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BLENDED POLYAMIDES

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This invention relates to polymeric materials and more particularly to the manufacture and treatment of solid structures consisting essentially of synthetic linear polyamides of types such as described hereinafter. For convenience, the said types will be referred to at times simply as polyamides. Still more particularly, this invention relates to the manufacture and processing of filaments, fibers, pellicles, ribbons, films, sheets, and other like structures, consisting essentially of the said polyamides, as well as to textile or other products fabricated therefrom.

The said polyamides as a class are capable of being spun into filaments that can be drawn to produce molecular orientation along their fiber axes. The resulting oriented fibers, or fabrics formed therefrom, generally are characterized by relatively low water absorption, pronounced resistance to deformation and moderately slow recovery from strain. While these properties of the polyamide articles render them especially suitable for many uses, there nevertheless are a number of more or less specialized fields of utility for which such articles are not altogether satisfactory. For instance, the low water absorption capacity of the polyamides makes it considerably more difficult to subject them successfully to certain types of processing for which natural fibers similar or analogous to wool are especially adapted, by reason of their relatively high affinity for moisture. Furthermore, the fact that the water absorption capacities of the various polyamides roughly correspond, in degree, to certain desirable physical properties, particularly the ease with which the polyamides can be set in a form to which they recover after deformation, lends emphasis to the need which has arisen for the development of processes making possible the enhancement of the water absorption capacity of polyamide structures.

This invention has as its primary object therefore the production of polyamide structures having enhanced water absorption capacities, as well as improved physical characteristics consequent thereon, e. g., greater speed of recovery from strain, increased pliability, and enhanced recovery from deformation, as, e. g., creasing, and also possessing greatly improved dyeing characteristics. This invention has as a further object the appropriate processing of bodies consisting of

such polyamides, in order to capitalize most effectively on the said capacities and characteristics. Still further objects will appear either expressly or impliedly hereinbelow.

5 The aforesaid primary object is accomplished by heating in the molten state at amide-forming temperatures a mixture of at least two pre-formed synthetic linear polyamides, at least one of which is per se soluble in a member of the class consisting of water, aliphatic alcohols containing less than five carbon atoms, and mixtures of water with aliphatic alcohols containing less than five carbon atoms, and at least one other polyamide of which is per se insoluble in said member, and continuing the heating until a homogeneous melt blend is obtained, and preferably until not more than 10 per cent of the first mentioned polyamide is extractable from the product by prolonged solvent treatment thereof with the aforesaid member, on cooling of the product.

15 The further object specified hereinabove is accomplished by treating the solidified melt blend, in whatever form desired, e. g., filaments or films, with the said member. In this treatment the latter, i. e., water, short chain aliphatic alcohol, or mixture of water and short chain aliphatic alcohol functions as a swelling agent, and will be referred to as such.

20 Generally, the preferred swelling agent is water or steam, the same being applied to the mixed-polyamide structure at elevated temperatures and for considerable periods of time. Consequently, the invention will be described in detail, and illustrated in the examples and tables set forth hereinafter, with particular reference to those embodiments involving the melt-blending of water-soluble polyamides with water-insoluble polyamides, and the utilization of water or steam as the swelling agent for the processing thereof. It is to be understood, however, that the invention may be practiced in embodiments which, though generally less advantageous, are nevertheless more or less effective, without the use of water or steam; the same being replaced, e. g., with mild organic swelling agents. Thus, low molecular weight aliphatic alcohols may be substituted for the water or steam, a methanol-, rather than water-, soluble polyamide substituted for the water-soluble component of the

mixed-polyamide, and an alcohol-, rather than merely water-, insoluble polyamide being chosen for the remaining component of the mixed-polyamide.

In any case, the mixed-polyamide structure generally is oriented, as by cold-drawing or cold-rolling, prior to subjection to the swelling treatment, and ordinarily is permitted to shrink more or less freely during the treatment.

The synthetic linear polyamides used in the practice of this invention are of the general type described in Patents 2,071,250, 2,071,253, 2,130,523, and 2,130,948. The polymers there described are high molecular weight products which are generally crystalline in structure showing X-ray powder diffraction patterns in the massive state, and which are capable of being cold drawn into fibers showing by characteristic X-ray patterns molecular orientation along the fiber axis. For the best fiber-forming properties the polymerization reaction should be continued until the intrinsic viscosity is at least 0.4.

These polyamides, generally speaking, comprise the reaction product of a polyamide-forming composition in which the molecules are bifunctional and contain two amide-forming groups, each of which is complementary to an amide-forming group in other molecules in said composition.

These polyamides as defined above or as otherwise identified hereinafter can be obtained, for example, by self-polymerization of monoaminomonocarboxylic acids, or by reacting a diamine with a dibasic carboxylic acid in substantially equimolecular amounts, it being understood that reference herein to the amino acids, diamines, and dibasic carboxylic acids is intended to include the equivalent amide-forming derivatives thereof. Amide-forming derivatives of the amino acids include the ester, anhydride, amide, lactam, acid halide, N-formyl derivatives, carbamate, and nitrile in the presence of water. Amide-forming derivatives of the dibasic carboxylic acids comprise the mono- and di-ester, the anhydride, the mono- and di-amide, acid halide, and the following compounds in the presence of water: nitrile, cyanocarboxylic acid, cyanoamide, and cyclic imide. Amide-forming derivatives of the diamines include the carbamate, N-formyl derivative and the N,N'-diformyl derivative.

These linear polyamides include also polymers obtained by admixture of other linear polymer-forming reactants, as for instance glycols in the use of polyester amides, with the mentioned polyamide forming reactants. In either instance the amide group is an integral part of the main chain of atoms in the polymer, and, in the case of the preferred polyamides, the average number of carbon atoms separating the amide groups is at least two. It should be noted, however, that the ratio of amide groups to other carbon-noncarbon linkages in the polymer chain should be at least 1:20 if the products are to exhibit polyamide properties to a significant degree.

