

UNITED STATES PATENT OFFICE

2,130,948

SYNTHETIC FIBER

Wallace Hume Carothers, Wilmington, Del., assignor to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

No Drawing. Application April 9, 1937,
Serial No. 136,031

56 Claims. (Cl. 18—54)

This invention relates to new compositions of matter, and more particularly to synthetic linear condensation polyamides and to filaments, fibers, yarns, fabrics, and the like prepared therefrom.

5 The present application is a continuation-in-part of my application Serial Number 91,617, filed July 20, 1936, which is a continuation-in-part of application Serial Number 74,811, filed April 16, 1936, which is a continuation-in-part of abandoned application Serial Number 34,477, filed 10 August 2, 1935, which in turn is a continuation-in-part of application Serial Number 181, filed January 2, 1935; and of U. S. Patent 2,071,251, filed March 14, 1933; and of U. S. Patent 2,071,250, 15 filed July 3, 1931.

Products obtained by the mutual reaction of certain dibasic carboxylic acids and certain organic diamines have in the past been described by various investigators. For the most part, these 20 products have been cyclic amides of low molecular weight. In a few cases they have been supposed to be polymeric, but they have been either of low molecular weight or completely infusible and insoluble. In all cases, they have been devoid 25 of any known utility. These statements may be illustrated by the following citations: Ann. 232, 227 (1886); Ber. 46, 2504 (1913); Ber. 5, 247 (1872); Ber. 17, 137 (1884); Ber. 27 R, 403 (1894); Ann. 347, 17 (1906); Ann. 392, 92 (1912); 30 J. A. C. S. 47, 2614 (1925). Insofar as I am aware, the prior art on synthetic polyamide fibers, and on polyamides capable of being drawn into useful fibers, is non-existent.

This invention has as an object the preparation 35 of new and valuable compositions of matter, particularly synthetic fiber-forming materials. Another object is the preparation of filaments, fibers, and ribbons from these materials. A further object is the manufacture of yarns, fabrics, 40 and the like from said filaments. Other objects will become apparent as the description proceeds.

The first of these objects is accomplished by 45 reacting together a primary or secondary diamine (described comprehensively as a diamine having at least one hydrogen attached to each nitrogen) and either a dicarboxylic acid or an amide-forming derivative of a dibasic carboxylic acid until a product is formed which can be 50 drawn into a continuous oriented filament. The second object is attained by spinning the polyamides into filaments, and preferably, subjecting the filaments to stress ("cold drawing") thereby 55 converting them into oriented filaments or fibers.

The third of these objects is accomplished by combining the filaments into a yarn and knitting, weaving, or otherwise forming the yarn into a fabric.

The term "synthetic" is used herein to imply 5 that the polyamides from which my filaments are prepared are built up by a wholly artificial process and not by any natural process. In other words, my original reactants are monomeric or relatively low molecular weight substances. 10

The term "linear" as used herein implies only those polyamides obtainable from bifunctional reactants. The structural units of such products are linked end-to-end and in chain-like fashion. The term is intended to exclude three-dimen- 15 sional polymeric structures, such as those that might be present in polymers derived from triamines or from tribasic acids.

The term "polyamide" is used to indicate a polymer containing a plurality of amide linkages. 20 In the linear condensation polyamides of this invention the amide-linkages appear in the chain of atoms which make up the polymer.

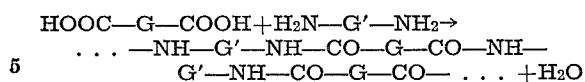
The terms "fiber-forming polyamide" is used to indicate that my products are capable of being 25 formed directly, i. e., without further polymerization treatment, into useful fibers. As will be more fully shown hereinafter, fiber-forming polyamides are highly polymerized products and for the most part exhibit crystallinity in the massive 30 state.

The term "filament" as used herein refers to both the oriented and unoriented filaments or threads which are prepared from the polyamides 35 regardless of whether the filaments or threads are long (continuous) or short (staple), large or small, while the term "fiber" will refer more specifically to the oriented filaments or threads whether long or short, large or small. 40

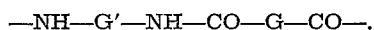
The expression "dibasic carboxylic acid" is used to include carbonic acid and dicarboxylic acids. By "amide-forming derivatives of dibasic carboxylic acids" I mean those materials such as anhydrides, amides, acid halides, half esters, 45 and diesters, which are known to form amides when reacted with a primary or secondary amine.

The following discussion will make clear the nature of the products from which my filaments 50 and fibers are prepared, and the meaning of the above and other terms used hereinafter. If a dicarboxylic acid and a diamine are heated together under such conditions as to permit amide formation, it can readily be seen that the 55

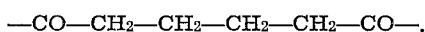
reaction might proceed in such a way as to yield a linear polyamide



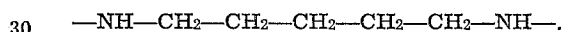
The indicated formula, in which G and G' represent divalent hydrocarbon radicals, represents the product as being composed of long chains built up from a series of identical units



This unit, derived from one molecule each of acid and diamine, may be called the "structural unit". It will be convenient to refer to the number of atoms in the chain of this unit as the "unit length". The expression "radical of a dibasic carboxylic acid" is taken to mean that fragment or divalent radical remaining after the two acidic hydroxyls have been removed from its formula. Thus the radical of carbonic acid is —CO— ; the radical of adipic acid is



The expression "radical of a diamine" indicates the divalent radical or fragment remaining after one hydrogen has been removed from each amino group. Thus the radical of pentamethylenediamine is

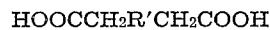


The "radical length" is, in the case of both acid and amine, the number of atoms in the chain of the radical. Thus the radical length of carbonic acid is 1; that of adipic acid is 6; and that of pentamethylenediamine is 7. The term "unit length", referred to above, obviously means the sum of the radical lengths of the diamine and the acid. Thus, the unit length of poly-pentamethylene sebacamide, the polyamide derived from sebacic acid and pentamethylenediamine, is 17.

As previously mentioned, fiber-forming polyamides can be prepared by reacting diamines with dicarboxylic acids or amide-forming derivatives of dibasic carboxylic acids, of which the most suitable are the diesters with volatile monohydric alcohols or phenols. The diamines suitable for the practice of my invention are those having at least one hydrogen attached to each of the nitrogen atoms. In other words, I may use di-primary amines, primary-secondary amines, or di-secondary amines, but never a diamine in which either amino group is tertiary. Of all these types of amines, the di-primary amines are in the great majority of instances far more satisfactory because of their greater reactivity and because they yield polyamides of higher melting points. Within the field of di-primary amines, the aliphatic amines are most suitable for the ready preparation of polyamides capable of being drawn into the highest quality fibers. By aliphatic diamine as used herein is meant a diamine in which the nitrogens are attached to aliphatic carbons, (i. e., carbon atoms which are not a part of an aromatic ring). Mixtures of diamines of any of the mentioned operable types may also be used. Fiber-forming polyamides may also be prepared from one or more diamines and (a) mixtures of different dicarboxylic acids (b) mixtures of amide-forming derivatives of different dibasic carboxylic acids (c) mixtures of dicarboxylic acids and/or amide-forming derivatives of dibasic carboxylic acids with one or more monoaminomonocarboxylic acids or amide-forming derivatives thereof.

While the fiber-forming polyamides used in my invention can be prepared from a wide variety of diamines and dicarboxylic acids or amide-forming derivatives of dibasic carboxylic acids, I have found that a preferred selection of amine and acid is that in which the sum of the radical lengths is at least 9. Such a pair of reactants has very little if any tendency to form low molecular weight cyclic amides, and the polyamides therefrom are more generally soluble or fusible, one of these properties being necessary for spinning. I have, however, met with some success in preparing fiber-forming polyamides from amines and acids the sum of whose radical lengths is less than 9. As an example of a fiber-forming polyamide having a relatively short structural unit may be mentioned that from pentamethylenediamine and dibutyl carbonate.

Of the fiber-forming polyamides having a unit length of at least 9, a very useful group from the standpoint of fiber qualities are those derived from diamines of formula $\text{NH}_2\text{CH}_2\text{RCH}_2\text{NH}_2$ and dicarboxylic acids of formula



or amide-forming derivatives thereof, in which R and R' are divalent hydrocarbon radicals free from olefinic and acetylenic unsaturation (i. e., non-benzenoid unsaturation) and in which R has a chain length of at least two carbon atoms. The R and R' may be aliphatic, alicyclic, aromatic, or araliphatic radicals. Of this group of polyamides, those in which R is $(\text{CH}_2)_x$ and R' is $(\text{CH}_2)_y$ where x and y are integers and x is at least two, are especially useful from the standpoint of spinnability and fiber qualities. They are easily obtained at an appropriate viscosity for spinning and have a type of crystallinity which enables them to be cold drawn with especial facility. As valuable members of this class may be mentioned polypentamethylene adipamide, polyhexamethylene adipamide, polyoctamethylene adipamide, polydecamethylene adipamide, polypentamethylene suberamide, polyhexamethylene suberamide, polydecamethylene suberamide, polypentamethylene sebacamide, polyhexamethylene sebacamide, and polyoctamethylene sebacamide.

