

SPECIFICATION

Process for the production of flexible copolyamides having improved mechanical properties

The present invention relates to a process which makes it possible to obtain flexible copolyamides having improved mechanical properties, high molecular weights and high melting points. For certain applications of plastics, it is necessary to have polymers which possess the characteristics of chemical resistance of polyamides, whilst having a greater flexibility than that of conventional polyamides such as polyhexamethylene adipamide or polycaprolactam. The use of a plasticiser makes it possible to obtain flexibility, but this is generally to the detriment of the chemical stability or other mechanical properties. The use of copolyamides has also been proposed.

British Specification No. 1 000 216 discloses a process which enables one to obtain copolyamides having the desired properties; nevertheless the process provides copolyamides with slight variations in properties and these variations can have a significant effect on their utility. In other words this process does not enable one to obtain consistent results.

It has now been found, according to the present invention, that it is possible to obtain consistently copolymers from a dimeric fatty acid, hexamethylenediamine and caprolactam which have greatly improved mechanical characteristics, equivalent to those of homopolymers used in industry, whilst retaining the properties of elasticity and of chemical resistance of the latter by controlling the stoichiometry of the salt used in the reaction.

According to the present invention there is provided a process for preparing an essentially linear flexible copolyamide which is based on caprolactam, dimeric fatty acid and hexamethylenediamine, and which has a tensile strength of more than 5 DaN/mm², which process comprises mixing caprolactam with a solution in either (i) water and an alcohol having less than 5 carbon atoms; or (ii) water and caprolactam, or (iii) caprolactam, of a salt of hexamethylenediamine and a dimeric fatty acid containing less than 0.5% by weight, and preferably less than 0.1% by weight, of a monobasic acid and less than 5% by weight of an acid having a basicity of more than 2, the stoichiometry of this salt having been established by measuring its pH, for example with a pH meter, in a solvent which is either water and an alcohol, or water and a diol, or water and caprolactam and, if necessary, adjusting the salt solution to be mixed with the caprolactam accordingly so that the stoichiometry of the salt is such that its pH is not more than 0.05 from the pH at the equivalence point, with the proviso that when the solution in (iii) contains sufficient caprolactam, mixing of the solution with further caprolactam can be omitted and subsequently heating to cause the caprolactam to react with the salt.

The caprolactam used in the process according to the invention can have the same characteristics as those of the product used for obtaining polycaprolactam in industry i.e. it can be of industrial quality. Likewise, the hexamethylenediamine can have the properties of the product used for obtaining polyhexamethylene adipamide in industry.

On the other hand, industrial dimeric fatty acid usually contains various impurities; the dimeric fatty acid used in the present invention must have a particular composition. It has been found that this dimer must contain not more than 0.5 and preferably not more than 0.1% by weight of monobasic acid and not more than 5% by weight of acid having a basicity of more than 2, and it must possess an iodine number of less than 30. A dimeric acid which does not contain any monobasic acid detectable by gas phase chromatography of the methyl esters, and which contains about 3% of the acid having a basicity of more than 2 and has an iodine number of about 10, is preferred. A specific example is the C₃₆ saturated dimer obtained from a C₁₈ unsaturated monomeric acid. The mean molecular weight of the dimer is preferably of the order of 565, but it is possible to use other dimeric acids having molecular weights between 370 and 800.

The industrial processes which are usually employed for manufacturing homopolymers derived from diacids and diamines consist, in a first stage, in obtaining the stoichiometric salt of this diacid with the diamine and then in carrying out the polycondensation. There are two techniques for obtaining the salt: either the salt is crystallised and purified from its solution, or a concentrated solution of this salt is obtained, the stoichiometry of which can be monitored and adjusted, for example using a pH meter. However, when the diacid is a dimeric acid as defined above and the diamine is hexamethylenediamine, the first process cannot be used because the salt possesses the characteristics of a soap which cannot easily be isolated and purified. In order to carry out the second method, it has been found that it is necessary to use a particular solvent, the water which is usually employed being a solvent neither for the dimeric acid nor for the salt obtained, under approximately ambient conditions. It has been found that, unexpectedly, it is possible to obtain a concentrated and stable solution under ambient conditions, that is to say that, at about 25°C, it is possible to obtain a concentration of at least 30% up to say, 70% of solids with a water/caprolactam mixture. However, it is quite obvious that it would be possible to operate at a higher temperature with an even higher concentration. The water/caprolactam mixtures preferably have a composition of 40 to 90% by weight of water and, more precisely, of 50 to 80% of water. These solutions in the water/caprolactam mixture are generally clear, stable, of low viscosity and therefore easy to handle. Moreover, they exhibit the advantage that they can be employed directly in the usual processes for the polycondensation of polyamides.

Alternatively pure caprolactam can be used as the solvent medium (assuming insufficient

caprolactam is to be mixed with the salt solution). In this case, it is generally necessary to operate at a temperature above 67°C but not too high because the rate of formation of the salt then no longer makes it possible to adjust the stoichiometry suitably. The reaction is preferably carried out at 70 to 75°C and with salt concentrations of 5 to 95% by weight and preferably 5 to 50% by weight.

It is also possible to use, as the solvent medium, mixtures of water and a volatile alcohol i.e. which has a boiling point below 120°C, and preferably below 100°C, or forms, with the water, an azeotrope having a boiling point below 100°C, in particular an alcohol having less than 5 carbon atoms. Amongst such water/alcohol mixtures (which may, for example contain 30 to 60% by weight of water and 5 to 90% by weight of isopropanol), water/methanol mixtures having a water content of 30% by weight to 60% by weight, and preferably 40 to 50%, water/ethanol mixtures having a water content of 30% by weight to 60% by weight, water/isopropanol mixtures having a water content of 5% by weight to 90% by weight, and preferably 25 to 75%, and water/butanol mixtures having a water content of 30% to 60% by weight are preferred. Salt concentrations of 30 to 70% by weight can easily be obtained with these mixtures.

Of course, as in customary procedures, the alcohol should be removed before carrying out the polycondensation. The alcohol or its azeotrope with water can be distilled at atmospheric pressure.

