FURFURAL AS A PAINT AND VARNISH REMOVER

By

Harold E. Carlson

and

Don P. Hammer

A Thesis Submitted for the Degree of

BACHELOR OF SCIENCE

in

Chemical Engineering

Iowa State College
1939

TABLE OF CONTENTS

INTRODUCTION

The subject of the utilization of agricultural wastes has become one of great interest and importance in the last few years. Much work has been done upon the conversion of materials such as oat hulls, peanut shells, corn stalks and corn cobs into products of industrial and commercial importance. Because of its availability as a raw material, the most conclusive work has been done on oat hulls. Such research has led to the development of commercial furfural.

Most of the previous research on furfural has been done in connection with its use in plastics. It is used in the production of a resin which has proven to be satisfactory enough to form a good lacquer base for metallic surfaces when mixed with the proper ingredients. Furfural has also been used more or less successfully as an anaesthetic, insecticide, and as a germicide. One major use is in the solvent refining of lubricating oils.

The primary object of this investigation was to determine the practicability of using furfural, or a combination of furfural with another material or materials, as an efficient paint and varnish remover. If it was found to be practicable, it was also to be determined in what proportions should the materials be mixed in order to obtain the most efficient and quickest remover. Many different combinations were to be tried and the results were to be compared with results obtained by using a standard commercial remover.

Particular attention was to be given to the effect that the remover would have upon the wood, as no combination could be considered a satisfactory remover which has a darkening or a grain-raising effect upon the floor.

The formulae for some of the paint and varnish removers which are in use today are as follows: (11)

1. Paraffin wax----------3 parts*
   Turpentine----------30 parts
   Acetone----------25 parts
   Carbon tetra chloride----15 parts
   Benzene----------20 parts
   Xylene----------10 parts

2. Paraffin wax----------4 parts
   Benzene----------8 parts
   Turpentine----------7 parts

3. Sodium hydroxide--------2.67 lbs.
   Water----------2.00 qts.
   Aqua ammonia----------2.00 qts.
   Sodium silicate---------2.5 gals.

4. Benzene or toluene--------1 part
   Ethyl acetate----------1 part
   Ethyl alcohol----------1 part

5. Amylene dichloride------80 parts
   Alcohol----------40 parts
   Naphtha----------20 parts
   Diglycol stearate--------2 parts

6. Ortho dichlorobenzene----7 parts
   Propylene dichloride-----6 parts
   Benzene----------1 part
   Carbon tetrachloride-----1 part

* All parts are parts by weight.

HISTORICAL

One of the most phenomenal rises of a chemical compound from a laboratory curiosity to an industrial commodity of the first rank is that of furfural. Furfural was first discovered in 1830 by Dobereiner (2). He was preparing formic acid by the action of sulfuric acid and manganese dioxide on sugar, when he noticed that a yellow oil separated from his distillate. This oil was given the name of "artificial oil of ants" because of odor and method of accidental preparation. Not long after Dobereiner's discovery, Emmett discovered some of the same "oil" while preparing formic acid by treating rye and corn with sulfuric acid.

In 1840 Stenhouse (7), by treating oatmeal and sawdust with sulfuric acid, obtained an appreciable quantity of oil, about one ounce from 12 pounds of raw material. He determined the constitution of the aldehyde, its physical properties, and the composition of the oil. He also gave it the formula $C_5H_4O_2$.

In 1845 Fownes (3) secured, by distilling bran with sulfuric acid, an oil identical with that identified by Stenhouse. From its method of preparation he suggested the name furfurol (furfur - bran, oleum - oil). Ultimately, after the aldehyde character of the compound was determined, the name was changed to furfural.

Early experimenters obtained furfural from wheat and sulfuric acid (1). Stenhouse (8) prepared similar oils from various sources. He also secured from sea weeds an oil he assumed to be an isomer of furfural and named it fucusol. Later Maquenne (5) and

Tollens (6) found the compound to be a mixture of furfural and methyl furfural. Other experimenters prepared furfural from wood(4), and numerous other substances, generally materials containing a relatively high percentage of pentosan. Among the agricultural wastes which may be used for the commercial manufacture of furfural are corn-stalks, corn-cobs, oat-hulls, peanut hulls, cottonseed hulls, beet pulp, sugar cane pulp, rice chaff, and wheat, oat, rye, and flax straw. At present all of the furfural is manufactured by The Quaker Oats Company, Cedar Rapids, Iowa, who obtained it from oat hulls as by-product of their cereal plant.