My fiber-forming polyamides are prepared by heating in substantially equimolecular amounts a diamine and a dicarboxylic acid or an amide-forming derivative of a dibasic carboxylic acid under condensation polymerization conditions, generally 180 to 300° C., in the presence or absence of a diluent, until the product has a sufficiently high molecular weight to exhibit fiber-forming properties. The fiber-forming stage can be tested for by touching the molten polymer with a rod and drawing the rod away; if this stage has been reached, a continuous filament of considerable strength and pliability is readily formed. This stage is reached essentially when the polyamide has an intrinsic viscosity of about 0.4, where intrinsic viscosity is defined as

$$\frac{\log_e \lambda_r}{C}$$

in which λ_r is the viscosity of a dilute solution (e. g., 0.5% concentration) of the polymer in m-cresol divided by the viscosity of m-cresol in the same units and at the same temperature (e. g., 25° centigrade) and C is the concentration in grams of polymer per 100 cc. of solution. If products capable of being formed into fibers of optimum quality are to be obtained, it is desira-

ble to prolong the heating beyond that point where the intrinsic viscosity has become 0.4. In general products having an intrinsic viscosity between 0.5 and 2.0 are most useful for the preparation of fibers.

In common with other condensation polymerization products the fiber-forming polyamides will in general comprise a series of individuals of closely similar structure. The average size of these individuals, i. e., the average molecular weight of the polymer, is subject to deliberate control within certain limits; the further the reaction has progressed the higher the average molecular weight (and intrinsic viscosity) will be. If the reactants are used in exactly equimolecular amounts and the heating is continued for a long time under conditions which permit the escape of the volatile products, polyamides of very high molecular weight are obtained. However, if either reactant is used in excess, the polymerization proceeds to a certain point and then essentially stops. The point at which polymerization ceases is dependent upon the amount of diamine or dibasic acid (or derivative) used in excess. The reactant added in excess is spoken of as a "viscosity stabilizer" and the polymer obtained with its use is spoken of as a "viscosity stable polymer", since its intrinsic viscosity is not altered appreciably by further heating at spinning temperatures. Polyamides of almost any intrinsic viscosity can be prepared by selecting the proper amount of stabilizer. In general from 0.1 to 5.0% excess reactant is used in making viscosity stable polyamides. The viscosity stable polyamides are particularly useful in spinning filaments from melt since they do not change appreciably in viscosity during the course of the spinning operation.

In general my fiber-forming polyamides are prepared most economically from a diamine and a dicarboxylic acid. The first reaction which occurs when a diamine and a dicarboxylic acid are mixed and brought into sufficiently intimate contact is the formation of the diamine-dicarboxylic acid salt. Such salts are generally solids and since their tendency to dissociate into their components is relatively low, both the acid and amine are fixed. The mixture can therefore be subjected immediately to heat in an open vessel without danger of losing amine or acid and so disturbing the balance in the proportion of reactants. Frequently, however, it is advantageous to isolate the salt and purify it prior to conversion into the polyamide. The preparation of the salts affords an automatic means for adjusting the amine and acid reactants to substantial equivalency and it avoids the difficulty attendant upon the preservation of the isolated amines in the state of purity. It also tends to eliminate impurities present in the original diamine and dicarboxylic acid.

A convenient method of preparing these salts consists in mixing approximately chemical equivalent amounts of the diamine and the dicarboxylic acid in a liquid which is a poor solvent for the resultant salt. The salt which separates from the liquid can then be purified, if desired, by crystallization from a suitable solvent. The salts are crystalline and have definite melting points. They are, as a rule, soluble in water and may conveniently be crystallized from certain alcohols and alcohol-water mixtures. They are relatively insoluble in acetone, benzene, and ether.

The preparation of fiber-forming polyamides

from the diamine-dicarboxylic acid salts can be carried out in a number of ways. The salt may be heated in the absence of a solvent or diluent (fusion method) to reaction temperature (usually 180-300° C.) under conditions which permit the removal of the water formed in the reaction, until examination of the test portion indicates that the product has good fiber-forming qualities. It is desirable to subject the polyamide to reduced pressure, e. g., an absolute pressure equivalent to 50 to 300 mm. of mercury, before using it in making filaments and other shaped objects. This is conveniently done by evacuating the reaction vessel in which the polyamide is prepared before allowing the polymer to solidify. Another procedure for preparing polyamides consists in heating a salt in an inert solvent for the polymer, preferably a monohydric phenol such as phenol, m-cresol, o-cresol, p-cresol, xylenol, p-butyl phenol, thymol, diphenylolpropane, and o-hydroxydiphenyl. With the solvents may be associated, if desired, non-solvents which are non-reactive, such as hydrocarbons, chlorinated hydrocarbons, etc. When the reaction has proceeded far enough to give a polymer of good fiber-forming qualities, the mixture can be removed from the reaction vessel and used as such (e. g., for spinning from solution) or the polymer can be separated from the solvent by precipitation, i. e., by mixing with a non-solvent for the polymer such as alcohol, ethyl acetate, or a mixture of the two. Still another method of preparation consists in heating the salt in the presence of an inert non-solvent for the polymer such as high boiling hydrocarbons of which white medicinal oil may be mentioned. The methods can also be applied directly to the diamine and dicarboxylic acid without first isolating the salt.

In place of using the diamine and dicarboxylic acid (or the salt), a diamine and an amide-forming derivative of a dibasic carboxylic acid may be used in the preparation of the polyamide. The reaction may be carried out in the absence of a solvent, in the presence of a solvent, in the presence of a diluent which is not a solvent for the polymer, or in the presence of a mixture of solvent and diluent. The reaction conditions, as indicated in my co-pending application Serial Number 181, differ somewhat with the nature of the amide-forming derivative used. For example, the esters of dibasic carboxylic acids, and particularly the aryl esters, react with diamines at a lower temperature than do the acids themselves, often at temperatures as low as 50° C. In a specific experiment hexamethylenediamine and dicyclic adipate yielded a fiber-forming polyamide in 2.5 hours heating at 155° C.

The polyamides of this invention compared with most organic compounds are fairly resistant to oxidation. Nevertheless, at the high temperatures used in their preparation (e. g., 250° C.) they show a strong tendency to become discolored in the presence of air. For this reason, it is desirable to exclude air or to limit the access of air during their preparation. This may be done by operating in a closed vessel during the early stages of the reaction, or, if an open vessel is used, by providing a stream of inert gas. It is helpful in some cases to add antioxidants to the reaction mixture, especially antioxidants such as syringic acid that show very little inherent tendency to discolor. It is also important to exclude oxygen from the polymer during spinning.

In general, no added catalysts are required in the above described processes of the present in-

vention. It should be mentioned, however, that the surface of the reaction vessel (e. g., glass) appears to exercise a certain degree of catalytic function in many cases. The use of added catalysts sometimes confers additional advantages. Examples of such materials are inorganic materials of alkaline reaction such as oxides and carbonates, and acidic materials such as halogen salts of polyvalent metals, for example, stannous chloride.

The polyamides can be prepared in reactors constructed of or lined with glass, porcelain, enamel, silver, gold, tantalum, platinum, palladium, rhodium, alloys of platinum with palladium and/or rhodium, chromium plated metals, and chromium containing ferrous metals, including chromium-nickel steels. In order to obtain light-colored products it is generally necessary to carry out the reaction in substantially complete absence of oxygen. This means that if commercial nitrogen is maintained over or passed through the reaction mixture it should be washed free of oxygen. As examples of other inert gases which may be used to blanket the polymer during preparation or spinning may be mentioned carbon dioxide and hydrogen.

The properties of a given polyamide will vary over a considerable range, depending upon its molecular weight and in part on the nature of its terminal groups which in turn is dependent upon which reactant was used in excess. The average molecular weights of the polyamides are very difficult to determine on account of their limited solubility in suitable solvents. A precise knowledge of average molecular weights is, however, not important for the purposes of this invention. In a rough way it may be said that two stages or degrees of polymerization exist: low polymers whose molecular weights probably lie in the neighborhood of 1000 to 4000, and fiber-forming polyamides whose molecular weights probably lie above 7000. The most obvious distinction between low polymers and the high polymers or "superpolymers" is that the former when molten are relatively less viscous. The high polymers even at temperatures 25° C. above their melting points are quite viscous. The high polymers also dissolve more slowly than the low polymers and solution is preceded by swelling. Practically the most important distinction between the two types is that the high polymers are readily spun into strong, continuous, pliable, permanently oriented fibers, while this property is lacking in the low polymers. In general the low polymers, and in particular those having a unit length of at least 9, can be converted into high polymers by a continuation of the reaction by which the low polymers were formed.

Two of the most characteristic properties of the fiber-forming polyamides used in this invention are their high melting points and low solubilities. Those derived from the simpler types of amines and acids are almost invariably opaque solids that melt or become transparent at a fairly definite temperature. Below their melting points the fiber-forming polyamides when examined by X-rays generally furnish sharp X-ray crystalline powder diffraction patterns, which is evidence of their crystalline structure in the massive state. Densities of these polyamides generally lie between 1.0 and 1.2, which is considerably lower than that of previously described artificial fiber-forming materials. Their refractive index is usually in the neighborhood of 1.53. Typical melting points are shown in Table I. All of the

polyamides in this table are capable of being spun into continuous filaments.