A further aspect of the process according to the invention is the monitoring which makes it possible to adjust the stoichiometry of the salt solution. It has been found that this monitoring can advantageously be carried out by measuring the pH, at, say, 20°C, of a salt solution which is not necessarily that obtained during the salification. The operation is usually carried out with solutions having a salt concentration of 5 to 50% and preferably 5 to 20% by weight. The best results are usually obtained with a concentration of about 10% by weight. The solvent medium used necessarily comprises a variable amount of water and a solvent which is preferably a (monohydric) alcohol, a diol or caprolactam. The preferred mixtures are binary mixtures, but it is also possible to use ternary mixtures of the same solvents. The amounts of this co-solvent or these co-solvents vary depending on the nature of the latter, but are generally from 15 to 80% by weight and preferably from 30 to 70%.

In the case of ethanol, from 30 to 55% and preferably from 45 to 55% by weight of ethanol is used. In the case of isopropanol, from 15 to 85% of isopropanol, and preferably from 40 to 80% by weight, is used. In the case of butanol, the butanol content is preferably from 50 to 90% and preferably from 70 to 80% by weight.

In the case of ethylene glycol, this content is generally 25 to 80% and preferably from 40 to 70% by weight of ethylene glycol.

In the case of caprolactam, the caprolactam content of the solution is preferably 10 to 50% and preferably from 20 to 40% by weight.

The pH corresponding to the stoichiometric salt varies depending on the nature of the solvent medium and the concentration of the solution. This pH can easily be determined by potentiometry in the solvent medium in question and at the chosen concentration.

Having determined the pH of the salt solution, it is then easy to obtain the stoichiometry of the solution intended for the polycondensation by adding the required reactant. The stoichiometry is finally such that its pH (in the selected solution) is not more than 0.05 from the pH at the equivalence point (of the selected solution).

The adjusted solution can then be directly employed in the polycondensation process, together with other constituents and additives of the polymer, if desired.

The main constituent which can be added is caprolactam, but it is also possible to add small amounts of other monomers which can co-condense with the caprolactam. It is also possible to introduce other additives such as monobasic acids or monofunctional amines acting as chain stoppers, in fairly low proportions which are generally less than 0.5 mol % and preferably less than 0.2 mol %, relative to the monomers. It will be appreciated that only by keeping the monobasic acid concentration in the dimer to low limits as defined above is it possible to regulate the chain length with any degree of certainty by adding these monobasic acids. It is also possible to introduce other ingredients such as nucleating agents, lubricants and colorants.

The copolyamides according to the invention can be obtained by various processes which are generally used for condensing polymers. Two processes are particularly suitable.

In the case of copolyamides in which less than about 90% by weight of the monomers is caprolactam, the preferred process consists in gradually raising the temperature of the reaction medium to, say, 250 to 300°C at atmospheric pressure, ensuring that the solvents and the water of polycondensation distil uniformly. The polycondensation is then terminated by keeping the molten mass at the same temperature for a period varying from, say, 1 hour to a few hours.

A second process which can be applied to all the copolyamides, but which is preferred for those in which more than 90% by weight of the monomers is caprolactam, consists in heating the reaction mass, at atmospheric pressure, in order to remove, by distilling the reaction mixture, the non-aqueous solvents which may be present and also some of the water present. The resulting mass, which preferably contains from 10 to 20% by weight of water, is then heated to a high temperature for example, 200 to 250°C under an autogenous pressure of the order of 5 to 20 bars. The water is then distilled under pressure and the polycondensation is allowed to proceed, the pressure being gradually let down to

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atmospheric pressure whilst raising the temperature to, say, 250—300°C. The polycondensation can be terminated by heating the molten mass, as in the above process.

In both processes, the final heating time can be reduced by sweeping dry nitrogen over the molten polymer or, preferably, by gradually applying a vacuum. This latter technique exhibits the additional advantage that it removes a large part of the monomers which have not undergone polycondensation. If this technique is not used, the residual monomers and certain low molecular weight oligomers can be removed by washing the polymer with hot water.

The products obtained by the process according to the invention exhibit numerous advantages, *inter alia* a flexibility and a permanent elasticity, which can be controlled by the proportion of dimeric acid, whilst retaining the mechanical characteristics of break under tension which are equivalent to those of polycaprolactam, an excellent impact strength under ambient conditions, an improved dimensional stability and resistance to water, and a good resistance to aromatic and aliphatic chlorohydrocarbons. Furthermore, an improved transparency is found, relative to that of polycaprolactam. The resistance to hydrolysis is good.

The suitability for moulding, extrusion or spinning is good. These polymers also possess a good thermomechanical strength, due to their high melting points, and a degree of crystallinity.

Copolyamides of this type can be used successfully in the fields of, for example, moulding, injection moulding, extrusion or spinning. It is possible to envisage various applications requiring the specific properties of these copolymers in fields as varied as the mechanical, building, electrical household equipment or textile industries.

The following Examples further illustrate the present invention. The test conditions for the copolymers obtained are indicated below:

The pH measurements are carried out at 20°C using a Radiometer PHM 62 pH meter, graduated to a hundredth of a pH unit.

The pH values at the equivalent points were determined at 20°C using a Radiometer PHM 62 pH meter, graduated to a hundredth of a pH unit, and under the dilution conditions used for the pH measurements.

The inherent viscosities of the polyamides were determined on a solution containing 0.5 g of dried polymer in about 100 ml of m-cresol at 25°C, using a capillary tube viscometer.

$$\eta_{inh.} (dl/g) = \frac{1}{c} \log \frac{t}{t_0}$$

c = exact concentration of the solution in g/dl

t = flow time of the solution in seconds

t_0 = flow time of the pure solvent in seconds

(Draft ISO/R 307)

The glass transition temperatures of the polyamides are obtained by differential thermal analysis under nitrogen, using temperature variations of 10°C/minute.

The contents of products which could be extracted with hot water were determined in the following manner:

100 g of polyamide granules, dried to constant weight, are treated with 1 litre of softened water at 80°C for 5 hours. The granules are rinsed, drained and then dried again to a constant weight p .

Content of extractables $E\% = 100 - p$.

This method of operation also defines the washing conditions of the polymers.

After removing the products which could be extracted with hot water, the degree of whiteness of the polyamides was determined on granules (dimensions about 2mm × 1mm × 3mm) using a ZEISS "ELREPHO" photoelectric photometer equipped with an anti-reflection dome and provided with illumination by means of an incandescent lamp.