It is interesting to note the history of the prices of furfural:

Year	Selling Price
1920	$ 30.00 a pound
1921	$ 30.00
1922	$ 1.00
1923	$ 0.50
1924	$ 0.25
1936	$ 0.10
1939	$ 0.10

For the past few years, due to the limited uses of furfural, the price has remained approximately constant. However, it is predicted that the price per pound will become much lower with the discovery of new uses and applications. Authorities estimate that with the present machinery and mass production the price should be about $ 0.04 a pound and with improvements the price could possibly be cut down to about a $ 0.01 to $ 0.015 a pound.

There are several possible methods for the technical preparation of furfural. The only one in use today is the combination process of acid hydrolysis and steam distillation of oat hulls used by the afore mentioned Quaker Oats Company at Cedar Rapids, Iowa. The waste oat hulls are first ground up; then digested for from three to five hours under a steam pressure of 60 pounds gauge. The furfural vapors are conducted to a continuous column still. The product is about 95 percent pure. This is then further rectified somewhat in a socalled "drier" and as it leaves the drier it has a purity of 98.5 - 99.0 percent. This product is sold as the technical grade furfural. The refined furfural is produced by vacuum distillation of the technical grade.

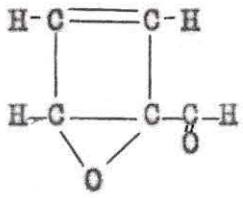
Past researches have dealt mostly with the applications of furfural in plastics, lacquers, crayons, fly repellents, weed killers, and fungicides. Furfural is used commercially as a selective solvent for nitrocellulose, cellulose acetate, mineral oils, and certain varnish gums. It is also used as a solvent for shoe dyes, and dyes in textile printing. It has been used as a substitute for formaldehyde in the manufacture of phenol and urea resins; as a preservative for starch and glue solutions; in tanning leathers; and in hardening gelatin-glycerol mixtures; and as an embalming fluid.

This work on the use of furfural as a paint and varnish remover represents the continuation of the attempt to add to the present industrial uses of furfural. The first work done along

this line was by Charles M. Robinson who experimented with various materials which when mixed with furfural would make efficient paint and varnish remover. Further experimentation by Howard F. Conway and John S. Wagler (10) checked the validity of the results obtained by Robinson.

PROPERTIES OF FURFURAL

Furfural is a heterocyclic aldehyde whose synonym is furfuraldehyde. The empirical formula is $C_5H_4O_2$. The molecular weight is 96.0. The generally accepted formula for the structure of furfural is as follows:



Pure furfural is a colorless liquid, but is oxidized quickly by air to a yellow or brown color. It has a distinct "empyruematic odor". It is non-poisonous compound.

Melting Point --------- 38.7° C.

Boiling Point -------- 161.7° C.

Specific Gravity ------ 1.159 (20° C)

Flash Point ---------- 55°-57° C.

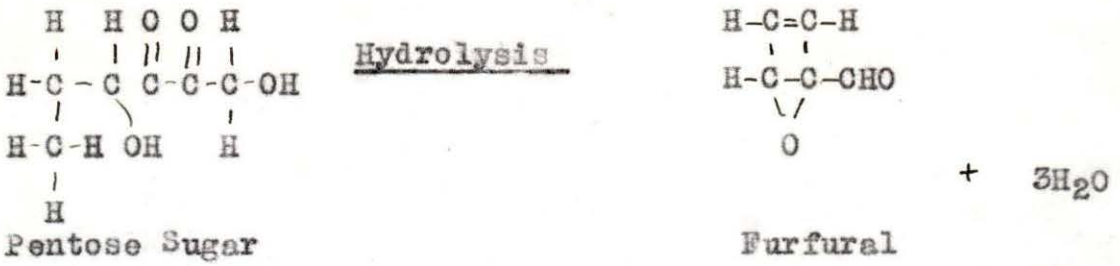
Solubilities:

Furfural is soluble in most organic solvents except gasoline, petroleum ether, glycerin, and kerosene.

Solubility in water ---------- 8.3% (20° C)

Solubility of water in furfural --------- 4.8% (20° C)

Furfural is obtained from pentosan containing substances when the latter are subjected to hydrolysis. The pentoses are hydrolytic products of the pentosans. They hydrolyze easily to furfural. The reaction which takes place is represented as follows:



Pentose Sugar

Furfural

The above reaction is almost quantitative.

The reaction is catalyzed to some extent by the use of a mineral acid such as hydrochloric acid or sulfuric acid. Some salts, such as zinc chloride and calcium chloride also act as catalyzers.

