

1

2,939,853

POLYAMIDE-LIKE CONDENSATION PRODUCTS AND PROCESS FOR PREPARING THE SAME

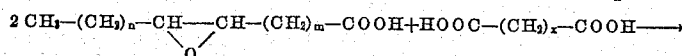
Hermann Delius, Hamburg, Germany, assignor to Reichhold Chemicals, Inc., Detroit, Mich.

No Drawing. Filed Apr. 17, 1956, Ser. No. 578,560

Claims priority, application Germany Feb. 18, 1956

3 Claims. (Cl. 260—18)

The invention relates to the process of preparing certain novel polyamide-like condensation products and is in the nature of an improvement on the disclosure of

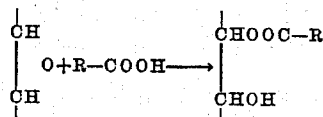


the application of Wolfgang Foerster Serial No. 567,750, filed February 27, 1956.

In said application Serial No. 567,750, filed February 27, 1956, a process for the preparation of novel, polyamide-like condensation products is described. The particular characteristic of this process consists in condensing unsaturated epoxy fatty acids or their esters particularly the esters of monoalcohols having a boiling point not exceeding 200° C. with di-, tri-, or higher polyamines.

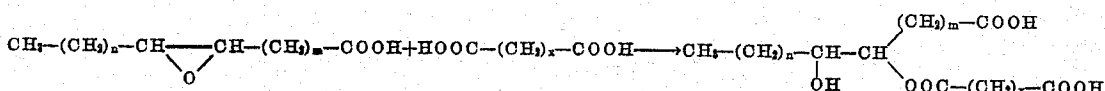
In developing the basic idea of the invention, it has now been found that it is advantageous first to react the unsaturated epoxy fatty acids or their monoalcohol esters with dicarboxylic acid and to subject the reaction products obtained in this manner to amidation with di-, tri-, or higher polyamines.

It is known that carboxyl radicals react with epoxy radicals. With a monocarboxylic acid this reaction proceeds approximately as follows:



Whence a dicarboxylic acid can react in an analogous manner with one or two moles of an epoxy fatty acid or an epoxy fatty acid monoalcohol ester. Basically all the existing dicarboxylic acids are suitable; however, the reaction proceeds most advantageously with dibasic acids that easily give a homogenous mixture with the epoxy fatty acids or their esters under the temperature and reaction conditions described below. As examples the following may be mentioned: succinic acid, glutaric acid, adipic acid, azelaic acid, sebacic acid, isosebacic acid (a mixture of branched isomeric C₁₀-dicarboxylic acids), phthalic acid, etc.

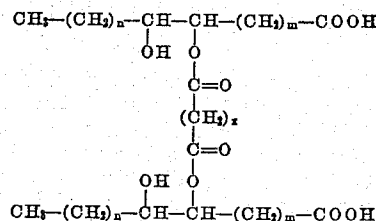
If epoxy fatty acids or their monoalcohol esters are reacted with dicarboxylic acid in a 1:1 molar ratio, about the following schematically illustrated reaction takes place predominantly:



2

In other words, a dicarboxylic acid can be formed that also contains an ester radical and a secondary alcohol radical. When using epoxy fatty acids, an intermolecular reaction between epoxy radicals and carboxyl radicals of the epoxy fatty acid may occur. In this reaction lactide-like compounds are formed. The formation of cyclic lactones as the result of an intramolecular reaction seems less likely. With due consideration to this side reaction, which obviously has an unimportant influence on the end result, the use of epoxy fatty acid esters doubtless possesses the advantage that no lactides or possibly lactones can be formed.

In working with a 2:1 molar ratio of epoxy fatty acid to dicarboxylic acid, a reaction approximately according to the following diagram is to be predominantly expected:



What has been said above concerning the 1:1 reaction ratio is also valid here, as regards the intramolecular reaction, for possible participation of the carboxyl radicals of the epoxy fatty acids in the reaction with the epoxy radicals. Likewise, in the above sense, the use of epoxy fatty acid esters here also favors a connection of two fatty acid residues over a dicarboxylic acid ester radical.

The reaction temperature for this first stage of the present invention lies between 100–200° C., preferably at 150 to about 200° C. The drop in the acid number is a convenient measure of the progress of the reaction. Especially when epoxy fatty acids are used, the reaction should be interrupted upon reaching a certain level in the acid number, whose value lies about 20–30 units above the theoretically calculated one. Otherwise an additional esterification of free carboxyl radicals with the secondary hydroxyl radicals that result from the reaction of the epoxy radicals will take place, which can lead to gelatinization of the ingredients by polymerization. In the reaction of epoxy fatty acid esters with dicarboxylic acids, it is uneconomical and inadvisable to permit the reaction to reach the theoretical acid number 0 in the first stage. This reaction is appropriately terminated upon reaching an acid number of about 20. The reaction products obtained in the first stage are subsequently reacted at higher temperatures with ethylene diamine, diethylene triamine or higher polyamines in such a way that in every case soluble and fusible resin-like, polyamide-like condensation products result that either alone or in mixture with other raw materials represent valuable novel synthetic resins.

