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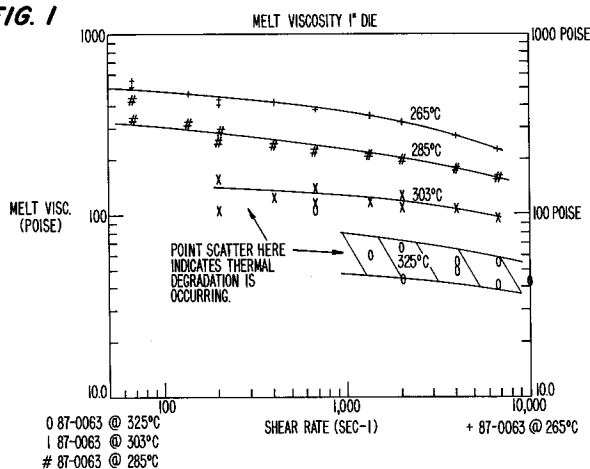
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AT BE CH DE DK ES FR GB GR IT LI LU NL SE(71) Applicant: **FIBERWEB NORTH AMERICA, INC.**
545 North Pleasantburg Drive
Greenville, South Carolina 29607(US)(72) Inventor: **Allan, John L.**
340 River Road
Appleton, WI 54915(US)Inventor: **Johnston, Milo R.****3902 Dogwood Lane**
Doyleston, PA 18901(US)Inventor: **Katz, Keon**
195 Dogwood Court
Stamford, CT 06903(US)Inventor: **Boettcher, Jeffrey J.**
417 E. Marquette Street
Appleton, WI 54911(US)(74) Representative: **Patentanwälte Grünecker,**
Kinkeldey, Stockmair & Partner
Maximilianstrasse 58
W-8000 München 22(DE)(54) **Meltblown hydrophilic web made from copolymer of an amine-ended polyethylene oxide and a polyamide.**

(57) A process is disclosed for preparing a nonwoven web comprising melt-blowing a composition comprising a block copolymer, the block copolymer comprising: (a) recurring units formed from an amine-ended polyethylene oxide; and (b) recurring units formed from a polyamide.

FIG. 1**EP 0 484 952 A1**

Technical Field

The present invention relates to processes for preparing nonwoven webs by melt-blowing a composition, particularly a composition comprising a block copolymer, wherein the block copolymer comprises: (a) recurring units formed from an amine-ended polyethylene oxide; and (b) recurring units formed from a polyamide. This invention also relates to melt-blown nonwoven webs containing such a block copolymer. Also within the scope of the invention are wipes (preferably hydrophilic), absorptive liners (such as for a garment, dressing, or personal care items), filters, and battery separators that contain the melt-blown nonwoven web of the present invention.

The technique of melt-blowing is known in the art and involves extruding a molten polymeric material into fine streams and attenuating the streams to fine fibers by flows of high velocity heated air that also break the streams into discontinuous fibers. The die melt temperature, i.e., the temperature of the polymer melt at the die, is generally about 80°-100° C above the melting temperature of the resin. Typically, a composition is melt-blown at about 310°-340° C. Melt-blowing is discussed in the patent literature, e.g., Buntin et al., U.S. Patent No. 3,978,185; Buntin, U.S. Patent No. 3,972,759; and McAmish et al., U.S. Patent No. 4,622,259. These patent disclosures are hereby incorporated by reference.

Some resins known to be capable of being melt-blown are, for example, polypropylenes, polyethylenes, polyamides, and polyesters. (See, for example, McAmish et al., paragraph bridging columns 10-11.)

For compositions containing block copolymers of an amine-ended polyethylene oxide and a polyamide, it is known to melt-spin these compositions to produce fibers, yarns and woven fabrics. For example, Lofquist et al., *Hydrophilic Nylon for Improved Apparel Comfort*, 55 *Textile Research Journal*, No. 6, 325 (June 1985) discloses the melt-spinning of a block copolymer of nylon 6 and polyethylene oxide diamine to produce hydrophilic fibers, yarns and woven fabrics. Melt-spinning involves pumping molten polymer at a constant rate under high pressure through a spinneret. The liquid polymer streams emerge downward from the face of the spinneret, usually into air. They solidify and are brought together to form threads, which are wound up on bobbins. The temperatures involved in melt-spinning are generally lower than in melt-blowing.

Those skilled in the art, who have been accustomed to melt-spinning compositions containing block copolymers of an amine-ended polyethylene oxide and a polyamide as illustrated in Lofquist et al., have generally believed that these compositions could not be melt-blown. It has been thought that the polyether groupings of the amine-ended polyethylene oxide are heat-sensitive to temperatures above 285° C and, consequently, that the compositions containing the polyether groupings would thermally degrade to an undesirable degree at the 310°-340° C temperature range typically used for melt-blowing. For example, as seen in Figure 1, Hydrofil® 87-0063, a block copolymer believed to contain about 85% nylon 6 and about 15% of an amine-ended polyethylene oxide by weight based on the weight of the copolymer, starts to thermally degrade at about 303° C, a temperature below the 310°-340° C temperature range typically used for melt-blowing.

Applicants have surprisingly discovered, however, that compositions containing a block copolymer of a polyamide and an amine-ended polyethylene oxide can in fact be melt-blown, despite the presence of the polyether grouping. Moreover, the nonwoven webs produced according to the present invention have excellent hydrophilic properties.

It is an object of the present invention to provide a melt-blowing process for preparing nonwoven webs, preferably hydrophilic nonwoven webs.

Another object of this invention is to produce webs which are instantly wettable by a drop of cold water, and webs that retain this property even after repeated rinsings with water.

A further object of this invention is to produce melt-blown, nonwoven webs that are strong, abrasive, and abrasion resistant.

Other objects will be apparent from the specification and claims.

Disclosure of the Invention

The present invention is directed to a process for preparing a nonwoven web comprising melt-blowing a composition comprising a block copolymer, wherein the block copolymer comprises: (a) recurring units formed from an amine-ended polyethylene oxide; and (b) recurring units formed from a polyamide. The present invention is also directed to nonwoven webs obtained by this process.