Degree of whiteness $\% = 100 - Pe$

Pe = excitation purity (%) deduced from the tri-stimulus values standardised by the C.I.E. The iodine number is the weight of iodine fixed by 100 g of product and is determined by the conventional method using WIJS' reagent.

The mechanical characteristics were determined on comparison test-pieces which had been moulded by injection into a cold mould (15°C) using a laboratory transfer press.

Before moulding, the polyamides were dried at 110°C in an oven for 5 hours, under a vacuum of about 10 mm Hg.

The moulded test-pieces are stabilised for 1 hour at 100°C in an inert atmosphere before being conditioned.

The test-pieces are conditioned in the following manner:

EH 0: test-pieces kept in a P_2O_5 desiccator at 25° for 24 hours after moulding.

EH 50: test-pieces kept in a desiccator containing a saturated solution of sodium dichromate at 25°C until equilibrium is reached.

The hardness is measured on 80mm × 10mm × 4mm moulded bars using a Shore D hardness meter in accordance with draft ISO/R 868.

The mechanical bending characteristics were determined at 20°C on 80mm × 10mm × 4mm

test-bars in accordance with draft ISO 178.

The mechanical tensile characteristics were determined at 20°C on 2 mm thick H₃ type test-pieces in accordance with French Standard Specification T 51 034 (traction speed 10 mm/minute) using an Instron (registered Trade Mark) type tensometer.

5 In the Examples, various batches of dimeric acid, marketed under the registered Trade Mark Empol 1010 by Unilever Emery, were used; these either do not contain any monobasic acid (monomer) detectable by gas phase chromatography of their methyl esters, or contain less than 0.1% of monobasic acid determined by this analytical method, and which have an iodine number of about 10. All parts and percentages are by weight.

10 EXAMPLE 1

Preparation of the salt of hexamethylenediamine with the dimeric fatty acid as a 50% strength solution in a 50/50 (by weight) mixture of water and isopropanol.

41,650 g of a dimeric fatty acid, containing 0.03% of monomer and about 3% of trimer (and marketed under the name Empol 1010 by Unilever Emery), and 25,000 g of isopropanol are charged 15 into a 150 litre reactor which is equipped with a propeller stirrer (three blades — rotation speed 300 revolutions/minute) and is capable of operating under a nitrogen atmosphere.

The mixture is homogenised and the free space in the reactor is purged with nitrogen. 8,349 g of pure hexamethylenediamine, dissolved in 25,000 g of softened water beforehand, are then run uniformly into the stirred mass in the course of about 1 hour.

20 The clear solution obtained is homogenised for about 30 minutes.

A small sample of about 10 cm³ is taken and diluted with a mixture of water and isopropanol (50/50 by weight) so as to bring the concentration of the salt to 10%. The pH value of this diluted solution is greater than that at the equivalence point.

25 600 g of Empol 1010 dimeric fatty acid, diluted with 300 g of isopropanol, and 300 g of softened water are introduced into the concentrated solution (50% strength). The solution is homogenised for 30 minutes and a further pH measurement is then carried out on a solution which has been diluted to 10% strength with the mixture of water and isopropanol (50/50 by weight). The pH value of the diluted solution is still greater than that at the equivalence point.

30 A further 600 g of Empol 1010 dimeric fatty acid, diluted with 300 g of isopropanol, and 300 g of softened water are introduced into the concentrated solution. The solution is homogenised for 30 minutes and a further pH measurement is carried out on a diluted solution. The pH value of the diluted solution reaches that at the equivalence point to within five hundredths of a pH unit.

35 The concentrated solution, adjusted in this way, is withdrawn and kept under a nitrogen atmosphere at 25°C. Under these conditions, it is clear, homogeneous and stable and possesses an apparent viscosity of about 2 Poises.

EXAMPLE 2

Preparation of the salt of hexamethylenediamine with the dimeric fatty acid as a 33.3% strength solution in a 50/50 (by weight) mixture of water and caprolactam.

40 30,207 g of softened water, 30,207 g of caprolactam and 4,937 g of pure hexamethylenediamine are charged, whilst stirring, into the equipment described in Example 1.

The mixture is homogenised for about one hour and the free space in the reactor is purged with nitrogen.

45 25,270 g of an Empol 1010 dimeric fatty acid of Unilever Emery, which contains 0.065% of monomer, are run uniformly into the stirred solution in the course of about one hour. The mass is homogenised for 30 minutes to one hour.

A small sample is taken and diluted with a mixture of water and isopropanol (42.85/57.15 by weight) so as bring the concentration of the salt to 10%. This diluted solution then has the following composition:

	salt of dimeric acid	0.1 part	
50	caprolactam	0.1 part	50
	water	0.4 part	
	isopropanol	0.4 part	

The pH value of this solution is less than that at the equivalence point.

55 260 g of a 66.6% strength aqueous solution of hexamethylenediamine are introduced into the concentrated solution. The solution is homogenised for 30 minutes and a further pH measurement is then carried out on a solution which has been diluted so as to contain 10% of salt as above. The pH value of the diluted solution reaches that at the equivalence point to within five hundredths of a pH unit.

The concentrated solution, adjusted in this way, is withdrawn and kept at 25°C under a nitrogen

atmosphere. Under these conditions, it is stable, clear and homogeneous and possesses an apparent viscosity of about 1.5 Poises.

EXAMPLE 3

Preparation of the salt of hexamethylenediamine with the dimeric fatty acid as a 50% strength solution in molten caprolactam.

500 g of caprolactam are charged into a 2 litre reactor equipped with a system for heating by means of a thermostatically controlled oil bath, an anchor-type stirrer (rotation speed 100 revolutions/minute), a nitrogen circuit making it possible to operate under a nitrogen atmosphere, a thermometer and a 500 ml dropping funnel.

The free space in the reactor is purged with nitrogen and the mass is heated to 70°C. The stirring is started when the caprolactam is molten, and 85.34 g of pure hexamethylenediamine are then introduced into the stirred mass. Homogenisation is carried out for about 15 minutes.

414.66 g of an Empol 1010 dimeric fatty acid of Unilever Emery, which contains 0.065% of monomer, are then run uniformly into the stirred mass by means of the dropping funnel, keeping the temperature of the mass below 80°.

The mass is homogenised at 70°—75°C for one hour after the addition of the dimeric acid has ended.

A small sample is taken and diluted with a 78.75/21.25 mixture of water and caprolactam so as to bring the concentration of the salt to 10%. The pH value of this diluted solution is less than that at the equivalence point.

