Company, Cedar Rapids, Iowa, who obtain it from oat hulls. The process consists briefly of charging the ground hulls into a rotating autoclave with a small percentage of sulphuric acid and then subjecting them to steam at 60 pounds gage pressure for a period of three to five hours. During the latter part of the digestion, steam is passed through the autoclave and into a continuous still which is designed to deliver furfural with a purity of 95%.

Then, after passing the product through a drier to remove water, the material thus obtained is sold as technical furfural and has a purity of 98.5 - 99.0 % furfuraldehyde. A vacuum distillation of the technical product further purifies it and produces a drier and lighter material known as refined furfural.

Below is a table comparing the two commercial grades:

|                         | Technical                     | Refined                   |
|-------------------------|-------------------------------|---------------------------|
| Boiling point           | 158 - 162°C.                  | 158 - 162°C.              |
| Specific Gravity, 20°C. | 1.158 - 1.160                 | 1.159 - 1.161             |
| Flash point             | 55 - 57°C.                    | 55 - 57°C.                |
| Acid (as acetic)        | 0.2% (max.)                   | 0.1% (max.)               |
| Weight per gallon       | 9.7 lbs.                      | 9.7 lbs.                  |
| Shipping containers     | 1 and 5 gal.<br>500 lb. drums | 9 and 45 lb.<br>tank cars |

## EXPERIMENTAL

### Materials and Equipment

The materials and equipment needed to carry out this experimental research were relatively simple and easily obtainable. An ordinary oak floor on a small scale was constructed as it would have been on a large scale; that is, with foundation cross-pieces made of two by fours and a sub-floor made of 1 x 12 inch pine boards, the strips of oak flooring being laid on top of that in the correct manner. For the experimental work the best grades of filler, shellac, and a hard-finish varnish were used. The procedure for finishing the oak floor was as follows:

An already stained filler was first put on; then three or four coats of shellac were applied to form a hard base satisfactory for a rigid test; and upon this were placed two or three coats of the varnish mentioned above.

No special or elaborate equipment or supplies were necessary, the rest being merely a paint brush, a scraper, and the ingredients to be tried in the experiment; these being crude furfural, Ponsolve (a commercial solvent made up mainly of denatured alcohol), ordinary benzene, and paraffin wax. A good grade of standard commercial paint remover was obtained

to furnish a comparison with the experimental mixtures.

#### Procedure and Observations

Preliminary (made to determine whether a mixture of furfural and some other ingredient was necessary and if necessary which ingredient or ingredients should be used.)

I. In order to form a basis of comparison, an application of the standard commercial paint remover was first made; the remover being Pitcairn remover, a Pittsburgh Paint Company product. The time necessary for this remover to penetrate the finish on the oak floor was approximately 20 minutes, and for a clean removal of all of the varnish and shellac two applications were necessary. It was taken off by wiping with cloths or paper towels. However, an easier way in which to remove it was to use an ordinary paint scraping tool. This remover left some of the stain. However, the section to which it was applied was left fairly light in color. It did not raise the grain of the wood.

2. As a second experiment, furfural alone was used. In comparison with the standard remover it took less time; about 10 minutes or less. The removal of the finish was very satisfactory and its application did not raise the grain of the wood. It did not appear to discolor the wood to any great extent. The one great difficulty in the application of furfural alone was that, due to its surface tension, it would collect in pools rather than spread on in an even surface. This fact

led to the belief that some other substance should be mixed with the furfural to reduce its surface tension and to cause it to flat in a better manner.

3. A mixture of equal amounts of furfural and Ponsolve was tried in order to determine the effect of an added agent. The test was not satisfactory since the penetration required too much time and the effect of inefficient spreading was not overcome.

4. A mixture of  $2/3$  furfural and  $1/3$  benzene was next applied to the finish. As far as time necessary for removal and satisfactory removal were concerned this experiment compared in approximately the same manner as did the straight furfural. However, the benzene evaporated too quickly to give any benefit to the pooling characteristic of the furfural thus ultimately proving unfavorable.

5. For the next trial a saturated solution of paraffin wax in benzene was prepared; this solution being mixed with the furfural in approximately equal proportions. This addition of the wax to the benzene before further mixing with furfural succeeded in solving the problem of causing the furfural to spread evenly. The removal, however, was somewhat slower than that of the standard remover. Due to those facts three formulas were prepared, the mixtures consisting of furfural and the saturated solution of paraffin wax in benzene. These mixtures were prepared on a volumetric

basis, the final volume being 200 cc. The following are the mixtures which were made up:

Formula No. 1:

|                           |   |            |   |                  |
|---------------------------|---|------------|---|------------------|
| Sat. Soln. wax in benzene | = | $1/3(200)$ | = | 66.7 cc.         |
| Furfural                  | = | $2/3(200)$ | = | <u>133.3 cc.</u> |
|                           |   |            |   | 200.0 cc.        |