On hydrolysis with hydrochloric acid the amino acid polymers yield the amino acid hydrochloride, and the diamine-dibasic acid polymers yield the diamine hydrochloride and the dibasic acid.

Although the fiber-forming polyamides are preferred, particularly in the case of the "insoluble" polyamides, this invention may also be practiced with the lower molecular weight polyamides obtained from selected reactants or by

stopping the polymerization reaction before the fiber-forming stage is reached.

Those of the polyamides which are soluble in water, the preferred swelling agent for the practice of the invention, are generally found among the class of polyamides in which heteroatoms of the oxygen family are present in the main polymer chain. Specific illustrations of such water-soluble varieties, as well as of other types of water-soluble polyamides, will be found hereinafter, along with illustrative species of polyamides which, though insoluble in water, are generally soluble in those organic compounds which usually function as swelling agents rather than solvents for polyamides of the fiber-forming varieties.

Ordinarily the mixed blend is prepared with the use of between 5% and 80% of the more soluble component. Where such component is designated hereinafter as being water-soluble, such designation will mean that it is soluble at least to the extent of 20% by weight in water at 25° C. The melt blending is effected at amide-forming temperatures, the same being, in general, above 180° C. It is desirable to use temperatures in excess of 200° C. and preferably in the range of 250 to 300° C. The upper limit generally is below 320° C. This limit will vary, however, by reason of the fact that the polyamides differ somewhat in the temperature at which deleterious thermal decomposition takes place. It is desirable to exclude oxygen during the heating.

The following illustrates a preferred mode of practicing the invention:

A water-insoluble polyamide and a water-soluble polyamide, each in comminuted form, are heated together at amide-forming temperatures to effect complete fusion of the ingredients, the same being stirred until the mixture is substantially homogeneous to the eye, i. e. until the melt appears to form a single phase without discontinuity. The time required usually is 10 to 60 minutes. As will be shown later, there is evidence that at least some chemical reaction between the polymers occurs during the melt-blending. The resultant mixed polymer has a melting point lying in general near the melting point of the higher-melting component, which will in general be the water-insoluble polymer, and well above the melting point of the true interpolyamide which would be formed by heating together in corresponding proportions the monomeric reactants from which the said water-soluble and the said water-insoluble polyamides respectively were obtained. The melting point of a polymer blend of this invention lies close to that of the water-insoluble component when this component comprises at least one-half of the original mixture. Since high-melting points are desirable in textile fibers, it is preferred to blend not more than 50% of the water-soluble component with the complementary amount of the high melting, water-insoluble polyamide, in order to avoid extensive lowering of melting point. In some instances sufficient blending can be accomplished merely by mixing small flakes or chips of the water-soluble and water-insoluble polyamides and feeding the mixture to a melt-spinning assembly in which the mixture is melted prior to extrusion into filaments or the like and is kept in the molten condition long enough to secure a substantially homogeneous blend. In general, however, superior results are obtained by effecting melt blending, with stirring, prior

to feeding the polymer to a melt-spinning or extrusion device.

With reference to the hereinabove-stated discovery that by far the larger proportion of the water-soluble polyamide in the product cannot be extracted by boiling water, it may be remarked that even in the case of melt-blends containing especially high proportions of water-soluble polyamides, only one-tenth or less of this component ordinarily is removed during 72 hours exposure to boiling water. In fact, the duration of the melt-blending in the preferred practice of the invention, may be defined as that period which will yield a product from which, on solidification, not more than 10% of the soluble component can be selectively extracted.

It may be observed further that the products of this invention are characterized by their ability, as hereinabove indicated, to absorb large amounts of water under typical atmospheric conditions (e. g. 50% relative humidity at 25° C.), while retaining their strength and resiliency.

The water-soluble polyamide, poly(N-methyltriglycol adipamide)¹ which is advantageously used in this invention, as shown in Examples V and VI, hereinbelow, may be prepared as follows: Four hundred thirty-eight parts of adipic acid and 546 parts of N,N'-dimethyltriglycoldiamine ($\text{CH}_3\text{NHCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{NHCH}_3$) are dissolved in 1600 parts of ethanol, and the solution is evaporated nearly to dryness. The diamine-diacid salt obtained is purified by recrystallization from ethanol. The salt is polymerized by heating it for 3 hours at 220° C. in a sealed vessel, for 3 additional hours at 250° C. under atmospheric pressure, and finally for 0.75 hour at 250° C. in vacuo. The polymer is a colorless, transparent, viscous fluid which sets to a brittle glass at -75° C. and is miscible with water in all proportions at 25° C. It has an intrinsic viscosity of 0.35.

The practice of this invention is illustrated in the following examples, in which the parts are given by weight.

EXAMPLE I

One hundred twelve parts of polyhexamethylene adipamide (water-insoluble; intrinsic viscosity, 0.80; melting point 250° C. in air) in the form of small chips and 48 parts of pulverized polytriglycol adipamide (water-soluble; intrinsic viscosity 0.73; melting point 160° C.) are placed in a vessel from which atmospheric oxygen is exhausted by successive evacuation and admission of oxygen-free carbon dioxide. The filled vessel is then heated in a bath of boiling dibenzofurane vapor (237° C.), complete fusion of the contents thus being effected. The molten mass is stirred until substantial homogeneity results. After cooling the mixture (melting point 250° C.), the solidified melt-blend is transferred to the appropriate apparatus and converted into a yarn of continuous filaments as described in U. S. 2,130,948.