0.345 g of pure hexamethylenediamine and 0.345 g of caprolactam are added to the stirred mixture at 70°—75°C. The mass is homogenised at 70°—75°C for 30 minutes and a further small sample is then taken and diluted to 10% strength as above. The pH value of this solution reaches that at the equivalence point to within five hundredths of a pH unit.

The concentrated solution, adjusted in this way, is homogeneous and clear and possesses an apparent viscosity of about 3.5 Poises at 75°C but crystallises at about 67°C on cooling.

500 g of solution are removed whilst hot and used immediately for preparing a copolyamide in accordance with Example 11.

150 g of softened water are run uniformly into the reactor containing the remainder of the solution. Homogenisation is carried out whilst allowing the mixture to cool. A clear, homogeneous and stable solution, which possesses an apparent viscosity of about 2 Poises, is finally obtained at 25°.

EXAMPLE 4

Preparation of the salt of hexamethylenediamine with the dimeric fatty acid as a 70% strength solution in a 25/75 (by weight) mixture of water and isopropanol.

4,074 g of an Empol 1010 dimeric fatty acid of Unilever Emery (which contains 0.03% of monomer) and 1,050 g of isopropanol are charged into a 10 litre reactor equipped with a frame-type stirrer (rotation speed 60 revolutions/minute), a 1 litre dropping funnel and a circuit making it possible to operate under a nitrogen atmosphere.

The mixture is homogenised and the free space in the reactor is purged with nitrogen. 826 g of pure hexamethylenediamine, dissolved beforehand in a mixture containing 525 g of softened water and 525 g of isopropanol, are then run uniformly into the stirred mass in the course of one hour.

The solution obtained is homogenised for one hour.

A small sample is taken and diluted with a mixture of water and isopropanol (51.25/48.75 by weight) so as to bring the concentration of the salt to 10%. This diluted solution then has the following composition:

salt of dimeric acid 0.1 part

water 0.45 part

isopropanol 0.45 part

The pH value of this diluted solution is less than that at the equivalence point.

5.85 g of 70% strength solution of hexamethylenediamine in the 25/75 mixture of water and isopropanol are then introduced into the concentrated solution. The solution is homogenised for 30 minutes and a further pH measurement is then carried out on a solution which has been diluted to 10% strength as above. The pH value of the diluted solution reaches that at the equivalence point to within five hundredths of a pH unit.

The concentrated solution, adjusted in this way, is withdrawn and kept at 25°C under a nitrogen atmosphere. Under these conditions, it is clear, homogeneous and stable and possesses an apparent viscosity of about 17 Poises.

EXAMPLE 5

Preparation of the salt of hexamethylenediamine with the dimeric fatty acid as a 35% strength solution in a 65/35 (by weight) mixture of water and caprolactam.

633.75 g of softened water, 341.25 g of caprolactam and 88.33 g of pure hexamethylenediamine are charged into a 2 litre reactor equipped with an anchor-type stirrer (rotation speed 100 revolutions/minute), a 500 ml dropping funnel, a thermometer and a nitrogen circuit making it possible to operate under a nitrogen atmosphere.

The mixture is homogenised for about one hour and the free space in the reactor is purged with nitrogen. 436.67 g of a batch of an Empol 1010 dimeric fatty acid of Unilever Emery, which contains no monomer detectable by chromatography of the methyl esters, are run uniformly into the stirred solution in the course of about one hour. The mass is homogenised for one hour.

A small sample is taken and diluted with a mixture of water and caprolactam (77.6/22.4 by weight) so as to bring the concentration of the salt to 10%. This diluted solution then has the following composition:

15	salt of dimeric acid	0.1 part
	caprolactam	0.225 part
	water	0.675 part

The pH value of this diluted solution is less than that at the equivalence point.

0.77 g of a 35% strength solution of hexamethylenediamine in the 65/35 mixture of water and caprolactam is introduced into the concentrated solution. The solution is homogenised for 30 minutes and a further pH measurement is carried out on a solution which has been diluted so as to contain 10% of salt as above. The pH value of the diluted solution reaches that at the equivalence point to within five hundredths of a pH unit.

The concentrated solution, adjusted in this way, is kept at 25°C under a nitrogen atmosphere. Under these conditions, it is stable, clear, homogeneous and fluid.

EXAMPLE 6

Preparation of the salt of hexamethylenediamine with the dimeric fatty acid as a 50% strength solution in a 50/50 by weight mixture of water and ethanol.

The equipment described in Experiment No. 1 is used.

33,230 g of an Empol 1010 dimeric fatty acid of Unilever Emery (which contains 0.03% of monomer) and 20,000 g of pure ethanol are charged into the reactor.

The mixture is homogenised and the free space in the reactor is purged with nitrogen. 6,770 g of pure hexamethylenediamine, dissolved in 20,000 g of softened water beforehand, are then run uniformly into the stirred mass in the course of one hour. The clear solution obtained is homogenised for one hour.

A small sample is taken and diluted with a mixture of water and ethanol (50/50 by weight) so as to bring the concentration of the salt to 10%. The pH value of this diluted solution reaches that at the equivalence point to within five hundredths of a pH unit.

The concentrated solution, adjusted in this way, is withdrawn and kept at 25°C under a nitrogen atmosphere. Under these conditions, it is clear, homogeneous and stable and possesses an apparent viscosity of about 2 Poises.

EXAMPLE 7

Preparation of the salt of hexamethylenediamine with the dimeric fatty acid as a 50% strength solution in a 40/60 (by weight) mixture of water and n-butanol.

The equipment described in Example No. 3 is used.

500 g of an Empol 1010 dimeric acid of Unilever Emery, which contains 0.03% of monomer, and 361.2 g of n-butanol are charged into the reactor. The mixture is homogenised and the free space in the reactor is purged with nitrogen.

102 g of pure hexamethylenediamine, dissolved in 240.8 g of softened water beforehand, are introduced uniformly into the stirred solution in the course of 15 minutes. The clear solution obtained is homogenised for one hour.

A 10 g sample of the solution is taken and diluted by adding 30.75 g of n-butanol and 9.25 g of softened water, whilst stirring. The pH value of this diluted solution is greater than that at the equivalence point.

