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SYNTHETIC POLYMERS AND SHAPED
ARTICLES THEREFROM

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5 This invention relates to synthetic linear con-
densation polymers and more particularly to a
method for improving the properties of syn-
thetic fiber-forming linear condensation poly-
amides.

10 The materials used and improved by the prac-
tice of this invention are the new polymeric ma-
terials described in Patents 2,071,250, 2,071,253,
and 2,130,948. In these cases there is described
15 a new class of fiber-forming materials referred
to as synthetic linear condensation polymers of
which the polyamides described in the last two
mentioned cases are the most useful. These
fiber-forming polyamides are made by subject-
20 ing bifunctional polyamide-forming reactants,
which may, for example, be a polymerizable
amino acid alone or a mixture of diamine and
dibasic acid, to polymerizing conditions until
the polyamide formed is capable of being drawn
25 into filaments which possess the unusual property
of being capable of being cold drawn, that is
drawn or elongated under application of stress
in the solid state, into fibers showing upon X-ray
examination orientation along the fiber axis.

30 While the properties of the synthetic linear
condensation polyamides will of course vary
somewhat with the extent to which they have
been polymerized and with the nature of the
reactants used in their preparation, common
characteristics of fibers derived from these poly-
amides are high tenacity, both wet and dry;
high degree of orientation; extraordinary re-
sistance to solvents and chemical reagents; ex-
ceptionally good elastic recovery; good dyeing
35 properties; and good aging characteristics in air
even at elevated temperatures. These polymers
are generally crystalline and can be formed not
only into filaments but also into other useful
articles such as ribbons, foils, films, sheets, and
40 the like. However, the sheeted products, e. g.,
films, sheets, etc., have the disadvantage of
being opaque unless some special means such as
described herein is used in their preparation.
With regard to the oriented fibers as heretofore
45 made the cold drawing of the polyamide fila-
ments as previously practiced is satisfactory in
the production of fibers of the smaller deniers,
but as explained in more detail below filaments
of the larger sizes cannot be satisfactorily cold
50 drawn into oriented products.

The term "filament" as used herein refers
to both the oriented and unoriented filaments or
threads which are prepared from these polymers
regardless of whether the filaments or threads
55 are long (continuous) or short (staple), while
the term "fiber" refers more specifically to the
oriented filaments or threads.

In the manufacture of filaments and fibers a
valuable property of these polyamides is that
60 they can be spun into filaments directly from

melt. Thus, fibers can be prepared from the
polyamides by extruding the molten polymer
through a suitable orifice into air and cold draw-
ing the resultant filaments. For most pur-
poses the fibers are more useful than the un-
6 drawn filaments from which they are derived,
since they are tougher and more elastic. In
preparing fibers of the size (usually 0.2 to 20
denier) used in the manufacture of fabrics, no
difficulty is encountered in melt spinning tough
10 filaments which cold draw readily. However,
when it is endeavored to prepare large filaments
or articles, such as bristles, ribbons, and rods,
from the polyamides by this method, the prod-
ucts are inclined to be somewhat brittle, at least
15 they are much less tough than the fine filaments
mentioned above. As a result of this lower de-
gree of toughness, these larger articles are much
less susceptible to cold drawing for the pro-
duction of products which for many purposes are
20 more useful because of fiber orientation.

An object of this invention is to improve the
utility of synthetic linear condensation polymers.
Another object is to improve the properties, par-
ticularly the toughness, of fiber-forming syn-
25 thetic linear condensation polyamides. A fur-
ther object is to provide an improved method
for preparing shaped articles from molten poly-
amides of this type. A further object is to improve
the drawability of filaments made from said poly-
30 amides. A further object is the manufacture
of new and useful shaped objects from synthetic
linear condensation polymers. Other objects
will appear hereinafter.

In its broader aspects this invention accom-
35 plishes these objects by rapidly chilling a hot
fiber-forming synthetic linear condensation
polymer. In its preferred embodiment this in-
vention attains these objects by rapidly chilling
a hot fiber-forming synthetic linear condensa-
40 tion polyamide in predetermined shape with a
liquid which has no appreciable solvent action
on the polyamide under the conditions of opera-
tion.