Brief Description of the Drawing

Figure 1 shows the melt viscosity profile of a composition comprising a block copolymer of about 85% nylon 6 and about 15% of an amine-ended polyethylene oxide by weight based on the weight of the copolymer. Compositions of this type are presently sold by Allied Corporation under the name Hydrofil®.

The point scatter at about 303° C and about 325° C indicates the occurrence of thermal degradation.

Best Mode for Carrying Out the Invention

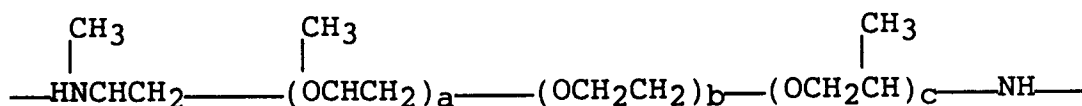
The present invention is directed to a process for preparing a nonwoven, preferably hydrophilic, web by melt-blowing a composition comprising a block copolymer, the block copolymer comprising: (a) recurring units formed from an amine-ended polyethylene oxide; and (b) recurring units formed from a polyamide.

A block copolymer is a polymer containing relatively long chains of the recurring units of a particular polymer with the chains being separated by recurring units of a polymer having a different chemical composition. In a different type of block copolymer, the block copolymer contains relatively long chains of the recurring units of a particular polymer, and the chains are separated by a low molecular weight coupling group. Each of the aforementioned polymer chains can be a homopolymer or a random copolymer. Within the scope of the present invention are block copolymers of more than two dissimilar monomers.

The block copolymer of the invention preferably contains polyether blocks which are randomly inserted into a polyamide chain, e.g., -A-PE-A-A-A-PE-A-PE-A-A-, where A is a recurring unit formed from a polyamide and PE is a recurring unit formed from an amine-ended polyethylene oxide.

The relative proportion of the recurring units formed from the amine-ended polyethylene oxide of the invention can vary widely, limited only by the melting point of the copolymer and the degree of hydrophilicity required. Typically, the percentage by weight varies from about 5% to about 30% based on the weight of the copolymer. It is preferred, however, that the block copolymer comprise from about 10% to about 15% by weight of the recurring units formed from the amine-ended polyethylene oxide based on the weight of the copolymer. Most preferably, about 15% of the block copolymer is made up of the amine-ended polyethylene oxide recurring units, based on the weight of the copolymer.

Preferably, the amine-ended polyethylene oxide has of the general formula



where the sum of a plus c ranges from about 2 to about 20 and b varies from about 5 to about 500. Preferably, the sum of a plus c ranges from about 2 to about 3, and b is from about 8 to about 140.

The molecular weight of the amine-ended polyethylene oxide can vary widely. In a preferred embodiment, however, the amine-ended polyethylene oxide has a molecular weight of from about 600 to about 2000. More preferably, the amine-ended polyethylene oxide has a molecular weight of from about 700 to about 1000. In a most preferred embodiment, the amine-ended polyethylene oxide has a molecular weight of from about 800 to about 900.

The amine-ended polyethylene oxide useful in this invention can be prepared by any process known to those skilled in the art. Yeakey, U.S. Patent No. 3,654,370, teaches a preferred process for preparing the amine-ended polyethylene oxide, the disclosure of which is hereby incorporated by reference. Yeakey discloses treating polyethylene glycol with a minimum amount of propylene oxide to generate a polyether with terminal secondary hydroxyl groups. These hydroxyl groups are then converted to amines, creating a polyethylene glycol with amine ends. The process of Yeakey is conducted in the presence of ammonia and hydrogen at a temperature of 150-275° C and at a pressure of about 500 to 5000 p.s.i.g. over a catalyst prepared by the reduction of the oxides of nickel, copper and chromium.

The relative proportion of the recurring units formed from the polyamide of the invention can vary widely. Typically, the percentage by weight of the recurring units formed from the polyamide varies from about 40% to about 95% based on the weight of the block copolymer. It is preferred, however, that the block copolymer from about 70% to about 95% by weight of the recurring units formed from the polyamide. More preferred is a copolymer comprising from about 80 to about 90% by weight of the recurring units formed from the polyamide based on the weight of the copolymer. Most preferably, the block copolymer contains about 85% of the polyamide recurring units.

Not all polyamides are nylons, and not all nylons are polyamides. For example, some nylons such as nylon 4 or those with a high content of relatively inflexible rings are too unstable or have too high a melt viscosity to be melt processible and, therefore, are not normally included in the polyamide category. Moreover, a class of polyamides distinct from the nylons is prepared by the polymerization or dimerization of vegetable oil acids and polyalkylene polyamines, such as ethylenediamine or diethylenetriamine. However, the term polyamide, as used throughout the specification and claims, is hereby defined to include all nylons.

A large number of polyamides is useful in the present invention. Table I sets forth potentially useful polyamides as follows:

Table I

Nylon Code	Name	Melting Point, °C
<i>Aliphatic amino acid polyamides</i>		
22	poly(22-aminodocosanoic acid)	145
3	poly(3-aminopropionic acid)	330
2,2DM3	poly(2,2-dimethyl-3-aminopropionic acid)	270
MM3	poly(<i>N</i> -methyl-3-aminopropionic acid)	225
NP3	poly(<i>N</i> -phenyl-3-aminopropionic acid)	205
AP	poly(aminopivalic acid)	270
7S	poly(7-aminothioenanthic acid)	235
<i>Aliphatic diamine-diacid polyamides</i>		
10,1	poly(decamethylene carbonamide)	200
10,2	poly(decamethylene oxamide)	290
12,6	poly(dodecamethylene adipamide)	210
12,10	poly(dodecamethylene sebacamide)	173
2,6	poly(ethylene adipamide)	310

