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PROCESS FOR PREPARING DELUSTERED SYNTHETIC FIBERS AND THE LIKE

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8 Claims. (Cl. 260—37)

This invention relates to shaped artificial objects, and more particularly to an improved process for making delustered synthetic superpolyamide fibers, sheets, etc.

This invention has as an object an improved method of producing the delustered shaped articles. Another object is a method for making these articles, and particularly fibers, which results in a more complete dispersion of the delustering material throughout the polyamide and hence yields superior products. Other objects will appear hereinafter.

These objects are accomplished by a process which consists in incorporating the delustering material with the reactant or reactants used in the preparation of the superpolyamide instead of mixing the preformed polymer with the delusterant.

The method of making the fiber-forming polyamides and the fibers therefrom is described in detail in Patents Nos. 2,071,250 and 2,071,253 and Application Serial Number 74,811, filed April 16, 1936, by W. H. Carothers. These fiber-forming polyamides are linear condensation products and are made by continued heating under polymerizing conditions of bi-functional reactants with removal of the volatile reaction products until the product obtained is capable of being drawn into a filament which may be further "cold-drawn" (that is, subjected to stress in the solid state) into a useful fiber showing by X-ray examination orientation along the fiber axis. It is to be understood that the term "filament" as used herein refers to both oriented and unoriented fibers or threads which are drawn from the superpolymers regardless of whether the fibers or threads are long (continuous) or short (staple), and that the term "fiber" refers more specifically to the oriented fibers which are useful in the manufacture of yarn and cloth as are natural textile fibers. A valuable property of these superpolyamides is that they can be spun from melt, that is, by extruding the molten polymer through suitable orifices and cold-drawing the filaments thus obtained. The fiber-forming polyamides, i. e. the superpolyamides, as described in the mentioned applications, are made from polyamide-forming reactants, such as a diamine plus a dibasic acid or a polymerizable amino acid. The preferred polyamides, however, are those made from diamines and dibasic acids, the dibasic acids for the purpose of this invention including their amide-forming derivatives.

As indicated above, the present process is carried out by synthesizing the polyamide in the presence of the delusterant which is preferably a finely divided material such as a pigment having a refractive index differing from that of the superpolyamide, is incompatible therewith, and is inert thereto. The term "incompatible" is used in the specification and claims to indicate that the finely divided material is insoluble in the superpolyamide at ordinary temperatures and forms a separate phase therefrom. The agent which is added to produce the heterogeneous phase will be referred to as the "delusterant." It may be a gas, liquid, or solid, but preferably it will be a solid. For proper delustering the added agent must be in a finely divided state and be so distributed throughout the polyamide surface and fiber so as not to impair the continuity of the superpolyamide or destroy its fiber qualities.

The delustered fibers are most advantageously spun from a melt of the polyamide. The present invention is particularly valuable because, as will be pointed out more particularly below, it is difficult to obtain a good dispersion of the delusterant and molten polymer by methods other than that disclosed herein, namely, that of incorporating the delusterant with the monomeric ingredient or ingredients used in the synthesis of the polyamide. The monomeric ingredient or ingredients may be a polymerizable amino acid, an amide-forming derivative of a polymerizable acid, a diamine plus a dicarboxylic acid, a diamine plus an amide-forming derivative of a dibasic carboxylic acid, or a mixture of such ingredients. Other agents such as solvents, non-solvents, plasticizers, e. g. o-hydroxydiphenyl, and viscosity stabilizing agents, e. g. those described in U. S. Patent 2,174,527 may also be present. The polyamide-forming reactants exert a surprising dispersing action on the delusterant, particularly pigment delusterants. Thus, it is possible to react a diamine with a dicarboxylic acid or an amide-forming derivative of a bibasic carboxylic acid in the present of a pigment, e. g. titanium dioxide, and obtain a superpolyamide in which the pigment is homogeneously dispersed. This homogeneous dispersion is noteworthy for it might be expected that the pigment would tend to flocculate at the high temperature required for polyamide formation or that it would react with the polyamide-forming ingredients or adversely affect the polymerization reaction, or that in the absence of an added dispersing agent no dispersion would occur.