Example 1

300 g. epoxy soy bean fatty acid (oxirane-oxygen content 3.94%, acid number 143) and 107.5 g. adipic acid are gradually heated to 200° C. with stirring, an inert gas, such as nitrogen or carbon dioxide, being forced through and kept at 200° C. until the acid number of the reaction product has dropped to 205–215. Thereupon the reaction

3

product is allowed to cool to about 80° C., and 154.5 g. diethylene triamine are added. Now the reaction mixture is heated under reflux to a temperature of 140° C. After a lapse of 2 hours the temperature is raised to 200° C. in the downtake cooler and kept there for about 2 hours. In order to remove small amounts of low-molecular constituents possibly causing trouble later on, these are distilled off during the second hour by working under a vacuum. After cooling, a light yellow, soft resin is obtained. The yield amounts to about 480 g. The condensation product dissolves well in mixtures of aromatic substances and aliphatic alcohols, e.g. in a 1:1 mixture of toluol and i-butanol.

Example 2

620 g. of epoxy soy bean fatty acid methyl ester (oxirane-oxygen content 6.5%) and 504 g. sebacic acid are heated together as described in Example 1 until an acid number of 125-130 has been reached. After cooling to 70-80° C., 257 g. diethylene triamine are added and, as described in Example 1, heated. A light-colored soft resin results. Approximate yield: 1100 g.

Example 3

620 g. epoxy linoleic fatty acid methyl ester (oxirane-oxygen content 6.1%) and 172 g. adipic acid are heated to 180° C. and kept at this temperature until the acid number has dropped to a value <20. After cooling to 70-80° C., 206 g. diethylene triamine are added and the process continued as described in Example 1. Yield: approx. 850 g. of a light-colored soft resin.

Example 4

600 g. epoxy soy bean fatty acid (oxirane-oxygen content 4.2%, acid number 119) and 115 g. adipic acid are heated to 180° C. with stirring under a stream of inert gas and held at this temperature until an acid number of ~130 has been reached (theoretical value: 100). Then heating is discontinued and the temperature allowed to drop to 80° C. At this temperature, 206 g. diethylene triamine are allowed to flow in, and the process is continued as described in Example 1. Yield: about 800 g. of a light-yellow colored resin that possesses about the same consistency as the condensation products described in the other examples.

The invention has been described in detail for the purpose of illustration but it will be obvious that numerous modifications and variations may be resorted to within the scope of the appended claims.

I claim:

1. A process for the preparation of polyamide-like condensation products which comprises reacting (1) at least one member of a group consisting of epoxidized fat acids and esters of epoxidized fat acids of saturated

4

monohydric aliphatic alcohols having a boiling point not above about 200° C. and (2) at least one member of a group consisting of hydrocarbon dicarboxylic acids having not more than 10 carbon atoms in a mol ratio of 0.5 to 1.0 mol of dicarboxylic acid per mol of oxirane groups in said epoxidized fat acids and esters under elevated temperature conditions of about 200° C. until an acid number of not more than 30 is obtained above that theoretically obtainable, cooling the reaction product to between about 70° and about 80° C., adding a polyamine having the formula $R-NH-CH_2-CH_2-NH_2$ wherein R is a member of the group consisting of H and $-(CH_2-CH_2-NH_2)$, heating the resultant mixture at temperature of about 200° C. and terminating the reaction while the said condensation product is still fusible.

2. A polyamide-like condensation product produced in accordance with the process of claim 1.

3. A process for the preparation of polyamide-like condensation products which comprises reacting (1) at least one member of a group consisting of epoxidized fat acids and esters of epoxidized fat acids of saturated monohydric aliphatic alcohols having a boiling point not above about 200° C. and (2) at least one member of a group consisting of aliphatic dicarboxylic acids having not more than 10 carbon atoms in a mol ratio of 0.5 to 1.0 mol of dicarboxylic acid per mol of oxirane groups in said epoxidized fat acids and esters under elevated temperature conditions of about 200° C. until an acid number of not more than 30 is obtained above that theoretically obtainable, cooling the reaction product to between about 70° and about 80° C., adding a polyamine having the formula $R-NH-CH_2-CH_2-NH_2$ wherein R is a member of the group consisting of H and $-(CH_2-CH_2-NH_2)$, heating the resultant mixture at a temperature of about 200° C. and terminating the reaction while the said condensation product is still fusible.

References Cited in the file of this patent

UNITED STATES PATENTS

2,445,892	Swern et al.	July 27, 1948
2,500,449	Bradley	Mar. 14, 1950
2,682,514	Newey	June 29, 1954

FOREIGN PATENTS

133,819	Australia	July 10, 1946
---------	-----------	---------------

OTHER REFERENCES

Swern: Oxygenated Fatty Acids, reprint from "Progress in the Chemistry of Fats and Other Lipids," pages 213-217, Pergamon Press Ltd., London (1955).

Chemical Abstracts, volume 39, No. 24, pages 5923-5924 (1945), Lee et al., Epoxy Resins, page 31, McGraw-Hill (1957). (Copy in Science Library.)