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CONDENSATION PRODUCTS OF SUPER-POLYAMIDE CHARACTER AND PROCESS OF PRODUCING THEM

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The present invention relates to condensation products of superpolyamide character and to a process of producing same.

In the co-pending application Ser. No. 252,630 one of the present inventors and two others have described a process for the production of high molecular compounds of the polyamide type according to which amines having at least two reactive amino groups separated from each other by at least two carbon atoms are reacted with unsaturated, especially alpha-beta-unsaturated, monocarboxylic acids or their derivatives at temperatures at which the amines are added on to the unsaturated monocarboxylic acids or their derivatives and amide formation between two or more molecules of the amino acids thus formed takes place. In the same application there is also described that the properties of the polyamides obtainable according to the said process may be varied either during or after their manufacture by reacting them with one or more organic compounds containing one or more groups capable of reacting with NH-groups. Among the compounds of the said type there are mentioned inter alia polycarboxylic acids.

We have now found that valuable condensation products can also be obtained by heating polyamides obtainable according to the process of the said application Ser. No. 252,630 or their said reaction products with organic compounds containing one or more groups capable of reacting with NH-groups, either during or after their manufacture, with superpolyamides, i. e. film-forming high molecular amides of polypeptide-like structure, as for example condensation products of diamines and dicarboxylic acids or of salts of diamines and dicarboxylic acids, and/or of aminocarboxylic acids or with the initial materials forming such superpolyamides.

In practicing the present invention the condensation products obtainable according to the process of the copending application Ser. 252,630 are, for example, melted together with the superpolyamides or the superpolyamides may already be added during the production of the condensation products according to application Ser. 252,630 or while they are reacted with a compound having one or more groups capable of reacting with NH-groups. Especially favorable results are obtained by carrying out the condensation according to application Ser. 252,630 in the presence of superpolyamide forming substances, as for example dicarboxylic acids and/or of ω -aminocarboxylic acids.

Dicarboxylic acids suitable for this reaction are in particular those of the formula



5 wherein x means a whole number greater than 3, for example adipic acid or sebacic acid, and also dicarboxylic acids interrupted one or more times by hetero atoms or groups containing hetero atoms, for example diglycollic acid, thio-dipropionic acid, iminodipropionic acid or methy-
10 yliminodipropionic acid. Mixtures of several dicarboxylic acids and salts of dicarboxylic acids with the diamines may also be used. Among suitable diamines there may be mentioned those of
15 the formula $\text{NH}_2(\text{CH}_2)_x\text{NH}_2$, wherein x means a whole number greater than 3, for example tetramethylenediamine, pentamethylenediamine, hexamethylenediamine, octamethylenediamine, deca-
20 methylenediamine, para-phenylenediamine, para-xylylenediamine, ω,ω' -diamino-para-diethylbenzene or their perhydrogenated derivatives. Di-
25 amines the carbon atoms of which are interrupted one or more times by hetero atoms, as for example oxygen or sulfur or groups containing
30 hetero atoms, for example $-\text{SO}-$, $-\text{SO}_2-$ or $-\text{NX}-$ (X being hydrogen or a hydrocarbon radicle), may also be used. Among diamines of the latter kind we may mention for example
35 beta-beta'-diaminodithylether or -dipropylether and homologues thereof or similar thioethers. Mixtures of several of these amines may also be used.

As aminocarboxylic acids which may be heated with the condensation products obtainable according to application Ser. No. 252,630 there may be mentioned those of the general formula
40 $\text{NH}_2(\text{CH}_2)_x\text{COOH}$, wherein x is a whole number preferably greater than 3, for example ϵ -aminocaproic acid. The carbon chain of amino acids, too, may be interrupted one or more times
45 by the said hetero atoms or groups containing hetero atoms.

Instead of the free carboxylic acids, their functional derivatives, as for example their esters or amides, may also be employed undergoing the same reaction as the acids, save that alcohol or ammonia or an amine is split off instead of
50 water.