It will be noted that the above method for incorporating the delusterant into the superpolyamide is quite different from that used in intro-

ducing delusterants into cellulosic derivatives. In the delustering of viscose, for instance, dispersions of pigments are generally prepared by grinding the pigment with water and a dispersing agent or with a small portion of viscose, in a ball or colloid mill, and this dispersion is added in the required amount to the main viscose solution. Oils and waxes are emulsified in water and added to the viscose. In delustering cellulose acetate rayon the pigment is generally ground in a dilute solution of cellulose acetate in acetone and this dispersion added to the spinning solution. Such methods cannot be employed advantageously with superpolyamides when the latter are spun by the preferred procedure, i. e. melt spinning. The superpolyamides are solids at ordinary temperatures and are frequently so tough that ball mill grinding is accomplished with difficulty. Ball mill or colloid mill grinding methods are also difficult to apply to the molten polymers because of their high melting point and high viscosity. Addition of the pigment dispersions in a solvent followed by removal of the solvent is disadvantageous because of the long time intervals required during which the polymer tends to undergo objectionable transformations. Furthermore, the polymer is so viscous in the molten state that direct addition of the pigment and thorough dispersion thereof are often extremely difficult or impossible. The discovery that the pigment is thoroughly dispersed in the superpolyamide melt by incorporating it with the monomeric reactants used in preparing the superpolyamide proved very valuable therefore since it furnished a simple and efficient method for producing delustered superpolyamide products. Mixtures of delusterant and polymer obtained by preparing the superpolyamide in the presence of the delusterant as described above are particularly valuable because they can be readily spun from melt into delustered fibers of good quality. If desired, these mixtures can also be treated with solvent and spun by the wet or dry methods.

As previously pointed out, this invention is best practiced by making the fibers from the molten polymer as contrasted with the solution method to which cellulosic materials such as viscose is restricted in the production of artificial fibers. Spinning from melt is simpler and more economical than spinning from solution. It will be observed further that methods which involve the incorporation of the delusterant into the superpolyamide before spinning also differ from the preparation of the known delustered fibers (cellulosic materials) in that the fibers of this invention are stretched or cold-drawn (i. e. subjected to stress while in the solid state) to a much greater degree. The superpolyamide filaments that are extruded from the spinneret are generally cold-drawn from 150 to 600% and are thereby converted into oriented fibers (they exhibit X-ray fiber diffraction patterns which indicate definite orientation along the fiber axis) of high strength and elasticity. It might be thought that this great elongation would restore the luster to the product. In fact, unless the filaments contain a sufficient amount of delusterant, the fibers do take up a low or subdued luster during the cold-drawing operation. In practice, however, no difficulty is encountered in preparing delustered superpolyamide fibers by the process of this invention. The delusterant surprisingly does not interfere with the cold-drawing operation.

The delusterants used in the practice of this invention must have an index of refraction which is different, that is, lower or higher, than that of the superpolyamide. The refractive index of most superpolyamides is approximately 1.55. This difference in refractive index between the delusterant and the superpolyamide should be at least 0.05 and preferably more than 0.2. The most useful delusterants, e. g. titanium dioxide, zinc sulfide, and many other pigment-like materials, have indices of refraction which differ from that of the superpolyamides by at least 0.5. Furthermore, the delusterant must be present in the superpolyamide in a finely divided form. This is particularly essential if the delusterant is added before the superpolyamide is spun or otherwise there is danger that the spinneret orifices will become clogged. For the preparation of delustered superpolyamide fibers the particle size of the delusterant should be less than five microns and preferably less than one micron. If, however, the object to be delustered is a bristle, sheet, film, or molded article, delusterants of larger particle size may be used. For these purposes the particle size may be as large as 25 microns. For the preparation of permanently delustered superpolyamide fibers and fabrics it is further essential that the delusterant be firmly coated or imbedded in the fiber; it should not be removed by the action of soap, water, or solvents of the type used in dry cleaning. The delusterant must be inert to the polyamide fiber-forming material and it must be incompatible therewith. In this connection it may be noted that the fiber-forming materials used herein not only differ radically in chemical composition from cellulosic fiber-forming materials but differ in compatibility characteristics in reactivity toward other agents, the present superpolyamides and cellulosic materials being in fact incompatible with each other. For these reasons agents which have been used in conjunction with cellulosic fiber-forming materials are not necessarily indicated as useful in the production of the new fibrous products described herein.

Inorganic pigment-like materials are especially valuable as delusterants for superpolyamides. These products are in general inert toward the superpolyamides even at the elevated temperatures required for melt spinnig, have a high refractive index, are easily obtained in a finely divided state, and are not affected by water or solvents. As examples of such materials might be mentioned titanium dioxide, barium sulfate or calcium sulfate extended titanium dioxide, barium titanate, zinc titanate, magnesium titanate, calcium titanate, zinc oxide, zinc sulfide, lithopone, zirconium dioxide, calcium sulfate, barium sulfate, aluminum oxide, thorium oxide, magnesium oxide, silicon dioxide, talc, mica, and the like. Colored materials such as carbon black, copper phthalocyanine pigment, lead chromate, iron oxide, chromium oxide, and ultramarine blue may also be used. Another valuable class of delusterants comprises the non-phenolic polynuclear compounds, such as triphenyl benzene, diphenyl, substituted diphenyls, substituted naphthalenes, and particularly chlorinated compounds of the aromatic and polynuclear type, e. g. chlorinated diphenyl. In general the organic delusterants are lighter and softer than the inorganic pigment-like materials. Various oils, waxes, and resins can also be used, but it is often desirable to use these agents in conjunction with delusterants of the types already mentioned.

