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PROCESS FOR THE PRODUCTION OF FINELY DIVIDED PARTICLES OF SYNTHETIC INTERPOLYAMIDES

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This invention relates to a process for the production of finely divided particles of synthetic polymers, to the new products and to paper and other non-woven sheets produced therefrom.

For some time, experiments have been carried out for utilising synthetic fibres, and more especially polyamide and polyester fibres, in the paper industry either by incorporating these fibres, cut to the required length, in the usual cellulose pulps or by using them alone as base fibres in cases where particularly high strength characteristics are required.

Especially in the latter case, by reason of the generally smooth surface of such fibres, it is necessary to use a bonding agent by means of which they can be held together in the paper sheet.

Various types of bonding agents have been proposed. Use has been made of solutions of mineral salts, with which the fibrous sheet is impregnated, the sheet thereafter being subjected to calendering at a temperature at which the solutions of mineral salts swell and locally plasticise the base fibres without, however, causing degradation thereof.

Dispersions of fusible synthetic resins (notably N-alkoxyalkylpolyamides) or thermoplastic fibres which melt or soften at temperatures at which the base fibres undergo no deterioration have also been employed, the calendering of the sheets being carried out at such a temperature that the bonding agent melts or softens.

It is possible by means of a recent process to obtain fibrous and/or foliated structures which can be used either alone or in admixture with synthetic fibres and, if desired, natural fibres for the production of paper. It consists in subjecting a polymer, in the incompletely solidified or coagulated state, to an intense shearing and/or beating action which may take place, in the case of soluble polymers, at the instant when they are precipitated from their solution, the said shearing and/or beating action being regarded as essential for producing acceptable fibrous or foliated structures.

Now, it has been found that it is possible to obtain from completely solidified interpolyamides, without using any precipitation technique, finely divided particles which are entirely acceptable more especially as bonding agents in papers, in other non-woven fibrous structures, etc.

According to the present invention interpolyamide grains are treated with a compound or mixture of compounds which produces swelling but not dissolution thereof under the operating conditions, and the grains thus swelled are fragmented by a mechanical action. The term "grains" is used throughout the description and claims to signify particles whose size is greater than that of the particles produced after treatment according to this invention. A grain size of 2–3 mm. is very suitable.

The swelled interpolyamide grains may retain up to about 150%, and preferably more than 70% of their weight of swelling agent.

It could not be imagined that the simple swelling of the polyamide grains would be a sufficient means of ensuring that a subsequent mechanical action would bring these grains into a state of division and into a physical

form in which they could be employed as bonding agents in paper.

The term "interpolyamide" polycondensing together at least one diamine, at least one dicarboxylic acid and at least one monoaminomonocarboxylic acid. These are, for example, binary copolymers made from polymers obtained by hexamethylene-diamine adipate and caprolactam and ternary copolymers made from these two compounds together with hexamethylene-diamine sebacate, etc.

In practice, the swelling agents employed for this treatment are generally methyl or ethyl alcohols, for reasons of cost. However, use may be made of other compounds such as anhydrous methylene chloride and isobutanol, as also of mixtures of compounds, for example mixtures of alcohol and trichloroethylene, alcohol and methylene chloride, alcohol and acetone, and alcohol and methylisobutyl ketone, employed in the anhydrous state.

The operation is carried out at a temperature below the boiling point of these swelling agents. The duration of the treatment varies, particularly with temperature and also with the nature of the swelling agent, the composition of the interpolyamide employed, the grain size, etc.

With regard to this interpolyamide grain size, it has been found that dimensions of 2 to 3 mm. are very suitable.

The division of the swelled polyamide grains by mechanical action advantageously takes place with the aid of the conventional equipment employed in paper making. There may be mentioned, for example, pulpers, "depastilleurs," disc breakers, refiners, etc.

There are obtained particles which are sufficiently divided to be able to retain, after draining, a quantity of water which may reach several times their weight. They may be used as such or intermediately subjected to drying under moderate conditions not entailing any substantial modification of their physical structure. They can readily be redispersed in water, for example in aqueous suspensions of synthetic fibres intended for the production of paper sheets.