	2,1	poly(ethylene carbonamide)	400
	2,12	poly(ethylene dodecanediamide)	261
	2,10	poly(ethylene sebacamide)	280
5	6,1	poly(hexamethylene carbonamide)	300
	6,12	poly(hexamethylene dodecanediamide)	217
	6,20	poly(hexamethylene eicosanediamide)	189
	6,5	poly(hexamethylene glutaramide)	241
	6,3M6	poly(hexamethylene 3-methyladipamide)	230
10	6,2	poly(hexamethylene oxamide)	320
	8,12	poly(octamethylene dodecanediamide)	202
	8,20	poly(octamethylene eicosanediamide)	179
	5,3	poly(pentamethylene malonamide)	191
	6,14	poly(hexamethylene tetradecanediamide)	209
15	4,1	poly(tetramethylene carbonamide)	400
	4,12	poly(tetramethylene dodecanediamide)	245
	6,S025	poly(hexamethylene sulfonyldivaleramide)	215
	6,4D03	poly[hexamethylene tetramethylenedi- (oxypropionamide)]	410
20	6,4DS026	poly[hexamethylene tetramethylenedi- (sulfonylcaproamide)]	241
	6,S4	poly(hexamethylene thiodibutyramide)	200
	6,S3	poly(hexamethylene thiodipropionamide)	219
	2,S5	poly(ethylene thiodivaleramide)	220
	2,S7	poly(ethylene thiodienanthamide)	210
25	6,10DSO26	poly(hexamethylene decamethylenedi- (sulfonylcaproamide))	210

Aromatic-aliphatic polyamides

30	4,4'DP,6	poly(4,4'-diphenylene adipamide)	400
	4,4'DP,10	poly(4,4'-diphenylene sebacamide)	435
	10,I	poly(decamethylene isophthalamide)	186
	10,pP2	poly(decamethylene p-phenylene- diacetamide)	242
35		poly[decamethylene p-phenylene- di(oxyacetamide)]	188
		poly(decamethylene p- phenylenedipropionamide)	265
	10,T	poly(decamethylene terephthalamide)	276
40		poly(2,2-dimethyltrimethylene 4,4'-sulfonyldibenzamide)	284
		poly(4,4'-ethylenediphenylene adipamide)	400
		poly(4,4'-ethylenediphenylene sebacamide)	360
45	2,T	poly(ethylene terephthalamide)	455
	2,P	poly(ethylene phthalamide)	250
	7,pP2	poly(heptamethylene p-phenylene- diacetamide)	234
50	6,5tBI	poly(hexamethylene 5-tert- butylisophthalamide)	210

	6,4,4'DBZ	poly(hexamethylene 4,4'-dibenzoamide)	360
		poly(hexamethylene 2,5-	143
5		dimethylterephthalamide)	
		poly(hexamethylene 4,4'-	175
		ethylidenedibenzoamide)	
		poly(hexamethylene 4,4'-	180
		isopropylidenedibenzoamide)	
	6,MT	poly(hexamethylene	248
10		methylterephthalamide)	
	6,mP2	poly(hexamethylene <i>m</i> -	182
		phenylenediacetamide)	
	6,pP3	poly(hexamethylene <i>p</i> -	295
		phenylenedipropionamide)	
15	7,T	poly(heptamethylene terephthalamide)	341
	6,T	poly(hexamethylene terephthalamide)	371
	6,NMT	poly(hexamethylene <i>N</i> -	260
		methylterephthalamide)	
	4,4'MDP,6	poly(4,4'-methylenediphenylene	356
20		adipamide)	
		poly(3,3'-dimethyl-4,4'-methylene-	326
		diphenylene adipamide)	
		poly(4,4'-methylenediphenylene	275
		azelamide)	
		poly(4,4'-methylenediphenylene	280
25		sebacamide)	
		poly(3,3'-dimethyl-4,4'-methylene-	227
		diphenylene sebacamide)	
	4,T	poly(tetramethylene terephthalamide)	436
	3,T	poly(trimethylene terephthalamide)	399
30	3MmP,6	poly(3-methyl- <i>m</i> -phenylene adipamide)	225
	3MmP,10	poly(3-methyl- <i>m</i> -phenylene sebacamide)	200
	8,T	poly(octamethylene terephthalamide)	315
	mP,6	poly(<i>m</i> -phenylene adipamide)	296
	oP,6	poly(<i>o</i> -phenylene adipamide)	179
	pP,6	poly(<i>p</i> -phenylene adipamide)	262
35	pPDE,6	poly(<i>p</i> -phenylenediethylene adipamide)	310
	pPDE,9	poly(<i>p</i> -phenylenediethylene azelamide)	250
	pPDE,10	poly(<i>p</i> -phenylenediethylene sebacamide)	285
	mP,10	poly(<i>p</i> -phenylene sebacamide)	256
	5,T	poly(pentamethylene terephthalamide)	353
40	pX,22	poly(<i>p</i> -xylylene decanediamide)	240
	pX,12	poly(<i>p</i> -xylylene dodecanediamide)	272
	pX,5	poly(<i>p</i> -xylylene glutaramide)	280
	pX,6	poly(<i>p</i> -xylylene adipamide)	340
	mX,9	poly(<i>m</i> -xylylene azelamide)	172
45	pX,18	poly(<i>p</i> -xylylene octadecanediamide)	235
	mX,7	poly(<i>m</i> -xylylene pimelamide)	192
	pX,7	poly(<i>p</i> -xylylene pimelamide)	284
	mX,10	poly(<i>m</i> -xylylene sebacamide)	193
	mX,8	poly(<i>m</i> -xylylene suberamide)	213
	pX,8	poly(<i>p</i> -xylylene suberamide)	305
50	pX,4	poly(<i>p</i> -xylylene succinamide)	360
	mX,14	poly(<i>m</i> -xylylene tetradecanediamide)	192