The quantity of delusterant used in the prep-

aration of the fibers of this invention will depend upon the nature (degree of dispersion, refractive index, etc.) of the delusterant and upon the degree of opacity desired for the final product. In general, quantities of delusterant ranging from 0.1 to 5.0% by weight of the polyamide are used, when the delusterant is dispersed throughout the fiber. In the case of titanium dioxide, for example, quantities of 0.1 to 2.0 are ordinarily employed. Smaller amounts can be used if the delusterant is present merely on the surface of the fiber. Quantities of delusterant outside of this range can be used, but the delusterant must not be present in an amount sufficient to impair the continuity of the superpolyamide or products of inferior flexibility and elasticity will result.

This invention is described more specifically in the following examples in which parts are given by weight:

Example I

A mixture of 524 parts of hexamethylene diammonium adipate (diamine-dibasic acid salt), 4.72 parts of hexamethylene diammonium acetate (viscosity stabilizer), and 6.75 parts of finely divided titanium dioxide having an index of refraction of approximately 2.54 and particles whose size ranged largely from 0.3 to 0.5 micron in diameter, was placed in a stainless steel autoclave equipped with a stainless steel stirrer and a steam heated reflux condenser wihich in turn was connected through a water cooled condenser to a receiver. The autoclave was evacuated and filled with oxygen-free nitrogen, this process being repeated twice. A pressure of 100 pounds was then applied by means of oxygen-free nitrogen and the autoclave was heated to 288° C. during two hours. The pressure was then slowly released but the heating was continued for an additional two hours. The stirrer was run at a rate of 16 revolutions per minute during the initial heating period and at a rate of 36 revolutions per minute during the last two hours. The autoclave was then cooled and the polymer removed as a white, opaque solid. The product had an intrinsic viscosity of approximately 1.0.

The above sample of superpolyamide, which contained 1.5% of titanium dioxide homogeneously dispersed throughout, was spun from melt as follows: The polymer-delusterant mixture was extruded at a pressure of 100–125 pounds per sq. in. (applied with oxygen-free nitrogen) at a temperature of 284° C. from a spinneret having 7 orifices each 0.0078 inch in diameter and placed at the bottom of 0.125 inch cone-shaped protrusions extending downward from the face of the spinneret. The extruded filaments were collected on a motor driven drum having a peripheral speed of 583 ft. per min. and were continuously transferred to and collected on a second drum having a peripheral speed of 1749 ft. per min. The extent of cold-drawing thus produced was therefore 200%. The fibers thus obtained were opaque and completely free from luster. The fibers were oriented and had the following properties: denier, 3.1; tenacity at break, 5.3 g. per denier; residual elongation, 42%. These fibers were readily twisted into a delustered thread or yarn. Fabrics produced from this yarn were free from luster and had good dyeing properties.

Example II

A sample of polyhexamethylene adipamide containing 5% of the dinaphthyl ether of ethylene glycol, prepared by heating hexamethylene diammonium adipate in the presence of 5% of the dinaphthyl ether as described in the preceding example, was spun from melt following the general technique described in Example I. The polymer had an intrinsic viscosity of 0.8. The delusterant, the above mentioned ether, had three principal indices of refraction (1.55, 1.65, and 1.80), and a particle size of 1–2 microns. The spinning conditions (melt process) were as follows: temperature, 284° C.; spinning pressure, 60 pounds per sq. in.; rate of spinning, 634 ft. per min.; extent of cold-drawing, 250%. The delustered fibers obtained in this way had a denier of 4.7, a tenacity of 4.9 g. per denier at break, and a residual elongation of 63%.

