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MANUFACTURE OF PENTAERYTHROL

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The present invention relates to the manufacture of artificial resins by condensing pentaerythrol with organic acids and to a process for producing a pentaerythrol of high melting point and to the product of said process.

Formerly, the condensation of pentaerythrol with acids, such as phthalic or succinic acid, was carried through until the removal of water vapor from the reaction mixture was finished. Afterwards, when trying to harden these masses, they became porous. Therefore, these artificial masses could not be used for producing clear moulded bodies or articles requiring clarity of composition.

An object of the invention is to improve the quality of the resins, of the method of production, and of the quality of the pentaerythrol.

Another object of the invention is to provide a new material useful for electrical purposes, especially for covering electric wires with an insulating layer of lacquer containing pentaerythrol resins.

It is also an object of the invention to provide a process for producing a relatively pure form of pentaerythrol having a high melting point.

A further object of the invention is to produce pentaerythrol with a melting point up to about 257° C. or higher.

Other and further objects and advantages will become apparent from the following description.

Broadly stated, according to the present invention, the mixture of pentaerythrol and organic acids, especially polybasic acids, is subjected to a ripening process after condensation. This ripening process consists of a continued heating at higher temperatures, preferably in vacuo.

It is not yet quite clear which reactions cause this ripening. In many cases, after ripening for some time, the liberation of small quantities of water can be noticed. Thus, the ripening can also be effected by heating at ordinary, elevated, or reduced pressures, preferably in the presence of hygroscopic substanees, such as gypsum, sodium sulfate, or acetic anhydride. The masses, ripened according to the present invention, can be hardened in any known manner, e. g., by raising the heating temperature or by continuing the time of heating.

The hardening process is favored by adding acidic substances, such as sulphuric acid, phosphoric acid, boric acid, sodium bisulphate, monochloracetic acid, and benzol sulphonic acid. It is also possible to bleach the masses by adding bleaching substances, especially if the masses are not purified instead.

For the purpose of giving those skilled in the art a better understanding of carrying the invention into practice the following illustrative examples are given.

Example No. I

About 136 grams of pentaerythrol are melted with about 290 grams of adipic acid and left at about 140° C. for about half an hour. After this time, when the liberation of water vapor is about finished, the reaction mixture is ripened at about 130° C. in vacuo for about 1½ hours, whereafter the product is left under ordinary pressure and at a moderate temperature, i. e. in this case, at about 120° C., for about one-half hour.

Instead of adipic acid, other acids, such as phthalic acid, succinic acid, oxalic acid, maleic acid, sebacic acid, tartaric acid, citric acid, and aconitic acid, or mixtures thereof, can also be used. Together with pentaerythrol, other polyhydric alcohols, such as glycerol, glycol, and mannitol, can be reacted according to the invention. The reaction mixture can contain other substances able to condense or polymerize to form resins, such as phenolic-formaldehyde, vinyl ester or other vinyl compounds, such as acrylic derivatives, styrene, etc.

It has been found that polycarbonic acids with long chains, such as adipic acid or pimelic acid, cause soft polymerization products to be obtained, having qualities similar to those of caoutchou or butadiene polymers. On the other hand, hard masses, which may be used as artificial glass, can be produced by reacting pentaerythrol with oxalic or phthalic acids. Generally, the hardness of the product is varied by regulating the duration and the temperature of the ripening process.

The resols, obtained according to the ripening process disclosed herein, can be immediately subjected to a hardening process by heating for from about 1 to about 3 hours at temperatures of about 160° to about 180° C. These hardened resols are easily handled for storing or shipping. They can later be moulded by hardening in any desired manner.

Example No. II

About 137 grams of pentaerythrol and about 332 grams of phthalic acid, or about 296 grams of phthalic anhydride, are melted together and kept at about 140° to about 150° C. for about 25 minutes. After the liberation of water vapor has ceased, the reaction product is cooled to about 120 to about 130° C. and left at this temperature in vacuo for about 20 to about 40 minutes, after the addition of gypsum. The masses obtained by this process can then be treated as in Example No. I.

It has also been found that an excellent lacquer for covering and insulating metal electric wires is obtained by condensing pentaerythrol with aliphatic saturated carbonic acids containing more than 5 carbon atoms in the molecule. Mono-, as well as polybasic acids can be used for this purpose, e. g. caprylic acid, acid, adipic acid, stearic acid and lauric acid. It is preferred to use those mono-basic acids which contain about 8 to about 12 carbon atoms, especially the mixture of fatty acids taken from the oxidation of paraffin.

The lacquer made from these condensation products possesses excellent adhesive qualities with respect to the metal wires. The wires can be bent without destroying the covering resin layer, and the lacquer films do not get brittle with time, in contrast with lacquer made with the aid of softening agents. It is a special advantage of these products that they can be used as metal wire lacquers without any addition of a softening agent, if necessary.