The yarn is processed by cold-drawing, plying and twisting to a thread of 30 filaments which is 133 denier in weight and twisted 6 turns per inch. The sensitivity of this thread to moisture is manifested in its behaviour when exposed to superheated steam. At 140° C., the steamed threads shrink 17% in length during 4 hours, while under the same conditions threads of polyhexamethylene adipamide shrink only 5%. The yarn subsequently is woven in a plain weave taffeta fabric

measuring in the warp 120 threads per inch and in the woof 56 threads per inch. Exposure of this fabric to super-heated steam at 140° C. for 4 hours causes it to shrink 21% in the direction of the filling threads and become quite elastic and rubbery, so that it recovers rapidly and completely from a 10% extension. A similarly treated fabric of polyhexamethylene adipamide yarn shrinks only 14% and does not become rubbery.

EXAMPLE II

An intimate mixture comprising 35 parts of polytriglycol adipamide having an intrinsic viscosity of 0.82 and 65 parts of polyhexamethylene adipamide of intrinsic viscosity of 0.84 is prepared by melt blending to substantial homogeneity during 30 minutes heating at 287° C., with thorough stirring at intervals during the heating. A film of this composition absorbs 9% of its weight of water when allowed to come to equilibrium with moist air at 50% relative humidity and 25° C. Under these typical atmospheric conditions, the completely oriented film possesses unusual elasticity in the direction of orientation and recovers nearly completely after being stretched almost to the breaking point, which with different specimens is 30 to 40% and in some instances 45%. In contrast with this unique elasticity, a film melt-cast from polyhexamethylene adipamide stretches reversibly only to the extent of 5 to 10%, or at most 20%, and absorbs only 2 to 3% water at 50% relative humidity and 25° C.

The blend of water-soluble and water-insoluble polyamides is converted to yarn (100 denier, 30 filaments, 10 turns per inch twist) and woven in a plain weave, taffeta fabric measuring 109 threads per inch in the warp and 77 threads per inch in the woof. The water sensitivity of the constituent fibers permits unusual effects to be developed in this fabric. For instance, when it is exposed for 1 hour to the action of steam at 15 to 55 lbs./sq. in. absolute pressure (i. e. 100 to 140° C.), the fabric acquires the elasticity of mildly vulcanized rubber, and shrinks much more than a similar standard fabric of polyhexamethylene adipamide yarn. The following table shows how the degree of shrinkage may be pre-determined by adjustment of the steam pressure and the temperature, besides furnishing comparative data with respect to a similar fabric of polyhexamethylene adipamide yarn.

TABLE I

Shrinkage of steam-treated fabrics

Steam pressure lb./sq. in. ² (absolute)	Temperature	Shrinkage of fabric from melt-blended PTGA ¹ and PHMA ²			
		Shrinkage of fabric from melt-blended PTGA ¹		Shrinkage of fabric from PHMA ²	
		Direction of warp threads	Direction of filling threads	Direction of warp threads	Direction of filling threads
	°C.	Per cent	Per cent	Per cent	Per cent
15	100	30	19	8	8
25	115	32	18	8	8
35	126	36	21	8	8
45	131	43	28	11	10
55	141	51	32	15	12

¹ PTGA: Polytriglycol adipamide.

² PHMA: Polyhexamethylene adipamide.

When the foregoing mixed polyamide fabric is soaked or boiled in water and then subjected to moist heat along with mechanical pressure against its face for 30 seconds, it develops extraordinarily good recovery from creasing. Such

¹ Also denominated N-Methyl polytriglycol adipamide, hereinbelow.

a treatment advantageously may be carried out by calendering the wet fabric. The "crease angle," a measure of the percentage of crease recovery, is determined by measuring the angle from the horizontal to which a folded 1 inch square of fabric returns in 30 seconds, upon being allowed to unfold after the crease has been set in by the pressure of a 1 kilogram weight for 1 minute. Wet calendering temperatures of 150 to 220° C. applied to the said fabric produce finished cloth whose crease recovery is considerably greater than that of an otherwise identical fabric woven from polyhexamethylene adipamide yarn, as shown in the following table.

TABLE II

Crease recovery of wet fabrics

Pre-treatment	Calendering temperature	"Crease angle" of fabric from melt-blended PTGA ¹ and PHMA ²	"Crease angle" of fabric from PHMA ²
	°C.	Degrees	Degrees
Soaking 16 hrs. in water at 25° C.	152	13	36
Do.	185	21	33
Boiling 1 hr. in water	152	12	29
Do.	185	8	21
Do.	220	11	18

¹ PTGA—Polytriglycol adipamide.

² PHMA—Polyhexamethylene adipamide.

EXAMPLE III

A mixture of 150 parts of polytriglycol adipamide (intrinsic viscosity, 0.83) and 850 parts of polyhexamethylene adipamide (intrinsic viscosity, 0.84) is melt blended by heating with intermittent stirring for about 30 minutes at 285° C. and then is melt-spun at about 280° C. into filaments which are converted by the usual procedures to yarn (90 denier, 30 filament, 10 turns per inch twist) and thence to a plain weave taffeta fabric measuring 100 threads per inch in the warp and 70 threads per inch in the woof. The water-sensitivity conferred on the fabric by the presence of the water-soluble but unextractable component of the yarn is such that wet-calendering confers on the fabric unusual and highly desirable crease recovery, the same being approximately of the order of that shown in the case of the mixed-polyamide fabric of Table II, and contrasting sharply with the crease recovery of polyhexamethylene adipamide fabrics of the prior art.

