

ALIEN PROPERTY CUSTODIAN

PRODUCTS

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This invention relates to organic compounds, and more particularly to synthetic resins.

Aldehyde resins may be obtained by the condensation of aldehydes, frequently with an alkaline catalyst. See Ellis—The Chemistry of Synthetic Resins—Chapter 23.

This invention has as an object the preparation of modified aldehyde resins. A further object is the preparation of improved aldehyde resins. Other objects will appear hereinafter.

These objects are accomplished by the following invention wherein an aldehyde resin containing water of constitution has a portion or all of the water replaced by molecules of an organic or inorganic acid, alcohol, halogen, or other exchangeable compound alone or mixed.

The resins which may be produced from aldehydes such as acetaldehyde, crotonaldehyde, etc., particularly the solid, amorphous masses formed by thermal treatment, e. g., according to DRP-381,720, can, by reaction with chemical reagents, be converted in a surprising manner into new type compounds. The aldehyde resins are derivatives of acetylene and, in combination with the polythine nuclei resulting from the condensation of the acetylene, they contain chemically combined water in different ratios. The new process deals with the partial or complete replacement of this water. The derivatives formed by this conversion may be considered as polyethine compounds of the composition $(C_2H_2)_x.K_y$, where K is an organic acid, inorganic acid, alcohol, halogen, or other exchangeable compound alone or mixed, and y may vary from 0 to x . K may also include water, but not alone, i. e., it is present along with an alcohol, acid, etc., which has but partially replaced it in the original aldehyde resin.

The following examples which are illustrative and not limitative exemplify the invention with respect to the preferred aldehyde resin "Wacker Artificial Shellac KR" obtained by a thermal hardening with or without alkalies of resins from acetaldehyde and its polymerization and condensation products according to German Patent 381,720. The elementary analysis of this resin is carbon 68.50%, hydrogen 8.26%.

Example I

100 g. of resin KR were dissolved in about 500 g. of hot glycerol and to the hot solution about 1/2 cc. of concentrated sulfuric acid was added in drops, the mixture being agitated. When the sulfuric acid was added, local reactions were set up with the formation of black lumps. On the next

day the contents of the flask had become almost solid and only a small amount of liquid remained. Water was added to the reaction product and boiled. By repeated washing or boiling with water, after drying on a clay plate in the open and in the drying oven at 120° C, 86 g. of a coffee brown powder were obtained. Its composition is carbon 72.04%, hydrogen 7.55%.

The product is partially soluble in alcohol and then gives a brittle brown resin melting at 120° C. The alcohol-insoluble portion is rather resistant to solvents and is amorphous.

Example II

10 g. of resin KR were dissolved in 70 cc. of glycol by heating. By the addition of several drops of sulfuric acid to the hot solution reaction took place with the formation of a dark precipitate. On another day the reaction product was covered with water, ground, boiled until the wash water was clear and, after drying at 120° C, gave about 7 g. of fawn-colored powder. Analysis gave carbon 71.11%, hydrogen 6.82%.

The product is partially soluble in alcohol and then gives a brown fusible resin. The alcohol-insoluble, amorphous portion is only partially soluble in other customary solvents such as acetone, benzene, etc.

Example III

10 g. of resin KR were dissolved in 60 cc. of hot formic acid and to this hot solution 4-5 drops of concentrated sulfuric acid were added. On the addition of sulfuric acid to the hot solution a mild reaction took place. After warming for 3 hours a dark resin was precipitated from the black solution by the addition of 200 cc. of water. This precipitate was washed with hot water and dried. The yield was 8.4 g. Analysis gave carbon 70.73%, hydrogen 7.17%. The saponification number was 442 to 465.

The product is originally blackish but by repeated boiling with water becomes fawn-colored. It is partially soluble in alcohol. The alcohol-soluble portion is a brittle brown resin with good solubility in the customary organic solvents. In methanol, tetrachloroethane, it is only partially soluble, in benzene it is only soluble in traces. The alcohol-insoluble portion is amorphous and difficultly soluble. In acetic acid, Methylanon, Palatinol M, and pyridine it dissolves partially when heated.