In addition, the subdivision of the swelled grains may be facilitated by using a swelling agent having a low boiling point and suddenly immersing the particles obtained after mechanical treatment of these grains in an aqueous bath, for example, brought to a temperature above the boiling point of the swelling agent. It is also possible to incorporate in the grains before or during swelling an alkali or alkaline-earth carbonate and to treat the particles obtained after mechanical subdivision by means of an acidulated aqueous bath. In the first case the swelling agent also acts as a blowing agent, and in the second case the carbonate is added as an auxiliary blowing agent.

The sudden evaporation of the solvent in the first case, and the evolution of carbon dioxide in the second case, produce breakage of the polymer particles into minute flakes whose spongy structure permits considerable water retention.

The following examples are given in order to illustrate the invention, but are not intended to limit it in any way.

Example I

Into a fluid-tight receptacle are introduced 250 g. of interpolyamide grains whose dimensions are about 2 to 3 mm. The interpolyamide was obtained from

20% of hexamethylenediamine adipate
50% of caprolactam
30% of hexamethylenediamine sebacate

The polymer grains are covered with 400 cc. of substantially anhydrous methyl alcohol and allowed to swell at ambient temperature for 24 hours. They are then

separated from the alcohol bath and poured into a beating engine (manufactured by the firm Allimand), which is first adjusted to the grazing position for 20 minutes and then to the beating position for the succeeding 10 minutes.

Very flaky structures are obtained, whose dimensions are between 10 and 50μ. They possess a high water retentive power (of the order of 83% by weight after draining).

(a) Into a disintegrator containing 2 litres of water and rotating at 2000 r.p.m. are introduced 10 g. of drained flakes (representing 1.7 g. of interpolyamide) and 7 g. of polyhexamethylene adipamide fibre having a count of 1.5 deniers and a staple length of 4 mm. The proportion of flakes serving as bonding agent is thus 20% in relation to the mixture with fibre. When the dispersion is homogeneous, one-fifth thereof is introduced into a laboratory former provided with a detachable 100-mesh screen (U.S.A. system), i.e. one having apertures of 0.149 mm.

The sheet obtained is suction-filtered on a Büchner funnel and then detached, and then has good wet strength, similar to that of sheets prepared from mechanical pulp subjected to only a small amount of beating. It is dried for 30 seconds between a plate heated at 130° C. and a felt. It is then subjected to pressing for 40 seconds under 25 kg./cm.^{2} between two chromium-plated, polished and silicone-coated plates, which are brouhgt to a temperature of 150° C. Melting of the bonding agent results in uniting of the fibres. There is obtained by cooling a sheet weighing 99 g./m.^{2} and possessing the following characteristics.

Tearing index ("Index 100"): 583 (this index is obtained by dividing, by the weight of the paper in g./m.^{2}, the value given in kg. by the Lhomme and Argy ED_1 apparatus).

Bursting index: 32 (this index is obtained by dividing by the weight of the paper in g./m.^{2} the value given in g./cm.^{2} by the Mullen burst tester.

Breaking length in m.: 4220.

(b) In the same apparatus as under (a), 20 g. of the same swollen flakes (representing 3.4 g. of interpolyamide) are mixed with 5.1 g. of polyhexamethylene adipamide fibre having a count of 1.5 denier and a length of 4 mm., so as to obtain a proportion of bonding agent in the sheet in the neighbourhood of 40%.

This mixture is introduced into a laboratory former and treated under the same conditions as under (a). The sheet obtained possesses the following characteristics:

Tearing index	302
Bursting index	64
Breaking length	5200

Example II

Interpolyamide grains identical to those of Example I are swelled under the conditions indicated in the said example.

Swelled grains separated from the alcohol bath are introduced into a disc-type beater (produced by the firm Sprout Waldron), containing discs No. 16,381. The relative speed of rotation of these discs is 1800 r.p.m. They are sprinkled with water at an extremely low rate which is just sufficient to cool them.

