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㉕ Mineral filled abrasion-resistant monofilament.

㉖ Polyamide monofilament with excellent transverse abrasion resistance obtained by incorporation of aluminum silicate, particularly useful in paper clothing.

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TITLE

Mineral Filled Abrasion-Resistant Monofilament

BACKGROUND OF THE INVENTION

In the preparation of paper, woven support
5 belts are used for the initial casting and subsequent
treatment of the paper. These belts are known as
paper clothing. A variety of materials has been used
in the manufacture of such belts, including metals,
and, more recently, thermoplastic monofilaments.
10 Thermoplastic materials which have been used in the
weaving of these belts include nylon as well as
polyester monofilaments.

A particularly satisfactory combination of
materials for paper clothing is a polyester
15 monofilament, woven in the machine direction of the
belt, with transverse monofilaments composed either
partly or entirely of a polyamide monofilament.
Particularly in such applications, a need exists for
a polyamide monofilament having improved resistance
20 to abrasion when the abrasive force is applied
transversely to the longitudinal dimension of the
monofilament.

SUMMARY OF THE INVENTION

The present invention provides a polyamide
25 monofilament which exhibits outstanding resistance to
abrasive forces applied transversely to the
longitudinal dimension of the monofilament.

Specifically, the instant invention provides
an oriented polyamide monofilament comprising fiber
30 or filament-forming polyamide and about from 2 to 20
weight percent, based on the total weight of the
monofilament, of aluminum silicate having an average
particle size of about from 1 to 8 microns.

The instant invention further provides, in a
AD-5099 35 woven, heat set, papermaking belt of machine and

transverse direction thermoplastic filaments, the improvement wherein at least about 25% of the transverse direction filaments are monofilaments comprising filament forming polyamide and about from 5 2-20 weight percent, based on the total weight of the filament, of aluminum silicate having an average particle size of about from 1 to 8 microns.

DETAILED DESCRIPTION OF THE INVENTION

The polyamides used for preparation of the 10 oriented monofilaments of the present invention are non-cyclic polyamides of fiber-forming molecular weight having relative viscosity generally between 25 and 150 as determined by ASTM D-789-62T. These polyamides include, for example, polycaprolactam 15 (6 nylon), polyhexamethylene adipamide (66 nylon), polyhexamethylene decanoamide (610 nylon), and polyhexamethylene dodecanoamide (612 nylon). Polyamide copolymers and polymer blends can also be used, such as those prepared from 6 nylon and 66 20 nylon. Of these, polyhexamethylene adipamide (66 nylon) and polyhexamethylene dodecanoamide (612 nylon) have been found to be particularly satisfactory for use in paper clothing.

In accordance with the present invention, 25 about from 2 to 20 weight percent, and preferably about from 4 to 10 weight percent, of aluminum silicate is blended with the polyamide used for the preparation of the monofilaments. Less than about 2 weight percent of the aluminum silicate does not 30 provide the markedly improved transverse direction abrasion resistance of the present invention, while quantities of aluminum silicate in excess of 20 weight percent of the monofilament unnecessarily weaken the filament with no further beneficial 35 effects.

The aluminum silicate used in the present invention should be of the type generally commercially available in a uniform particulate configuration. The aluminum silicate should have a
5 particle size such that 90% by weight or more of the particles are less than 15 microns and the average particle size is about from 1 to 8 microns. Particularly satisfactory aluminum silicate clays are those in which 98% of the particles are less than 10
10 microns and have an average particle size of about from 1 to 6 microns. Aluminum silicates of this type are described in detail in United States Patent 3,419,517, and are commercially available as "Satintone" from Engelhard Minerals and Chemicals
15 Corp. of Edison, New Jersey.

The products of the present invention are preferably prepared by combining the nylon polymer with a coupling agent prior to the incorporation of the aluminum silicate. The incorporation of the
20 coupling agent provides improved adhesion of the aluminum silicate to the nylon. Coupling agents which can be used include those organosilane and phosphorus coupling agents described in Miller U.S. Patents 3,344,107, 3,471,435 and 3,488,319, hereby
25 incorporated by reference.