Polyhexamethylene adipamide has poor receptivity for vat colors, and, furthermore, these dyeings crock badly. These difficulties are overcome by the use of polytriglycol adipamide melt blended with polyhexamethylene adipamide. Skeins of yarn melt-spun from the blend containing 15% of the water-soluble polyamide component and 85% polyhexamethylene adipamide are dyed with vat colors by the sodium hydrosulfite method commonly used in commercial dyeing practice. Table III lists a comparison of the receptivity of the yarn with that of rayon¹ and with that of polyhexamethylene adipamide, when skeins of the various fibers are dyed in individual baths. As can be seen from the table, the yarn prepared from the water-soluble and water-insoluble polyamide components has a receptivity for vat colors equal to that of rayon. Furthermore, these vat dyeings on the yarn of the blended polymer do not crock.

¹ The term, "rayon," as used in this specification, is intended to designate regenerated cellulose rayon, of the type spun from viscose.

TABLE III

Dye color index No.	Concentration of dye bath	Dye absorbed by yarn of 15% PTGA ¹ and 85% PHMA ²	Dye absorbed by PHMA ² yarn	Dye absorbed by rayon yarn
	Percent	Percent	Percent	Percent
Anthraquinone vat dye having color index No. 1113.	3	96	40	96
Anthraquinone vat dye having color index No. 1132.	5	90	40	80
Anthraquinone vat dye having color index No. 1163.	5	96	46	90
Indigold vat dye having color index No. 1184.	5	98	90	96

¹ PTGA—Polytriglycol adipamide.

² PHMA—Polyhexamethylene adipamide.

Skeins of yarn melt-spun from the product obtained from 15% of the water-soluble component and 85% polyhexamethylene adipamide, skeins of polyhexamethylene adipamide yarn, and skeins of rayon are dyed in individual baths containing direct colors. As can be seen in Table IV the yarn containing the water-soluble and water-insoluble polyamide component has a receptivity comparable to that of rayon for direct colors.

TABLE IV

Dye color index No.	Concentration of dye bath	Dye absorbed by yarn melt-spun from 15% PTGA ¹ and 85% PHMA ²	Dye absorbed by PHMA ² yarn	Dye absorbed by rayon yarn
	Per cent	Per cent	Per cent	Per cent
Direct dye having color index No. 375.	2	95	25	95
Direct dye having color index No. 382.	2	95	25	90
Direct dye having color index No. 365.	2	95	25	90

¹ PTGA—Polytriglycol adipamide.

² PHMA—Polyhexamethylene adipamide.

Skeins of yarn melt-spun from the blend prepared from 15% of the water-soluble component and 85% of polyhexamethylene adipamide, skeins of polyhexamethylene adipamide yarn, and skeins of silk are dyed in individual baths containing neutral dyeing acid colors. As can be seen in Table V the yarn prepared from the melt blend of the water-soluble and water-insoluble polyamide components has a receptivity comparable to that of or greater than that of, silk for neutral dyeing acid colors.

TABLE V

Dye color index No.	Concentration of dye bath	Dye absorbed by melt-spun yarn of 15% PTGA ¹ and 85% PHMA ²	Dye absorbed by PHMA ² yarn	Dye absorbed by silk yarn
	Per cent	Per cent	Per cent	Per cent
Neutral dyeing acid dye having index No. 833.	4	93	37	93
Neutral dyeing acid dye having color index No. 430.	2	95	12	63

¹ PTGA—Polytriglycol adipamide.

² PHMA—Polyhexamethylene adipamide.

When knit goods prepared from polyhexamethylene adipamide yarns differing in the de-

gree to which they have been drawn, in the solid state, by as much as 4% are dyed with acid, direct, or vat colors, a pronounced color junction appears at the union of the sections of fabric containing the differently drawn yarns, the section knit from the lesser drawn yarn absorbing more color than the section knit from the more highly drawn yarn. Knit goods prepared from the melt-spun yarn of 15% polytriglycol adipamide and 85% polyhexamethylene adipamide differing in the degree to which they have been drawn, in the solid state, by as much as 4% are dyed uniformly and evenly with acid, direct, and vat colors. Accordingly, the level-dyeing properties are improved as well as the dye receptivity of the modified polymer over similar properties of polyhexamethylene adipamide.

The polyamides of this invention have a greater affinity for basic colors and chrome dyes than do polyamides such as polyhexamethylene adipamide. Typical examples of useful basic colors are those having color indices of 657, 749, and 815. Examples of useful chrome dyes are those of color indices 109, 180, 216, 219, and 720.

The polyamides of this invention also have good affinity for dyestuffs of the cellulose acetate class. Thus fabrics knitted from cold drawn yarn spun from the melt blended polyamide of Example III are satisfactorily dyed in a 1% bath of cellulose acetate color having Color Index Pr 43.

EXAMPLE IV

By the procedure described in the foregoing examples, a series of melt-blends are prepared by heating with intermittent stirring at 185° C. for about 30 minutes polytriglycol adipamide (intrinsic viscosity, 0.84) and polyhexamethylene adipamide (intrinsic viscosity, 0.83) in varying proportions. The physical properties which characterize the resulting compositions are indicated in the following table, along with corresponding data for the unblended components and for the interpolymers made from the same proportions of the corresponding monomeric ingredients. It will be noted that the melting points of the melt-blends of pre-formed polymers are significantly higher than the melting points of the interpolymers.

TABLE VI

Properties of melt-blends of polytriglycol adipamide and polyhexamethylene adipamide

Proportions of ingredients		Melt-blend melting point	Inter-polymer melting point	Melt-blend	
PTGA ¹	PHMA ²			Water absorption (saturated at 25° C.)	Proportion of weight lost on water extraction
0	100	247	247	Per cent	Per cent
0.5	99.5	247	247	9.0	0
1	99	246	246	9.1	0
2	98	245	245	9.1	0.1
4	96	244	244	8.9	0
8	92	242	242	10.1	0.5
20	80	244	224	10.7	0.6
35	65	242	213	13.7	1.2
50	50	240	190	21.1	2.2
65	35	235	169	33.6	4.5
80	20	215	155	-----	-----
90	10	185	152	-----	-----
100	-----	166	160	-----	100

¹ PTGA—Polytriglycol adipamide.