1.2 g of Empol 1010 dimeric fatty acid, diluted with 0.7 g of n-butanol, and 0.5 g of softened water are introduced into the concentrated solution.

The solution is homogenised for 30 minutes and a further pH measurement is then carried out on a solution which has been diluted as above. The pH value of the diluted solution reaches that of the equivalence point to within five hundredths of a pH unit.

The concentrated solution, adjusted in this way, is kept at 25°C under a nitrogen atmosphere. Under these conditions, it is clear, homogeneous and stable and possesses an apparent viscosity of about 2 Poises.

EXAMPLE 8

- 5 a) Experiment for the preparation of the salt of hexamethylenediamine with the dimeric fatty acid 5
as a 40% strength solution in a 25/75 (by weight) mixture of water and caprolactam.

The equipment described in Example 3 is used.

- 1,000 g of a batch of an Empol 1010 dimeric acid of Unilever Emery and 677 g of caprolactam, dissolved in 225.5 g of softened water beforehand, are charged into the reactor. The free space in the
10 reactor is purged with nitrogen. The mixture is stirred slowly. The mass obtained is heterogeneous. A 10
mixture of 677 g of caprolactam, 203.5 g of pure hexamethylenediamine and 225.5 g of softened water
is then introduced into the stirred mass in the course of 15 minutes.

- The mass is stirred for one hour. A fairly fluid heterogeneous mass is obtained which, when
allowed to stand at 25°C, rapidly separates out into two immiscible phases. These two immiscible
15 phases remain when the mass is diluted at 25°C with the mixture (25/75) of water and caprolactam in 15
order to obtain overall salt concentrations of between 10% and 40%.

b) Experiment for the preparation of the salt of hexamethylenediamine with the dimeric fatty acid
as a 40% strength solution in softened water.

The equipment described in Example 3 is used.

- 20 300 g of a batch of an Empol 1010 dimeric acid of Unilever Emery and then a solution of 61 g of 20
pure hexamethylenediamine in 541.5 g of softened water are charged into the reactor. The free space in
the reactor is purged with nitrogen.

The mass obtained is heterogeneous and difficult to stir. The temperature of the mass is raised to
80°C in the course of 15 minutes. The mass is then pasty and difficult to stir and yields a gel on cooling.

- 25 c) Experiment for the preparation of the salt of hexamethylenediamine with the dimeric fatty acid 25
as a 40% strength solution in a 90/10 mixture of water and isopropanol.

The equipment described in Experiment No. 3 is used.

- 300 g of a batch of an Empol 1010 dimeric acid of Unilever Emery and then 54.2 g of isopropanol
are charged into the reactor. The free space in the reactor is purged with nitrogen and the mixture is
homogenised. 61 g of pure hexamethylenediamine, dissolved in 487.3 g of softened water beforehand, 30
are introduced uniformly into the stirred mixture in the course of one hour.

Homogenisation is carried out for one hour. The mass obtained is heterogeneous and separates
out into two immiscible phases when it is allowed to stand at 25°C.

EXAMPLE 9

- 35 Preparation of a 6,6-Empol 1010 copolyamide, (70—30 by weight). 35

The equipment comprises:

- a 150 litre reactor equipped with a system for heating by means of a heat-transfer fluid, a stirrer
(propeller type with three blades — rotation speed 300 revolutions/minute), a distillation column and a
system making it possible to purge with nitrogen, which is connected by a heat-insulated pipe to:
40 a 100 litre autoclave equipped with a system for heating by means of a heat-transfer fluid, a 40
frame-type stirrer rotating at 16 revolutions/minute, a circuit for condensing and collecting the volatile
products, which also makes it possible to apply a vacuum by means of steam ejectors, and a system
making it possible to purge with nitrogen.

- 27,424 g of the solution of the salt of hexamethylenediamine with the dimeric fatty acid, prepared
45 as a 50% strength solution in a mixture (50/50) of water and isopropanol as in Example 1, are 45
introduced into the 150 litre reactor, preheated to 50°C. Homogenisation is carried out for 15 minutes
and 32,000 g of caprolactam and 30 ml of a 6% strength solution of an anti-foam agent in
tetrachloromethylene are added. 3 nitrogen purges are carried out by applying a pressure of 3 bars and
then letting the pressure down. The temperature of the stirred mass is gradually raised to 130°C in the
50 course of about two hours, whilst ensuring uniform distillation through the column. The temperature of 50
the mass is kept at about 130°C until the weight of distillate reaches 7,800 g. The temperature of the
mass is then raised uniformly to about 235°C, whilst maintaining uniform distillation through the
column.

- The stirring is then stopped, a nitrogen pressure of 2 bars is applied and the mass is discharged
55 from the reactor into the 100 litre autoclave which has been preheated to 250°C and purged with 55
nitrogen.

The temperature of the stirred mass in the autoclave is gradually raised to 260°C in the course of
30 minutes and then to 270°C in the course of two hours.

- A pressure of 40 mm Hg is then established gradually in the course of about 30 minutes, whilst
60 continuing to homogenise the mass at 260°C—270°C. 60

The stirring is stopped, a nitrogen pressure of 5 bars is established in the autoclave and the
polymer is withdrawn. The latter, extruded from the autoclave in the form of a strip, is cooled by passing
it through a bath of cold water, granulated and dried.

The polymer obtained is transparent and slightly opalescent and possesses the following characteristics:

$\nu_{inh.} = 1.164 \text{ dl/g}$

$E\% = 1.54$

5 Melting point = 199°C

Crystallisation point on cooling: 137°C

Degree of whiteness = 85%

The mechanical characteristics, measured on stabilised and conditioned injection-moulded test-pieces, are given in the Tables below.

10 EXAMPLE 10

Preparation of a 90/10 6,6-copolyamide, with Empol 1010.

The equipment described in Example 9 is used.

9,047 g of the solution of the salt of hexamethylenediamine with the dimeric fatty acid, prepared as a 50% strength solution in a mixture (50/50) of water and isopropanol as in Example 1, are introduced into the 150 litre reactor, preheated to 50°C . Homogenisation is carried out for 15 minutes, whilst heating the mass to 60°C . 10,000 g of softened water, 40,713 g of caprolactam and 30 ml of a 6% strength solution of an anti-foam agent in tetrachloroethylene are then introduced. Homogenisation is carried out for 10 minutes and three nitrogen purges are carried out by applying a pressure of 3 bars and then letting the pressure down.