Example IV

30 g. of resin KR were dissolved in 150 cc. hot glacial acetic acid. To the cooled solution a mix-

ture of 2 cc. concentrated sulfuric acid in 50 cc. glacial acetic acid was added. When the sulfuric acid solution was added to the cooled mixture no visible reaction occurred, except for the development of a dark color. A vigorous reaction did not take place until the mixture was heated. The reaction mixture was held for several hours at the boiling point of acetic acid and the hot solution, solidifying below 100° C, was poured into water, whereby a blackish brown hard powder precipitated. By boiling with water and drying a coffee-brown powder, which swelled strongly in water, was obtained. The yield was approximately 25 g.

The product is partially alcohol-soluble. On combustion, the alcohol-soluble portion gave carbon 73.34%, hydrogen 6.74%, and a saponification number of 246.

In the case of the alcohol-insoluble portion, combustion gave carbon 72.76% and hydrogen 7.10%, and a saponification number of 213.

A polyethine acetate of the formula



has the composition: carbon 73.1%, hydrogen 7.3%.

Example V

50 g. of resin KR were dissolved in 250 cc. of glacial acetic acid and to the hot solution a mixture of 5 cc. concentrated sulfuric acid in 150 cc. glacial acetic acid was added. The reaction mixture was heated for 3 hours at the boiling point of the glacial acetic acid and then the distillable portion was distilled from the reaction flask on an oil bath. In the acetic acid which was driven off about 12 g. of saponifiable ester were determined. The solid reaction product, after washing with water and drying, gave a blackish brown, hard powder.

The yield was 46 g. Combustion gave carbon 73.98%, hydrogen 7.24%, and a saponification number of 257.

However, in comparison with the reaction product obtained according to Example IV, this product is less soluble. Both hot and cold it is only soluble in traces in benzene, butyl acetate, Methylanon, and tetrachloroethane.

Example VI

50 g. of resin KR were dissolved in 200 cc. of glacial acetic acid and then a mixture of 2 cc. concentrated sulfuric acid and 100 cc. of glacial acetic acid was introduced into the middle of the resin solution. This reaction mixture was boiled for 4 hours and the resulting dark solution poured into alcohol. Overnight a dark sludge separated, which was boiled several times with alcohol, and after drying at 120° C produced a fawn-brown powder.

On combustion this product gave carbon 73.24%, hydrogen 7.36% and had a saponification number of 316. Its composition corresponded, therefore, very well with the formula for a polyethine acetate as given in Example IV.

The alcohol-containing filtrate was concentrated on a water bath and poured into water. After drying the powder separating out gave a fawn-brown powder of the composition: carbon 70.97%, hydrogen 7.11% and had a saponification number of 297.

Example VII

10 g. of resin KR were dissolved in 50 cc. of hot glacial acetic acid and to the hot solution several drops of concentrated sulfuric acid were

added, a short vigorous reaction takes place at once accompanied by a darkening of the mixture. The solution was allowed to stand overnight and by the addition of 150 cc. of water a voluminous black compound was precipitated. By repeated washing with water and drying at 120° C about 8 g. of a brown product were obtained. This product was particularly voluminous in comparison with the other acetates produced according to Examples IV-VI.

Analysis gave carbon 70.67%, hydrogen 7.03%, and a saponification number of 263.

This product is very easily soluble. Cold it is partially soluble in acetone, benzene, butyl acetate, chloroform, acetic acid, methanol, Methylanon, Palatinol M, alcohol, tetrachloroethane; cold it is soluble in glycol only in traces also carbon tetrachloride, on the other hand it is almost soluble in pyridine when cold.

Hot it is completely soluble in Methylanon, Palatinol M, pyridine, tetrachloroethane; it is almost completely soluble in acetic acid.

By way of comparison the solubility characteristics of the product, obtained according to Example IV, are different. This product, both hot and cold, is for the most part only partially soluble in the solvents cited; in methanol it is only soluble in traces.