Aromatic-aromatic polyamides

5	4,4'DP,T	poly(4,4'-diphenylene terephthalamide)	500
		poly(3,3'-dimethyl-4,4'-diphenylene terephthalamide)	440
10		poly(3,3'-dimethyl-4,4'-diphenylene N,N'-diethylterephthalamide)	254
		poly(4,4'-diphenylene N,N'-diethylterephthalamide)	316
15		poly[decamethylene 4,4'-ethylenedi-(phenyleneoxyacetamide)]	220
		poly(4,4'-dimethylheptamethylene 4,4'-sulfonyldibenzamide)	268
20	2,4,4'SO ₂ DBZ 2,T	poly(ethylene 4,4'-sulfonyldibenzamide)	380
		poly(ethylene terephthalamide)	455
25		poly(ethylene N,N'-dibutylterephthalamide)	190
		poly(ethylene N,N'-diethylterephthalamide)	230
30		poly(ethylene N,N'-dimethylterephthalamide)	379
		poly(hexamethylene 2,5-dihydroxyterephthalamide)	334
35	6,pPD02	poly[hexamethylene p-phenylenedi-(oxyacetamide)]	237
		poly(hexamethylene 4,4'-sulfonyldibenzamide)	310
40	4,4'MDP,T	poly(4,4'-methylenediphenylene terephthalamide)	420
		poly(4,4'-methylenediphenylene N,N'-dibutylterephthalamide)	195
45		poly(3,3'-dimethyl-4,4'-methylene-diphenylene terephthalamide)	380
		poly(3,3'-dimethyl-4,4'-methylene-diphenylene N,N'-dimethylterephthalamide)	229
50		poly(4,4'-methylenediphenylene N,N'-dimethylterephthalamide)	264
		poly(p-phenylenediethylene m-phenylenediacetamide)	222
55	pPDE,mP2	poly(hexamethylene dithio-terephthalamide)	190
		poly[hexamethylene 4,4'-oxydi-(phenyleneoxyacetamide)]	220
60	mX,I	poly(m-xylylene isophthalamide)	225
		poly(p-xylylene isophthalamide)	279
65	pX,I	poly(p-xylylene phthalamide)	230
		poly(m-xylylene terephthalamide)	300
70	mX,T	poly(p-xylylene terephthalamide)	350
		poly(4,4'-diphenylene isophthalamide)	400
75	pX,T	poly(4,4'-diphenylene isophthalamide)	400
		poly(3,3'-dimethyl-4,4'-diphenylene isophthalamide)	365

	4,4'MDP,I	poly(4,4'-methylenediphenylene isophthalamide)	400
5	4,S0 ₂ DBZ	poly(tetramethylene 4,4'-sulfonyl-dibenzamide)	358
	3,S0 ₂ DBZ	poly(trimethylene 4,4'-sulfonyl-dibenzamide)	298
	3,T	poly(trimethylene terephthalamide)	399
10		poly(trimethylene N,N'-dimethyl-terephthalamide)	220
	mP,I	poly(m-phenylene isophthalamide)	365
<i>Alicyclic-aliphatic and heterocyclic-aliphatic polyamides</i>			
15	1,3CH,6	poly(1,3-cyclohexylene adipamide) (<i>trans</i>)	300
	1,4CH,6	poly(1,4-cyclohexylene adipamide)	400
	1,3CH,9	poly(1,3-cyclohexylene azelamide) (<i>trans</i>)	300
20	CHDM,12	poly(1,4-cyclohexylenedimethylene dodecanediamide)	278
	CHDM,10	poly(1,4-cyclohexylenedimethylene sebacamide)	300
25	CHDM,7	poly(1,4-cyclohexylenedimethylene pimelamide)	293
	CHDM,5	poly(1,4-cyclohexylenedimethylene glutaramide)	290
	1,3CH,10	poly(1,3-cyclohexylene sebacamide) (<i>trans</i>)	290
30	CPDM,10	poly(1,2-cyclopropylene-dimethylene sebacamide)	223
	CP,10	poly(cyclopropylene sebacamide)	220
	10,THF3	poly(decamethylene tetrahydrofuran-2,5-dipropionamide)	178
35	2,CP1	poly(ethylene cyclopropane-dicarboxamide) (<i>trans</i>)	350
	2,THF3	poly(ethylene tetrahydrofuran-2,5-dipropionamide)	218
	7,THF3	poly(heptamethylene tetrahydrofuran-2,5-dipropionamide)	148
40	6,1,2C2	poly(hexamethylene cyclohexane-1,2-diacetamide)	255
	6,1,2C1	poly(hexamethylene cyclohexane-1,2-dicarboxamide) (<i>trans</i>)	242
45	6,1,3C1	poly(hexamethylene cyclohexane-1,3-dicarboxamide) (<i>trans</i>)	312
	6,1,4C1	poly(hexamethylene cyclohexane-1,4-dicarboxamide) (<i>trans</i>)	360
	6,CP1	poly(hexamethylene cyclopropanedicarboxamide) (<i>trans</i>)	300
50	6,2,5F3	poly(hexamethylene furan-2,5-dipropionamide)	190

	6,3MCP	poly(hexamethylene 3-methylcyclopropanedicarboxamide) (<i>trans</i>)	270
5		poly(hexamethylene 1-methylpyrrole-2,5-dipropionamide)	180
		poly(hexamethylene 1-methylpyrrolidine-2,5-dipropionamide)	200
		poly(hexamethylene piperazine-1,4-diacetamide)	168
10	6,THF3	poly(hexamethylene tetrahydrofuran-2,5-dipropionamide)	182
	8,THF3	poly(octamethylene tetrahydrofuran-2,5-dipropionamide)	180
	5,THF3	poly(pentamethylene tetrahydrofuran-2,5-dipropionamide)	153
15		poly[1,4-cyclohexylenedi-(oxytrimethylene)terephthalamide]	384
		poly[1,4-cyclohexylenedi-(oxytrimethylene) 4,4'-tetramethylenedi(oxybenzoamide)]	224
20	Pip,CP1	poly(piperazine cyclopropane-dicarboxamide) (<i>trans</i>)	330
	Pip,10	poly(piperazine sebacamide)	180
	Pip,8	poly(piperazine suberamide)	300
25	4,THF3	poly(tetramethylene tetrahydrofuran-2,5-dipropionamide)	210

Alicyclic and Heterocyclic Polyamides

30		poly[1,4-cyclohexylenedi-(oxytrimethylene)adipamide]	196
		poly[1,4-cyclohexylenedi-(oxytrimethylene) 4,4'-ethylenedi(oxybenzoamide)]	250
35		poly[1,4-cyclohexylenedi-(oxytrimethylene) 4,4'-hexamethylenedi(oxybenzoamide)]	215
		poly[1,4-cyclohexylenedi(oxytrimethylene) oxamide]	246

