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CURING OF EPOXIDE RESINS WITH A CHELATE

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This invention relates to the curing of polyepoxide resins and especially to the conversion of such resins into insoluble, infusible products which are useful in varnishes, adhesives, encapsulating compounds, potting compounds, protective coatings, electrical insulating coatings, and the like. The invention has particular reference to an improved method for curing polyepoxide resins, and to a stable heat-curable amine-epoxy composition and method of making the same.

It is well known in the resin art that amine compounds are capable of converting polyepoxide resins to their infusible, insoluble state. The curing of these resins with amines, particularly polyamines, is disclosed, for example, in S. O. Greenlee Patents Nos. 2,510,885 and 2,585,115, dated June 6, 1950, and February 12, 1952, respectively. However, while a rapid conversion of the epoxide resins is provided by these amine compounds, particularly the diprimary amines such as ethylene diamine and diethylene triamine, the unconverted amine-epoxy compositions have the disadvantage of being unstable at room temperature. Accordingly, they are unsuitable for those applications (of which there are many) where varnish stability or compound stability prior to conversion is required.

It is also known that other curing agents, such as urea-formaldehyde, phenol formaldehyde and other heat reactive resins, will provide greater stability in varnishes or compounds using the polyepoxide resins, but at the sacrifice of curing speed. Moreover, the use of these other curing agents with the polyepoxide resins will not give the type of conversion required in many instances, as when the cured product is to be a wire enamel.

The principal objects of the present invention are to provide a reactive amine-epoxy composition which enables a rapid conversion of the epoxide resin and affords desired characteristics in the converted product, and yet avoids the inherent instability of the prior amine-epoxy compositions; to provide a stable amine-epoxide composition which is readily converted by heating above room temperature; and to provide methods for making the aforesaid composition and using it for the conversion of polyepoxide resins to their infusible, insoluble state.

According to the present invention, the curing agent for the polyepoxide resin is essentially a metal-amine chelate compound in which the amine nitrogen is held by the metal through a coordinate valence bond. This chelate compound may be prepared by reacting a polyamine with the organic salt of the metal, to form an amine-metal organic salt complex or coordination compound. The active hydrogen atoms of the amine groups are thus rendered inactive by the metal toward the reactive epoxide groups of the resinous polyepoxide at room temperature; but upon application of heat a number of active hydrogens provided by the amine groups are released and react with a number of epoxide groups, cross-linking the resinous polyepoxide and converting it to its insoluble, infusible state. The new amine-metal organic salt complex-polyepoxide composition has excellent stability and can be readily applied in solutions when thin films are desired. The reaction of the amine-metal organic salt complex with the polyepoxide resin, upon heating, gives unusual

properties in the finished products, enabling the production of films or thick sections of excellent solvent resistance, flexibility in the films, hardness and toughness, heat resistance, and adhesion with a minimum amount of active amine.

The metal used in making the amine-metal organic salt complex or chelate compound is one which, when reduced to a salt by an organic acid and reacted with the polyamine, forms a coordinate valence bond holding the nitrogen of the amine groups. Examples of such metals are zinc, cobalt, manganese and copper. Examples of organic acids suitable for formation of the metal salt are aliphatic acids such as acetic, hexoic, 2-ethyl hexoic, and similar mono-functional organic carboxylic acids containing at least two carbon atoms, naphthoic, ricinoleate, phenol, cresol, and higher molecular weight phenolic derivatives of sufficient acidity to form an organic salt with the coordinating metal atom.

Polyamines suitable for reaction with the metal organic salt, to form the complex or chelate compound, are those which in themselves are capable of reacting with epoxide groups through active hydrogens provided by the different amine groups. Diethylene triamine has been found suitable.

The following describes the preparation of two examples of the soluble amine-metal organic salt complex according to the present invention:

Complex "A".—One mole of zinc oxide and two moles of 2-ethyl hexoic acid are reacted together in the presence of xylene to form the zinc salt of 2-ethyl hexoic acid, to which is added one mole of diethylene triamine. Thus, 90 grams of zinc oxide are reacted with 320 grams of 2-ethyl hexoic acid in the presence of 475 grams of commercial xylene to give the zinc salt of 2-ethyl hexoic acid. To this solution are added 115 grams of diethylene triamine, stirring gently until the reaction is complete. The resulting amine-metal organic salt complex is a clear solution containing 50.5% solids and .335 equivalent of diethylene triamine per 100 grams of amine-metal organic salt complex solution.

Complex "B".—One mole of finely divided zinc oxide is dispersed in 7.88 moles of mixed cresols, 1.38 moles of diethylene triamine are added slowly, and external heat is then applied to raise the complex solution to 140° C. and hold it at this temperature for 30 minutes. Thus, a clear amine-metal organic salt complex may be prepared by dispersing 81.4 grams of finely divided zinc oxide in 851.8 grams of mixed cresols, then, while agitating, adding 142.3 grams of diethylene triamine slowly, causing a controllable exothermic reaction in which the temperature increases to 80° C., and then increasing the temperature over a period of one hour to 140° C. and holding it there for 30 minutes. This results in a clear solution having a viscosity of 30 poises, a non-volatile content of 39.5%, and containing .389 equivalent of diethylene-triamine per 100 grams of amine-metal organic salt complex solution.

The polyepoxides used for reaction under heat with the amine-metal organic salt complex contain an average of more than one epoxide group per molecule which will react with the amine groups to form addition reaction products. The polyepoxides disclosed in the aforesaid Greenlee Patents Nos. 2,510,885 and 2,585,115 are suitable for this purpose. Thus, the resin used according to the present invention may be defined as an epichlorhydrin-di(hydroxyphenyl) dimethyl methane product which is free from functional groups other than epoxide and hydroxyl groups and having a 1, 2 epoxide equivalency of greater than 1. In the following Table I are examples of polyepoxide compositions resulting from the reaction of bisphenol with varying proportions