TABLE I

Approximate melting points of some fiber-forming polyamides

Polyamide derived from—	M. P. °C.
Ethylenediamine and sebacic acid.....	254
Tetramethylenediamine and adipic acid.....	278
Tetramethylenediamine and suberic acid.....	250
Tetramethylenediamine and azelaic acid.....	223
Tetramethylenediamine and sebacic acid.....	239
Tetramethylenediamine and undecanedioic acid.....	208
Pentamethylenediamine and malonic acid.....	191
Pentamethylenediamine and glutaric acid.....	198
Pentamethylenediamine and adipic acid.....	223
Pentamethylenediamine and pimelic acid.....	183
Pentamethylenediamine and suberic acid.....	202
Pentamethylenediamine and azelaic acid.....	178
Pentamethylenediamine and undecanedioic acid.....	173
Pentamethylenediamine and brassylic acid.....	176
Pentamethylenediamine and tetradecanedioic acid.....	170
Pentamethylenediamine and octadecanedioic acid.....	167
Hexamethylenediamine and sebacic acid.....	209
Hexamethylenediamine and beta-methyl adipic acid.....	216
Hexamethylenediamine and 1, 2-cyclohexanediocetic acid.....	255
Octamethylenediamine and adipic acid.....	235
Octamethylenediamine and sebacic acid.....	197
Decamethylenediamine and carbonic acid.....	200
Decamethylenediamine and oxalic acid.....	229
Decamethylenediamine and sebacic acid.....	194
Decamethylenediamine and para-phenylene diacetic acid.....	212
Para-xylylenediamine and sebacic acid.....	268
3-Methylhexamethylenediamine and adipic acid.....	180
Piperazine and sebacic acid.....	153
Hexamethylenediamine and diphenic acid.....	157

The melting points are dependent to some extent upon the heating schedule used and the conditions of thermal contact, but when carried out by the same operator under the same conditions they are fairly sharp and reproducible. The melting points indicated in the table were determined by placing fine particles of the polyamide on a heated metal block in the presence of air and noting the temperature of melting or fusion. Values obtained in this way are usually from 5 to 20° C. lower than those obtained by noting the temperature at which the polyamide melts when heated in a glass tube in the absence of oxygen. The melting points are considerably affected by the nature of the acid and the diamine used in their preparation. In particular melting points generally diminish with increasing unit length and increasing degree of substitution on the hydrocarbon chain. Increased solubility also runs in the same direction, but is not greatly affected by the molecular weight. For the most part, the polyamides used in the preparation of the filaments and fibers of this invention can be dissolved in hot glacial acetic acid, in formic acid, or in phenols, but are quite insoluble in most of the other usual types of organic solvents. However, polyamides derived from reactants having a hydrocarbon side chain, e. g., 3-methylhexamethylenediamine, betamethyl adipic acid, and the like, are soluble in a wider range of solvents including alcohols. This is often true also of interpolymers or copolymers, i. e., polyamides derived from a mixture of reactants capable of yielding more than one polyamide if reacted in suitable combinations. Thus, the interpolyamide derived from equimolecular amounts of hexamethylene diammonium adipate and decamethylene diammonium sebacate is soluble in ethanol and butanol.

In the finely divided state or in the form of filaments and fibers the polyamides of this invention are attacked by strong mineral acids, such as hydrochloric or sulfuric acid, and on

heating with such acids they are hydrolyzed to the dibasic acids and diamines from which they are derived. When reference is made in the claims to the formation of a "diamine" by acid hydrolysis, it is to be understood that the term includes the mineral acid salt of the diamine. The polyamides are resistant to attack by strong caustic alkalies but these agencies also will finally hydrolyze them to the diamines and dibasic acids.

The polyamides of this invention can be spun into continuous filaments in a number of ways. They can be spun directly from the reaction vessel in which they are prepared by attaching a suitable spinneret to the bottom thereof or they can be removed and spun from a separate device. One method of spinning (wet process) consists in dissolving the polyamide in a suitable solvent and extruding the resulting solution through orifices into a liquid which dissolves the solvent but not the polyamide, and continuously collecting the filaments thus formed on a suitable revolving drum or spindle. Another method (dry process) consists in extruding a solution of the polyamide into a heated chamber where the solvent is removed by evaporation. Still another method (melt process) consists in extruding the molten polyamide through orifices into the atmosphere where it congeals into a filament. In these various methods of spinning the fiber-forming mass may be forced through the orifices by means of gas pressure or by means of a constant volume delivery pump. By similar processes the polyamides can be formed into rods, bristles, sheets, foils, ribbons, films, and the like. In the various methods of forming shaped articles from fiber-forming polyamides, and particularly when this is done from solutions of the polymers, the characteristics of the filaments, etc., may be altered by blending the polyamides with other polyamides or with resins, plasticizers, cellulose derivatives, etc. As cellulose derivatives which can be blended with the polyamide solutions might be mentioned ethyl cellulose, benzyl cellulose, and cellulose acetate.

A remarkable characteristic of filaments of this invention is their ability to accept a very high degree of permanent orientation under stress. Although the unoriented or slightly oriented filaments are sufficiently pliable and strong for some purposes the highly oriented filaments or fibers are in general more useful. Filaments obtained by spinning the polyamides under such conditions that no stress is applied closely resemble the polymer from which they are spun. In particular, when examined by X-rays they generally furnish X-ray crystalline powder diffraction patterns. However, although ordinary spinning conditions, and especially with certain polyamides, e. g., polypentamethylene sebacamide, may produce a filament that shows by the X-ray test orientation in some degree, nevertheless it is advantageous to subject the filaments subsequently to a cold drawing process (i. e., stretching below the melting point of filament). By this cold drawing the filaments can be elongated as much as 200 to 700%. The elongation is accompanied by a progressive increase in tensile strength until a definite limit is reached beyond which the application of additional stress causes the fiber to break. The cold-drawn filaments remain permanently extended, they are much stronger than the material from which they are drawn, more elastic, and when examined by X-rays they furnish a sharp diffraction fiber pattern. They also exhibit strong birefringence and

parallel extinction when observed under crossed Nicol prisms. This evidence of fiber orientation shows that the cold drawn filaments are true fibers. The fibers can be doubled and/or twisted into threads or yarns suitable for the manufacture of fabrics. Sometimes it is desirable to set the twist in these yarns by means of heat, preferably by steam treatment. If desired, the filaments used in the preparation of the fibers can be twisted before cold drawing.

When the wet process is used in spinning synthetic linear condensation polyamides, it is desirable to use polymers having an intrinsic viscosity of at least 1.0. Polymers of lower intrinsic viscosity can be used with some success, however, by using high concentrations of polymer and by extruding the solvent from the spinneret at elevated temperatures, e. g., 100-200° C. Especially useful solvents for the wet spinning process are phenol and formic acid. In the case of certain polyamides, e. g., polyhexamethylene betamethyl adipamide, alcohols can be used as solvents. Other solvents which may be used include various phenols, e. g., cresol and xylenol; lower fatty acids, such as acetic, chloroacetic, propionic, and butyric; and, if elevated temperatures are avoided, certain chlorohydrins, such as epichlorohydrin and glycerol dichlorohydrin, and certain mineral acids, e. g., hydrochloric, sulfuric, and hydrofluoric. Anhydrous hydrogen fluoride is a good polyamide solvent. Mixtures of these solvents can also be used. Moreover, the solvents may be diluted with non-solvents, such as water, dioxane, isobutanol, chloroform, benzene, and the like. The presence of the non-solvent increases the rate of coagulation in the spinning bath. The concentration of the polyamide solutions required for successful spinning vary with the intrinsic viscosity of the polyamide used. Polymers of high intrinsic viscosity can be spun at lower concentrations than those of lower intrinsic viscosity. When phenol alone is used as solvent, it is necessary to operate at elevated temperature, generally above 75° C. and preferably in the range of 100-200° C. depending upon the concentration and intrinsic viscosity of the polyamide. These phenol solutions gel at room temperature. At the elevated temperature required to spin such solutions, it is generally impossible to immerse the spinneret in the coagulating bath as is done in normal wet spinning practice unless the temperature of the coagulating bath is kept sufficiently high. If, however, the phenol solution is diluted with a suitable amount of non-solvent, preferably water, it is possible to spin at ordinary temperatures and to immerse the spinneret in the coagulating bath. Solutions of polymer in 85-95% phenol (5-15% water) can be spun in this way at ordinary temperatures. This method of spinning is more satisfactory than spinning from anhydrous phenol.

The spinning or coagulating bath used in wet spinning consists of a liquid which dissolves the polyamide solvent but not the polyamide itself. The spinning bath should gel the polymer rather than precipitate it. The coagulating process differs from that which occurs in viscose spinning in that the fiber-forming material does not undergo a chemical change during the process. The coagulating liquid selected will depend in part on the nature of the solvent from which the polyamide is spun. In spinning polyamides from a phenol or acid solution, aqueous alkaline spinning baths, particularly dilute solutions of sodium hydroxide or sodium sulfide (preferably 2-10%) con-

centration are very useful. Various salts, e. g., sodium tartrate, disodium phosphate and sodium citrate, can be added to these alkaline baths. The addition of wetting agents is sometimes helpful. Many organic liquids which are non-solvents for the polyamides, such as esters, ethers, ketones, and amines can also be used. As examples of such substances might be mentioned ethyl butyrate, glycol acetate, diethyl succinate, dioxane, dibutyl ether, methyl hexyl ketone, pyridine, toluene, xylene, and kerosene. In general, the aqueous alkaline baths cause more rapid coagulation of the polyamides than do baths composed of organic solvents. Increasing the temperature of the bath also increases the rate of coagulation; temperatures of 40–80° C. are very suitable.