The rapid chilling of hot or molten fiber-
45 forming linear condensation polymers as re-
ferred to above results in a much tougher prod-
uct than is obtained by slow cooling. This rapid
cooling or "tempering" can be effected by means
of a cold liquid which does not dissolve or react
50 with the polymer under the conditions of opera-
tion. The process of cooling hot or molten poly-
amides with the use of a liquid will be referred to
herein as "quenching." Quenching provides an
excellent means of preparing articles of high
55 toughness and improved utility directly from
the molten polymer. The method is particularly
well adapted to the preparation of large fila-
ments, films, ribbons, rods, and the like. The
improved toughness obtained by quenching such
60

products greatly improves their drawability. Thus, filaments of 0.020 inch diameter spun from molten polymer having an intrinsic viscosity of 0.8 and cooled in air cannot generally be cold drawn at the ordinary speed of drawing, whereas quenched filaments of the same diameter and intrinsic viscosity can be readily drawn. Although air cooling is generally sufficient to produce the necessary tempering in the case of small diameter articles, such as filaments to be used in fabric manufacture, these articles can also be prepared to advantage by the quenching method herein described.

This invention therefore consists essentially in rapidly chilling a hot polyamide, preferably in predetermined shape, with a non-solvent liquid medium. The preferred procedure consists in extruding a molten polyamide in suitable form directly into the liquid medium. The polymer may be molten when it comes in contact with the liquid or it may be set or partially set due to the preliminary cooling action of air. To obtain the most pronounced effect, the temperature of the polyamide should not be materially below the melting point of the polyamide when it comes in contact with a liquid cooling medium. Thus, in the case of polyhexamethylene adipamide, which has a melting point (in absence of oxygen) of about 263° C., it is desirable that the temperature of the polyamide be above 245° C. when it comes in contact with the quenching medium. The melting point of the polyamides will of course vary depending upon the reactants from which they have been prepared. The most useful polyamides have melting points between 150 and 300° C. Although a large difference in temperature between the molten polyamide and the cooling medium is desirable, it is generally inadvisable to heat the polyamide much above 300° C. since this tends to bring about thermal decomposition in most instances.

The liquid used to quench the polyamide should preferably be chemically inert toward the polyamide and should not have an appreciable solvent action thereon under the conditions of quenching. Water meets these requirements and in addition is readily available and has a high specific heat. It is therefore the preferred quenching medium. However, a large variety of other liquids may be employed. As examples might be mentioned alcohols, ketones, ethers, esters, hydrocarbons, chlorinated hydrocarbons, etc. The quenching liquid may consist of a mixture of compounds. It may also contain wetting agents, dyes, etc. The quenching liquid is ordinarily employed at ordinary temperatures but may be cooled with the use of brine or other suitable means to sub-normal conditions, e. g., 0° C., in the case of water in order to obtain a larger temperature differential between the polyamide and the liquid. It is also within the scope of this invention to use the quenching medium at moderately elevated temperatures, e. g., 50-100° C., providing there is a sufficient temperature differential. The temperature of the liquid should preferably be kept below 100° C. If desired, the temperature of the liquid cooling medium may be regulated or kept constant by any suitable means. The liquid may be used in the form of a bath or spray.

As already indicated, polyamides which have been quenched are tougher than those which have not received this treatment. Thus, ribbons of 0.1 inch thickness extruded from molten polyamide and allowed to cool in air are rather

brittle and cannot be given sharp bends without breaking. On the other hand, a similar ribbon prepared from the same molten polymer by extrusion into water is quite tough and can readily be bent without breaking. This toughness improves the cold drawing properties of the polymer. In other words, the force required to cold draw ribbons and the like made by quenching is less than that required to draw similar articles prepared from the same polymer without quenching. For this reason it permits the cold drawing of articles of larger diameter than is otherwise possible. The improvement in drawing qualities results primarily from the quenching treatment and not from the action of the water itself, for an improvement in drawing qualities is also obtained when a liquid such as carbon tetrachloride or pyridine is employed as the quenching medium. However, as indicated in Patent No. 2,137,235 treatment of the filaments with water until saturation is reached further improves their drawing properties. The following data illustrate the difference in drawing qualities of unquenched and quenched filaments of 0.028 inch diameter prepared from the same polyamide (intrinsic viscosity about 0.95). In each case the filaments were soaked in water before drawing. The force required to cold draw the unquenched (i. e., spun under non-tempering conditions) was 3.0 pounds, whereas the force required to cold draw the quenched filament was only 1.4 pounds. Not only are the drawing qualities of the quenched filament better, but the strength of the cold drawn product is higher. The average tenacity of oriented bristles made from quenched filaments of polyhexamethylene adipamide having an intrinsic viscosity of approximately 0.9 is 4.7 g. per denier at the breaking point, whereas the average strength of oriented bristles prepared from the same polymer under non-quenching conditions is 3.0 g. per denier at break.

