

# ALIEN PROPERTY CUSTODIAN

## PRODUCTION OF SUPERPOLYAMIDES

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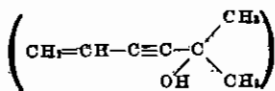
The present invention relates to a process for the production of superpolyamides.

Superpolyamides, i. e. condensation products similar to polypeptides which can be drawn into threads, are obtained by condensing diamines with approximately equimolecular proportions of dicarboxylic acids or of functional derivatives of the said acids capable of forming amides, or by condensing salts of diamines with dicarboxylic acids, or by condensing aminocarboxylic acids or their functional derivatives capable of forming amides, while operating at an elevated temperature, for example between 200 and 300°, preferably between 250 and 280 to 290° C. By a proper selection of the initial materials and the use of mixtures of the single components, the properties of the final products may be varied within wide limits.

We have now found that superpolyamides having especially valuable properties are obtained by adding to the diamines and dicarboxylic acids or their functional derivatives capable of forming amides or the salts of diamines with dicarboxylic acids or the aminocarboxylic acids to be condensed less than 10 per cent, preferably up to 2 per cent by weight, of aliphatic or cycloaliphatic carboxylic acids containing at least 3 carboxylic groups, or of aliphatic or cycloaliphatic compounds containing at least one hydroxyl group and in addition at least 2 further hydroxyl groups or unsaturated linkages, advantageously in conjunction with polybasic (including dibasic) carboxylic acids.

Suitable carboxylic acids containing at least 3 carboxylic groups are, for example, ethane-, propane-, butane-, hexanetri- or -tetracarboxylic acid and cyclohexanone-1.1.1.1'-tetrapropionic acid. These acids are preferably added only in slight proportions, advantageously less than 2 per cent, in order to procure products with a sufficient length of chain. The said polycarboxylic acids can be employed in combination with diamines or polyamines, either in the form of their salts or in admixture with such amines.

Among compounds containing at least one hydroxyl group and, besides, two further hydroxyl groups or unsaturated linkages, we may mention trihydric alcohols or alcohols of a higher valency, as for example glycerine, trimethylethane, trimethylol-propane or hexanetriol, or compounds of the type of vinyl ethinyl-dimethylcarbinol



A preferred method of practicing the process according to the present invention consists in adding trihydric alcohols or alcohols of a higher valency together with dibasic acids or acids of higher basicity. Acids containing more than two carboxylic groups, when used together with higher than dihydric alcohols, should be employed in an amount which together with the amount of the said alcohols is less than 10 per cent (by weight) of the bifunctional substances forming the superpolyamides. Instead of the said alcohols and the said acids of either the dibasic or higher-basic type, there may also be employed products of the alkyd resin type of low degree of condensation prepared therefrom. By the addition of the at least tri-valent alcohols together with di- or higher-basic acids or condensation products thereof, greater stiffness and hardness are imparted to the final product without its further good mechanical properties being deteriorated. Such products are especially adapted to the manufacture of stiff articles by injection-molding and the manufacture of stiff bristles. The influence of the said additions on the properties of the products depends on the proportions of the substances added. While additions of more than 10 per cent generally will yield infusible and completely insoluble products, additions of less than 10, preferably less than 2, per cent are very advantageous. The properties of the products can be influenced also by the quantitative relation between the tri- or higher-valent alcohols and the di- or higher-basic acids (exceeding the amount of dicarboxylic acid required for the amide formation). Usually it is of advantage to use more alcohol than can be esterified by the quantity of acid added. The said compounds containing more than 2 functional groups exert a stabilizing action on the products.

The said substances are usually added to the basic materials forming the superpolyamides in the very outset of the operation; alternatively, they may also be added after the materials forming the superpolyamides have undergone already partial condensation.