In order to obtain filaments of satisfactory strength in the wet spinning process, drawing of the filaments in the bath should be avoided as much as possible until coagulation is complete. Stretching in the bath can be minimized by running the filaments over a motor driven guide roll immediately after entering the bath. The size (i. e., the length) of the spinning bath required will depend somewhat upon the nature of the polyamide solution and of the coagulating liquid but also upon the rate of spinning. In general, a bath seven feet in length is sufficient. The filaments can be cold drawn after coagulation is substantially complete. Cold drawing may be carried out in the coagulating bath, but is preferably done outside of the bath either before or after washing the filaments. It is preferable to carry out the cold drawing operation while the filaments are still wet. Very fine filaments can be spun by the wet process; in fact, spinning improves as the denier of the fiber is decreased. The process is best adapted to the preparation of filaments having a denier below 1.5. In contrast to the melt spinning process, the fibers obtained by this method usually have an irregular crenulated surface; in other words, a cross-section of the fiber presents an irregular area. For certain uses, e. g., in the preparation of staple, this is an advantage. The crenulated surface aids in the formation of threads and yarns from the staple. Polyamide staple can be spun into yarns and fabrics in much the same fashion as cotton.

The dry spinning process, like the wet spinning process, is best carried out with polyamides having an intrinsic viscosity of at least 1.0. However, polymers of lower intrinsic viscosity can be spun with some success by employing high concentrations and elevated temperatures. The solvents used in the dry spinning process should preferably be of relatively low boiling point so that they can be volatilized without too much difficulty. Formic acid is an exceptionally useful solvent for this purpose. However, phenol and the other solvents mentioned in connection with the wet spinning process can also be used. Non-solvents may be added to the polymer solution but are in general undesirable. Plasticizers may be added to the solutions if desired, but the nature of the fibers is such that no flexibilizing agents are necessary. Dry spinning is suitably carried out in a heated vertical chamber or cell which is provided with a spinneret at the top and an opening at the bottom for removing the filaments. The spinneret may be of the conventional rayon type (flat face); the filaments are readily thrown free of the spinneret with substantially no fouling of the spinneret face. A current of air or other gas is maintained in the

drying chamber to aid in the removal of the solvent. The dry spinning of formic acid solutions of polyamides can be performed satisfactorily with head temperatures (temperature of solution in the spinneret) of 20 to 110° C. and cell temperatures (temperature of drying or evaporating chamber) of 65 to 120° C. If the drying chamber is maintained under reduced pressure, lower cell temperatures can be used. The concentration of the solution most satisfactory for dry spinning will depend upon the intrinsic viscosity of the polymer and the spinning temperatures to be employed. Generally, it is desirable to use solutions having an absolute viscosity of at least 200 poises at the spinning temperature. The polyamide solution passes through the orifices into the spinning chamber, evaporation of solvents starts immediately and the extruded portion sets up to a filament. After the major portion of the solvent has been removed, and preferably after substantially complete removal of the solvent has taken place, the filaments can be cold-drawn into oriented fibers. The cold drawing can be carried out within the heating chamber, but preferably it is done outside the heating chamber, either as an integral part of the spinning operation or as a separate step. Fibers obtained by the dry process, like those obtained in the wet method, generally have surfaces which are crenulated.

The polyamides of this invention are of such extraordinary nature that they are also capable of being spun into continuous filaments directly from the molten mass without addition of any solvent or plasticizer. For this purpose a mass of the molten polymer may be touched with a rod. Upon drawing the rod away a filament is formed. The filament may be caught on a moving drum or reel and in this manner a continuous filament may be drawn from the molten mass until the latter is exhausted. The cross-section of the filaments thus obtained can be regulated by controlling the temperature of the molten mass and the rate of reeling. The higher the temperature and the more rapid the rate of reeling, the finer will be the filament.

Continuous filaments may also be produced by extruding the molten polyamide through an orifice, or through a spinneret containing a plurality of orifices, and continuously collecting the extruded filaments on a rotating drum. The fineness of the filaments may be controlled by controlling the temperature of the molten polymer, the amount of pressure applied or the rate of pumping, the size of the orifices, and the rate of reeling. It is possible to spin polyamide filaments at very high speeds, e. g., 3000 feet per minute. The properties of the polyamides of this invention also make it possible to obtain exceedingly fine filaments, as fine as 0.2 denier or less. The optimum temperature for the spinning of each polyamide must be worked out experimentally. Below this optimum temperature filaments of inferior quality are obtained; above this temperature the polyamide mass is too fluid for ready spinning and may be subject to decomposition. Thus, for polyhexamethylene adipamide the optimum melt spinning temperature lies between 285 and 295° C., although this depends somewhat on the spinning assembly. In spinning the polyamides from melt it is also important that oxygen be excluded from the molten polymer.

In the melt spinning process the formation of continuous oriented fibers from the filaments of this invention may be easily conducted as an inte-

gral part of the spinning operation. Thus, the extruded filaments as they are collected may be transferred continuously to a second drum driven at a higher rate of speed, so as to provide any desired degree of stretching or cold drawing. Friction devices may also be used to provide the necessary stretch. Cold drawing can also be effected by drawing the filaments through a die having an orifice smaller than that of the undrawn filament but larger than that of the cold drawn filament. It may be observed that these processes of cold drawing differ from the stretch-spinning known to the artificial fiber art in that they may be carried out very rapidly and completely in the total absence of any solvent or plasticizer. However, the stretching can also be effected in the presence of solvent or plasticizer. It is generally desirable to carry out the spinning and handling of the polyamides in a moist atmosphere or to sprinkle the filaments with water since this destroys the electrostatic charges on the filaments. Moreover, the wet filaments cold draw better than dry filaments.

Still another method for obtaining filaments from synthetic linear condensation polyamides and other polymers of this type consists in feeding the polymer in convenient form, e. g., a small rod, through a spray gun in which it is melted by an oxyacetylene flame, or other suitable device, and atomized or reduced to very fine filaments immediately by a blast of nitrogen or other gas. The polymer leaves the gun in the form of fine filaments resembling a spider web. These filaments can be used in making yarns, etc., which can be cold drawn. By impinging the blast from the spray gun directly on a proper backing, the polymer can be obtained in the form of a continuous coating.

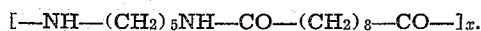
The properties of the fibers of this invention vary considerably with the nature of the reactants used in preparing the polyamides, and with the conditions of reaction and spinning. General characteristics illustrated in Example I are high tenacity, high orientation, lack of sensitivity toward conditions of humidity, exceptionally good elastic recovery, extraordinary resistance to solvents and chemical agents, and exceptionally good ageing characteristics in air even at elevated temperatures. It is possible to tie hard knots in polyamide fibers without materially decreasing their tenacity. The tenacity of the fibers is greater than 1.1 g. per denier and usually above 3.0 g. per denier. Most of the fibers have tenacities ranging from 3 to 7 g. per denier. The fibers have a strong affinity for dyes; they can be dyed rapidly, permanently and directly, with the dyes ordinarily used for wool and silk. In general, fibers prepared from dibasic acid-stabilized polymers take up basic dyes more readily than those made from diamine-stabilized polymers, while the latter have a stronger affinity for acid dyes.

The following examples, in which the parts are given by weight, are illustrative of this invention:

Example I

A mixture of 14.3 parts of pentamethylenediamine, 29.3 parts of sebacic acid, and 44 parts of mixed xylenols (B. P. 218–222° C.) was placed in a vessel fitted with a conductivity cell, a means for returning solvent lost by distillation, a means for introducing nitrogen, a thermometer, and a viscometer. The mixture was heated for 13 hours by means of the vapors of boiling naphthalene (218° C.), during which period the conductivity and viscosity were measured at appropriate inter-

vals. The conductivity dropped rapidly and the viscosity rose steadily. At the end of 13 hours, the intrinsic viscosity was 0.62, and the conductivity had dropped from an initial value of 0.0028 mhos to a final one of 0.000053 mhos. At this point, examination of a small portion of the product, separated by precipitation in alcohol and subsequent fusion, showed that it could be drawn into fibers of excellent strength. The entire reaction mass was then poured gradually with stirring into a large volume of ethyl alcohol. The polyamide precipitated as a white granular powder, and was filtered, washed with alcohol, and dried. It melted at 195–196° C. in air on a heated metal block. Analysis of the above product shows that it has the formula



Continuous filaments were prepared from the product as follows: A sample was heated at 234° C. in a cylindrical metal vessel surrounded by an electrically heated metal block and provided at the bottom with an orifice 0.47 mm. in diameter. The top of the vessel was connected with a tube through which nitrogen was passed under a gauge pressure to 3 lbs. The extruded filament was collected on a motor-driven drum having a peripheral speed of 32 feet per minute and was continuously transferred to and collected on a second drum having a peripheral speed of 164 feet per minute. The extent of the cold drawing thus produced was 100%. The resulting fiber was lustrous and silky in appearance. It showed strong birefringence with parallel extinction under crossed Nicol prisms and when examined by X-rays it furnished a sharp fiber diffraction pattern, while the same material before spinning furnished only a crystalline powder diffraction pattern. When further stress was applied to these fibers cold drawing occurred up to a total final length of 452%. Physical data on the completely cold drawn fibers were: denier at break, 0.63; tensile at break, 50.5 kg./sq. mm. or 5.2 g. per denier. The elastic recovery of these fibers under moderate elongations or stresses was very remarkable and in this respect it was much superior to existing artificial silks. In their physical behavior these fibers are almost completely insensitive to moisture. The fibers are completely resistant to the common organic solvents except such materials as hot acetic acid, formic acid or phenol, and they can for example be immersed in boiling toluene for a week without any noticeable effect. They are also very resistant to the effects of air and high temperature. They show no signs of tendering after storage for a month in air at 110° C. However, on heating with strong mineral acid, such as hydrochloric, hydrobromic, sulfuric, or phosphoric, these fibers disintegrate and are hydrolyzed to sebacic acid and pentamethylenediamine (mineral acid salt).