Quenching is also of importance in connection with the preparation of polyamides in sheet form. If films or sheets are prepared by allowing a layer of molten polyamide to cool slowly, e. g., on a glass plate in air, the product is opaque. On the other hand, if the molten layer of polyamide is rapidly chilled by quenching with water or other suitable liquid, it is much less opaque and is usually clear and transparent. Microscopic examination indicates that this transparency of the tempered films is due to the fact that they are made up of minute crystal aggregates (less than 20 microns and usually less than 2 microns in diameter), whereas the crystal aggregates in opaque polyamide films, e. g., those prepared without tempering, are much larger.

Reference has been made to the degree of polymerization and to the intrinsic viscosity of polyamides. Intrinsic viscosity, which furnishes a rough comparison of the molecular weight of different polyamides, is defined as

$$\frac{\log \eta_r}{C}$$

where η_r is the viscosity of a dilute meta-cresol solution of the polyamide divided by the viscosity of meta-cresol in the same units and at the same temperature and C is the concentration in grams of polyamide per 100 cc. of solution. In general, polyamides do not exhibit fiber-forming qualities unless their intrinsic viscosity is greater than 0.4. The strength and toughness of polyamides improve with increase in intrinsic viscosity. For the preparation of most shaped ar-

articles it is desirable to use polyamides having an intrinsic viscosity above 0.6, polyamides having intrinsic viscosities between 0.8 and 2.0 being particularly useful. Quenching frequently permits the preparation of shaped articles from polyamides of lower intrinsic viscosity than would otherwise be possible. For example, in the preparation of bristles, it is possible by application of quenching to prepare satisfactory bristles using polyamides having intrinsic viscosities as low as 0.65, whereas polyamides having an intrinsic viscosity above 0.90 are usually required to prepare satisfactory bristles if quenching is not employed.

Although I do not wish to be bound by my explanation of the quenching phenomenon, I believe that the polyamides exist in at least two different crystalline forms and that quenching leads to the production of a crystalline form which is different from that obtained by slow cooling. X-ray diffraction data offer support of this theory. The X-ray patterns of both quenched and unquenched massive polyamides are characterized chiefly by two heavy rings which arise from diffraction of the X-rays by the principal spacings of the polymers, and by fogging which arises from other spacings either normal or strained. In the pattern of quenched polyhexamethylene adipamide, for example, the two prominent rings represent spacings of about 4.32 Å. and 3.82 Å., while in unquenched polyhexamethylene adipamide one is 4.32 Å. but the other is 3.68 Å. When specimens of the two materials are cold drawn, the diffraction patterns show orientation; breaking of the rings into arcs occurs to the same degree in each and the spacing difference observed in the massive form remains.

The following examples describe the invention in greater detail:

Example I

A sample of polyhexamethylene adipamide (derived from hexamethylenediamine and adipic acid) having an intrinsic viscosity of approximately 0.80 was formed into bristles as follows. The molten polymer was spun directly from the autoclave in which it was prepared by extrusion through a spinneret aperture 0.055 inch in diameter attached to the bottom of the autoclave. The spinning was effected at 290° C. under a pressure of 200 lb./sq. in., applied with oxygen-free nitrogen. The filament was extruded at a rate of 120 ft./min. into a bath of cold water placed 2.5 inches below the spinneret orifice. The filament obtained in this way had a diameter of approximately 0.023 inch. The filament was quite tough and could be cold drawn without breakage. However, it was found that soaking the filament in water for eighteen hours prior to drawing facilitated the cold drawing operation. Filaments which were cold drawn 300%, i. e., until the length was four times that of the original filament proved very useful as artificial bristles.

When filaments of the same size were melt spun from the above polyamide without quenching, the product was less tough than that described above and could not be cold drawn satisfactorily due to breakage.

Example II

A film of polyhexamethylene adipamide of intrinsic viscosity 1.6 was prepared by flowing a

solution of the polymer in formic acid on a glass plate and allowing the solvent to evaporate. The film obtained in this way was opaque. The glass plate and film were then heated above the melting point of the polymer until the latter melted and became clear and transparent. The plate and film were then plunged into cold water. The polyamide solidified yielding a transparent film of good clarity which could be oriented by application of stress.