² PHMA—Polyhexamethylene adipamide.

³ For comparison.

⁴ Loses strength.

⁵ Dissolves.

EXAMPLE V

Intimate mixtures of N-methyl polytriglycol adipamide (intrinsic viscosity, 0.35) and polyhexamethylene adipamide (intrinsic viscosity, 0.81) in the proportions shown in the following table are prepared by melting them together with intermittent stirring in the absence of oxygen at 285° C. for about 30 minutes. The table furnishes a guide to the proper choice of proportions necessary for obtaining products with desired melting points and water absorption or extraction properties.

TABLE VII

Proportions of ingredients		Melting point	Water absorption of melt-blend (saturated) at 25° C.	Proportion of weight lost on water extraction
N-MPTGA ¹	PHMA ²			
Percent	Percent	° C.	Percent	Percent
10	90	242	13.5	0
20	80	235	18.0	1.5
40	60	230	36	3.8

¹ N-MPTGA—N-methyl polytriglycol adipamide.

² PHMA—Polyhexamethylene adipamide.

Oriented films of a melt blend comprising 20% N-methyl-polytriglycol adipamide and 80% polyhexamethylene adipamide are dyed with vat, acid, and direct colors by the usual methods of commercial practice. The following Table VIII shows the improvement in receptivity of the oriented films of the melt blend over that of the oriented films of polyhexamethylene adipamide.

TABLE VIII

Dye color index No.	Concentration of dye bath	Dye absorbed by films of melt-blend of 20% N-MPTGA ¹ and 80% PHMA ²	Dye absorbed by films of PHMA ²
VAT COLORS			
Anthraquinone dye having color index No. 1163.	Percent 5	Percent 96	Percent 50
Anthraquinone dye having color index No. 1113.	5	96	40
DIRECT COLORS			
Direct dye having color index No. 365.....	2	95	25
Direct dye having color index No. 382.....	2	95	25
Direct dye having color index No. 376.....	2	95	25

ACID COLORS

Acid dye having color index No. 114.....	2	85	25
Acid dye having color index No. 439	2	90	12

¹ N-MPTGA—N-methyl polytriglycol adipamide.

² PHMA—Polyhexamethylene adipamide.

EXAMPLE VI

A melt-blend is formed by stirring and heating for about 30 minutes at 285° C. in the absence of oxygen 100 parts of N-methyl polytriglycol adipamide (intrinsic viscosity, 0.35) and 900 parts of an interpolymers product (melting point, 161° C.; intrinsic viscosity, 1.00) of 40% hexamethylenediammonium adipate, 30% hexamethylenediammonium sebacate, and 30% epsilon-caprolactam. Pellicles of this composition (melting point, 145° C.) are conditioned to different moisture contents at 25° C. by the following methods: (1) thorough drying in a chamber dehydrated by phosphorus pentoxide, (2) exposure

for 24 hours to atmosphere at 50% relative humidity, and (3) soaking in water. The pellicles with the highest moisture content (conditioned by method 3 are very resistant to the usual embrittling influence of low temperatures. For example, they are still capable of being cold drawn when cooled to -65°C . and therefore are

Melt-blended mixtures of water-soluble polyamides with water-insoluble polyamides other than those already specified, together with figures furnishing a guide to the proper choice of proportions for obtaining optimum balance between melting point and other characteristics, will be found in the following table.

TABLE X
Melt blends of water-soluble and water-insoluble polyamides

	Water-soluble polyamide (1)	Water-insoluble polyamide (2)	Ratio of (1):(2)	Melting point
				$^{\circ}\text{C}$.
A.....	N-methyl polytriglycol adipamide.	Interpolymerization product of 60% hexamethylenediammonium adipate and 40% epsilon-caprolactam.	10:90	180
B.....	do.	do.	20:80	175
C.....	do.	do.	40:60	135
D.....	do.	do.	40:60	115
		Interpolymerization product of 40% hexamethylene-diammonium adipate, 30% hexamethylenediammonium sebacate and 30% epsilon-caprolactam.		
E.....	do.	do.	20:80	135
F.....	Polytriglycol adipamide.	Polyhexamethylene sebacamide.	5:95	215
G.....	do.	do.	10:90	214
H.....	do.	do.	20:80	210
I.....	do.	do.	35:65	214
J.....	do.	do.	50:50	210
K.....	do.	Poly-epsilon-caprolactam.	5:95	202
L.....	do.	do.	10:90	205
M.....	do.	do.	20:80	204
N.....	do.	do.	35:65	192
O.....	do.	do.	50:50	200
P.....	do.	Interpolymerization product of 60% hexamethylenediammonium adipate and 40% epsilon-caprolactam.	5:95	186
Q.....	do.	do.	10:90	185
R.....	do.	do.	20:80	184
S.....	do.	do.	35:65	183
T.....	do.	do.	50:50	171

well adapted for applications at the low temperatures which may be met in practice, e. g., during outdoor winter exposure. The importance of the water absorbed is demonstrated by the fact that the pellicles of the same material containing less moisture (conditioned by methods 1 or 2) are adversely affected by cold. These contrasts are emphasized by determinations of the cold crack temperature, i. e., the lowest temperatures to which the conditioned pellicles can be cooled without losing their capacity to withstand fracture when flexed. The results of these determinations are set forth in the following table.