Furfural when pure and distilled under vacuum is clear and of a light straw color, but it darkens quickly upon exposure to light.

Furfural is very readily detected in a solution by the deep red color which it gives when treated with aniline acetate.

EXPERIMENTAL

A. Materials and Equipment

The materials and equipment which were used to carry on this research were very simple and comparatively easy to prepare or to obtain. A small oak floor was used. The floor consisted of strips of oak flooring laid upon a sub-floor of 1 in. x 12 in. pine boards which were in turn laid upon cross-pieces of two by fours. For the experimental tests standard wood fullers, shellacs and varnishes were used. The preparation of the oak floor for experimentation was as follows:

Due to the fact that the floor had been used in previous research it was necessary to first thoroughly sand it with coarse and then fine sand paper. The commercial wood filler was then applied as directed, rubbing across the grain of the wood. Three coats of clear shellac were next applied. This number of coats was used in order to obtain a rigid base which would be satifactory for the tests. Upon this base three caots of dark oak varnish were applied. This finish was used in order to most easily observe the action of the remover against the background of the lighter colored wood.

No elaborate equipment was used, the remainder of the articles employed consisted of a paint brush, scraper and the materials to be used in the experiments. These materials consisted of crude furfural, acetone, benzene, paraffin wax, and various other chemicals as will be described under the experimental procedure. A good grade of standard commercial remover, manufactured by the

Pittsburgh Plate Glass Company, was obtained to be used as a basis for comparison with the experimental mixtures.

B. Procedure

In order to establish a basis of comparison for the experimental tests to be carried out, results obtained by using the standard remover were noted. The time necessary for complete penetration was about twelve (12) minutes. The removal was satisfactory, but the liquid evaporated very quickly, necessitating two (2) applications at stubborn points. Contrary to advertized claims, rubbing the varnish off with a cloth seemed to be unsatisfactory, and best results were obtained with a scraper. This commercial remover did not stain or raise the grain of the wood in any way.

Furfural alone was tried next. The time necessary for penetration and softening 4 to 6 minutes. The performance compared favorably with that of the commercial remover but because of its high surface tension the furfural tends to pool on the floor rather than to spread as evenly as is desirable. This observation suggested the addition of some material or materials capable of lowering the surface tension of the furfural. In this experiment the wood was not affected in any way.

With the above observation in mind, several different solutions containing furfural and one or more other materials, having not only a low surface tension but also a more or less effective solvent action of their own were tried.

The following solutions were prepared and tested:

1. 50% furfural - 50% acetone *
2. 60% furfural - 40% turpentine *

3. 60% furfural-25% turpentine-15% aqueous ammonia *

4. 50% furfural-25% acetone-25% benzene *

* Percent by volume.

The results obtained from the use of the above preparations may be summarized as follows:

1. Time: 2 minutes for cessation of reaction.

   Results: This mixture succeeds quite well in lowering the surface tension of the furfural and does not raise the grain of the wood or affect it in any manner.

2. Time: 5 minutes.

   Results: This preparation stains the wood and so it could not be considered a satisfactory remover.

3. Time: 15 minutes.

   Results: Darkens the wood. There is also an excessive odor of ammonia present. This mixture was not considered further.

4. Time: 10 minutes.

   Results: Unsatisfactory in general.

Although the results of mixture No. 1 above were unsatisfactory when used upon the experimental floor, older varnish did not respond so readily. Before the preparation had time to act thoroughly upon the varnish, the acetone had evaporated to such an extent as to render the final result unsatisfactory. This suggested the addition of some material to hold down the rate of evaporation of the more volatile constituent.

Several different mixtures were prepared as follows:

5. 45% furfural-52% water-3% emulsone B *

6. 25% saturated solution of paraffin in benzene
   75% furfural *

7. 60% furfural-30% acetone-10% glaurin wax *

The experimental results obtained by using the mixtures as described above were as follows:

5. Time: 15 minutes for cessation of reaction.

   Results: This mixture was considered as unsatisfactory as it stained the wood.

6. Time: 5 minutes.

   Results: This mixture is in the form of a sludge. The addition of the furfural seems to decrease the solubility of paraffin in benzene. It removes the varnish about 85 percent as efficiently as the commercial remover.

7. Time: 4 minutes.

   Results: This composition stains the wood slightly and also becomes quite tacky in about 4 minutes. This seems to indicate that the wax used is not capable of lowering the evaporation rate enough.