20 The temperature of the stirred mass is gradually raised to 130°C in the course of about two hours, whilst ensuring uniform distillation through the column. The temperature of the mass is kept at about 130°C until the weight of distillate reaches 9,660 g.

25 The stirring is then stopped, a nitrogen pressure of 2 bars is applied and the mass is discharged from the reactor into the 100 litre autoclave which has been preheated to 200°C and purged with nitrogen.

The stirred mass is heated to 250°C under autogenous pressure in the course of one hour. A pressure of about 10 bars is reached. Uniform distillation is carried out under a pressure of 10 bars until the temperature of the mass reaches 268°C in about one hour. The pressure is let down uniformly to atmospheric pressure in the course of 45 minutes, whilst keeping the temperature of the mass at 268°C — 270°C . The mass is kept at 268°C — 270°C under atmospheric pressure for one hour, whilst stirring, and a pressure of 18 mm Hg is then established gradually in the course of 40 minutes, whilst keeping the mass at 265°C — 270°C and whilst stirring.

35 The stirring is stopped, a nitrogen pressure of 5 bars is established in the autoclave and the polymer is withdrawn. The latter, extruded from the autoclave in the form of a strip, is cooled by passing it through a bath of cold water, granulated and dried.

The polymer obtained is translucent and possesses the following characteristics:

$\nu_{inh.} = 1.21 \text{ dl/g}$

$E\% = 0.54$

Melting point = 213°C

40 Crystallisation point on cooling = 163°C

The mechanical characteristics, measured on stabilised and conditioned injection-moulded test-pieces, are given in the Tables below.

EXAMPLE 11

Preparation of a 50/50 6,6-copolyamide, with Empol 1010.

45 The equipment is a 1 litre autoclave equipped with a system for heating by means of a heat-transfer fluid, a spiral stirrer (speed 10 revolutions/minute to 75 revolutions/minute), a system making it possible to apply a nitrogen pressure and a circuit making it possible to condense and collect the volatile products.

50 450 g of a solution of the salt of hexamethylenediamine with the dimeric fatty acid, prepared as a 50% strength solution in molten caprolactam in accordance with Example 3, are charged into the autoclave, preheated to 75°C .

Homogenisation is carried out for 10 minutes (50 revolutions/minute) and three nitrogen purges are carried out by applying a pressure of 3 bars and then letting the pressure down. After having carried out the third purge, a nitrogen sweep of about 2 litres per hour is established.

55 The temperature of the stirred mass is raised uniformly to 270°C in the course of two hours, whilst collecting the distillate, the first fractions of which appear when the temperature of the mass reaches about 190°C .

60 The mass is homogenised at 270°C for three hours, whilst sweeping nitrogen, during which time the stirring is gradually brought down to 20 revolutions/minute. The nitrogen sweep and the stirring are stopped. A nitrogen pressure of 5 bars is established in the autoclave and the polymer is withdrawn. The latter, extruded from the autoclave in the form of a strand, is cooled by passing it through a bath of cold water, granulated and dried.

The polymer obtained is transparent and possesses the following characteristics:

$\eta_{inh} = 1 \text{ dl/g}$

$E\% = 3.9$

Melting point = 175°C

Crystallisation point on cooling = 112°C

- 5 The polymer obtained is washed with water at 80°C under the conditions defined above. The mechanical characteristics of the washed polymer, measured on stabilised and conditioned injection-moulded test-pieces, are given in the Tables below. 5

EXAMPLE 12

Preparation of a 80/20 6,6-copolyamide, with Empol 1010.

- 10 The equipment is a 1 litre autoclave equipped with a system for heating by means of a heat-transfer fluid, a spiral stirrer (speed 10 revolutions/minute to 75 revolutions/minute), a distillation column, a system making it possible to apply a nitrogen pressure and a circuit making it possible to condense and collect the volatile products. 10

- 15 300 g of a solution of the salt of hexamethylenediamine with the dimeric fatty acid, prepared as a 33.3% strength solution in a mixture (50/50) of water and caprolactam as in Example 2, are charged into the autoclave, preheated to 50°C . 15

- Homogenisation is carried out for 10 minutes (50 revolutions/minute) whilst heating the mass to 60°C . 300 g of caprolactam are introduced, whilst stirring, homogenisation is carried out for 10 minutes and three nitrogen purges are carried out by applying a pressure of 3 bars and then letting the pressure down. After having carried out the third purge, a nitrogen sweep of about 2 litres per hour is established. 20

The temperature of the stirred mass is raised gradually to 270°C in the course of 90 minutes, whilst ensuring uniform distillation through the column (distillation starting when the temperature of the mass reaches about 110°C).

- 25 The mass is homogenised at 270°C for 3 hours, whilst sweeping nitrogen, during which time the stirring is gradually brought down to 20 revolutions/minute. The nitrogen sweep and the stirring are stopped. A nitrogen pressure of 5 bars is established in the autoclave and the polymer is withdrawn. The latter, extruded from the autoclave in the form of a strand, is cooled by passing it through a bath of cold water, granulated and dried. 25

- 30 The polymer obtained is slightly translucent and possesses the following characteristics: 30

$\eta_{inh} = 1.06 \text{ dl/g}$

$E\% = 5.9$

Melting point = 206°C

Crystallisation point on cooling: 158°C

- 35 Degree of whiteness = 91% 35

The polymer obtained is washed with water at 80°C under the conditions defined above. The mechanical characteristics of the washed polymer, measured on stabilised and conditioned injection-moulded test-pieces, are given in the Tables below.

EXAMPLES 13 to 18

- 40 Preparation of a 6,6-copolyamide, with Empol 1010. 40

- Various copolyamides are prepared from solutions of the hexamethylenediamine salt of Empol 1010, obtained in accordance with the methods of operation described in the Examples 1 to 6 and by analogous processes to those described in Examples 9 to 12. The term analogous processes is to be understood as meaning processes in which the temperature and pressure programmings are similar, the charges and the amounts of distillate being adjusted according to the position of the polymers to be obtained. 45

The characteristics of the polymers obtained are summarised in the Tables below.

Table 1 gives the characteristics relating to the preparation of the copolymers and also their thermal characteristics.

- 50 Table 2 gives the mechanical characteristics of the dry copolymers at EH 0. 50

Table 3 gives the mechanical characteristics of the copolymers conditioned at EH 50.