TABLE IX
Cold crack temperatures of moisture-conditioned films

Method of conditioning	Water absorption of melt-blend at 25°C .	Cold crack temperature
	Percent	$^{\circ}\text{C}$.
3.....	14.7	Below -55
1.....	0	-30 to -35
2.....	3.1	-25 to -30

With reference to Table X, it should be remembered that some of the water-insoluble polyamides, e. g., A, B, C, D, F, Q, R, S, and T, are soluble in mixtures of water and alcohol (20% water and 80% ethanol) and can be used as the soluble component in the practice of this invention when blended with polyamides insoluble in alcohol or alcohol-water mixtures. This embodiment of the invention is illustrated in the following example.

EXAMPLE VII

The interpolymerization product (soluble in 80:20 mixture of ethanol and water) of 60% of hexamethylene diammonium adipate and 40% of epsilon-caprolactam is melt-blended at 285°C . with stirring with an equal weight of fiber-forming polyhexamethylene adipamide (insoluble in ethanol-water mixtures) until a homogeneous product is obtained. The resulting melt-blend is spun into yarn and the yarn oriented by cold-drawing until the yarn had a residual elongation of about 20%. As shown by the following table, this yarn has better dyeing properties than yarns spun from polyhexamethylene adipamide alone.

TABLE XI

Dye color index No.	Concentration of dye in bath	Dye absorbed by melt-blend of interpolymerization product and polyhexamethylene adipamide	Dye absorbed by polyhexamethylene adipamide	Dye absorbed by—	
				Rayon	Silk
	Per cent	Per cent	Per cent	Per cent	Per cent
Neutral dyeing acid having C. I. No. 114.....	2	75	25	75	75
Neutral dyeing acid having C. I. No. 430.....	2	50	25	50	75
Direct dye having C. I. No. 518.....	2	80	10	90	-----
Vat dye having C. I. No. 1113.....	5	80	40	98	-----
Vat dye having C. I. No. Pr. 124.....	5	80	40	98	-----
Vat dye having C. I. No. 1101.....	5	80	40	98	-----

Suitable water-soluble polytriglycolamides other than those varieties which have been disclosed hereinabove, include polytriglycol N,N'-piperazinediacetamide*, polytriglycol N-methyliminodiacetamide*, polytriglycol 5-hydroxy-1,9-nonanedicarbonamide, polytriglycol diglycolamide*, and the interpolymerization products of: triglycoldiammonium adipate (85 parts), hexamethylenediammonium adipate (14 parts), and triglycoldiammonium 4-ketopimelate (1 part); or triglycoldiammonium adipate (85 parts), hexamethylenediammonium adipate (10 parts), and triglycoldiammonium 4-ketopimelate (5 parts)*; or triglycoldiammonium adipate and 6-aminocaproic acid containing at least 75% of the former; or triglycoldiammonium diglycolate (50 parts) and hexamethylenediammonium glycolate (50 parts)*; or triglycoldiammonium diglycolate (70 parts) and hexamethylenediammonium adipate (30 parts)*; or triglycoldiammonium adipate and decamethylenediammonium sebacate containing at least 90% of the former; or triglycoldiammonium adipate and hexamethylenediammonium sebacate containing at least 85% of the former; or triglycoldiammonium adipate and hexamethylenediammonium adipate containing at least 85% of the former.

Of the water-soluble polyamides just listed, those marked with an asterisk ordinarily are to be preferred, since they are soluble at least to the extent of 50% by weight in water at 25° C. The remaining polymers in the list are satisfactory in many instances, however, since they are at least 20% soluble by weight, in water at 25° C. The significance of the stated 20% or, preferably, 50% solubilities arises from the fact that the extent of unique characteristics possessed by, or producible in, the products of the invention corresponds generally to the degree of inherent solubility of the more soluble polyamide of the mixture in water, or whatever other swelling agent may be employed in place thereof.

Additional examples of water-soluble polyamides suitable for use in the practice of the invention include polydiglycol diglycolamide, polyethylene N-methyliminodiacetamide, polydiglycol N-methyliminodiacetamide, and poly-4,7-dioxadecamethylene adipamide.

Mixtures of two or more water-soluble polyamides of course may be employed as the water-soluble component. It is to be remarked, furthermore, that the suitable water-soluble polyamides are not limited to fiber-forming polyamides, although it is desirable that these polyamides have intrinsic viscosities of at least 0.2.

As the water-insoluble component, any fiber-forming polyamide or interpolyamide, or a mixture of two or more of them, advantageously may be used. In addition to the water-insoluble polymers mentioned in the foregoing examples, the following are suitable: polytetramethylene adipamide, polytetramethylene suberamide, polytetramethylene sebacamide, polyoctamethylene adipamide, polydecamethylene p-phenylenediacetamide, poly-p-xylylene sebacamide, polypentamethylene adipamide, polypentamethylene sebacamide, and 9-aminononanoic acid polymer. Since it is frequently desired to achieve a high melting point in the product, water-insoluble polyamides having melting points above about 235° C. are preferred. The first six of the polyamides just listed are examples of such preferred ingredients.

As is evident from Examples IV and V, the properties of the polyamide mixtures which are

responsive to the hot water or steam treatments in accordance with the invention, depend on the proportions of water-soluble and water-insoluble ingredients. The optimum qualities are achieved by the use of water-soluble polyamide in the preferred proportions of 15% to 50%. Since the highly water-soluble polyamides are more effective than their less soluble analogs, however, when used in the same proportions, it has been found desirable to use higher proportions, preferably at least 15% or higher, of the water-soluble component, if it is soluble in water to the extent of less than 50% by weight.