Example III

The superpolyamide used in this experiment was prepared by heating hexamethylene diammonium adipate containing 1% of hexamethylene diammonium acetate as viscosity stabilizer, 1.5% of finely divided titanium dioxide, and 0.75% of finely divided dinaphthyl ether of ethylene glycol under the conditions described in Example I. This superpolyamide-delusterant mixture was melt spun from an 18-orifice cone-type spinnert, having orifices 0.0078 inch in diameter and several heavy screen packs placed directly above the orifices, under the following conditions: spinning temperature, 284° C.; spinning pressure, 125 pounds per sq. in.; spinning rate, 700–900 ft. per min.; extent of cold-drawing, 350%. The delustered fibers obtained in this way had a denier of 3.3, a tenacity at break of 4.93 g. per denier, and a residual elongation of 25%. Yarns and fabrics prepared from these fibers were completely free of luster.

Other superpolyamides can be delustered by the method given in the above examples. A valuable class of delustered superpolyamides comprise those derived from diamines of formula $NH_2CH_2RCH_2NH_2$ and dicarboxylic acids of formula $HOOCCH_2R'CH_2COOH$ or their amide-forming derivatives, in which R and R' are divalent hydrocarbon radicals free from olefinic or acetylenic unsaturation and in which R has a chain length of at least two carbon atoms. An especially valuable group of superpolyamides within this class are those in which R is $(CH_2)_x$ and R' $(CH_2)_y$ wherein x and y are integers and x is at least 2. As examples of superpolyamides which fall within one or both of these groups might be mentioned polytetramethylene adipamide, polytetramethylene suberamide, polytetramethylene sebacamide, polypentamethylene adipamide, polypentamethylene sebacamide, polyhexamethylene adipamide, polyhexamethylene sebacamide, polyoctamethylene adipamide, polydecamethylene adipamide, polydecamethylene sebacamide, polydecamethylene para-phenylene diacetamide, and poly-paraxylylene sebacamide. Polyhexamethylene adipamide, because of its high melting point and excellent film-forming qualities, is a particularly valuable member of this group. Polydecamethylene adipamide is likewise a very valuable product. The present invention is not limited, however, to the use of superpolyamides of the diamine-dibasic acid type; those derived from polymerizable amino acids or their amide-forming derivatives are also readily obtained in the delustered form by the methods herein described. As examples of this type of superpolymer might be mentioned the polymers derived from 6-aminocaproic acid ($NH_2(CH_2)_5COOH$), 9-aminononanoic acid, and

11-aminoundecanoic acid. It is within the scope of this invention to prepare delustered shaped articles from mixtures of superpolyamides with each other or with other fiber-forming materials. Delustered articles can also be prepared from interpolymers derived from a mixture of superpolyamide-forming reactants, e. g. two diamines and two dicarboxylic acids.

The delustered objects whose preparation is described in the foregoing examples are fibers. As already indicated, superpolyamide ribbons, bristles, foils, sheets, films, and molded objects can also be delustered according to the methods of this invention; in fact, objects of larger size or diameter can generally be delustered more easily than fibers since they permit the use of delusterants of larger particle size and require less stringent operating conditions.

In the process of this invention the delusterant is incorporated with the monomeric reactant or reactants used in the preparation of the superpolyamide and the resultant mixture is transformed into a shaped object. By this method the delusterant is dispersed throughout the shaped object more completely and efficiently than if the delusterant is incorporated with the preformed polymer or applied to the surface of the shaped object. The method described herein is particularly advantageous because the delustered articles are exceptionally uniform and retain their opacity or low luster even when subjected to abrasion or severe handling conditions.

It may be seen from the foregoing description of the properties which a delusterant must have that a wide variety of compounds can be used as delusterants for superpolyamides. Numerous pigments and extenders have already been mentioned and their use is specifically illustrated in certain of the examples. Example II illustrates the use of an organic delusterant. To be effective as a delusterant the organic compound must of course be used in such proportions that it is not compatible with the superpolyamides. As additional examples of suitable luster modifying agents which include the preferred materials, there may be mentioned the following: picene, decachlorodiphenyl, hexachlorocarbazole, s-dibenzothiazylmercaptoethane, phenyldinaphthoxanthene, tetraphenyl thiophene, thiodinaphthylamine, di-biphenyl ketone, di-binaphthyl urea, oxamide, N-di-alpha-naphthylmethane sulfonamide, di-alpha-naphthyl sulfone, lead formate, the lead salt of N-phenyl phthalamic acid, di-alpha-naphthylmethyl phthalate, urea-aldehyde resins, and polybenzyl resins.