Table 4 gives the resistance of the copolymers to solvents by measuring the solvent uptake and the mechanical characteristics after immersion for 21 days in the solvents in question.

CHARACTERISTICS OF THE 6,6-COPOLYAMIDES WITH EMPOL 1010

TABLE 1

Example No.	COMPOSITION OF THE COPOLYAMIDE (%)		PROCESS OF PREPARATION			CHARACTERISTICS OF THE COPOLYAMIDE			
			Hexamethylenediamine Salt of EMPOL 1010 in Accordance with Example No.	Polycondensation in Accordance with Example No.	Pressure in mm Hg at the end of Polycondensation	INH. ν dl/g	Melting Point °C	Crystallisation Point on Cooling °C	E % ^②
	6	6 EMPOL 1010							
13	95	5	4	10	760	1.18	218	178	0
14	95	5	1	10	60	1.34	214	167	1.68
15	90	10	1	12	760	1.12	212.5	168	0
10	90	10	1	10	18	1.21	213	163	0.54
12	80	20	2	12	760	1.11	209	160	0
16	80	20	6	9	70	1.21	205	153	2.66
17	70	30	5	12	760	1.02	201	148	0
9	70	30	1	9	40	1.16	199	137	1.54
11	50	50	3	11	760	1.02	176	104	0
16	50	50	2	12	40	1.04	174	112	1.96
Technyl C 216 polyamide 6 of RHONE-POULENC POLYMERS									
						1.12	225	173	0.7
Rilsan N of ATO Chimie							162	102	

① Empol 1010 salt 6 - Salt of hexamethylenediamine with the Empol 1010 dimeric fatty acid of Unilever Emery

② E = 0 The polymers were washed under the conditions defined above. It is found that the inherent viscosities of the copolyamides are analogous to that of an industrial polyamide 6. The melting points of the copolyamides remain high.

CHARACTERISTICS OF THE 6,6-COPOLYAMIDES WITH EMPOL 1010

TABLE 2

Example No.	CHARACTERISTICS OF THE DRY POLYMERS E H O					
	Tg°C	Shore D Hardness	MECHANICAL CHARACTERISTICS			
			Bending Modulus DaN/mm ²	TENSILE CHARACTERISTICS		
				Flow Threshold Stress DaN/mm ²	Stress at Break DaN/mm ²	Elongation at Break %
13			272 ± 5			
14	28	85 ± 0.5	160 ± 16	6.2 ± 0.2	6.7 ± 0.3	420 ± 60
15			218 ± 12			
10	36	85 ± 0.5	200 ± 10	5.8 ± 0.1	6.9 ± 0.4	310 ± 70
12	25	80 ± 0.6	142 ± 5	4.6 ± 0.1	7.35 ± 0.3	590 ± 60
16		80 ± 0.5	82 ± 9	3.8 ± 0.1	7.8 ± 0.1	570 ± 20
17	21	76 ± 0.6	101 ± 6	3.9 ± 0.1	7.6 ± 0.5	660 ± 70
9	16	78 ± 0.5	86 ± 7	3.7 ± 0.1	7.1 ± 0.4	590 ± 40
11	-3	69 ± 0.5	29.3 ± 1.2	2.65 ± 0.1	5.5 ± 0.3	670 ± 40
18	-4	70 ± 0.5	29.9 ± 2.4	2.25 ± 0.2	5.6 ± 0.4	620 ± 50
Poly- amide 6	42	86 ± 0.5	290 ± 10	6.9 ± 0.1	6.5 ± 0.4	400 ± 50
Rilsan N	3	68 ± 0.2	20 ± 2	1.8 ± 0.3	5.1 ± 0.5	600 ± 55

The values are given with a confidence interval for a probability of 0.95.

It is noted that the bending modulae which represent the flexibility can be controlled by the dimeric acid content, but the characteristics at break remain at the level of those of the industrial polyamide.

CHARACTERISTICS OF THE 6,6-COPOLYAMIDES WITH EMPOL 1010

TABLE 3

Example No	CHARACTERISTICS OF THE POLYMERS AT EH 50						
	Moisture Uptake %	Tg°C	Shore D Hardness	MECHANICAL CHARACTERISTICS			
				Bending Modulus DaN/mm ²	TENSILE CHARACTERISTICS		
					Flow Threshold Stress DaN/mm ²	Stress at Break DaN/mm ²	Elongation at Break %
12	1.57	-9	70.1 ± 0.3	48.5 ± 2	2.9 ± 0.2	7.3 ± 0.5	690 ± 60
17	1.2	-8	71 ± 0.5	38.8 ± 1.5	3.1 ± 0.2	6.8 ± 0.45	710 ± 70
11	0.42	-18	63.4 ± 0.4	25.6 ± 0.9	1.7 ± 0.1	4.7 ± 0.5	610 ± 70
Poly-amide 6	2.5	-3	77 ± 0.2	125 ± 3	5.0 ± 0.2		470 ± 20
Rilsan N	0.66	-9	63.2 ± 0.2	16 ± 0.5	1.4 ± 0.05	4.5 ± 0.6	340 ± 40