The most positive results obtained in previous research have been secured by using a mixture of wax and benzene in furfural. This mixture forms a sludge and makes it quite unhandy to work

with. In view of this fact, an effort was made to find other materials which would produce the same results as would wax.

Many other materials were tried in order to lower the evaporation rate after acetone. Among those tried were starch, ethylene glycol, acetone oil, corn sugar, Halowax No. 1014. The starch seemed to hasten the evaporation rather than retard it, leaving a tacky surface after about 2 minutes. Corn sugar exhibited about the same characteristic. Acetone oil held down the evaporation rate to a small extent, but gave off a somewhat disagreeable odor when mixed with furfural. Halowax No. 1014 exhibited very satisfactory properties when used to hold down the evaporation, but left an undesirable wax film upon the surface of the floor. Ethylene glycol seemed to give the most satisfactory results. It slowed down the volatilization of the solvents did not affect the floor, and had no noticable odor.

Many different solvents were tried. Among the most important were trichloroethylene, toluene, benzene, acetone, zylene, and ethyl methyl ketone. Trichloroethylene was observed to have a very good solvent action. Toluene, benzene, acetone, and zylene, gave satisfactory results when used as solvents, but were not as efficient as trichloroethylene. Ethyl methyl ketone was observed to have the most satisfactory solvent action of any of the materials tried.

Of the many combinations tried in order to obtain a satisfactory remover, the one which showed the greatest possibilities was composed of 40 percent furfural, 55 percent ethyl methyl ke-

tone and 5 percnet ethylene glycol.

DISCUSSION

The most important characteristics of a good paint and varnish remover are its ability to penetrate the coating within a short period of time, its ease of removal after penetration and softening and its tendency to flow evenly over the entire surface to be treated. Furthermore it must not stain or discolor the wood, or raise the grain of the wood.

A review of previous research upon this subject disclosed that no mention had been made of the fact that furfural has a discoloring action upon the skin. This action has no harmful effect upon the skin, but it requires several days for the stain to wear off.

Taking into consideration the cost of manufacture, it has been indicated that furfural can be made at a low price; this price being approximately 10 cents per pound or perhaps a little less. The fact that in the production of furfural various agricultural wastes may be used assures its continuous manufacture.

The price of ethylene glycol is higher than that of furfural and wax, but so little is necessary that the price does not prohibit its use. The price is $ 0.22 to $ 0.23 per pound.

The price of ethyl methyl ketone, the other constituent of the most successful remover found is $ 0.0665 per pound.

The addition of ethyl methyl ketone was observed to materially raise the flash point of the mixture. This decreases the danger of using the remover indoors.

CONCLUSIONS

1. Having observed the effect of mixing various ingredients with furfural in order to eliminate the pooling action, it was found that a mixture of ethyl methyl ketone, furfural and ethylene glycol was the best preparation having the characteristics of a good remover.

2. This mixture as compared with the standard commercial remover seems to exhibit superior properties as demanded of a good paint and varnish remover.

3. It is believed that the mixture as described above could be produced on a large scale at a price which would make the production profitable. It is also believed that such a mixture could be sold more cheaply than many of the removers on the market at present.

Further work should be done on the development of furfural as a paint and varnish remover. However, the staining action of furfural on the skin may have to be overcome before it will be possible to develop an acceptable remover.

Many other possible ingredients could be used which might prove of value. These include glycerin, xylene, trichloroethylene, and some of the higher ketones.

SUMMARY

A paint and varnish remover was prepared from a mixture of 40 percent furfural, 55 percent ethyl methyl ketone and 5 percent ethylene glycol.

This mixture was applied to an experimental finished oak floor and also to various other floors with older coatings of varnish. The results indicated that the product is satisfactory and possesses the characteristics of a good paint and varnish remover.

LITERATURE CITED

(1) Cahours, Ann., 74:279 (1850)

(2) Dobereiner, Ann., 3:141 (1832)

(3) Fownes, Ann., 54:52 (1845)

(4) Heill, Ber., 10:936 (1870)

(5) Maquenne, Ber., 22:751 (1889)

(6) Tollens, Ber., 22:3062 (1889)

(7) Stenhouse, Ann., 35:301 (1840)

(8) Stenhouse, Ann., 74:279 (1850)

(9) Robinson, Charles M. Furfural as a paint and varnish remover. Unpublished Thesis. Library, Iowa State College, Ames, Iowa. (1936)

(10) Conway, Howard F., and Wagler, John J., Furfural as a paint and varnish remover. Unpublished Thesis. Library, Iowa State College, Ames, Iowa. (1937)

(11) The Chemical Formulary. Vol. 4:423.