In a preferred embodiment of the present invention, the monofilaments further comprise about from 0.5 to 10 weight percent of an ethylene copolymer having a Melt Index of about from 0.3 to 30. At
30 least about 50% of the ethylene copolymer should be a graft copolymer prepared from (a) a backbone of polymer selected from the group consisting of thermoplastic polymers of ethylene and copolymers derived from ethylene and C₃-C₈ alpha-olefins and
35 (b) a graft monomer selected from the group

consisting of unsaturated carboxylic acids,
anhydrides and dianhydrides. Less than 1.0 weight
percent of this ethylene copolymer additive provides
little or no appreciable improvement in abrasion
5 resistance for the finished monofilament, while
quantities in excess of 10 weight percent result in a
drop in tensile strength for the monofilament.
Particularly outstanding improvement in monofilament
characteristics is realized through the use of about
10 from 1.2 to 5 weight percent of the graft copolymer.

The graft copolymer, when used, should have
a Melt Index of about from 0.3 to 30. Ethylene
polymers having a Melt Index outside of this range
can result in processing difficulties. Particularly
15 satisfactory are those graft copolymers having a Melt
Index of about from 0.5 to 20.

Melt Index is measured according to ASTM
D-1238-79, condition E. In that test, the rate of
extrusion in grams per 10 minutes (through an orifice
20 0.0825 inch [0.210 cm] in diameter and 0.315 inch
[0.800 cm] in length) is determined for the material
under test at 190°C and under the force of a piston
having a diameter of 0.373 inch (0.947 cm) and a
total weight of 2,160 grams.

25 Polymeric materials which can be used as a
backbone polymer in the graft copolymers are
generally selected from thermoplastic polymers of
ethylene and copolymers derived from ethylene and
C₃-C₈ alpha-olefins. Backbone polymers which are
30 substantially saturated include polymers of ethylene
and copolymers derived from ethylene and
alpha-olefins. Backbone polymers which exhibit
unsaturation include those having a substantially
saturated backbone chain with unsaturated side
35 chains, including copolymers derived from ethylene

and alpha-olefins. The term alpha-olefin includes monoolefins and diolefins and does not include ethylene.

Graft monomers which can be used for the preparation of the graft copolymer additives of the present invention include unsaturated carboxylic acids, anhydrides and dianhydrides thermally stable at the temperature of the grafting reaction. Graft monomers which can be used for the preparation of these additives include methacrylic acid; acrylic acid; glycidyl methacrylate; 2-hydroxy ethylacrylate; 2-hydroxy ethyl methacrylate; diethyl maleate, monoethyl maleate; di-n-butyl maleate; maleic anhydride; maleic acid; fumaric acid; itaconic acid; dodecanyl succinic anhydride; 5-norbornene-2,3-anhydride; and nadic anhydride (3,6-endomethylene-1,2,3,6-tetrahydrophthalic anhydride).

The graft copolymers can be prepared by a variety of reaction techniques. However, particularly preferred is that process described in Flexman, Jr. et al. U.S. Patent 4,026,967, wherein the reaction of the components is conducted in baffled tubular reactors which exhibit dispersed plug flow character and which provide rapid heating and cooling of reactants, short reaction time with uniform material residence time, and radial uniformity of temperature. In general, the graft comonomers can comprise about from 0.15 to 2.0 weight percent of the graft copolymer. A graft copolymer found to be particularly satisfactory in the invention is that prepared from polyethylene having a density of about from 0.94 to 0.97 g/cc and grafted with about from 0.15 to 0.75 weight percent graft monomer, and especially fumaric acid or maleic anhydride monomers.

The blending of the components of the monofilament can be carried out in any sequence convenient to the particular manufacturing operation involved. However, in general, it has been found
5 convenient to prepare concentrates of each additive in nylon prior to final blending to aid in the accurate measurement of each of the components.

After blending of the components, the monofilaments are prepared according to customary
10 techniques. The molten nylon, blended with the aluminum silicate and any other additives, is extruded through a die into a quench medium, after which it is oriented. The monofilaments should be oriented about from 3.4 to 6.0 times their original
15 length, and preferably about from 3.5 to 4.7 times their original length. In general, the diameter of the final monofilament should be about from 5 to 30 mils, and preferably about from 10 to 20 mils.

The monofilaments of the present invention
20 can be woven into papermaking belts according to conventional weaving techniques. The type and density of the weave will, of course, depend on the type of paper and papermaking operation for which the belt is to be used. The present monofilaments are
25 particularly satisfactory when used in combination with polyester monofilaments in a woven belt in which the polyester monofilaments make up the machine direction strands and the monofilaments of the present invention comprise at least about 25%, and
30 preferably about from 25% to 50% of the transverse direction strands.