The condensation may furthermore be influenced, especially the degree of condensation be varied, by the addition of small proportions of monocarboxylic acids, for example acetic acid, or of ammonia or monoamines, for example methyl
55 amine, dimethylamine, ethylamine, dipropylamine, octodecylamine, decylamine or also by

employing, the dicarboxylic acids or diamines in excess of the amount theoretically required for the interaction of both substances.

The condensation products are prepared by heating, preferably, at temperatures ranging between 100° and about 300° C. Depending on the temperature and the duration as well as on the method of heating, products of varying properties are obtained. Temperatures of more than 300° C should be avoided as they easily give rise to decomposition and darkening in color. The reaction may be carried out under ordinary, increased or reduced pressure. It is advantageous to employ at first increased pressure or to work with reflux cooling in order to thus bring the mass into as uniform as possible a state of melting, and then to complete the condensation under ordinary or reduced pressure while removing the resulting volatile constituents as water, alcohol, ammonia or amine by distillation. Solvents and/or diluents may be present, if so desired.

As solvents suitable in particular when free carboxylic acids are employed for the condensation may be mentioned such as form azeotropic mixtures with the water split off by the condensation, as for example xylene or xylenol. Generally speaking, it is most desirable to exclude air or oxygen as far as possible, in order to obtain products as colorless as possible.

The mixed high molecular condensation products of the superpolyamide type thus obtained are suitable for the manufacture of threads, films, ribbons, tubes, coverings, coatings, and moulded articles of a great variety of kinds. They are more plastic and softer than the pure superpolyamides from dicarboxylic acids and diamines or from aminocarboxylic acids. The condensation products from alpha-beta-unsaturated monocarboxylic acids and diamines having their amino groups separated from each other by at least 2 carbon atoms, obviously exert therein a softening or plasticizing effect. In contrast to softening and plasticizing agents otherwise employed for highly polymerized substances they have the great advantage of being chemically combined and, by reason of their high-molecular nature, being not subject to volatilization or dissolution.

The following Example will further illustrate how the present invention may be carried out in practice. The parts are by weight.

Example

A solution of 250.5 parts of an aqueous acrylic

acid of 71.8 per cent strength in 450 parts of alcohol is slowly added, while stirring, to a solution of 293 parts of hexamethylenediamine in 750 parts of alcohol and the mixture is boiled under reflux for 2 hours, whereupon the alcohol is distilled off under reduced pressure. The viscous yellowish oil thus obtained is heated with an equal proportion of adipic acid hexamethylenediamine salt for 90 minutes in a closed vessel at a temperature of from 275° to 280° C in the presence of nitrogen and then kept at this temperature for another 4 hours under atmospheric pressure. The condensation product thus obtained is extremely soft and flexible and eminently suitable for the manufacture of films.

The same reaction product is obtained by carrying out the reaction in only one stage, i. e. if the acrylic acid, adipic acid and the whole amount of hexamethylenediamine are mixed and then heated.

Instead of adipic acid hexamethylenediamine salt there may also be used the diglycollic acid hexamethylenediamine salt or mixtures of adipic acid and hexamethylenediamine or of diglycollic acid and hexamethylenediamine.

The ratio in which the condensation product from acrylic acid and hexamethylenediamine or the starting materials therefor and the adipic acid or diglycollic acid hexamethylenediamine salts may be combined with one another may be varied at will.

Using only from 10 to 20 per cent of the condensation product from acrylic acid and hexamethylenediamine and condensing the said product with adipic acid or diglycollic acid and hexamethylenediamine at from 210 to 220° C or even higher temperatures, for example at from 275 to 280° C, condensation products are obtained which are especially soft, flexible and solid. Instead of the only condensation product from acrylic acid and hexamethylenediamine, use may be made also of a solid crystalline product which may be obtained in the following manner.

A solution of 215 parts of acrylic acid methyl ester in 750 parts of alcohol is slowly added at 25° C while stirring to a solution of 293 parts of hexamethylenediamine in 750 parts of alcohol. The mixture is further stirred at 70° for 5 hours, whereupon the alcohol is distilled off under reduced pressure.

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