Polypentamethylene sebacamide (intrinsic viscosity 0.67) prepared by heating purified pentamethylenediamine-sebacic acid salt for three hours under conditions similar to those described above was spun into fibers (250% cold drawing, applied in two stages) having a denier of 4.9 and a tenacity at break of 7.1 g. per denier. These fibers were plied into a 123-denier, 24-filament yarn having four twists per inch. This yarn was then knit into a fabric and compared with a similar fabric knitted from 95-denier, 7-thread, 10-turn silk. The polyamide fabric was found to have far better elastic recovery than natural silk, particularly under conditions of high

stretch (100%), high humidity (85%) or wet, and for long periods of time (15 hours). This is illustrated by Table II.

5
10
15
TABLE II
Elastic recovery of knitted fabric

Percent stretched	Time held	Relaxation	Silk recovery		Polyamide recovery	
			85% R. H.*	Wet **	85% R. H.*	Wet
25	3 min.	1 min.	65	---	77	79
35	3 min.	1 min.	58	43	71	79
45	3 min.	1 min.	48	38	76	79
75	3 min.	1 min.	24	34	73	80
100	3 min.	1 min.	---	32	71	80
25	15 hrs.	5 min.	25	---	---	---
50	15 hrs.	5 min.	---	---	53	---

* Relative humidity.

** Wet with water.

20
25
At the end of the above tests (held three minutes), the silk fabric was drastically and permanently distorted while the polyamide fabric returned to essentially its former shape. Threads removed from the polyamide fabric also retained their wavy form much better than did the silk threads.

30
35
40
45
50
The polyamide fibers and fabrics are almost insensitive to moisture. This is shown by the following experiment in which a sample of fiber having a denier of 1.1 obtained from poly-pentamethylene sebacamide was dried by heating at 110° C. for 16 hours and immediately weighed. It was then stored at 25° C. at 50% relative humidity for five hours and again weighed. The weights were 1.1184 g. and 1.1272 g. respectively, indicating that the fibers had absorbed 0.97% moisture. Viscose rayon fibers stored under conditions comparable absorbed about 8% moisture. The polyamide also had a higher ratio of wet to dry strength than the rayon. In general the wet strength of the polyamide fibers is at least 85% of their dry strength. The breaking point elongation of the fibers is usually above 20%. The elastic properties of the fibers of this invention are noteworthy and are usually such that when the fiber is stretched 4% for one minute it recovers at least 80% of its extension during the first minute of release.

Example II

55
60
65
70
75
A salt was prepared from hexamethylenediamine and adipic acid as follows: 144 parts of the amine was mixed with 174 parts of the acid in the presence of 1300 parts of 95% ethyl alcohol and 210 parts of water and the mass warmed until complete solution occurred. The mixture was then cooled and the pure white crystals which separated out were filtered off and recrystallized from 1300 parts of 95% alcohol and 200 parts of water. The recrystallized material consisted of 247 parts. It melted at 183–184° C. and had the composition required for hexamethylene diammonium adipate. It was converted into a fiber-forming polyamide by heating for three hours with an equal weight of mixed xyleneol under the conditions described in Example I. The conductivity of the mixture fell from 0.0022 to 0.0000215 mhos and the absolute viscosity increased from 0.14 to 20.4 poises. The precipitated polymer had an intrinsic viscosity of 1.2 and a melting point of about 263° C. as determined in a glass tube in the absence of oxygen. It was spun into oriented fibers as follows: The molten polymer was extruded from a spinneret

at 284–292° C. under a gas pressure of 50 lbs. per sq. in. applied with oxygen-free nitrogen at a spinning rate of 300 ft. per minute and a drawing rate of 1020 ft. per minute (equivalent to 240% cold drawing). The spinneret employed had ten orifices each 0.0078 inch in diameter placed at the bottom of 0.125 inch cone-shaped protrusions extending downward from the face of the spinneret. The resultant fibers had a denier at break of 1.08 and a tenacity at break of 4.32 g. per denier. The wet strength of these fibers was slightly more than 90% of the dry strength. A 113-denier, 70-filament, 4-twist per inch yarn made from fibers of this polymer could readily be knit or woven into fabrics of excellent properties.

Example III

20
25
30
35
40
45
A mixture of two mols of hexamethylene diammonium adipate and 0.02 mol. of adipic acid (viscosity stabilizer) was placed in a two-liter, silver-lined autoclave equipped with an 18:8 stainless steel (i. e., 74% iron, 18% chromium, 8% nickel, and less than 0.2% carbon) stirrer and an 18:8 stainless steel steam-heated reflux condenser, the top of which was connected through a water-cooled downward condenser to a receiver. Air was removed from the autoclave by evacuation, followed by filling with nitrogen and evacuating again. A nitrogen pressure of 80 lbs. was then applied. The nitrogen used for this purpose was commercial nitrogen which had been washed with sodium hydrosulfite "sliver salt" solution to remove substantially the last traces of oxygen. The stirrer was started and the autoclave heated to 288° C. during 1.5 hours. The pressure was then reduced to atmospheric during 0.5 hour and the heating and stirring continued for 2.5 hours. The pressure was then reduced to 200 mm. absolute pressure for a few minutes. After cooling the polymer was removed from the autoclave as a white solid cake. It had an intrinsic viscosity of about 0.9, was essentially viscosity stable, and yielded good fibers on spinning from melt using a constant volume delivery pump of the type used in viscose spinning (Zenith gear pump, type A-1).

Example IV

50
55
60
65
Chemically equivalent amounts of sebacic acid and pentamethylenediamine were heated for two hours in a closed vessel at 220–240° C. This gave a low polymer. The vessel was then opened to permit the removal of the water formed in the reaction. On heating the polymer for one hour at 230–240° C. under an absolute pressure of 1 mm. it was converted into high polymer. The product, poly-pentamethylene sebacamide, yielded fibers of good quality.

Example V

70
75
A 40% solution of polyhexamethylene adipamide (intrinsic viscosity, 1.38) in anhydrous phenol was placed in a brass tube which held a rayon spinneret having an orifice 0.006 inch in diameter. The spinneret was situated a short distance above the surface of a coagulating bath seven feet in length containing a 3% aqueous solution of sodium sulfide maintained at 70° C. The bath was provided with a motor driven guide roll placed close to the spinneret. Two other motor driven rolls or bobbins were placed outside the bath: a "take-up roll" for winding up the filaments as they left the bath and a "drawing roll" driven at a higher rate of speed for cold

drawing the filaments. The polyamide solution was extruded from the spinneret at a temperature of 140° C. under a nitrogen pressure of 50 lbs. into the coagulating bath. Drawing of the filaments in the bath was minimized by passing the filaments over the guide roll which was synchronized with the take-up roll. The wet filaments passed from the take-up roll to the drawing roll. The peripheral speed of the take-up roll was 46 ft./min. and that of the drawing roll 167 ft./min. which is equivalent to 263% cold drawing. The cold drawn filaments or fibers were then washed with water and dried. The fibers had a denier of 3.6, a residual elongation of 44%, a denier at break of 2.5, and a tenacity of 4.34 g. per denier at break.

Example VI

A 25% solution of polyhexamethylene adipamide (intrinsic viscosity, 1.35) in a solvent mixture consisting of approximately 89% phenol and 11% water was spun from a spinneret having 40 orifices of 0.004 inch diameter into a coagulating bath consisting of a 4% aqueous sodium hydroxide solution maintained at 75° C. The spinneret was immersed in the coagulating bath. The spinning rate was 24 ft./min. and the drawing rate 83 ft./min., equivalent to 246% cold drawing. The cold drawing was carried out before washing the filaments. The resultant fibers after washing and drying had the following properties: denier, 0.9; denier at break, 0.518; tenacity based on the denier at break, 4.9 g. per denier; residual elongation, 74%.