The product obtained according to Example VI is even less soluble. Both hot and cold it is insoluble in acetone, benzene, oil of turpentine, and vinyl acetate; hot and cold it is somewhat soluble in chloronaphthalene, chloroform, dichloroethylene, Palatinol C & M, and trichloroethylene; otherwise it is only soluble in traces.

The product obtained according to Example V is the least soluble. Both hot and cold it is only soluble in traces in benzene, butyl acetate, Methylanon, and tetrachloroethane; otherwise it is insoluble when cold.

Examples IV, V, VI, and VII show how the reaction with acetic acid may be modified in order to bring out the fact that products with different physical properties may be obtained to a large degree, e. g., products which are highly soluble or which are of low solubility, products which are in an easily pulverizable or are in a hard form, voluminous products or more compact products, products which are resinous and fusible or which are infusible and amorphous, different colored products, e. g., so that these products have a wide application in the fields where resins and other plastics are customarily used.

Example VIII

50 g. of resin KR are dissolved in 450 g. of glacial acetic acid. At room temperature chlorine is introduced into this solution. The solution, which originally had the characteristic red-yellow color of aldehyde resins, became light brown after an initial dark coloration. After the solution had taken up 56 g. of chlorine in 340 minutes, the reaction product was precipitated with 3 liters of water and washed with 9 more liters of water until it was chlorine and acid free. The reaction product was an almost white powder which contained 46.17% carbon, 4.8% hydrogen, and 34.37% chlorine. The yield was 88 g.

The chlorination product is very easily soluble in almost all organic solvents, e.g., acetone, butyl acetate, monochlorobenzene, benzene, chloroform, acetic acid, pyridine, and trichloroethylene.

The process and the form of the product obtained may be varied by the choice of different solvents, different halogens, by the addition of

halogen carriers, and also by varying the solvent, temperature, etc. of the chlorinating agent used. Therefore, another example of the chlorination may be given below.

Example IX

50 g. of resin KR were dissolved in 450 g. of glacial acetic acid. After the addition of 7.5 g. of phosphorous pentachloride, chlorine was led in while cooling the mixture to 0°C until there was an 80 g. increase in weight. By irradiation of the solution the reaction of the chlorine saturated solution could be so conducted that a light reaction product was obtained, which after isolation had a saponification number of 558. By precipitation of the mother liquor with methanol, a second almost white reaction product with a saponification number of 573 was isolated. A third white reaction product with a saponification number of 721 was obtained by the addition of water to the mother liquor.

Similar compounds may be obtained with other halogens. If bromine, dissolved in glacial acetic acid, is reacted on a solution of resin KR in acetic acid a black, bromine-containing product is obtained. By the action of iodine dissolved in a solution of acetic acid and alcohol, a blackish gray green, iodine-containing pulverulent product is precipitated from an acetic acid solution of resin KR.

While certain alcohols, acids, etc. have been exemplified above, the process of the present in-

vention is generically applicable to the replacement of at least a portion of the combined water of an aldehyde resin by alcohols, organic acids and halogens. Lower fatty acids, i.e., those up to four carbon atoms are a preferred class and of these acetic acid is particularly useful. Lower polyhydric alcohols, i.e., those having up to four carbon atoms are also useful. Monohydric alcohols may also be used. When an organic hydroxyl compound, e.g., a fatty acid or polyhydric alcohol is to replace the combined water in whole or in part, a catalyst, e.g., sulfuric acid, is particularly desirable.

The invention is exemplified above with KR resin, i.e., a thermo hardened acetaldehyde resin, but the process of the invention is applicable to any aldehyde resin, i.e., the resinification product of an aldehyde or mixture of aldehydes.

By the present process a new method is disclosed for obtaining new organic compounds particularly polyethine compounds. Their field of use is the same as that of previously known plastics, particularly the fields in which resins and polyvinyl compounds are used.

The above description and examples are intended to be illustrative only. Any modification of or variation therefrom which conforms to the spirit of the invention is intended to be included within the scope of the claims.

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