Aromatic and aliphatic amino acid polyamides

40	2P5	poly(<i>p</i> -aminoethylphenylvaleric acid)	275
		poly(aminotoluic acid)	300
		poly(<i>p</i> -amino- α -methylhydrocinnamic acid)	250
45	P2	poly(aminophenylacetic acid)	410
	P3	poly(<i>p</i> -aminophenylpropionic acid)	310
		poly(<i>p</i> -aminomethylhydrocinnamic acid)	300
	IP2	poly(<i>p</i> -aminomethylphenylacetic acid)	355
	IP3	poly(<i>p</i> -aminomethylphenylpropionic acid)	300
50	IP4	poly(<i>p</i> -aminomethylphenylbutyric acid)	267
	IP5	poly(<i>p</i> -aminomethylphenylvaleric acid)	233

2P2	poly(<i>p</i> -aminoethylphenylacetic acid)	283
2P3	poly(<i>p</i> -aminoethylphenylpropionic acid)	382
2P4	poly(<i>p</i> -aminoethylphenylbutyric acid)	224

Alicyclic-aromatic and heterocyclic-aromatic polyamides

	poly(1,4-cyclohexylene 3,3'-dibenzoamide)	390
	poly(1,4-cyclohexylenedimethylene isophthalamide) (<i>trans</i>)	310
	poly(1,4-cyclohexylene 3,3'-methylenedibenzoamide)	174
	poly(1,2-dimethylenecyclopropylene isophthalamide)	220
	poly(cyclopropylene isophthalamide)	250
	poly(4,4'-diphenylene pyridine-2,6-dicarboxamide)	365
	poly(3,3'-dimethyl pyridine-2,6-dicarboxamide)	376
DMT, 6	poly(2,5-dimethylenethiophene adipamide)	253
	poly(2-methylpiperazine phthalamide)	350
2MPip, T	poly(2-methylpiperazine terephthalamide)	350
Pip, P	poly(piperazine phthalamide)	325
DMT, 10	poly(2,5-dimethylenethiophene sebacamide)	210
DMT, 7	poly(2,5-dimethylenethiophene pimelamide)	212
DMT, 9	poly(2,5-dimethylenethiophene azelamide)	197

Heterocyclic diamine-diacid polyamides

CP, CP1	poly(cyclopropane cyclopropane-dicarboxamide)	285
1,2DMCP, CP1	poly(1,2-dimethylenecyclopropane cyclopropanedicarboxamide)	220
Pip, 3MCP1	poly(piperazine 3-methylcyclopropanedicarboxamide) (<i>trans</i>)	280

Preferred polyamides are nylon 4,6 [poly(tetramethylene adipamide)]; nylon 66 [poly(hexamethylene adipamide)]; nylon 6,10 [poly(hexamethylene sebacamide)]; nylon 6 [poly(pentamethylene carbonamide)]; nylon 11 [poly(decamethylene carbonamide)]; nylon 12 [poly(undecamethylene carbonamide)]; MXD-6 [poly(meta-xylene adipamide)]; PACM-9 [bis(para-aminocyclohexyl)methane azelamide]; PACM-10 [bis-(para-aminocyclohexyl)methane sabacamide]; and PACM-12 [bis(para-aminocyclohexyl)methane dodecanoamide]. More preferably the polyamide is a nylon, with nylon 6 being the most preferred nylon.

Polyamides are condensation products that contain recurring amide groups as integral parts of the main polymer chains. Linear polyamides can be formed by the condensation of bifunctional monomers. If the monomers are amino acids, e.g., 6-aminohexanoic acid, the polymers are called AB types (A representing amine groups and B representing carboxyl groups). If the polymers are formed from the condensation of diamines and dibasic acids, they are called AABB types.

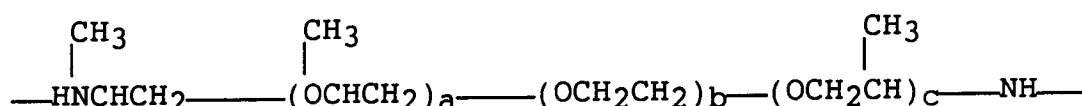
Although polyamides generally are considered to be condensation polymers, they can also be formed by addition or ring-opening polymerization. The ring-opening polymerization method of preparation is especially important for some AB type polymers made from cyclic lactams as recurring units, e.g., epsilon-caprolactam, hexahydro-2H-azepin-2-one or 2-pyrrolidinone gamma-aminobutyrolactam.

Methods for preparing polyamides are well known and described in various publications. For example, Billmeyer, Textbook Polymer Science 409 (3d ed. 1984), discloses the of preparation of nylon 6 and nylon 66, the disclosure of which is incorporated by reference. To prepare nylon 6, Billmeyer teaches the polymerization of caprolactam by adding water to open the rings and then removing the water again at elevated temperature, during which a linear polymer forms. To prepare nylon 66, Billmeyer teaches the polymerization of adipic acid and hexamethylenediamine.

The preparation of polyamides can be batchwise or a continuous process. An autoclave or a continuous reactor can be used.

The composition may consist of up to about 100% by weight of the block copolymer, based on the weight of the extruded resins. In a preferred embodiment, the composition comprises a block copolymer comprising

(a) the amine-ended polyethylene oxide having the general formula



wherein the sum of a plus c ranges from about 2 to about 3, and b is from about 8 to about 140; and

(b) the polyamide, nylon 6.

Even more preferably, the composition comprises a block copolymer comprising about 85% nylon 6 and about 15% of an amine-ended polyethylene oxide by weight based on the weight of the block copolymer. Compositions of this type are commercially available from the Allied Corporation under the name Hydrofil®.

In another preferred embodiment, the block copolymer useful in the present invention has a number average molecular weight of from about 5,000 to about 50,000. It is also preferred that the block copolymer has a relative viscosity when measured at 10% w/v concentration in 90% formic acid of less than 50, more preferably between about 34 to about 39.