The values are given with a confidence interval for a probability of 0.95

CHARACTERISTICS OF THE 6,6-COPOLYAMIDES WITH EMPOL 1010

TABLE 4

CHARACTERISTICS OF THE DRY POLYAMIDES AFTER IMMERSION FOR 21 HOURS IN THE SOLVENTS AT 25°													
HEXANE					TRICHLOROETHYLENE				TOLUENE				
Example No.	MECHANICAL TENSILE CHARACTERISTICS				Solvent Uptake %	MECHANICAL TENSILE CHARACTERISTICS				Solvent Uptake %	MECHANICAL TENSILE CHARACTERISTICS		
	Solvent Uptake %	Flow threshold stress DaN/mm ²	Stress at break, DaN/mm ²	Elongation at break %		Flow threshold stress DaN/mm ²	Stress at break DaN/mm ²	Elongation at break %	Flow threshold stress DaN/mm ²		Stress at break DaN/mm ²	Elongation at break %	
14	0.6	4.4 ± 0.1	6.3 ± 0.6	420 ± 60	3.3	3.6 ± 0.2	7.4 ± 0.3	540 ± 70	0.9				
10	0.55	4.9 ± 0.2	7.4 ± 0.3	520 ± 60	6.5	2.6 ± 0.1	7.7 ± 0.4	750 ± 50	1.4				
12	0.3	4.2 ± 0.2	8.2 ± 0.5	600 ± 70	15.6	2.4 ± 0.2	6.3 ± 0.4	670 ± 60	3.1	3.2 ± 0.2	7.0 ± 0.2	580 ± 70	
16	1.2	2.9 ± 0.3	8.5 ± 1	750 ± 70	18.5	2.0 ± 0.2	6.7 ± 0.6	640 ± 70	6.4				
17	0.7	3.5 ± 0.1	7.7 ± 0.6	680 ± 40	23	1.9 ± 0.05	4.5 ± 0.3	590 ± 60	5.6	2.2 ± 0.2	5.6 ± 0.5	670 ± 70	
9	1.55	3.1 ± 0.3	6.5 ± 0.6	530 ± 70	29	1.45 ± 0.15	5.4 ± 0.3	760 ± 70	9.7				
11	5.7	1.75 ± 0.2	4.1 ± 0.3	640 ± 70	33.1	1.2 ± 0.05	2.5 ± 0.2	450 ± 60	12.6	1.4 ± 0.1	3.1 ± 0.1	610 ± 40	
18	5.7	1.5 ± 0.15	4.6 ± 0.4	660 ± 50	38.5	1.1 ± 0.1	2.7 ± 0.2	450 ± 50	13.3				
Polyamide 6	0.75	5.9 ± 0.4	7.6 ± 1	470 ± 80	2.05	4.45 ± 0.6	7.8 ± 1.2	550 ± 80	1.3				
Rilsan	4.2	1.25 ± 0.07	4.0 ± 0.3	630 ± 60	43	0.8 ± 0.03	1.9 ± 0.2	500 ± 70	15.6	0.9 ± 0.03	2.5 ± 0.03	540 ± 50	

The values are given with a confidence interval for a probability of 0.95.

It is found that, with respect to the solvents, the copolyamides possess a very satisfactory resistance which is greater than that of Rilsan N and, in certain cases, is of the same order as that of industrial polyamide 6. "RILSAN" is a registered Trade Mark.

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CLAIMS

1. A process for preparing an essentially linear flexible copolyamide which is based on caprolactam, dimeric fatty acid and hexamethylenediamine, and which has a tensile strength of more than 5 DaN/mm², which process comprises mixing caprolactam with a solution in either (i) water and an alcohol having less than 5 carbon atoms, or (ii) water and caprolactam, or (iii) caprolactam of a salt of hexamethylenediamine and a dimeric fatty acid, the acid having an iodine number of less than 30, the concentration of any monobasic acid being less than 0.5% by weight based on the weight of the dimeric fatty acid and any acid having a basicity of more than 2 being present in an amount less than 5% by weight based on the weight of the dimeric fatty acid, the stoichiometry of the said salt having been established by measuring the pH of the salt in a solution of water and at least one of an alcohol, diol and caprolactam and, if necessary, adjusting the salt solution to be mixed with the caprolactam accordingly so that the stoichiometry of the salt is such that its pH is not more than 0.05 from the pH at the equivalence point, with the proviso that when the solution in (iii) contains sufficient caprolactam, mixing of the solution with further caprolactam can be omitted and subsequently heating to cause the caprolactam to react with the salt.
2. Process according to claim 1 in which the copolyamide is derived from 40 to 95% by weight of caprolactam and 5 to 60% by weight of the salt.
3. Process according to claim 1 or 2, in which the dimeric acid consists essentially of a saturated dimer of an unsaturated fatty acid having 18 carbon atoms.
4. Process according to any one of claims 1 to 3, in which the salt is provided as a solution containing 30 to 70% by weight of said salt having a temperature of about 25°C.
5. Process according to claim 4 in which the solution is of a mixture of water and caprolactam containing from 40 to 90% by weight of water.
6. Process according to claim 5 in which the solvent mixture contains 50 to 80% by weight of water.
7. Process according to claim 4 in which the solution is of a mixture of water and ethanol containing 30 to 60% by weight of water.
8. Process according to claim 4 in which the solution is of a mixture of water and methanol containing 40 to 50% by weight of water.
9. Process according to claim 4 in which the solution is of a mixture of water and isopropanol containing 25 to 75% by weight of water.
10. Process according to any one of claims 1 to 3, in which the salt is provided as a solution in molten caprolactam, having a salt concentration of 5 to 95% by weight.
11. Process according to any one of claims 1 to 10 in which the stoichiometry of the salt employed has been established by measuring the pH of a solution of the salt in either water and an alcohol, or water and a diol, or water and caprolactam.
12. Process according to any one of claims 1 to 11, in which the stoichiometry of the salt employed has been established by measuring the pH of a solution of the salt, having a solids content of 5 to 50% by weight in a binary or ternary solvent mixture of water and an alcohol, a diol or caprolactam.
13. Process according to claim 12 in which the concentration of the salt in the binary or ternary mixture is 5 to 20% by weight.
14. Process according to claim 12 or 13, in which the pH is determined on a solution of water and ethanol, containing from 30 to 55% by weight of ethanol.
15. Process according to claim 14 in which the said solution contains 45 to 55% by weight of ethanol.
16. Process according to claim 12 or 13 in which the pH is determined on a solution of water and isopropanol, containing 15 to 85% by weight of isopropanol.
17. Process according to claim 16 in which the said solution contains 40 to 80% by weight of isopropanol.
18. Process according to claim 12 or 13 in which the pH is determined on a solution of water and butanol, containing 50 to 90% by weight of butanol.
19. Process according to claim 18 in which the said solution contains 70 to 80% by weight of butanol.
20. Process according to claim 12 or 13, in which the pH is determined on a solution of water and ethylene glycol containing 25 to 80% by weight of ethylene glycol.
21. Process according to claim 20 in which the said solution contains 40 to 70% by weight of ethylene glycol.
22. Process according to claim 12 or 13, in which the pH is determined on a solution of water and caprolactam, containing 10 to 50% by weight of caprolactam.



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- 23. Process according to claim 22 in which the said solution contains 20 to 40% by weight of caprolactam.
- 24. Process according to claim 1 substantially as described in any one of Examples 9 to 18.
- 25. A copolyamide whenever prepared by a process as claimed in any one of the preceding claims.

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