Example III

Polyhexamethylene adipamide of intrinsic viscosity 0.90 was prepared by heating with stirring 786 parts by weight of hexamethylene diammonium adipate and a viscosity stabilizer consisting of 5.7 parts by weight of adipic acid and 4.6 parts by weight of hexamethylene diammonium acetate in an oxygen-free atmosphere for 1.5 hours at 290° C. The autoclave was then evacuated to 60 mm. for five minutes, oxygen-free nitrogen was introduced, and the melt held at 290° C. for one hour. The molten polyamide was then extruded from the bottom of the autoclave through a tube having an inside diameter of 0.25 inch, the lower end of which was situated 0.25 inch above the bite of two forming rolls which were immersed to one-half their diameter in cold water and were operated by a variable speed motor. The extruded polymer passed between the rolls and was quenched, as soon as it was shaped, by the water in which the rolls were immersed. The extruded polymer was thus formed into ribbons, 0.5 inch wide and 0.048 inch thick. (When ribbon of a given width was desired it was found desirable to have grooves of the desired width machined into the periphery of one of the rolls.) The ribbon was very tough, strong, and pliable. It could be bent double without breaking and could be cold drawn into an oriented ribbon. On the other hand, ribbons prepared in the same way but without quenching were much less pliable.

Although this invention has been described with particular reference to polyamides, it is applicable broadly to fiber-forming synthetic linear condensation polymers. As examples of such polymers might be mentioned polyesters, polyacetals, polyethers, polyester-polyamides, and other copolymers.

It is to be understood that the aforementioned examples are illustrative merely of the manner of carrying out the practical application of this invention. The process has been described with particular reference to polyamides because they form an especially useful class of polymers. A valuable class of polyamides for use in this invention comprise those derived from diamines of formula $\text{NH}_2\text{CH}_2\text{RCH}_2\text{NH}_2$ and dicarboxylic acids of formula $\text{HOOCCH}_2\text{R}'\text{CH}_2\text{COOH}$ and amide-forming derivatives of these reactants, R and R' in said formulae representing divalent hydrocarbon radicals free from olefinic and acetylenic unsaturation and R having a chain length of at least two carbon atoms. An especially valuable group of polyamides within this class are those in which R is $(\text{CH}_2)_x$ and R' is $(\text{CH}_2)_y$ wherein x is at least two. As examples of polyamides which fall within one or both of these groups might be mentioned polytetramethylene adipamide, polytetramethylene suberamide, polytetramethylene sebacamide, polypentamethylene sebacamide, polyhexamethylene adipamide, polyhexamethylene beta-methyl adipamide, polyhexamethylene sebacamide, polyoctamethylene adipamide, poly-

decamethylene adipamide, polydecamethylene p-phenylene diacetamide, and poly-p-xylylene sebacamide.

- This invention is also of importance in connection with linear condensation polyamides derived from monoaminomonocarboxylic acids and their amide-forming derivatives. As examples of such polyamides might be mentioned those derived from 6-aminocaproic acid, 9-aminononanoic acid, and 11-aminoundecanoic acid. It is also within the scope of this invention to quench mixtures of polyamides or interpolymers or copolymers, i. e., polyamides prepared from a mixture of polyamide-forming reactants, e. g., a mixture of two or more diamines with one or more dicarboxylic acids, or a mixture of a diamine, a dicarboxylic acid, and an amino acid.

- This invention is not limited to the quenching of polyamides and polyamide-articles consisting solely of fiber-forming linear condensation polyamides. Other materials such as plasticizers, melting point depressors, e. g., o-hydroxydiphenyl and diphenylolpropane, pigments, extenders, fillers, dyes, resins, oils, cellulose derivatives, and the like may be present in addition to the polyamide. Thus, a quenched polyamide filament containing 3% of titanium dioxide as a delusterant is tougher and more pliable than an unquenched filament of the same composition. The foreign material if present in moderate amounts does not interfere with the beneficial effects of the quenching operation.

- It will be evident to those skilled in the art that the quenching can be effected in a variety of ways. It is not absolutely essential that the polyamide come in contact with the liquid medium, although this is the preferred procedure particularly when operating with articles, such as filaments, films, ribbons, and the like. It is within the scope of this invention, however, to impart toughness to polyamides by rapidly cooling the container containing the hot polyamide. Thus, it has been found that if the polyamide is heated in a suitable vessel and the vessel rapidly cooled with water, brine, or the like, the polymer obtained is tougher than that obtained by allowing the polymer to cool more slowly. For certain applications it is desirable in preparing polyamides to chill the polymer rapidly in the reaction vessel in which it is formed, but in general it is more desirable to discharge the molten polymer directly from the reaction vessel into a suitable cooling liquid. This is particularly desirable when the polyamide is to be used as such in the manufacture of shaped articles.