After weaving, the papermaking belts are heat set according to conventional techniques to stabilize the weave. Typical heat setting conditions
35 will vary with the polymer, filaments, diameter and

weave, but will typically involve heating under tension in a hot air oven for about from 15 minutes to 1 hour at a temperature of about from 300 to 400°F.

The improved monofilaments of the present invention, when used as transverse direction strands in papermaking belts, exhibit excellent resistance to the transverse direction abrasion encountered in belts of this type. This abrasion resistance permits improved operation for apparatus using such belts, in that the period between belt replacements is increased significantly.

The present invention is further illustrated in the following examples, in which parts and percentages are by weight unless otherwise indicated.

15 EXAMPLES 1-9 AND COMPARATIVE EXAMPLES A-D

A concentrate of aluminum silicate and nylon 612 was prepared by tumbling 12 pounds of nylon 612 for 30 minutes with 50 grams of gamma-aminopropyl triethoxy silane coupling agent. Eight pounds of aluminum silicate of 1.3 microns particle size was added and tumbled for an additional 30 minutes. The blend was then extruded in a 53 mm twin-screw extruder at 150 pph, with a screw speed of 200 rpm and a barrel temperature of from 250 to 265°C under full vacuum at the vent port. The resulting strands were water quenched and cut into flake.

Next, concentrates were prepared of nylon 612 with three ethylene copolymers, designated Additives A, B and C. Additive A was a graft copolymer having a Melt Index of 11.4 and an average anhydride graft level of 0.4%. Additive B was also a graft copolymer having a Melt Index of 0.59 and an average anhydride graft level of 1.75%. Additive C was an ungrafted ethylene- α -olefin copolymer having a melt flow of 1.0 g in 10 minutes at 280°C with a

5000 g load and the same orifice dimensions used in the Melt Index method.

Nylon 612 having an inherent viscosity of 1.10 to 1.25 in metacresol was first dried overnight in a vacuum oven at 120°C. The additives were dried at 60°C under vacuum overnight. Concentrates were prepared by first cooling the nylon 612 to 60°C and then tumbling the nylon with additives for 30 minutes end over end. Two concentrates were prepared. The first concentrate contained 90 pounds of nylon 612 and 10 pounds of Additive A. The second concentrate contained 81 pounds of nylon 612, 10 pounds of Additive B and 9 pounds of Additive C. Each blend was extruded in a 53 mm twin-screw extruder at 27 pph, with a screw speed of 100 rpm, and a barrel temperature of from 215 to 250°C. The resulting strands were water quenched and cut to flake.

Nylon concentrates of the additives prepared above were blended with additional nylon 612 in the ratios indicated in Table I and then dried overnight at 120°C in a vacuum oven. They were extruded as monofilament through a 1 1/2-inch single-screw extruder with a screw speed adjusted to maintain constant pressure to a two-capacity Zenith gear pump. The polymer was filtered through five 50-mesh screens and extruded through a .059" single-hole die, quenched in water after passage through 8 inches of air. The extruder barrel temperature ranged from 240° to 280°C. The filament was immediately drawn 4X while passing through a steam tube, conditioned for 4 seconds at 180°C, allowed to relax 6% as it came out of the conditioner and then wound on a spool at 860 feet/minute. The tensile properties of the blends were tested, and the results are summarized in Table I.

The filament of Comparative Example B contains 2 weight percent of Additive A, but no aluminum silicate. Comparative Examples C and D are filaments of commercially available nylon 612 and polyethylene terephthalate, without the additives of the present invention.

The filaments were tested by bending four samples of each filament to be tested over a .016" steel wire and loading to a tension of 50 grams. The samples are forced against a stainless steel roller turning at 30-35 rpm at a load of 100 grams/sample. The four samples are kept wet with a 10% slurry of Kaolin in water throughout the test, which lasts 6 hours. Break load and elongation of the four samples are then measured in an Instron tester and the means divided by the unabraded value to obtain percent retention for break load and elongation. The average of these two values is tabulated below:

	<u>Example</u>	<u>Av. % Retention of Break Load & Elongation</u>
20	1	72
	2	56
	3	68
	4	76
	5	65
	6	60
	7	60
25	8	58
	9	70, 63
	A	42, 40
	B	29
	C	38
	D	39

If the test procedure is repeated, except that the 10% Kaolin is omitted from the water used to wet the samples, the samples will retain at least about 90% of their break load and elongation.