Example VII

A 29.2% solution of polyhexamethylene adipamide (intrinsic viscosity, 1.48) in formic acid was dry spun in an apparatus consisting of a brass tube holding a spinneret which was attached to an electrically heated drying cell 6 ft. in length and having a cross-section 7 inches square. The cell had an orifice at the bottom through which the filaments could be removed and wound up on a motor-driven drum. A second drum also outside the cell driven at a higher rate was provided for cold drawing the filaments. The top of the cell was provided with small air inlets, and a downward current of air was maintained in the cell by means of a suitable suction tube attached near the bottom. The polyamide solution in the spinneret was maintained at room temperature, i. e., approximately 25° C. The solution was extruded through the spinneret orifice (diameter, 0.004 inch) under 150 lbs. nitrogen pressure. The temperature of the cell was maintained at approximately 70° C. The spinning rate (peripheral speed of first drum) was 80 ft./min. and the drawing rate (peripheral speed of second drum) 196 ft./min., corresponding to 145% cold drawing. After cold drawing the fibers were kept at 100° C. for 15 minutes. The resultant fibers had a denier of 2.25, a denier at break of 0.80, a tenacity of 4.73 g. per denier at break, and a residual elongation of 180%. The wet strength of these fibers was 4.2 g. per denier and the strength of knotted fibers was 3.7 g. per denier. The high residual elongation of these fibers is characteristic of fibers spun from formic acid solution by the dry method even when the fibers have been cold drawn more than 100% during spinning.

While filaments of small diameter (0.00015-0.0015 inch, corresponding roughly to 0.1-10.0 denier) are the most useful for the preparation

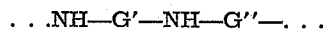
of yarns and fabrics, filaments of other sizes can be prepared from the polyamides of this invention. For example, it is possible to prepare larger filaments which are useful as bristles, artificial straw, tennis strings, fishline leaders, musical instrument strings, dental floss, horse hair substitutes, mohair substitutes, and the like from the fiber-forming polyamides by the methods herein described. It is also possible to prepare large filaments by fusing together or uniting by means of an adhesive a plurality of small filaments. Large filaments can also be prepared by cutting films or sheets into small strips. While these strips are not round, they are useful for many purposes.

Filaments having diameters ranging from 0.003 to 0.060 inch are especially suitable as bristles. Products of this type can be used in either the undrawn or drawn (oriented) form. They have good snap, toughness, and resistance to water, which make them useful in the manufacture of brushes, combs, and the like. For the preparation of these large filaments, spinning of the polyamide from melt through spinnerets having large orifices is most satisfactory, although solution spinning can also be employed as a method of preparation. The large diameter filaments are less susceptible to cold drawing than the smaller filaments. However, the drawing is greatly facilitated by soaking the filaments in water, and/or warming them, e. g., to 100° C., prior to the drawing operation, as described in copending application Serial Number 125,887, filed February 15, 1937. The following is an example of the manufacture of large filaments or bristles:

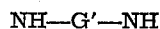
Example VIII

Following the general method described in the preceding example, a 40% solution of polyhexamethylene adipamide (intrinsic viscosity, 1.38) in phenol was dry spun from a spinneret having a 0.02 inch orifice under a pressure of 20 lbs. The head temperature employed was 130° C. and the cell temperature 203° C. The large filaments or bristles thus formed were not cold drawn. The small amount of phenol retained in the bristles was removed by washing them with water and then drying them at 100° C. for one hour. The bristles had good snap, flexibility, and toughness.

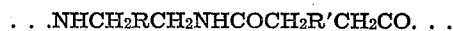
It will be seen from the foregoing description that the recurring structural units of my polyamides may be represented by the general formula . . . N(a)—G'—N(a')—G'' . . . in which *a* and *a'* are hydrogen or monovalent hydrocarbon radicals, G' is a divalent hydrocarbon radical and G'' is a divalent acyl radical. The most easily prepared fiber-forming polyamides in this field are those having structural units of the general type



in which G' and G'' are defined as above, the sum of the radical lengths of G'' and

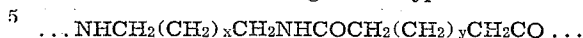


being at least 9. A particularly valuable group of polyamides from the standpoint of fiber-forming qualities are those having structural recurring units which may be represented by the general formula



in which R and R' are divalent hydrocarbon radicals of the types already described. It will

be noted that all of the polyamides in the foregoing examples are of this type. It will be noted further that these polyamides have recurring structural units of the general type



in which x and y are integers and in which x is at least two. High viscosity polyamides (intrinsic viscosity preferably above 0.6) of this select class are readily spun and give fibers of excellent quality.

It can be readily seen from the above examples that the important feature of the process of this invention is that the diamine and dibasic acid or amide-forming derivative, or the low molecular weight non-fiber-forming polyamide therefrom, must eventually be reacted or further reacted under conditions which permit the formation of a very highly condensed polyamide. In other words, the heating must be continued at such a temperature and for such a period of time that the product can be drawn into oriented fibers, and this point is reached essentially only when the intrinsic viscosity has risen to at least 0.4. In the preparation of some of my new fiber-forming polyamides, it may be advantageous to apply the principles of molecular distillation described in U. S. 2,071,250.

It will be evident that the present invention describes a wholly new and very valuable type of synthetic fiber, and is therefore an outstanding contribution to this art because the new fibers are made by a wholly synthetic process and because they have unusual properties, being strong, flexible, elastic, insensitive to moisture, etc. to a remarkable degree. They can be used to advantage either as continuous fibers or as staple fibers, e. g., lengths of 1 to 6 inches. The fact that they show by X-ray diffraction patterns orientation along the fiber axis (a characteristic of natural fibers and fibers derived from high molecular weight natural substances) places them in the field of true fibers.

It is to be understood that my invention comprises also fibers, etc., prepared from interpolyamides, e. g., a polyamide derived from the reaction of two or more diamines with one or more dibasic acids. My fibers can also be prepared from mixtures of preformed polyamides.

It is to be understood further that yarns and fabrics prepared from the synthetic polyamide fibers are within the scope of my invention. The yarns can be prepared from either the continuous or staple fibers. A convenient method for making a polyamide yarn comprising staple fibers consists in drawing a continuous thread or sliver consisting of a multiplicity of substantially parallel continuous filaments, either oriented or unoriented, until the filaments are reduced to staple and twisting (drafting) the sliver. If unoriented filaments are used in this process the filaments draw down to a much greater extent before breaking than in the case of previously described filaments, e. g., viscose or acetate rayon. My fibers and yarns can be knit, woven, or otherwise formed into fabrics of widely different types. The excellent elastic recovery of my fibers makes them especially useful in the preparation of knitted wear, such as stockings, gloves, sweaters, underwear, suits, etc. My fibers are also useful in making sewing thread.

It is within the scope of my invention to use synthetic polyamide fibers and yarns in admixture with other types of fibers or yarns in the preparation of "mixed fabrics". As examples of

other types of fibers and yarns which may be used in conjunction with my artificial fibers might be mentioned regenerated cellulose, spun or staple regenerated cellulose, acetate rayon, staple acetate rayon, silk, silk waste, wool, linen, and cotton. In these combinations the polyamide fibers may be used as continuous filaments or in the form of staple fibers. The mixed fabrics may be prepared by using different types of yarn, e. g., a polyamide yarn and a spun viscose rayon yarn, or by using yarns made up of mixtures of different types of fibers. When the latter method is employed, the mixed yarns can be prepared by incorporating the polyamide fibers with the other fibers at any stage in the preparation of the yarn. For this purpose twisting or doubling methods may also be employed. The mixed yarns may then be used in the preparation of woven or knitted fabrics or may be used in conjunction with other yarns, e. g., in the preparation of woven fabrics. Polyamide yarn may be used in either the warp or the filling. Novel effects are obtained by using polyamide yarns and other types of yarn intermittently in either the warp, filling, or both. Likewise in the preparation of knitted fabrics the different yarns may be fed into the knitting machine. The polyamide fibers impart increased strength to the fabrics.

My invention includes also the dyeing of the fibers, yarns, and fabrics mentioned above. The synthetic polyamides have a strong affinity for dyes and can be dyed rapidly, permanently and directly with the dyes ordinarily used for wool and silk. For example, they can be dyed very satisfactorily with dyes of the acid group, e. g., dyes of Color Index Numbers 714 and 640; dyes of the chrome or acid mordant group, e. g., dyes of Color Index Numbers 203 and 720; and dyes of the direct or substantive group, e. g., dyes of Color Index Numbers 365 and 512. Furthermore, they can be dyed with vat dyes, particularly those of the Indigoid and Thioindigoid classes, e. g., dyes of Color Index Numbers 1177 and 1211. In this respect my products are superior to silk and wool, for the alkaline medium in which vat dyes can be used is more damaging to silk and wool. My products can also be dyed satisfactorily with dyes of the sulfur class. Union or mixed fabrics containing my fibers and other types of fibers, e. g., animal or cellulosic fibers, can also be dyed satisfactorily, particularly with dyes of the acid and direct groups. Thus, union fabrics composed of my fibers and wool or of my fibers and regenerated cellulose are satisfactorily dyed with dyes of these groups.

The following typical example, which is not to be considered as limitative, is given to illustrate the dyeing of a synthetic polyamide yarn. The yarn was entered into a dyeing bath prepared with 1% of blue dye of Color Index Number 1088, 10% Glauber's salt, and 3% of sulfuric acid, the percentages being based on the weight of the yarn. The bath was boiled for 0.5 hour, 1% sulfuric acid was added, and the boiling continued for an additional 0.25 hour. The yarn was then removed, rinsed, and dried, resulting in a satisfactory dyeing of good fastness to light. Fabrics can be dyed similarly.