The melt-blends of this invention are not identical with simple mixtures or with the corresponding interpolyamides, as demonstrated by the following facts: (1) The major proportion of the soluble component (s) of the melt-blends is not extractable, while non-melt-blended mixtures (including heterogeneous melts) such as are obtained by mixing the components in a mutual solvent which is subsequently evaporated, can easily be separated into the original component polyamides by treatment with a selective solvent; (2) as indicated in Example IV, the melt-blends have significantly higher melting points than the corresponding interpolyamides. A plausible explanation for these facts is that the process of melt-blending involves some chemical reaction, presumably amide interchange, which unites the molecules of the constituents to a slight degree; but in postulating this explanation the applicants do not intend to be in any way bound thereby or limited thereto.

Although the water-soluble plus water-insoluble polyamide mixtures in most instances are preferred, in view especially of the relatively low cost of water as compared with other swelling agents and its use in dyeing and finishing operations, there are several counter-balancing advantages in the use of mild organic swelling agents, rather than water, which advantages on occasion may outweigh those inherent in the use of water. In such case the water-soluble polyamide component can be replaced with a component soluble per se in the said organic swelling agent, as hereinabove explained. The said relative advantages of the organic swelling agent may include ease of removability, as in the case of low boiling alcohols, increased activity at lower temperatures as compared with water, and decreased tendency to corrode equipment and consequently to contaminate the mixed-polyamide article undergoing treatment.

The mild swelling agent which may be employed in the practice of the invention generally are hydroxylated organic substances, which include not only the low molecular weight aliphatic alcohols such as methanol, ethanol, isopropanol, and butanol, but also ethylene chlorohydrin and benzyl alcohol.

Typical alcohol-soluble polyamides suitable for melt-blending with alcohol-insoluble polyamides, such as polyhexamethylene adipamide, in the practice of the invention, include poly(N-methyltriglycol adipamide) and the interpolymerization product of hexamethylenediammonium adipate (40 parts), hexamethylenediammonium sebacate (30 parts), and epsilon-caprolactam (30 parts). Polyamides soluble in alcohol-water or alcohol-chloroform mixtures can also be used as the soluble components. An example of this type is the polyamide derived from hexamethylenediammonium adipate (preferably 40 to 60 parts) and 6-aminocaproic acid (preferably 60 to 40 parts).

Polyester-amides such as those derived from diamine, dibasic acid and glycol, also are useful, provided a swelling agent is chosen which, though a solvent for them per se, is a non-solvent for the polyamide with which they are to be melt-blended. As a rule, the solubility of the ester-amide polymers increases as the percentage of ester content increases.

One of the foremost advantages of the mixed-polyamide products of the invention is their elasticity in the form of fabrics and foils. The elastic fabrics obtained by finishing treatments such as described in Examples I, II and III are suited for the types of garments which require a greater extensibility than can be attained with natural fibers. Fabrics possessing unusually high recovery from creasing, such as that of Example II, are, like wool, in great demand for textile uses, e. g. for garments in which impermanence of accidental creasing is highly desirable. Such fabrics are distinctly superior in this respect to the more crease-retentive synthetic fabrics of the prior art.

In connection with the superior dyeing characteristics of the mixed polyamide products of the invention, illustrated in Tables III-V, VIII, and XI, hereinabove, it may be remarked that the products have especially good receptivity for dyes in printing. A wide variety of dyes can be used in the printing pastes. Useful dyes include vat colors, e. g. those of color indices 1095, 1101, 1133, 1151, 1184, and 1212, acid colors, e. g., those of color indices 27, 234, 561, 581, 801, and 1053; direct colors, e. g. those of color indices 561, 581, and 814; basic colors, e. g. those of color indices 815 and 922; chrome colors, e. g. color having index number 720; oxidation colors, e. g. oxy black base (p-amino diphenyl amine); Celanthrene colors, e. g. 1-methyl amino anthraquinone; and acetamide colors, e. g. dispersible dyestuff from aniline azo alpha naphthylamine azo phenol. A few typical examples follow.

EXAMPLE VIII

The printing paste used consisted of 20 parts of vat color having Color Index No. 1184 and 80 parts of a composition prepared by incorporating 15% potassium carbonate, 15% sodium sulfoxylate formaldehyde and 5% glycerine in a suitable thickening gum such as starch, British gum, tragacanth or karaye. The paste is printed on polyhexamethylene adipamide fabric and on a fabric made with melt-blended polyamide of the type described in Example III. After printing the fabrics are partially dried, aged for 5 minutes in vat color ager, oxidized, rinsed, soaped, rinsed, and dried to give a blue pattern in the imprinted areas. The blue pattern is brighter on the fabric made from modified polyamide than on the polyhexamethylene adipamide fabric.

Discharge prints can be made with the above paste printed on grounds dyed with dye of Color Index No. 487 (Scarlet) or Acetamide Blue GFA.

EXAMPLE IX

A printing paste consisting of 2 parts of 1-methyl amino anthraquinone, 28 parts of water, and 70 parts of textile gum is printed on fabric made of melt-blend polyamide made by the process of this invention. After drying, the fabric is aged for 10 minutes in a vat color ager, soaped, rinsed, and dried. A brilliant scarlet print is obtained.

For discharge printing the above printing paste can be mixed with 10% of stannous chloride or

titanous chloride and printed on a ground dyed with p-amino acetanilide azo para cresol to give a scarlet illumination design on a yellow ground.

The mono nucleus anthraquinone bodies used as dyestuffs may be mono- or poly-amino anthraquinones which may be substituted in the nucleus or in the amino group or in both.

The resilient pellicles made of the blends of this invention are especially useful as self-supporting films for wrapping purposes and the like.

Since 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 we do not limit ourselves to the specific embodiments thereof except as defined in the appended claims.