EXAMPLES 10 TO 19 AND COMPARATIVE EXAMPLES E TO H

The general procedure of Examples 1 to 9 was repeated, except that blends were prepared from three

commercially available nylon 66 compositions. Nylon A is substantially unmodified nylon 66. Nylon B is a copolymer of nylon 6 and nylon 66 blended with about 36% aluminum silicate. Nylon C is nylon 66 blended with about 10% of grafted ethylene alpha-olefin copolymer and 9% of ungrafted copolymer of the types used as Additives B and C in Examples 5 and 6 below. Nylons A, B and C were tumbled and dried in the ratios indicated in Table II. The resulting blends were then extruded as in Examples 1 to 9, except that the melt was filtered through a finer set of screens, the die was 0.95 inches in diameter, and the extruder temperature ranged from 235 to 305°C. The resulting filaments were drawn 2.5 or 3.0 times and conditioned at 220°C. The physical properties of the resulting filaments were evaluated and the results are summarized in Table II.

Comparative Examples E and F were unmodified nylon 66, containing no aluminum silicate.

Comparative Example G was unmodified polyethylene terephthalate monofilament. Comparative Example H was a commercially available nylon 66 monofilament containing about 2% of additive A used in Examples 3 and 4 above.

The resulting monofilaments were tested for transverse abrasion as in Examples 1 to 9 above, except that the roller was tool steel rather than stainless steel. Water without Kaolin was used to wet filaments, and the filaments were tested for 3 hours instead of 6 hours. The abrasive used was iron oxide, which accumulated on the roller surface as the test proceeded. It was removed with emery cloth before each new sample was installed. The average retention of break load and elongation after three hours of abrasion is summarized in the following table:

	Example	Av. % Break Load	Retention of % Elongation	RV	% Poly-olefin	% Mineral
	E	65		853	--	--
5	10	72			2.5	36
	11	30			2.6	20
	12	12		90	2.4	10
	13	22		72	5.5	20
	14	68		79	5.5	10
10	15	81		95	1.2	18
	16	91		112	1.3	10
	17	59		122	0.74	11
	18	65		142	0.37	5.8
	19	62		159	0.12	1.8
15	F	53		67	--	--
	G	61		--	--	--
	H	66		65	2.0	--

EXAMPLE 20

Monofilaments were prepared by direct
 blending of the components. A blend was prepared by
 20 tumbling 142 pounds of nylon 612 for 30 minutes with
 51 grams of gamma-aminopropyl triethoxy silane
 coupling agent. Seven and one-half pounds of
 aluminum silicate of 1.3 microns particle size was
 25 added and tumbled for an additional 30 minutes. The
 blend was then extruded without drying in an 83 mm
 twin-screw extruder at 141 pounds/hour with a screw
 speed of 130 rpm and a barrel temperature of 255 to
 265°C under 6 inches vacuum at the vent port. The
 30 molten polymer was fed to eight two-stream, five
 capacity Zenith gear pumps, filtered through a stack
 of 33 screens, extruded through a .060" single-hole
 die, and quenched in water after passage through a
 4-1/2" air gap. The filament was immediately drawn
 3.5X in a radiant heater at 840°C, passed through a
 35 hot-air conditioning oven at 200°C for 1.4 seconds,

and removed from the oven at 40-50 grams tension to cooling rolls after which it was wound on spools at 2070 feet per minute. The monofilament had a caliper of 14.0 mils.

5 On testing according to the procedures of Examples 1-9, the filament exhibited a Break Load of 14 pounds, an Elongation to Break of 34%, an Initial Modulus of 420 Mpsi, and a Tensile Strength of 52 Mpsi. The Shrinkage was 6% and the Inherent
10 Viscosity 1.10. The average retention of break load and elongation was 55%.