In covering metal wires with the lacquer, it is preferred to do so by dissolving the condensation products in a suitable solvent, or by using them in the molten state. In the latter method, it is necessary that the condensation products be partially or wholly in the socalled A-stage, that is, in the first stage immediately after the condensation, when no hardening or no insolubility has been begun. The covered wire is put in an oven having a temperature of about 180 to about 250° C., whereby the lacquer becomes infusible or, at least, fusible with difficulty. Of course, it is desirable, but not necessary, to ripen the resins before applying them to the wire in the manner described above. The coverings may contain, in addition, other artificial resins which are electrically highly valuable, such as polystyrene, as well as phenol-formaldehyde resin, urea resins, vinyl resins, or chlorinated caoutchouc, which may be added to the molten lacquer or to the solution of the resins. It is also possible to add hardening oils.

Example No. III

About 136 grams of pentaerythrol are melted with about 292 grams of adipic acid at about 160° C., and thereafter ripened at about 130° C. A wire with a diameter of about 0.03 to about 3 mm. is drawn through this molten mixture at about 110° C. in such manner that it is homogeneously covered with the lacquer, while an eventual excess is removed by an apparatus for stripping it off. The wire is led through an oven having a temperature of less than about 400° C. The lacquering and enameling can be repeated several times. After being cooled, the layer is completely soft and dense, fast against high voltage, and free from pores, as shown by examination.

The condensation product for the lacquer can also be dissolved in a solvent, such as ethanol, and can be applied in the form of such a solution. The solvent is such as to give a homogeneous cover after evaporation. It is therefore preferable to add higher boiling alcohols to the solvent.

Special advantages of the lacquer are that it does not flow away when heated to higher temperatures and that its chemical and physical stabilities remain unchanged for years.

As a starting material, it is preferred to use a relatively pure pentaerythrol of high melting point, and the present invention provides for the production of such pentaerythrol. The pentaerythrol thus formed is well adapted for use in the production of the resins described herein or of explosives.

Broadly stated, the present invention provides for the production of a pentaerythrol having a melting point up to about 257° C. or even higher. This is obtained by concentrated solutions containing pentaerythrol in the presence of sufficient free acid to give a concentration of free acid from about 1 to about 10%, and preferably from about 2 to about 6%, in the concentrated solution, and thereafter crystallizing pentaerythrol from the solution. As free acids, sulphuric, phosphoric, benzene sulphonic, and acetic acids, and the like, can be used.

The process disclosed in this invention is very useful in the production of pentaerythrol from acetaldehyde and formaldehyde. In this process, formaldehyde and acetaldehyde are reacted together in an aqueous medium in the presence of alkaline substances, such as calcium hydroxide. The aqueous reaction solution contains pentaerythrol, di-pentaerythrol ether and other products. In order to separate the pentaerythrol therefrom, the alkaline condensing agent is neutralized, and the solution is concentrated so that crystallization occurs. According to the invention, care is taken that this crystallization takes place in the presence of sufficient quantities of free acid. It is preferred that the free acid be already present during the concentration of the solution by evaporation. It is assumed that, under these circumstances, chemical reactions take place which are important for obtaining very pure pentaerythrol, but which take a certain time for development.

As mentioned above, it is necessary that the quantities of free acid which must be present be between about 1% and about 10% of the volume of the concentrated solution. It is preferred to use strong acids, mineral acids or benzene sulphonic acid, when isolating the purest pentaerythrol immediately from the reaction mixture. The yield of solid matter appears to be smaller than that obtained by the prior art, and it is assumed therefrom that the older processes yielded only pentaerythrols which were contaminated with large quantities of impurities. If purification of these formerly produced impure products by repeated crystallizations is attempted, the yields obtained are lower than the limit of the yields obtainable by the present invention. Moreover, by the former methods it was not possible to obtain such pure products as can be produced by the present process.

Example No. IV

An apparatus which is provided with a stirring device and cooling coil is filled with about 1200 liters of water and about 400 kilograms of about 30% formaldehyde, so that the concentration of formaldehyde is about 7½% by weight. Over a 6 hour period about 44 kilograms of acetaldehyde in 25% solution and about 42 kilograms of finely powdered calcium hydroxide are added in half-hourly portions. The temperature is kept at about 15 to about 16° C.

After the condensation is finished, sulphuric acid is stirred into the reaction mixture in such quantity as to change all of the calcium hydroxide to calcium sulphate and, besides that, to provide sufficient excess acid so that the final concentrated volume will contain from about 2.6 to about 2.8% of free acid. After separating out the precipitated calcium sulphate, the clear solution is concentrated at about 90° C. to about $\frac{1}{10}$ of the initial volume. This remaining volume determines the percentage of the free acid present, according to the invention. The concentrated solution is then caused to crystallize, and the crystals are centrifuged and washed with a small amount of water. The product is further purified by one single recrystallization in water. A yield of about 45% of a pentaerythrol with a melting point of about 255° C. is obtained.

Of course, it is also possible to purify crude pentaerythrol by using the hereindescribed process. For this purpose, the crude product is dissolved in water, a sufficient quantity of sulphuric acid is added, and the solution is heated for some time, concentrated, and made to crystallize. Even a solid crude pentaerythrol can be subjected to a treatment with free acids in order to purify it. In this case, it is preferable to use relatively weak acids, such as acetic acid. Generally, however, the steps of the invention provided for the production of pentaerythrol itself are as shown in the preceding paragraphs.

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