While my polyamide fibers are normally lustrous, their luster can be reduced or destroyed by various means. The most satisfactory method for preparing low luster polyamide fibers, however, consists in preparing these fibers from a polyamide or polyamide solution containing dispersed therein a finely divided substance which is inert

toward the polyamide, is incompatible therewith at ordinary temperatures, and has an index of refraction differing from that of the polyamide. Pigment-like materials are generally good delusterants. As examples of such delusterants might be mentioned titanium dioxide, zinc oxide, zinc sulfide, barium sulfate, carbon black, and copper phthalocyanine pigment. However, many organic compounds, e. g., non-phenolic polynuclear compounds, also function as delusterants.

It will be apparent that the polyamides herein described are most useful in the form of filaments and fibers. Many other valuable artificially shaped objects may, however, be prepared from them by suitable modification of the general methods herein described. For example, films, foils, sheets, ribbons, bands, rods, hollow tubing, and the like can also be prepared from them. In general, however, these products are not clear but are translucent or opaque, unless they are prepared by the special processes described in copending applications Serial Number 125,927, filed February 15, 1937, by W. E. Catlin, and Serial Number 125,926, filed February 15, 1937, by G. D. Graves. In these various applications the polyamides may be used alone or in admixture with other ingredients, such as cellulose derivatives, resins, plasticizers, pigments, dyes, etc.

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. In the manufacture of polymeric materials the steps which comprise heating at polyamide-forming temperatures a diprimary diamine with approximately equimolecular proportions of a member of the group consisting of dicarboxylic acids in which each carboxyl group is attached to an aliphatic carbon atom, amide-forming derivatives of such dicarboxylic acids, and amide-forming derivatives of carbonic acid, and continuing such heating until a polymer is produced which is capable of yielding continuous filaments that can be tied into hard knots.

2. A process which comprises contacting a diprimary diamine in which each amino group is attached to an aliphatic carbon atom with approximately equimolecular proportions of a dicarboxylic acid in which each carboxyl group is attached to an aliphatic carbon atom, thereby forming a salt and heating said salt at polymerizing temperatures with removal of water of reaction until a polymer is produced which is capable of yielding continuous filaments showing by characteristic X-ray diffraction patterns orientation along the fiber axis.

3. In the manufacture of polymeric materials the steps which comprise heating at polyamide-forming temperatures a diprimary diamine with approximately equimolecular proportions of a member of the group consisting of dicarboxylic acids in which each carboxyl group is attached to an aliphatic carbon atom, amide-forming derivatives of such dicarboxylic acids, and amide-forming derivatives of carbonic acid, and continuing such heating with removal of the by-product of reaction until a polymer is produced which is capable of yielding continuous filaments showing by characteristic X-ray diffraction patterns orientation along the fiber axis.

4. A process which comprises heating at polyamide-forming temperatures under substan-

tially oxygen-free conditions a diprimary diamine, in which each amino group is attached to an aliphatic carbon atom, with approximately equimolecular proportions of a member of the group consisting of dicarboxylic acids in which each carboxyl group is attached to an aliphatic carbon atom, amide-forming derivatives of such dicarboxylic acids, and amide-forming derivatives of carbonic acid, the reactants being selected such that the sum of their radical lengths is at least 9, and continuing the heat treatment until a polymer is produced which is capable of yielding continuous filaments that can be formed into fabric.

5. A process which comprises reacting at polyamide-forming temperatures and between 180-300° C. a diprimary diamine of the formula $\text{NH}_2\text{CH}_2\text{RCH}_2\text{NH}_2$ with approximately equimolecular proportions of a dicarboxylic acid of the formula $\text{HOOCCH}_2\text{R}'\text{CH}_2\text{COOH}$, in which R and R' are divalent hydrocarbon radicals free from olefinic and acetylenic unsaturation and in which R has a chain length of at least two carbon atoms, and continuing the heat treatment with removal of the by-product of reaction until a polymer is produced which is capable of yielding continuous filaments that can be formed into a fabric.

6. The process set forth in claim 5 in which R is $(\text{CH}_2)_x$ and R' is $(\text{CH}_2)_y$, x and y being integers, and x being at least 2.

7. A process which comprises heating at polyamide-forming temperatures in the presence of an inert organic diluent a diprimary diamine, in which each amino group is attached to an aliphatic carbon atom, with approximately equimolecular proportions of a member of the group consisting of dicarboxylic acids in which each carboxyl group is attached to an aliphatic carbon atom, amide-forming derivatives of such dicarboxylic acids, and amide-forming derivatives of carbonic acid, the reactants being selected such that the sum of their radical lengths is at least 9, and continuing the heat treatment until a polymer is produced which is capable of yielding continuous filaments that can be formed into fabrics.

8. The process set forth in claim 7 in which the organic diluent is a solvent for the reactants and reaction product.

9. The process set forth in claim 7 in which the organic diluent is a non-solvent for the reaction product.

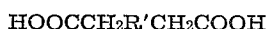
10. The process set forth in claim 7 in which the diamine is of the formula $\text{NH}_2\text{CH}_2\text{RCH}_2\text{NH}_2$ and the dicarboxylic acid is of the formula $\text{HOOCCH}_2\text{R}'\text{CH}_2\text{COOH}$, R and R' being divalent hydrocarbon radicals free from olefinic and acetylenic unsaturation and R having a chain length of at least two carbon atoms.

11. The process set forth in claim 7 in which the organic diluent consists essentially of a monohydric phenol as a solvent for the reactants and reaction product.

12. A process which comprises reacting at polyamide-forming temperatures a diprimary diamine of the formula $\text{NH}_2\text{CH}_2\text{RCH}_2\text{NH}_2$ with approximately equimolecular proportions of an amide-forming derivative of a dicarboxylic acid of the formula $\text{HOOCCH}_2\text{R}'\text{CH}_2\text{COOH}$, in which R and R' are divalent hydrocarbon radicals free from olefinic and acetylenic unsaturation and in which R has a chain length of at least two carbon atoms, and continuing the reaction until a polymer is produced capable of yielding continuous filaments which can be knitted into a fabric.

13. A process which comprises heating at polyamide-forming temperatures a diprimary diamine, in which each amino group is attached to an aliphatic carbon atom, with approximately equimolecular proportions of a member of the group consisting of dicarboxylic acids, in which each carboxyl group is attached to an aliphatic carbon atom, amide-forming derivatives of such dicarboxylic acids, and amide-forming derivatives of carbonic acid until a polymer is produced which has an intrinsic viscosity of at least 0.4.

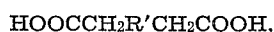
14. A process for manufacturing polymers which comprises bringing together approximately equimolecular proportions of a diprimary diamine of formula $\text{NH}_2\text{CH}_2\text{RCH}_2\text{NH}_2$ and a dicarboxylic acid of formula



and heating the mass at polyamide-forming temperatures in the substantial absence of oxygen and with removal of water of reaction until the polymer formed is capable of being spun into filaments which can be cold drawn into fibers showing by characteristic X-ray diffraction patterns orientation along the fiber axis, R and R' being defined as in claim 5.

15. A process for making a viscosity stable polyamide whose viscosity is substantially unaltered by heating at its melting point, said process consisting of heating at polyamide-forming temperatures a mixture of reactants which is capable of yielding a fiber-forming polyamide and which contains one of said reactants in 0.1 to 5.0 molar per cent excess, said mixture of reactants comprising a diprimary diamine, in which each amino group is attached to an aliphatic carbon atom, and a member of the group consisting of dicarboxylic acids in which each carboxyl group is attached to an aliphatic carbon atom, amide-forming derivatives of such dicarboxylic acids, and amide-forming derivatives of carbonic acid, and continuing said heating until a polyamide is produced which can be formed into continuous filaments capable of being made into fabric.

16. A process which comprises contacting a diprimary diamine of formula $\text{NH}_2\text{CH}_2\text{RCH}_2\text{NH}_2$ and a dicarboxylic acid of formula



in which R and R' are divalent hydrocarbon radicals free from olefinic and acetylenic unsaturation and in which R has a chain length of at least two carbon atoms, isolating the salt thereby formed, and heating said salt at polyamide-forming temperatures with removal of water of reaction until a polymer is produced which has an intrinsic viscosity of at least 0.4.

17. A process for making polymeric materials which comprises heating at polyamide-forming temperatures in the absence of any appreciable amount of oxygen, a salt obtainable from a diprimary diamine in which each amino group is attached to an aliphatic carbon atom and a dicarboxylic acid in which each carboxyl group is attached to an aliphatic carbon atom, and continuing said heating under conditions permitting the removal of water of reaction until the polymer former is capable of yielding oriented fibers.

18. A step in a process for making polymeric materials, which comprises subjecting a polyamide derived from a diprimary diamine of formula $\text{NH}_2\text{CH}_2\text{RCH}_2\text{NH}_2$ and a dicarboxylic acid of formula $\text{HOOCCH}_2\text{R}'\text{CH}_2\text{COOH}$, said polyamide being incapable of yielding continuous filaments, to continued polymerizing heat treatment

under conditions permitting the escape of volatile by-product until the polymer formed is capable of being drawn into continuous filaments showing by characteristic X-ray diffraction patterns orientation along the fiber axis, R and R' being defined as in claim 5.