The flakes obtained are received on an 80-mesh vibrating screen (0.177 mm. apertures) and the part which has remained on the screen is recycled in the beater in the next 40 to 70 seconds. The part which passed through the screen is readily redispersible in water. It retains about 78% by weight of water. It may be used for the preparation of papers containing, for example, 20% or 40% of these flakes as bonding agent, in accordance with the technique described in Example I.

Example III

There are used as starting material grains based on an interpolyamide made from 60% of hexamethylenediamine adipate and 40% of caprolactam, and they are swelled in the manner described in Example I in ethyl alcohol saturated with sodium carbonate.

The swelled grains are treated in the disc beater of Example II, the discs being cooled with water saturated with sodium carbonate.

After passing through an 80-mesh screen as in Example II, the particles obtained are introduced into a water bath acidified with 10% of hydrochloric acid. By the action of the acid on the sodium carbonate, an effervescent evolution of carbon dioxide is produced, which divides the polyamide particles into a multitude of flakes possessing a spongy structure and retaining up to 95% by weight of water.

There can be prepared by the technique of Example I, for example with 20–40% of these flakes as bonding agent, papers possessing good mechanical properties.

Example IV

Grains of the interpolyamide described in Example I are used, and they are swelled for 48 hours in methylene chloride. When separated from the swelling bath, they are worked in the disc breaker of Example II, whereafter they are received on a 200-mesh vibrating screen (0.074 mm. apertures).

The portion retained by the said screen is thrown into water at 50° C. The sudden evaporation of the occluded methylene chloride causes the fragments of polymer to burst. The structures obtained, when used as bonding agent under the conditions of Example I, give papers whose mechanical characeristics are similar to those indicated in that example.

Example V

Grains of the interpolyamide described in Example I are employed, in which 10% of calcium carbonate passing through a 200-mesh screen (idem) have been incorporated.

These grains are swelled in substantially anhydrous methyl alcohol for 24 hours at ambient temperature, whereafter they are removed from the alcohol bath and treated in the disc breaker of Example II, of which the discs are sprinkled with water at an extremely low rate, as in the same example.

The particles obtained are received on a 200-mesh vibrating screen (idem). The small proportion of particles retained is recycled through the breaker in the next 40 to 70 seconds.

The particles passing through the screen are received in the next 30 seconds in a water bath acidified with 3–15% of sulphuric acid. The lively effervescence resulting from the evolution of carbon dioxide divides the particles of polyamides into very spongy flakes, which are thereafter rinsed with water. They retain up to 97% by weight of water.

In the manner indicated in Example I, there can be prepared with 20–40% of these flakes as bonding agent paper sheets whose mechanical strength properties are remarkable and similar to those of Example I.

I claim:

1. Process for the production of finely divided particles of interpolyamides having high water retentive power, said interpolyamides being formed by copolymerized at least one diamine, at least one dicarboxylic acid and at least one monoaminomonocarboxylic acid, which comprises swelling grains of the said interpolyamide with a swelling agent which under the conditions used does not dissolve the interpolyamide, mechanically disintegrating the resultant swollen grains, and then removing the swelling agent, the temperature throughout being below that at which the interpolyamide becomes molten.

2. Process for the production of finely divided particles of interpolyamides having high water retentive power, said interpolyamides being formed by copolymerizing at least one diamine, at least one dicarboxylic acid and at

least one monoaminomonocarboxylic acid, which comprises forming from said interpolyamide swollen grains containing a blowing agent, mechanically disintegrating the swollen grains, and then activating said blowing agent, the temperature throughout being below that at which the interpolyamide becomes molten.

3. Process according to claim 2 wherein a volatile swelling agent is used both to swell the grains and to act as the blowing agent, and is activated as blowing agent by sudden exposure of the disintegrated grains to a temperature above the boiling point of said volatile swelling agent.

4. Process according to claim 3 wherein the volatile swelling agent is a compound selected from the class consisting of methyl alcohol and ethyl alcohol.

5. Process according to claim 2 wherein the blowing agent is provided by the incorporation of a carbonate into the grains, said blowing agent being activated by immersing the swollen, distintegrated grains in an aqueous acid.

6. Process according to claim 2 wherein the process is carried out throughout at substantially room temperature, and the mechanical disintegration is brought about by a paper-making beater.

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