United States Patent Office 3,234,171
Patented Feb. 8, 1966

3,234,171

COATING COMPOSITIONS

Ernest C. Koerner and Vello Nolvak, Fort Wayne, Ind., and Henry J. Bach, Mount Lebanon Township, Allegheny County, and William A. Merlack, Ross Township, Allegheny County, Pa.; said Koerner and said Nolvak assignors to Phelps Dodge Copper Products Corporation, New York, N.Y., a corporation of Delaware; said Bach and said Merlack assignors, by mesne assignments, to Socony Mobil Oil Company, Inc., New York, N.Y., a corporation of New York

Filed Nov. 2, 1960, Ser. No. 66,752
16 Claims. (Cl. 260—33.4)

The present invention relates to stable and preferably relatively concentrated liquid solvent solutions of high molecular weight, cold-drawable, essentially linear aromatic polyesters, such as polyethylene terephthalate.

The high molecular weight and essentially linear aromatic polyesters which are the subject of the invention are known compounds and are known to possess excellent physical, mechanical and electrical properties. Unfortunately, the strong tendency of these high molecular weight essentially linear aromatic polyesters to become molecularly oriented, as evidenced by their capacity to be cold drawn into products exhibiting crystallinity, has prevented effective organic solvent solution application. Aside from low solubility, the solutions tended to rapidly become more viscous and even gelatinous and the gelation problem is a progressive one in the sense that the more concentrated solutions gel more rapidly.

The present invention is based on the discovery that phenolic based solvent mixtures containing a substantial proportion of ortho-cresol, preferably a large proportion of ortho-cresol, are effective to dissolve the cold-drawable polyester to provide solutions of substantial concentration which possess good storage stability at room temperature and at moderately elevated temperature.

Another feature of the invention is improved low temperature storage stability obtained by limiting the proportion of ortho-cresol in the phenolic mixture to less than about 98% by weight, as by the inclusion in the mixture of small amounts of other hydrocarbon- and/or halogen-substituted aromatic compounds, preferably substituted phenolic compounds, such as meta, para-cresols, xylenols, and chlorophenols.

The high molecular weight, cold-drawable, essentially linear aromatic polyesters in accordance with the invention are polyesters consisting essentially of the reaction product of iso- and tere-aromatic dibasic compound and lower aliphatic and cyclo aliphatic diols containing from 2–10 carbon atoms. Preferably, and to accentuate polyester linearity and cold drawability, the reaction products of terephthalic acid or its derivatives and straight chain diols having from 2–5 carbon atoms and two primary hydroxyl groups are selected to constitute the polyester. Such polyesters possess the best physical and chemical properties and are the most difficult to place in stable and preferably concentrated solvent solution.

The iso- and tere-aromatic dibasic compounds which may be used are exemplified by terephthalic acid, isophthalic acid, acyl chlorides of these acids, lower alkyl esters of these acids containing from 1–10 carbon atoms in each ester radical (especially dimethyl terephthalate and dimethyl isophthalate) and mixtures thereof. While there are specific differences in the polyester depending upon the aromatic dibasic compound selected and while the required polyesterification procedure and commercial desirability thereof will also vary, depending upon the selection which is made, the polyester produced will possess substantially the same linearity and tendency to be cold-drawable, irrespective of the particular aromatic dibasic compound which is used. The terephthalic polyesters are more highly linear and are preferred because they provide superior properties and because they are more difficultly soluble, emphasizing the importance of the invention.

Various lower aliphatic hydrocarbon diols may be used, the preferred diol being ethylene glycol. 1,4-butanediol, 1,5-pentanediol, 1,4-butene-2-diol, illustrate other preferred diols for use alone or together with ethylene glycol. Other diols which may be used are illustrated by 1,2-propanediol, 1,3-propanediol, 1,6-hexanediol, 1,3-cyclobutane diol, 1,4-cyclohexane diol, 1,4-cyclohexane methanol, etc.

The language "essentially linear" identifies polyesters consisting essentially of iso- and tere-aromatic dibasic compound and lower aliphatic diols. It should be understood, however, that minor amounts of other components such as adipic acid, glycerin or orthophthalic acid may be present so long as the proportion thereof is too small to significantly alter the essentially linear and cold-drawable character of the polyester. The presence of substantial proportions of other components, as indicated above, tends to significantly lower the melting point of the polyester and the invention is directed to high molecular weight polyesters which are essentially linear, as indicated by a melting point in excess of 200° C., preferably in excess of 240° C.

The combination of high molecular weight and polyester linearity in accordance with the invention is intended to provide a cold-drawable polymeric product, and this raises the problem of the invention, namely, low solubility in organic solvents and poor stability in solution.

While cold-drawability is a sufficient measure of high molecular weight and polyester linearity to satisfy the requirements of the invention, numerical limits of relative viscosity can also be assigned. Relative viscosity is defined as the ratio of the efflux time of a polymer solution to the efflux time of the pure solvent. Conveniently, the polyester is placed in a solution containing 1 gram of polyester per deciliter of solvent, the solvent being a 60/40 mixture of phenol and tetrachlorethane. Using viscosity measurements made at 77° F., in a size 200 Ostwald-Kannon-Fenske viscometer, it has been found that polyesters having a relative viscosity in excess of 1.3, preferably in excess of 1.5, are adapted for the purposes of the invention. A relative viscosity of about 3.0 appears to represent an approximate upper limit of molecular weight from the standpoint of the feasibility of providing high molecular weight polyesters.

The invention is concerned with organic solvent solutions which contain a sufficient proportion of dissolved polyester to be useful in practice. Thus, the solution should contain at least 5% by weight of dissolved polyester and the solution should be stable, e.g., avoid gelation, or large increase in viscosity when allowed to stand for an extended period of time at temperatures in the range of 70–120° F., preferably in the range of 0–120° F. As a practical minimum, the liquid solution should not increase in viscosity by an amount in excess of 50% of the original viscosity when maintained at a temperature of from 70–120° F. for a period of at least 5 days. Preferably, the solutions are more concentrated, e.g., the solutions contain at least 10% by weight of dissolved polyester, desirably at least 13% by weight of dissolved polyester. As will be evident, the problem of maintaining solution viscosity and avoiding gelation becomes more difficult as the concentration of the solution is increased. Preferred solutions in accordance with the invention and containing at least 10% by weight of dissolved polyester, are stable at temperatures of 70–120° F. for periods in excess of 20 days. Still more preferably, the solvent solu-