19. In the manufacture of highly polymeric materials, the steps which comprise forming a low molecular weight polyamide by heating at polyamide-forming temperatures under super-atmospheric pressure approximately equimolecular proportions of a diprimary diamine of formula $\text{NH}_2\text{CH}_2\text{RCH}_2\text{NH}_2$ and a dicarboxylic acid of formula $\text{HOOCCH}_2\text{R}'\text{CH}_2\text{COOH}$, and then continuing the heating at polyamide-forming temperatures under conditions permitting the escape of water of reaction until the resultant polymer is capable of being spun into pliable filaments, R and R' being defined as in claim 5.

20. A process for manufacturing polymers which comprises heating at polyamide-forming temperatures approximately equimolecular proportions of hexamethylenediamine and adipic acid and continuing such heating with removal of the water of reaction until the polyamide formed is capable of yielding continuous fibers showing by characteristic X-ray diffraction patterns orientation along the fiber axis.

21. A polyamide obtainable by condensation polymerization from a diamine and a dibasic carboxylic acid, said polyamide being capable of being formed into fibers showing by characteristic X-ray patterns orientation along the fiber axis.

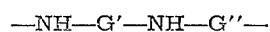
22. A polyamide capable of being formed into continuous filaments showing by characteristic X-ray diffraction patterns orientation along the fiber axis, said polyamide being one which is obtainable by condensation polymerization from a diprimary diamine and a dicarboxylic acid which has an intrinsic viscosity of at least 0.4.

23. A polyamide comprising the reaction product of a diprimary diamine, in which each amino group is attached to an aliphatic carbon atom, with approximately equimolecular proportions of a member of the group consisting of dicarboxylic acids in which each carboxyl group is attached to an aliphatic carbon atom, amide-forming derivatives of such dicarboxylic acids, and amide-forming derivatives of carbonic acid, said polyamide being capable of being formed into pliable fibers which can be made into textile fabrics.

24. A polyamide obtainable by condensation polymerization from a diamine and a dibasic carboxylic acid, said diamine being of the formula $\text{NH}_2\text{CH}_2\text{RCH}_2\text{NH}_2$ and said dibasic acid being of the formula $\text{HOOCCH}_2\text{R}'\text{CH}_2\text{COOH}$ in which R and R' are divalent hydrocarbon radicals free from olefinic and acetylenic unsaturation and in which R has a chain length of at least two carbon atoms, said polyamide being capable of yielding continuous filaments which can be tied into hard knots.

25. The polyamide set forth in claim 24 in which R is $(\text{CH}_2)_x$ and R' is $(\text{CH}_2)_y$, x and y being integers, and x being at least 2.

26. A linear polyamide having recurring structural units of the general formula



where G' is a divalent hydrocarbon radical in which the atoms attached to the —NH— groups are aliphatic and G'' is a divalent aliphatic acyl radical, the sum of the radical lengths of G' and —NH—G'—NH— being at least 9, said polyamide

being capable of yielding continuous filaments which can be formed into a fabric.

27. A polymer capable of being drawn into continuous filaments which can be formed into fabrics, said polymer yielding, upon hydrolysis with hydrochloric acid, a mixture of substances comprising a diamine hydrochloride and a dibasic carboxylic acid.

28. A synthetic linear condensation polymer having an intrinsic viscosity of at least 0.5, said polymer yielding, upon hydrolysis with hydrochloric acid, a mixture of substances comprising a diamine hydrochloride and a dicarboxylic acid.

29. A viscosity stable polyamide whose viscosity is substantially unaltered by heating at its melting point, said polyamide being obtainable by condensation polymerization from a mixture of diamine and dibasic carboxylic acid containing one of said reactants in 0.1 to 5.0 molar per cent excess, and said polyamide being capable of yielding continuous filaments which can be formed into fabric.

30. A polyamide obtainable by heating at polyamide-forming temperatures at least two different diamines with at least one dibasic carboxylic acid, said polyamide having an intrinsic viscosity of at least 0.4.

31. A polyamide obtainable by heating at polyamide-forming temperatures at least one diamine with at least two different dibasic carboxylic acids, said polyamide having an intrinsic viscosity of at least 0.4.

32. A synthetic linear condensation polyamide capable of being formed into fibers showing by characteristic X-ray patterns orientation along the fiber axis, said polyamide being polymeric hexamethylene adipamide.

33. A process for making synthetic fibers from polyamides derived from diamines and dibasic carboxylic acids which comprises spinning a filament from said polyamide and subjecting said filament to cold-drawing under tension until it shows by characteristic X-ray diffraction patterns orientation along the fiber axis.

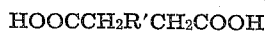
34. The process set forth in claim 33 in which the polyamide is in the molten state.

35. The process set forth in claim 33 in which the polyamide is in solution and solvent is removed from the filament before it is cold-drawn.

36. A process for making artificial fibers which comprises forming into a filament a polyamide having an intrinsic viscosity of at least 0.4, and subjecting said filament to stress to produce a fiber showing by characteristic X-ray diffraction patterns orientation along the fiber axis, said polyamide being obtainable by condensation polymerization from a diamine of formula



and a dicarboxylic acid of formula



in which R and R' are divalent hydrocarbon radicals free from olefinic and acetylenic unsaturation and in which R has a chain length of at least two carbon atoms.

37. A process which comprises extruding into filaments a solution of a synthetic polyamide which is obtainable by condensation polymerization from a diamine and a dibasic carboxylic acid, evaporating the solvent from the filaments, and subjecting the filaments to stress until they are formed into fibers useful in the manufacture of fabric.

38. A process which comprises extruding fila-

ments from a solution of a synthetic polyamide into a liquid which dissolves the solvent of the solution but not the polyamide, and subjecting the filaments to stress until they are formed into fibers useful in the manufacture of fabric, said polyamide being that obtainable by condensation polymerization from a diamine and a dibasic carboxylic acid.

39. A process for making fibers which comprises extruding filaments from a solution of a synthetic polyamide into a liquid which dissolves the solvent of said solution but not the polyamide, and subjecting the filaments to stress until they are formed into fibers capable of being tied into hard knots and useful in the manufacture of fabric, said polyamide having an intrinsic viscosity above 1.0 and being obtainable by condensation polymerization from a diamine and a dibasic carboxylic acid.

40. A polyamide obtainable by condensation polymerization from a diamine and a dibasic carboxylic acid, said polyamide being in the form of a filament showing by characteristic X-ray diffraction patterns orientation along the fiber axis.

41. A polyamide in the form of a filament which yields, upon hydrolysis with hydrochloric acid, a diamine hydrochloride and a dibasic carboxylic acid.

42. A polyamide in the form of a filament which yields, upon hydrolysis with hydrochloric acid, an aliphatic diprimary diamine hydrochloride and an aliphatic dibasic carboxylic acid, the sum of whose radical lengths is at least 9, said filament being capable of being tied into hard knots.

43. A delustered filament comprising a delustering agent and a polyamide obtainable by condensation polymerization from a diamine and dibasic carboxylic acid.

44. A polymer in the form of a crenulated pliable fiber which yields, upon hydrolysis with hydrochloric acid, a mixture of substances comprising a diamine hydrochloride and a dibasic carboxylic acid, said fiber being capable of being formed into a yarn which can be woven into a fabric.

45. A synthetic polymer in the form of a pliable filament, said polymer being obtainable by condensation polymerization from a diprimary diamine of formula $\text{NH}_2\text{CH}_2\text{RCH}_2\text{NH}_2$ and a dicarboxylic acid of formula $\text{HOOCCH}_2\text{R}'\text{CH}_2\text{COOH}$, wherein R and R' are defined as in claim 5.

46. A synthetic polymer in the form of staple fibers which are capable of being formed into useful yarns, said polymer being obtainable by condensation polymerization from a diamine and a dibasic carboxylic acid.

47. An artificial filament comprising polymeric hexamethylene adipamide.

48. A dyed fabric, said fabric containing filaments which yield, on hydrolysis with hydrochloric acid, a diamine hydrochloride and a dibasic carboxylic acid.

49. A fabric comprising filaments derived from a synthetic linear condensation polymer, said filaments yielding, upon hydrolysis with hydrochloric acid, a diamine hydrochloride and a dibasic carboxylic acid.

50. A mixed fabric comprising synthetic polyamide filaments, said polyamide being obtainable by condensation polymerization from a diamine and a dibasic carboxylic acid.

51. A synthetic polymer in the form of a film,

said polymer being obtainable by condensation polymerization from a diamine and a dibasic carboxylic acid.

5 52. A synthetic polymer in the form of an artificial filament having a diameter ranging from 0.003 to 0.06 inch, said polymer yielding, upon hydrolysis with hydrochloric acid, a mixture of substances comprising a diamine hydrochloride and a dibasic carboxylic acid.

10 53. A brush containing bristles which are obtainable by condensation polymerization from a diamine and a dibasic carboxylic acid.

54. A synthetic polyamide capable of being

formed into fibers showing by characteristic X-ray patterns orientation along the fiber axis, said polyamide being polymeric pentamethylene adipamide.

55. A synthetic polyamide capable of being 5 formed into fibers showing by characteristic X-ray patterns orientation along the fiber axis, said polyamide being polymeric tetramethylene sebacamide.

56. The delustered filament set forth in claim 10 43 wherein said delustering agent is titanium dioxide.

WALLACE HUME CAROTHERS.