As starting materials for the production of the superpolyamides may be mentioned, for example, the usual diamines, as for example penta-, hexa-, dekamethylenediamine and the like, and dicarboxylic acids, as for example maleic acid, glutaric acid, adipic acid, pimelic acid, sebacic acid, phthalic acid and terephthalic acid in admixture with one another or in the form of their salts, furthermore the usual aminocarboxylic acids, as for example ε-aminocaproic acid. These compounds can also be employed in the form of suit-

able functional derivatives, for example the aminocarboxylic acids can be used in the form of their lactams.

The condensation is carried out in the manner usual in the manufacture of superpolyamides, under increased, atmospheric or reduced pressure and, if desired, in the presence of water or solvents. When the operation is nearing its end, the water must be eliminated.

The following Examples serve to illustrate how the present invention may be carried out in practice, but the invention is not restricted to these Examples. These parts are by weight.

#### Example 1

2000 parts of the adipic acid salt of hexamethylenediamine, 1000 parts of water, 14.6 parts of adipic acid and 15 parts of trimethylol propane are slowly heated in a pressure-tight vessel up to from 275 to 280° C in an atmosphere of nitrogen free from oxygen, the pressure being maintained at 15.0 atmospheres by releasing the steam evolved in the reaction. When the temperature has been raised to 275-280° C, the pressure is lowered down to atmospheric pressure within 1½ hours and the condensation is completed by heating for another 1½ hours under atmospheric pressure. By introducing the melt into water a white, hard and stiff condensation product is obtained, from which extremely hard and stiff materials of very good mechanical strength are obtained, by working up for example by injection-molding.

Similar products are obtained if 21.0 parts of trimethylol propane are employed instead of 15.0 parts under otherwise identical conditions.

In the case of smaller additions of adipic acid and trimethylol propane condensation products are obtained, the hardness and stiffness of which shows a somewhat slighter increase as compared with a superpolyamide obtained from adipic acid and hexamethylenediamine alone; when adding larger amounts of adipic acid and trimethylol propane, for example more than 5 per cent, the products likewise show a high stiffness and hardness, but their strength is a little lessened.

#### Example 2

1000 parts of the adipic acid salt of hexamethylenediamine, 500 parts of water, 7.1 parts of adipic acid and 8.1 parts of a crude mixture mainly consisting of hexanetriol and some octanetriol (obtained as a residue in the distillation of 1,3-butyleneglycol formed by the hydrogenation of aldol) are treated in the manner indicated in Example 1. The condensation product obtained is distinguished by its high stiffness and hardness and very good strength.

#### Example 3

A mixture of 1000 parts of the adipic acid salt of hexamethylenediamine, 500 parts of water, 7.5 parts of adipic acid and 10.5 parts of trimethylol-ethane is treated in the manner indicated in Example 1. A white product is obtained which possesses great strength and is very well suited, for example, for the manufacture of bristles.

#### Example 4

2000 parts of ε-aminocaproic acid lactam (briefly referred to in the following Examples as ε-caprolactam), 15 parts of adipic acid and 21 parts of trimethylol propane are condensed in the presence of water in the manner indicated in Example 1. The product so obtained is consid-

erably harder and stiffer than a condensation product of the lactam alone. It is especially suited for producing bristles.

#### Example 5

1500 parts of ε-caprolactam and 19.1 parts of 1,2,3,4-butanetetracarboxylic acid are condensed in the presence of 450 parts of water in the manner indicated in Example 1. A colorless condensation product is thus obtained which melts at 195° C and is stiffer than a condensation product to which no addition was made, but well elastic. The stiffness of condensation products from the adipic acid or sebacic acid salt of hexamethylenediamine, or of mixed condensation products of ε-caprolactam with the said salts is similarly improved by the interaction with butanetetracarboxylic acid.

#### Example 6

1200 parts of the adipic acid salt of hexamethylenediamine, 800 parts of ε-caprolactam, 15.51 parts of the salt from equimolecular amounts of butanetetracarboxylic acid and hexamethylenediamine and 1000 parts of water are treated under the conditions indicated in Example 1. A tough, but comparatively stiff, colorless condensation product soluble in hot methanol is thus obtained.