We claim:

1. A process for obtaining an improved polyamide composition having a relatively high melting point and enhanced affinity for dyestuffs which comprises heating at amide-forming temperatures below that at which destructive decomposition occurs, a molten mixture of at least two preformed synthetic linear polyamides, at least one of said polyamides being water soluble at least to the extent of 20% by weight at 25° C. and at least another of said polyamides being water insoluble, said soluble to insoluble polyamides being by weight in the range 5:95 to 80:20, each of said preformed polyamides being one which on hydrolysis with hydrochloric acid yields substances of the class consisting of (a) monoaminomonocarboxylic acid hydrochlorides and (b) mixtures of diamine dihydrochloride and dibasic carboxylic acid, continuing the heating at said amide-forming temperatures until the molten polyamides form a single phase without discontinuity and until a substantially homogeneous product is obtained on solidification from which not more than 10% of said soluble polyamide can be selectively extracted by water, then solidifying said polyamide composition.

2. A process for obtaining an improved polyamide composition having a relatively high melting point and enhanced affinity for dyestuffs which comprises heating at amide-forming temperatures between 250° to 300° C., a molten mixture of at least two preformed synthetic linear polyamides, at least one of said polyamides being soluble at least to the extent of 20% by weight at 25° C. in a solvent selected from the group consisting of water, aliphatic alcohols of less than five carbon atoms and mixtures of water and said alcohols, and at least another of said polyamides being insoluble in said solvent, said soluble to insoluble polyamides being by weight in the range 15:85 to 50:50, each of said preformed polyamides being one which on hydrolysis with hydrochloric acid yields substances of the class consisting of (a) monoaminomonocarboxylic acid hydrochlorides and (b) mixtures of diamine dihydrochloride and dibasic carboxylic acid, continuing the heating at said amide-forming temperatures until the molten polyamides form a single phase without discontinuity and until a substantially homogeneous product is obtained on solidification from which not more than 10% of said soluble polyamide can be selectively extracted by said solvent, then solidifying said polyamide composition.

3. An improved polyamide composition having a relatively high melting point and enhanced affinity for dyestuffs comprising the reaction product obtained by heating at amide-forming temperatures below that at which destructive decom-

position occurs, a molten mixture of at least two preformed synthetic linear polyamides, at least one of said polyamides being water soluble at least to the extent of 20% by weight at 25° C. and at least another of said polyamides being water insoluble, said soluble to insoluble polyamides being by weight in the range 5:95 to 80:20, each of said preformed polyamides being one which on hydrolysis with hydrochloric acid yields substances of the class consisting of (a) monoaminomonocarboxylic acid hydrochlorides and (b) mixtures of diamine dihydrochloride and dibasic carboxylic acid, continuing the heating at said amide-forming temperatures until the molten polyamides form a single phase without discontinuity and until a substantially homogeneous product is obtained on solidification from which not more than 10% of said soluble polyamide can be selectively extracted by water, then solidifying said polyamide composition.

4. An improved polyamide composition having a relatively high melting point and enhanced affinity for dyestuffs comprising the reaction product obtained by heating at amide-forming temperatures between 250° to 300° C., a molten mixture of at least two preformed synthetic linear polyamides, at least one of said polyamides being soluble at least to the extent of 20% by weight at 25° C. in a solvent selected from the group consisting of water, aliphatic alcohols of less than five carbon atoms and mixtures of water and said alcohols, and at least another of said polyamides being insoluble in said solvent, said soluble to insoluble polyamides being by weight in the range 15:85 to 50:50, each of said preformed polyamides being one which on hydrolysis with hydrochloric acid yields substances of the class consisting of (a) monoaminomonocarboxylic acid hydrochlorides and (b) mixtures of diamine dihydrochloride and dibasic carboxylic acid, continuing the heating at said amide-forming temperatures until the molten polyamides form a single phase without discontinuity and until a substantially homogeneous product is obtained on solidification from which not more than 10% of said soluble polyamide can be selectively extracted by said solvent, then solidifying said polyamide composition.

5. The product of claim 3 wherein the soluble polyamide is polytriglycol adipamide.

6. The product of claim 3 wherein the insoluble polyamide is polyhexamethylene adipamide.

7. An article of manufacture comprising an

improved polyamide composition obtained by heating at amide-forming temperatures below that at which destructive decomposition occurs, a molten mixture of at least two preformed synthetic linear polyamides, at least one of said polyamides being water soluble at least to the extent of 20% by weight at 25° C. and at least another of said polyamides being water insoluble, said soluble to insoluble polyamides being by weight in the range 5:95 to 80:20, each of said preformed polyamides being one which on hydrolysis with hydrochloric acid yields substances of the class consisting of (a) monoaminomonocarboxylic acid hydrochlorides and (b) mixtures of diamine dihydrochloride and dibasic carboxylic acid, continuing the heating at said amide-forming temperatures until the molten polyamides form a single phase without discontinuity and until a substantially homogeneous product is obtained on solidification from which not more than 10% of said soluble polyamide can be selectively extracted by water, then solidifying said polyamide composition and incorporating therein a swelling agent.

8. A dyed article of manufacture comprising an improved polyamide composition obtained by heating at amide-forming temperatures below that at which destructive decomposition occurs, a molten mixture of at least two preformed synthetic linear polyamides, at least one of said polyamides being water soluble at least to the extent of 20% by weight at 25° C. and at least another of said polyamides being water insoluble, said soluble to insoluble polyamides being by weight in the range 5:95 to 80:20, each of said preformed polyamides being one which on hydrolysis with hydrochloric acid yields substances of the class consisting of (a) monoaminomonocarboxylic acid hydrochlorides and (b) mixtures of diamine dihydrochloride and dibasic carboxylic acid, continuing the heating at said amide-forming temperatures until the molten polyamides form a single phase without discontinuity and until a substantially homogeneous product is obtained on solidification from which not more than 10% of said soluble polyamide can be selectively extracted by water, then solidifying said polyamide composition and incorporating therein a dye composition.

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