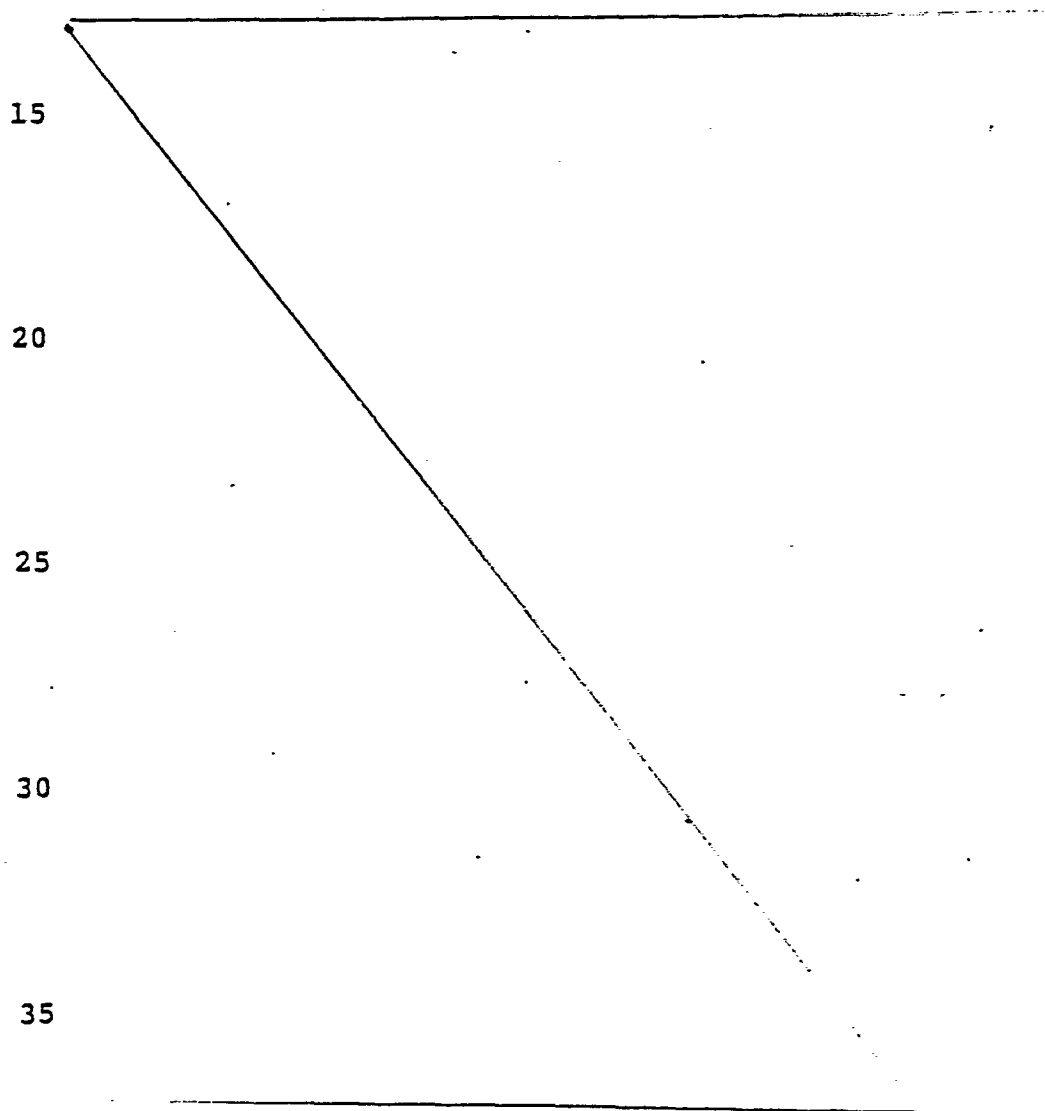


TABLE I

Example	Weight % Added			Break Load Lbs	Elongation To Break %	Initial Modulus M psi	Tensile Strength M psi	% Shrinkage 190°C 4 g/ 5 Minutes	Inherent Viscosity (meta-Cresol) Analyt.	% Mineral Analyt.
	Aluminum Silicate	Additive A	Additive B C							
1	4.8	None	None	6.8	28	377	50	16	1.19	4.9
2	9.6	None	None	6.1	31	358	42	16	1.18	10.1
3	4.8	2.0	None	6.8	31	378	50	16	1.16	4.8
4	9.6	2.0	None	6.4	24	396	46	16	1.16	10.8
5	4.8	None	2.0	6.8	30	363	48	16	1.17	4.9
6	9.6	None	2.0	6.0	24	384	45	17	1.03	10.3
7	14.4	2.0	None	5.2	27	401	38	--	--	--
8	19.2	2.0	None	4.2	29	399	32	--	--	--
9	14.4	3.0	None	5.1	24	370	38	--	--	--
A	None	None	None	8.3	39	436	57	13	1.19	--
B	None	2.0	None	9.6	24	610	67	12	0.97	--
C	None	None	None	16.3	48	1080	84	3	--	--
D	None	None	None	9.2	23	549	63	11	0.93	0