The composition, the copolymer, or both may also contain one or more additive agents. In a preferred embodiment, the additive is a homopolymer or a second copolymer and is mixed with the block copolymer to form a polyblend. The following are representative additive agents:

(a) delustrants such as barium sulfate, clays, and chalk;

(b) antioxidants such as phenols, aromatic amines, and salts and condensation products of amines and aminophenols with aldehydes, ketones, and thio compounds; (c) plasticizers such as phthalate esters, phosphate esters, adipates, azelates, oleates, sebacates, epoxy plasticizers, fatty acid esters, glycol derivatives, sulfonamides, and hydrocarbons and hydrocarbon derivatives; and (d) flame retardants such as halogenated aliphatics, antimony oxide (either alone or in combination with a halogen), brominated aromatics, and organophosphorus compounds. Specific examples of the above additive agents and other additive agents are found in Modern Plastics Encyclopedia 1984-85, the disclosure of which is incorporated by reference.

A preferred antioxidant is a phenolic antioxidant from Ciba Geigy, Irganox 1010. When the additive agent is an antioxidant, the copolymer preferably contains from about 0.1% to about 0.5% by weight of the antioxidant based on the weight of the block copolymer. More preferably, however, the block copolymer contains about 0.5% by weight of the antioxidant based on the weight of the block copolymer.

Tables II and III illustrate the physical properties of preferred block copolymers of nylon 6 and an amine-ended polyethylene oxide ("APEO"), as follows:

Table II. Physical Properties of Nylon 6 Containing Different Molecular Weight APEO's (Sold Under the Name of Jeffamine®)

APEO Concentration	Relative viscosity in formic acid	T _m ^a , °C	T _g ^a , °C
Control (all nylon 6 containing 0% APEO)	50	225	42
15% APEO; Molecular weight 2001	35	223	6
15% APEO; Molecular weight 900	38	217	19
15% APEO; Molecular weight 600	38	214	26

^a Crystalline melting point and glass transition temperature as determined by differential scanning calorimetry.

Table III. Polymer Properties of Nylon 6/APEO Block Copolymers.

Copolymer composition % APEO (MW=2001)	Number average molecular weight	Melting ^a point °C	Glass ^a transition temperature °C	Melt viscosity, ^b Pa.s, 260°C 2000 s ⁻¹
0	20,000	224	42	120
5	22,000	224	22	120
10	19,000	224	10	100
15	20,000	223	6	85
20	28,000	223	0	125

^a Crystalline melting point and glass transition temperature as determined by differential scanning calorimetry.

^b Melt viscosity as determined on a capillary melt rheometer using a 33 to 1 orifice.

the composition containing the block copolymer is itself prepared before the melt-blowing step. Methods for preparing the block copolymer of this invention are well known to those skilled in the art. Block copolymer preparations have been described in the patent literature using at least two techniques. One technique is melt blending two homopolymers. The melt blending of two homopolymers using elevated temperatures typically results in the formation of an intimately mixed physical mixture with an insignificant amount of chemical bonding between the polymer chains. When the conditions are closely controlled, however, block copolymers with long sequence lengths can occur due to a small amount of amide interchange accompanied by an insignificant number of random sequences. Such a technique is disclosed in Zimmerman, U.S. Patent No. 3,393,252.

Another method of preparing block copolymers has been described in Honda et al., U.S. Patent No. 3,683,047. This method consists of melt blending two homoprepolymer of molecular weight from 1000 to 4000, one prepolymer being carboxyl terminated and the other prepolymer being amine terminated. The result of the polymerization is a block copolymer having very little randomization, as indicated by the reduced decrease in melting point during the blend time.

According to the present invention, the composition is melt-blown to produce a nonwoven web. Melt-blowing involves extruding a molten polymeric material into fine streams and attenuating the streams to fine fibers by flows of high velocity heated air that also break the streams into discontinuous fibers.

The die melt temperature, i.e., the temperature of the polymer melt at the die, is generally about 80° - 100° C above the melting temperature of the resin. Preferably, however, the die melt temperature can be more than about 100° C above the melting temperature of the composition. In an especially preferred embodiment, the present composition is melt-blown at a temperature greater than about 285° C. In a still more preferred embodiment, the composition is melt-blown at a temperature of from about 310° to about 340° C.

The technique of melt-blowing is known in the art and is discussed in various patents, e.g., Buntin et al., U.S. Patent No. 3,978,185; Buntin, U.S. Patent No. 3,972,759; and McAmish et al., U.S. Patent No. 4,622,259, the disclosures of which are hereby incorporated by reference. Although one or more of these patents, e.g., Buntin, U.S. Patent No. 3,972,759, states that a polymer degradation step is required before melt-blowing to ensure that the polymer resin has the requisite viscosity, a polymer degradation step is optional in the present invention. This is because the present composition containing the block copolymer preferably has the requisite viscosity set forth in Buntin, U.S. Patent No. 3,972,759 for the production of high quality nonwoven webs without a polymer degradation step. Specifically, the block copolymer of the invention preferably has an apparent viscosity of from about 50 to about 500 poise, measured at a shear rate of from about 700 to about 3500 sec⁻¹ and a temperature of from about 250° to about 300° C.

In accordance with this invention, commercially useful resin throughput rates can be utilized. Suitable resin throughput (flow) rates range from nominally about 0.1 (e.g., as low as about 0.07) to about 5 grams per minute per nozzle orifice.

In the melt-blowing process of the present invention, the composition is attenuated while still molten to fibers having diameters of 0.5 to 400 microns. The diameter of the attenuated fibers generally decreases as the gas flow rate increases through the gas outlets or slots on either side of the nozzle die openings. Typically, gas flow rates may vary from 2.5 to 100 pounds per minute per square inch of gas outlet area, but may be even greater. At low to moderate gas rates of from about 2.5 to about 20 pounds per minute per square inch of gas outlet area, and for resin flow rates of from about 0.1 to about 5 grams per minute per orifice, the fibers can be 75 cm or longer between fiber breaks. Fibers produced in this low to moderate gas flow rate range typically have diameters of from about 8 to about 200-400 microns, preferably from about 8 to about 50 microns.

