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PROCESS OF PRODUCING ARTIFICIAL RESINS

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The present invention relates to a process for the production of condensation products of pentaerythritol with polybasic organic acids and monobasic aliphatic acids containing more than five carbon atoms.

The production of artificial resins by the condensation of pentaerythritol with polybasic acids has been known for a number of years. However, these resins because of certain undesirable characteristics, even though they had many valuable properties especially for application in the electrical industry, have not been introduced into the art. The prior art resins suffered from several drawbacks. For example, the condensation products were not completely clear and did not retain their form and shape. The prior art resins of this class were affected by moisture and were not completely resistant thereto. In addition, the hardened product did not possess constant properties.

I have discovered that the drawbacks of the prior art pentaerythritol resins may be overcome in a simple but efficacious manner.

It is an object of the present invention to provide a process for manufacturing condensation products of pentaerythritol with polybasic organic acids and monobasic aliphatic acids containing more than five carbon atoms.

It is another object of the present invention to provide pentaerythritol-polybasic organic acid resins which are completely clear and have great stability of form and shape.

It is a further object of the present invention to provide condensation products of pentaerythrithritol and polybasic organic acids which are highly resistant to and practically unchanged by moisture.

It is also within the contemplation of the present invention to provide a hardened product of the condensation of pentaerythritol and polybasic organic acids which has substantially constant properties.

The present invention likewise contemplates a process for the preparation of condensation products of pentaerythritol and polycarbonic acids together with aliphatic acids containing more than five carbon atoms.

Other objects and advantages will become apparent to those skilled in the art from the following description.

Broadly speaking, I have discovered that the various disadvantages and undesirable properties of the prior art pentaerythritol-polybasic organic acid condensation products may be overcome by employing pentaerythritol in a purified state. The pentaerythritol obtainable in commerce, even when it has a high melting point, contains greater or lesser quantities of contaminants such as sugars, aldehydes, formic acid and the like which influence the melting point of the pentaerythritol to no considerable extent. Even the so-called pure pentaerythritol is contaminated more or less by admixtures of one or more of the aforementioned contaminants. For example, even pentaerythritols having melting points of about 253° C. are not completely free from deleterious contaminants. Thus, it can be readily appreciated that the melting point of a pentaerythritol is not a sensitive enough characteristic of the material to be used as the sole means of determining its applicability in the process of the present invention.

The quantity of deleterious substances, particularly reducing substances, in the unpurified pentaerythritol may be determined by titration with Fehlings' solution or by means of electrometric titration. The best method we have found for this purpose is the titration with potassium permanganate. The pentaterythritol is purified, for example, by washing several times until the titration with a solution of potassium permanganate reaches a minimum which is not reduced by further washing.

In accordance with the present invention, it is preferred to employ pentaerythritol for the condensation process which has been prepared in accordance with the process of the German application D 76 325 IVc/12o, corresponding to U. S. application Serial No. 230 426, filed 17.9.38.

In accordance with the process of the aforesaid German application, pentaerythritol is prepared and recovered from solutions containing it by means of concentration and crystallization in the presence of 1 to 10% and preferably 2 to 6% of free acid. Pentaerythritol prepared in accordance with the process of the German application D 77 001, VId/12o is likewise adapted to condensation with polybasic organic acids in accordance with the principles of the present invention.

In order that those skilled in the art may have a better understanding of the principles of the present invention, the following illustrative example is provided.

Pentaerythritol obtained by the condensation of acetaldehyde with formaldehyde is recrystallized until there is no appreciable decrease in the quantity of reducing substances as indicated by titration with Fehlings' solution or a solution of potassium permanganate. There-

after, 136 grams of this specially purified product are melted with 292 grams of adipic acid. The melt is maintained at a temperature of about 140°C for a period of time, say about one-half hour. A water-clear, substantially transparent resin is obtained which may be treated in a manner well known to those skilled in the art to produce plastic masses, lacquers, foils, electric insulating masses, either by means of solvents or by taking advantage of the thermoplasticity of the product.

It is possible to employ other polybasic organic acids in place of the aforesaid adipic acid. Thus, phthalic acid, succinic acid, oxalic acid, maleic acid, sebacic acid, tartaric acid, citric acid, aconitic acid and the like may be used in quantities corresponding to the amount of adipic acid indicated in the illustrative example.

Example

After recrystallization as described above 136 grams pentaerythritol are melted with 296 grams of phthalin anhydride. The melt is maintained at a temperature of about 150° for 2 hours. A water-clear, transparent resin is obtained which preferably can be used for producing lacquers and the like, or by further heating at about the same temperature for a longer time it can be made insoluble but very resistant against the influence of acids and lyes.

Furthermore, mixtures of the aforesaid polybasic organic acids or with other polybasic organic acids may be employed. For the most part 2 moles of a polybasic organic acid are taken for one mol of pentaerythritol. When a mixture of different polybasic organic acids is used, generally the same proportion is chosen. Of course the choice of an other proportion is possible.

The products which are obtained by condensing pentaerythritol with a mixture containing polybasic organic acid or acids and higher aliphatic monobasic acids are particularly well adapted for use in preparing electric insulating lacquers. Furthermore by addition of monobasic acids containing more than five carbon atoms the mechanic properties of the resin are improved very much. Thus, such resins show a considerable elasticity and in addition, they possess a greater tending strength.

In order to provide those skilled in the art with an illustrative embodiment, attention is directed to the following example.

From the recrystallized pentaerythritol 136 grams are melted with 110 grams of pure adipic acid and 111 grams phthalic anhydride and 116 grams of caproic acid are mixed into the melt by stirring. Then the melt is maintained during 2 days at about 130° under diminished pressure and then warmed still during further days at about 160° at the normal pressure.

Finally two comparison samples are enclosed. Both are produced under exactly the same conditions, and the initial materials of both only differ in the used pentaerythritol. In the sample marked with No. 1 corresponding to our invention a very pure pentaerythritol, obtained by repeated recrystallization, is used the potassium permanganate value of which was only 1,2, while in the sample marked with No. 2, a customary pentaerythritol was employed which indicated a potassium permanganate value of 30.

For both samples always 136 grams of the respective pentaerythritol were mixed with 146 grams of pure adipic acid and 148 grams of phthalic anhydride and the mixture was melted at 160°. After filtration the melt was warmed at about 130° during three hours at a pressure of 15 m/m. Then it was poured into molds in which it was slowly heated to 160° and then maintained at this temperature during 24 hours. The difference in the both samples is so evident, that no further words are necessary therefor.

Although the present invention has been described in conjunction with certain embodiments thereof, it is to be understood that variations and modifications may be made as those skilled in the art will understand. Such variations and modifications are to be considered within the purview of the specification and the scope of the appended claims. Thus, mixtures of polybasic organic acids and aliphatic monobasic acids containing more than five carbon atoms may be employed with pentaerythritol to obtain condensation products having particular properties.

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