TABLE II

Example	Weight &		Caliper	Break		Initial Tensile	Shrinkage		Relative Viscosity	90% Formic Acid	Analyt.	Mineral
	Nylon A	Nylon B		Nylon C	Load		Elong.	Modulus				
	Mils	Lbs	Mpsi	Mpsi	Mpsi	Mpsi	Mpsi	%	Mpsi	%	%	%
E	100	None	None	14.5	12.1	27	580	73	5.8	853	—	0
10	None	100	None	14.3	4.2	13	529	26	3.8	—	—	36
11	36.5	57.0	6.5	13.8	4.5	36	237	30	4.4	—	20.3	20
12	61.0	28.5	10.5	13.0	4.2	58	212	32	5.2	90	9.3	10
13	21.5	57.0	21.5	13.8	4.2	35	333	28	3.6	72	21.1	20
14	46.0	27.5	25.5	13.4	5.9	38	405	42	4.0	79	10.3	10
15	50.0	50.0	None	13.6	6.7	29	402	46	4.2	95	17.5	18
16	68.5	28.5	3.0	14.3	7.3	30	415	45	3.8	112	10.5	10
17	70.0	30.0	None	13.6	8.2	20	546	57	4.9*	122	11.8	10.8
18	85.0	15.0	None	13.6	9.8	21	576	68	7.5*	142	5.8	5.4
19	95.0	5.0	None	13.7	8.4	20	585	58	7.2*	159	1.9	1.8
F				14.4	11.6	27	516	71	6.1	67	—	—
G				15.8	16.3	48	1080	84	3.0	—	—	—
H				14.4	10.6	29	501	65	5.6	65	—	—

*200°C

WE CLAIM:

1. An oriented polyamide monofilament comprising fiber or filament-forming polyamide and about from 2 to 20 weight percent, based on the total weight of the monofilament, of aluminum silicate having an average particle size of about from 1 to 8 microns.
2. A monofilament as claimed in claim 1 further comprising about from 0.5 to 10 weight percent of an ethylene copolymer having a Melt Index of about from 0.3 to 30.
3. A monofilament as claimed in claim 2 wherein the ethylene copolymer comprises at least about 50% of a graft copolymer prepared from (a) a backbone of polymers selected from the group consisting of thermoplastic polymers of ethylene and copolymers derived from ethylene and C₃ to C₈ alpha-olefins and (b) a graft monomer selected from the group consisting of unsaturated carboxylic acids, anhydrides and dihydrides.
4. A monofilament as claimed in any one of the preceding claims having a diameter of about from 5 to 30 mils.
5. A monofilament as claimed in claim 4 having a diameter of about from 10 to 20 mils.
6. A monofilament as claimed in any one of the preceding claims wherein the polyamide consists essentially of nylon 66.
7. A monofilament as claimed in any one of claims 1 to 5 wherein the polyamide consists essentially of nylon 612.
8. A monofilament as claimed in any one of claims 1 to 5 wherein the aluminum silicate comprises about from 4 to 10 weight percent.
9. A monofilament as claimed in any one of the preceding claims wherein the aluminum silicate has a particle size such that at least about 90% by weight of the particles are less

than 15 microns and the average particle size is about from 1 to 8 microns.

10. A monofilament as claimed in claim 9 wherein the aluminum silicate has a particle size such that 98% of the particles are less than 10 microns and exhibit an average particle size of about from 1 to 6 microns.

11. A woven, heat set, papermaking belt of machine and transverse direction thermoplastic filaments, characterised in that at least about 25% of the filaments in the transverse direction are monofilaments comprising filament forming polyamide and about from 2 to 20 weight percent, based on the total weight of the filament of an aluminum silicate having an average particle size of about from 1 to 8 microns.

12. A papermaking belt as claimed in claim 11 wherein the polyamide monofilaments comprise about from 25% to 50% of the transverse direction strands.

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