As gas rates increase for a selected resin flow rate of the composition, the number of fiber breaks increase, eventually producing coarse "shot." "Shot" consists of large globs of polymer having a diameter at least several times that of the average diameter size of the fibers and at least 0.3 millimeter in diameter. The production of coarse shot is objectionable when a uniform mat is desired. Further, if a mat is calendered or further treated, the coarse shot will produce imperfections or even holes in the surface of the mat.

At high gas rates of from more than about 20 to about 100 pounds per minute per square inch of gas outlet area, polymer fibers are produced which typically exhibit fine shot less than about 0.3 millimeter, preferably less than about 0.1 millimeter in diameter. At the high air rates for resin flow rates in the range from about 0.1 to about 5 grams per minute per orifice, the fiber diameter is generally between about 0.5 and 5 microns.

Subsequent collection of the fibers on a screen, belt, drum, or the like yields a mat of the fibers. Melt-blown webs according to the present invention can be point-bonded for added mechanical strength, or they can be laminated with other webs to obtain structures with multiple functions.

For example, the nonwoven webs of the present invention can be bonded by a point application of heat and pressure using patterned bonding rollers. At these points where heat and pressure is applied, the fibers fuse together, resulting in strengthening of the web structure. Also, Minto et al., U.S. Patent No. 4,469,734, discloses a method to prepare wipes from a melt-blown web, the web being formed or provided with apertures by, for example, hot needling or by passing the web between differentially speeded rolls. The disclosure of Minto et al., U.S. Patent No. 4,469,734, is hereby incorporated by reference.

The nonwoven webs produced by the present process are useful in a variety of ways. For example, the webs may be used in apparel, hydrophilic wipes, napkins, and personal care items. They may also be used as absorbents for water, urine, and similar fluids, and as compositions for the release of bactericides, drugs, fungicides, and insecticides. As such, they are ideal as absorptive liners for garments or for dressings.

Furthermore, they may be used as filters for the removal of particulate matter or water, or as filters for removing acidic or basic materials. In addition, they may be used in ion exchange resins, in odor removers, in battery separators, and in barrier composites. Another use is in making nonwoven fabric laminates, for example by hydroentanglement.

Moreover, the present melt-blown materials are useful as reinforcing agents for plastics, adhesives, concrete, and the like, and in geotextile applications. Also, they can be conductive or may be made conductive by the inclusion of conductive materials or by metal plating, and may then be used in EMI shielding or microwave-interactive heating constructions. In short, the present melt-blown materials may be used for just about anything that conventional nonwoven webs can be used for, as well as for many specific applications particularly requiring a hydrophilic nonwoven web.

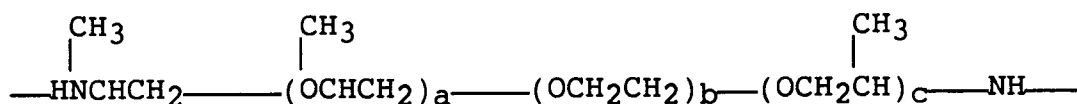
The following examples illustrate the present process for preparing a nonwoven web and the properties thereof.

EXAMPLES 1-5

A block copolymer with a sample designation Hydrofil® 87-0063, having a number average molecular weight of about 14,000, and the apparent viscosities shown in Figure 1, was obtained from the Allied Fibers Division of the Allied Corporation.

It is believed that Hydrofil® 87-0063 comprises:

(a) about 15% of the amine-ended polyethylene oxide of the general formula



wherein a plus c is about 2 to about 3 and b is about 8 to about 140, and

(b) about 85% of nylon 6.

As seen in Figure 1, the Hydrofil® composition used in these examples starts to thermally degrade at about 303° C. Surprisingly, however, the Hydrofil® composition was in fact melt-blown into continuous webs using a melt-blowing method similar to that disclosed in Buntin, U.S. Patent No. 3,972,759, at the melt temperatures and melt-blowing parameters shown in Table IV.

Table IV. Melt-Blowing Parameters

Equipment: One inch diameter extruder with L/D of 18/1.
Ten inch die with 25 spinneret holes per inch.

Resin: Hydrofil® 87-0063

	<u>Ex.1</u>	<u>Ex.2</u>	<u>Ex.3</u>	<u>Ex.4</u>	<u>Ex.5</u>
<u>Melt Temperature (°C):</u>	338	335	310	310	318
<u>Throughout (g/hole/min):</u>	---	0.51	0.23	0.23	0.35
<u>Collector Speed</u>					
<u>(meters/min):</u>	2.0	2.7	8.4	4.2	4.2
<u>Extruder Speed (RPM):</u>	90	90	75	75	90

The physical properties of the derived webs are set forth in Table V. Unless stated otherwise, the following test methods were used to generate the values seen in Table V.

Basis Weight

Samples were cut using a razor blade and a metal template (50 x 200 millimeters) and the sample weighed to the nearest 0.001 gram. The specimens were dried and equilibrated to ambient conditions before weighing. The basis weight is reported, in grams per square meter (g/m²), as the weight of the sample x 100.

Caliper

Web thickness was measured using an Ames gauge (Model 79-011; Ames Inc., Waltham, MA) with zero load.

Gurley Permeability

Permeability was measured using a Gurley Permeometer (Model 4301; Teledyne Gurley, Troy, NY) for a two-inch-diameter disc of the web with an air pressure of 0.5 inch of water. Data are reported as the flow rate in cubic feet per minute (ft³/min) through one square foot of material.

Pore Number

The pore number was measured as the minimum air pressure, in inches of water, necessary to force a bubble of air through a 0.75-inch-diameter disc of web supporting a column of isopropanol 1.375 inches high. The equipment used is similar to the simplified setup described in ASTM F316-80.

Tensile Measurements

Tensile strength (maximum strength) and elongation at break were measured using an Instron tensile tester (Model 1101; Instron Corp., Canton, MA). Jaw spacings and speeds were as follows:

	Sample Width (in)	Jaw Size (in)	Spacing (in)	Speed (in/min)
Strip	1.0	1.0	3.0	12

Samples were tested in the machine direction (MD) and the cross-machine direction (CD).