Formula No. 2:

|                           |   |            |   |                |
|---------------------------|---|------------|---|----------------|
| Sat. Soln. wax in benzene | = | $2/5(200)$ | = | 80 cc.         |
| Furfural                  | = | $3/5(200)$ | = | <u>120 cc.</u> |
|                           |   |            |   | 200 cc.        |

Formula No. 3:

|                           |   |            |   |                |
|---------------------------|---|------------|---|----------------|
| Sat. Soln. wax in benzene | = | $1/5(200)$ | = | 40 cc.         |
| Furfural                  | = | $4/5(200)$ | = | <u>160 cc.</u> |
|                           |   |            |   | 200 cc.        |

6. Formula No. 1 was first applied to the floor finish and proved to be very satisfactory as an efficient varnish remover. The time required for the removal was approximately 5 to 10 minutes. It left the wood in its natural color and did not in any manner raise the grain. The odor of the furfural was lessened a great deal by this addition and practically all trace of odor had disappeared by the next day. The preparation spread evenly and a second coat was applied merely to completely clean the surface of any adhering varnish or shellac. This formula was later applied to a

board upon which were several coats of paint and enamel which had remained on it for at least two years. The removal of this paint was effected almost instantly with very little difficulty. It could be easily wiped off with a cloth.

7. Formula No. 2 was next tried on the floor with relatively good success, but not as satisfactorily as Formula No. 1. It required only a short time to penetrate, but needed two or three coats for complete removal.

8. Upon the application of Formula No. 3, it was found that it required a greater amount of time for removal and also the same number of coats as did Formula No. 2. This was therefore discarded as a possible better remover than the standard commercial paint remover, because of its inefficiency of penetration.

## DISCUSSION

It can be easily understood that the most important characteristics of a good paint and varnish remover are its ability to penetrate within a short time, its ease of removal after penetration, its tendency to spread evenly without collection in globules, its failure to discolor the wood, and its property of leaving the grain flat and smooth instead of raising it in any way.

The use of furfural in the preparation of various colored lacquers has shown that its dark color has no effect upon the color of the lacquers. This is due to the fact that there is practically no pigmenting power in even very dark colored furfural. As was observed in the experiments carried on in this research, furfural imparted very little color to the clear oak wood, and it was noticed, too, that even if a clear oak finish was desired, the removal of the previous finish by the furfural-wax in benzene mixture would not prove a detriment to its light color.

Taking into consideration the cost of manufacture, it has already been seen that furfural can be made at a low price, this price being approximately 10 cents per pound or perhaps a little less. The method of manufacture, too, is



relatively simple, and a very pure product can be obtained by its use.

The mere fact, also, that in the production of furfural various agricultural wastes can be used is one which assures its continued manufacture. Although made mainly from oat hulls at the present time, processes have been and could be developed using not only corncobs, but also wood wastes, straw, flax, wood, cornstalks, bagasse, and rice hulls (3). All of these materials are easily obtainable and most of them are wasted in great quantities.

As far as the other necessary ingredients are concerned, the paraffin wax and benzene can be secured in large quantities. Benzene itself can be had cheaply and although not so desirable in the way of flammability and toxicity, its use in the amount in Formula No. 1 would be small enough to reduce those characteristics when mixed with the furfural. Paraffin wax is obtained in the petroleum refining industry and is manufactured in large amounts and fairly cheap (4).

### CONCLUSIONS

1. The effect of mixing various ingredients with furfural to determine the effect on eliminating the pooling action having been tried, it was found that a mixture of a saturated solution of wax in benzene and furfural was the best method for obtaining the characteristics of a good paint remover.

2. Of the three formulas made up of different preparations of this mixture, Formula No. 1 was found to give the best results. This formula consists of  $\frac{2}{3}$  by volume of furfural and  $\frac{1}{3}$  by volume of a saturated solution of wax in benzene.

3. Formula No. 1 as compared to the standard commercial paint remover seemed to excel in the properties demanded of a good paint and varnish remover.

4. It is believed that the mixture contained in the best formula, No. 1, could be produced on a large scale and sold more cheaply than many paint removers now on the market.

SUGGESTIONS

Further work should be done in the development of a satisfactory paint and varnish remover from furfural to place it on a commercial scale. The following suggestions may be of use in this development.

Many other possible ingredients could be used to mix with the furfural; some of these which might prove of value are given in the table of miscibilities on page 6.

It is suggested that small amounts of Tung oil be tried as a stiffener in further research and that a greater range of mixtures be attempted.

SUMMARY

A paint and varnish remover was made of a mixture of two-thirds furfural and one-third saturated solution of wax in benzene. This mixture was applied to an experimental finished oak floor and also to wood which possessed coats of paint approximately two years old. The results indicated that the product was satisfactory and possessed the characteristics of a good paint and varnish remover.

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