Other materials which may be mentioned as useful for the purpose of this invention are various materials such as the following: bianthryl, tetrachlorodiphenyl, octachloronaphthalene, di-naphthyl-p-phenylenediamine, isodinaphthalene oxide, thianthrene, N-phenylcarbazole, dinaphthocarbazole, s-dicarbazyl, anilinobenzothiazole, 2-phenyl benzimidazole, diphenylamine sulfoxide, diphenylamine sulfone, xanthone, anthraquinone, triphenylamine, di-alpha-naphthylbenzamide, diphenyl oxamide, N-di-alpha-naphthyl acetamide, N-tetraphenyl-succinic diamine, 1,3,5 trinaphthalene-sulfonyl benzene, 1,2-dinaphthyl sulfonyl ethane, trimethylene trisulfone, di-beta-naphthyl sulfoxide, barium and calcium salts of benzyl-p-aminobenzoic acid, di-beta-naphthyl succinate, 1,1'-di-naphthylmethane-3,3'-dibenzenesulfonate, phenol-aldehyde resins, polyether resins, and white mineral oil.

Not all of the above mentioned compounds, however, are useful for melt spinning, the materials suitable for this type of spinning are those which are stable at the elevated temperatures used in the process. In general, pigments, salts, hydrocarbons, chlorinated aromatic hydrocarbons, and related compounds are sufficiently stable for this purpose.

This invention is also applicable to the preparation of delustered shaped articles from other synthetic linear condensation fiber-forming polymers such as polyethers, polyacetals, and polyanhydrides, but owing to the fact that these products have different compatibility characteristics and refractive indices than the superpolyamides they sometimes require different delusterants than do the superpolyamides. In general, the pigment-like materials function as delusterants for these superpolymers also.

It will be seen from the foregoing description that this invention provides a convenient method for preparing fibers and other shaped objects of low or modified luster from superpolyamides. By varying the amount of delusterant used products ranging from brilliant to subdued, dull, or even chalky appearance can be obtained. The process of this invention is not only more advantageously practiced than that of incorporating the delusterant in the preformed polymer, but the resulting products are also in general superior. These fibers compare favorably with previously described superpolyamide fibers (lustrous) in tenacity, elasticity, resistance to solvents, aging qualities, etc., and are far superior to previously described delustered fibers, e. g. those of the cellulosic type, in the above qualities. The low luster superpolyamide flowers because of their excellent tenacity and elasticity give low luster fabrics of excellent quality. An advantage of these fabrics over highly lustrous fabrics is that they tend to "slenderize." When used in garments, for example, these fabrics yield an attractive dull appearance which tends to "slenderize" the figure of the wearer. Furthermore, the delustered fibers have better hiding or covering power than the lustrous fibers. Delustered films, sheets, molded objects, etc. have similar advantages. Unique effects may be obtained by using the delustered fibers of this invention in conjunction with lustrous fibers.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that I do not limit myself to the specific embodiments thereof except as defined in the appended claims.

I claim:

1. A process for obtaining a homogeneous dispersion of polyamide and inert finely divided material, said process comprising heating a polyamide-forming composition under polymerizing conditions in the presence of about 0.1 to 5.0% by weight of inert finely divided material which is incompatible with the polyamide resulting from said polyamide-forming composition and which is of different refractive index from that of said polyamide.

2. A process for making a composition which is capable of being formed into continuous pliable filaments of low luster and which comprises a mixture of polyamide and finely divided material, said process comprising heating a polyamide-forming composition under polyamide-forming conditions in the presence of about 0.1 to 5.0% by weight of inert finely divided pigment-like material which is incompatible with the polyamide re-

sulting from said polyamide-forming composition and which is of different refractive index from that of said polyamide.

3. The process set forth in claim 1 in which said composition comprises a diamine and a compound of the class consisting of dicarboxylic acids and amide-forming derivatives of dibasic carboxylic acids.

4. The process set forth in claim 2 in which said composition comprises a diamine of the formula $NH_2CH_2RCH_2NH_2$ and a dicarboxylic acid of the formula $HOOCCH_2R'CH_2COOH$, wherein R and R' are saturated divalent hydrocarbon radicals and R has a chain length of at least two carbon atoms.

5. The process set forth in claim 2 in which said polyamide-forming composition comprises hexamethylene diamine and adipic acid.

6. The process set forth in claim 2 in which said pigment-like material is titanium dioxide.

7. The process set forth in claim 2 in which said polyamide-forming composition comprises a polymerizable amino acid.

8. The process set forth in claim 2 in which said pigment-like material is barium sulfate.

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CERTIFICATE OF CORRECTION.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, second column, line 42, for the word "present" read --presence--; page 3, second column, line 14, for "4.9" read --4.3--; line 26, for "spinnert" read --spinneret--; page 4, second column, line 36, for "flowers" read --fibers--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 30th day of July, A. D. 1940.

Henry Van Arsdale,
Acting Commissioner of Patents.

(Seal)