- It will be evident from the foregoing discussion that this invention provides a simple and economical method for improving the properties of synthetic fiber-forming linear condensation polyamides. Application of this invention yields a tough, strong, and pliable polymer which has many applications in the art. The invention is particularly useful in the preparation of large polyamide filaments, bristles, films, sheets, ribbons, foils, and the like, since it greatly improves the drawing qualities of these articles. Another advantage in connection with films and sheets is that the process herein described improves the clarity of the products. Large filaments prepared by the process of this invention are useful as bristles, horsehair substitutes, mohair substitutes, tennis strings, musical instrument strings, surgical sutures, fish line leaders, dental floss, and the like.

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 fiber-forming synthetic linear polyamide in the form of sheet material having crystal aggregates whose average diameter is less than 10 two microns.
2. In the treatment of fiber-forming synthetic linear condensation polymers, the step comprising rapidly chilling the hot polymer with a liquid having substantially no solvent action on the polymer under the conditions used.
3. In the manufacture of shaped products from synthetic linear condensation polymers, the step comprising rapidly chilling the hot polymer in predetermined shape by quenching it in a liquid which has no substantial solvent action on the polymer under the conditions used.
4. In the manufacture of filaments from fiber-forming synthetic linear condensation polymers, the steps comprising extruding filaments from the molten polymer into a liquid which rapidly chills the filaments, said liquid having substantially no solvent action on the polymer, and cold drawing the filaments.
5. In the treatment of fiber-forming synthetic linear polyamides, the step comprising rapidly chilling the hot polyamide with a liquid when the polyamide is at a temperature not substantially below its melting point, said liquid having substantially no solvent action on the polymer under the conditions used.
6. In the manufacture of shaped products from synthetic linear condensation polyamides, the step comprising rapidly chilling the hot polyamide in predetermined shape by quenching it in a liquid which has no substantial solvent action on the polyamide under the conditions used.
7. In the manufacture of shaped products from synthetic linear condensation polyamides, the step comprising rapidly chilling the hot polyamide in predetermined shape by quenching it in water.
8. In the manufacture of filaments from fiber-forming synthetic linear polyamides, the steps comprising forming the molten polyamide into a filament and rapidly chilling the hot filament by quenching it in a liquid which has no substantial solvent action on the polyamide under the conditions of operation.
9. In the manufacture of large filaments including bristles, rods, and the like, the steps comprising forming a molten synthetic linear condensation polyamide into a filament, rapidly chilling the hot filament with a liquid having substantially no solvent action thereon, and cold drawing the filament.
10. In the manufacture of sheet material including films and ribbons, the steps comprising forming the sheet material from a molten fiber-forming linear polyamide, and then rapidly chilling the hot polyamide by quenching it in a liquid having no substantial solvent action on the polyamide.
11. In the manufacture of shaped products from synthetic polyamides capable of being cold drawn into oriented fibers, the steps comprising shaping the desired product from the polyamide, and rapidly chilling said product when it is at a temperature below its decomposition point but

not substantially below its melting point by means of a liquid having no appreciable solvent action on the polyamide.

12. The manufacture set forth in claim 6 in which said polyamide is obtained by reacting a diamine and a substance of the class consisting of dicarboxylic acids and amide-forming derivatives of dibasic carboxylic acids.

13. The manufacture set forth in claim 6 in which the polyamide is polymeric hexamethylene adipamide.

14. The manufacture set forth in claim 10 in which the polyamide is polymeric hexamethylene adipamide.

15. In the manufacture of sheet material including films and ribbons, the steps comprising forming sheet material from a molten fiber-forming linear condensation polymer, and then rapidly chilling the hot polymer by quenching it

in a liquid having no substantial solvent action on the polymer.

16. A fiber-forming synthetic linear polyamide in the form of a shaped article having crystal aggregates whose average diameter is less than two microns.

17. A filament comprising synthetic linear polyamide having crystal aggregates whose average diameter is less than two microns.

18. Dental floss comprising synthetic linear polyamide having crystal aggregates whose average diameter is less than two microns.

19. The manufacture set forth in claim 6 in which said polyamide is polyhexamethylene sebacamide.

20. The manufacture set forth in claim 8 in which said polyamide is polyhexamethylene sebacamide.

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