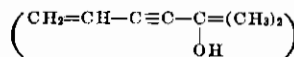
When 800 parts of the adipic acid salt of hexamethylenediamine, 800 parts of ε-caprolactam, 100 parts of 1,2,3,4-butanetetracarboxylic acid and 55 parts (or 84.8 parts) of hexamethylenediamine are condensed under the same conditions, yellowish, rather stiff, elastic condensation products are obtained which are soluble in hot methanol and methylbutinol.

#### Example 7

1200 parts of the adipic acid salt of hexamethylenediamine, 800 parts of ε-caprolactam, 19 parts of the salt from 1 molecular proportion of cyclohexanone-1.1.1'.1'-tetrapropionic acid and 2 molecular proportions of hexamethylenediamine are condensed in the presence of 1000 parts of water in the manner described in Example 1. The condensation product obtained yields a highly viscous melt.

#### Example 8

800 parts of the adipic acid salt of hexamethylenediamine, 800 parts of ε-caprolactam and 16 parts of vinyl ethynyl dimethylcarbinol



are treated in the manner described in Example 1. A colourless condensation product is obtained which is softer than one prepared without adding vinyl ethynyl dimethylcarbinol. Films of good appearance and strength may be cast from warm aqueous methanol solutions of the product.

#### Example 9

800 parts of the adipic acid salt of hexamethylenediamine, 800 parts of ε-caprolactam, 11.04 parts of the salt from 2 molecular proportions of hexamethylenediamine and 1 molecular proportion of 1,2,3,4-butanetetracarboxylic acid, 4.46 parts of 1,2,3,4-butanetetracarboxylic acid and 700 parts of water are treated in the manner described in Example 1. The product obtained melts at about 180°C and may be cast to form soft, strong, practically clear films.

A similar product of somewhat greater hard-

ness is obtained when using 9.42 parts of 1.2.3.4-butanetetracarboxylic acid instead of 4.46 parts.

*Example 10*

800 parts of the adipic acid salt of hexamethylenediamine, 800 parts of  $\epsilon$ -caprolactam, 48 parts of vinyl ethinyldimethylcarbinol and 800 parts of water are treated in the manner described in Example 1. A solid, soft, yellowish condensation product is obtained which may readily be molded into plates. Films may be produced from its solutions.

A similar condensation product is obtained from 1200 parts of the adipic acid salt of hexamethylenediamine, 800 parts of  $\epsilon$ -caprolactam, 40 to 60 parts of vinyl ethinyldimethylcarbinol and 1000 parts of water.

When 2000 parts of  $\epsilon$ -caprolactam, 40 to 60 parts of vinyl ethinyldimethylcarbinol and 80 parts of water are condensed, a yellow, very soft condensation product insoluble in hot aqueous methanol is obtained.

When a mixture of 2000 parts of the adipic acid salt of hexamethylenediamine, 60 parts of vinyl ethinyldimethylcarbinol and 1000 parts of water is treated in an analogous manner, a con-

5 condensation product is obtained which is especially suitable for the production of bristles. Such bristles possess a better resilience as compared with bristles from a corresponding condensation product produced without the co-employment of vinyl ethinyldimethylcarbinol.

*Example 11*

10 500 parts of the adipic acid salt of hexamethylenediamine, 1500 parts of  $\epsilon$ -caprolactam, 13.8 parts of the salt from 2 molecular proportions of hexamethylenediamine and 1 molecular proportion of 1.2.3.4-butanetetracarboxylic acid, 60 parts of vinyl ethinyldimethylcarbinol and 1000 parts of water are treated in the manner described in Example 1. An elastic condensation product of good mechanical strength is obtained. By coemploying the sebacic acid salt of hexamethylenediamine or replacing part of the adipic acid salt of hexamethylenediamine by the said sebacic acid salt or by adding 11-aminostearic acid the softness of the product is still improved.

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