Tear Strength

Tear strength was measured using a Thwing-Albert Elmendorf Tear Tester (Model 60-32), using samples 3 inches (CD) by 2.5 inches (MD) which were torn parallel to the machine direction. One ply
5 samples were tested using a 1600 g pendulum. The instrument scale was calibrated in percentages of the weight of the pendulum, and the Elmendorf tear, in grams, was given by the scale reading x 1600.

In addition to the properties discussed in Table V, all the webs were instantly wettable by a drop of cold water, a property which was retained even after repeated rinsing with water. When used as wipes, the samples absorbed and retained water readily and exhibited a desirable, mild abrasive action on the wiped
10 surface. The webs also were durable and retained excellent mechanical integrity, even when wet.

It will be appreciated that various changes may be made in detail regarding the materials, processes, and products described herein without departing from the invention as defined in the appended claims.

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Table V. Properties of Melt-blown Hydrofil® Derived Webs

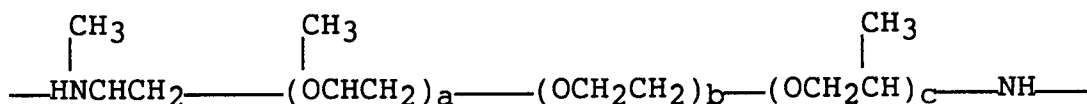
Example No.	Weight (g/m ²)	Caliper (mil)	Permeability (cfm)	Pore No. (in water)	Tensile Properties			
					Strength MD	(psi) CD	Elong MD	(%) CD
1	137	59	108	4.6	102	144	74	83
2	99	39	107	4.2	116	139	73	81
3	29	19	>400	2.2	85	89	106	104
4	66	35	326	2.6	82	92	109	107
5	71	37	326	2.5	87	99	126	103
								400
								320
								240
								496
								932

Claims

1. A process for preparing a nonwoven web comprising melt-blowing a composition comprising a block copolymer, wherein the block copolymer comprises:

- (a) recurring units formed from an amine-ended polyethylene oxide; and
- (b) recurring units formed from a polyamide.

2. The process according to claim 1, wherein the amine-ended polyethylene oxide has the general formula



wherein the sum of a plus c ranges from about 2 to about 20, and b is from about 5 to about 500.

3. The process according to claim 1, wherein the amine-ended polyethylene oxide has a molecular weight of from about 600 to about 2000.

4. The process according to claim 1, wherein the amine-ended polyethylene oxide has a molecular weight of from about 700 to about 1000.

5. The process according to claim 1, wherein the amine-ended polyethylene oxide has a molecular weight of from about 800 to about 900.

6. The process according to claim 1, wherein the block copolymer comprises from about 5% to about 30% by weight of the recurring units formed from an amine-ended polyethylene oxide based on the weight of the copolymer.

7. The process according to claim 6, wherein the block copolymer comprises from about 10% to about 15% by weight of the recurring units formed from an amine-ended polyethylene oxide based on the weight of the copolymer.

8. The process according to claim 1, wherein the block copolymer comprises from about 40% to about 95% by weight of the recurring units formed from a polyamide based on the weight of the copolymer.

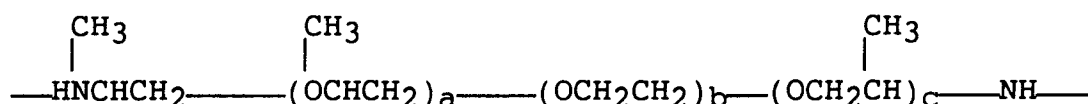
9. The process according to claim 8, wherein the block copolymer comprises from about 70% to about 95% by weight of the recurring units formed from a polyamide based on the weight of the copolymer.

10. The process according to claim 1, wherein the polyamide is selected from the group consisting of nylon 4,6; nylon 6,10; nylon 6; nylon 11; nylon 12; nylon 66; MXD-6; PACM-9; PACM-10; an PACM-12.

11. The process according to claim 1, wherein the polyamide is a nylon.

12. The process according to claim 11, wherein the nylon is nylon 6.

13. The process according to claim 1, wherein
- (a) the amine-ended polyethylene oxide has the general formula

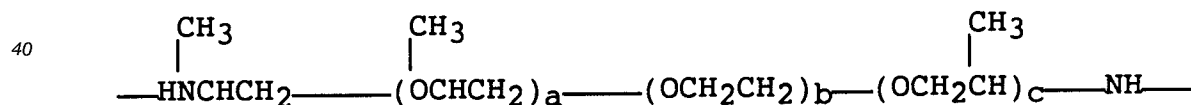


- wherein the sum of a plus c ranges from about 2 to about 20, and b is from about 5 to about 500;
- and
- (b) the polyamide is nylon 6.

14. The process according to claim 13, wherein the composition comprises

- (a) about 15% of the amine-ended polyethylene oxide, the sum of a plus c ranges from about 2 to about 3, and b is about 8 to 140; and
 (b) about 85% of nylon 6.

- 5 15. The process according to claim 1, wherein the melt-blowing melt temperature is more than 80 ° C above the melting temperature of the composition.
16. The process according to claim 1, wherein the composition is melt-blown at a temperature greater than about 285 ° C.
- 10 17. The process according to claim 1, wherein the composition is melt-blown at a temperature of from about 310 ° to about 340 ° C.
18. The process according to claim 1, further comprising incorporating into the composition, into the block copolymer, or both, at least one additive agent selected from the group consisting of delustrants, antioxidants, plasticizers, and flame retardants.
- 15 19. The process of claim 17, wherein the additive is a homopolymer or a second copolymer and is mixed with the block copolymer to form a polyblend.
- 20 20. The process according to claim 1, wherein the block copolymer has a number average molecular weight of from about 5,000 to about 50,000.
21. The process of claim 1, wherein the block copolymer has a relative viscosity at 10% w/v in 90% formic acid of less than about 50.
- 25 22. The process according to claim 1, further comprising preparing the composition before the melt-blowing step.
- 30 23. A melt-blown nonwoven web comprising a composition which comprises a block copolymer, the block copolymer comprising:
 (a) recurring units formed from an amine-ended polyethylene oxide; and
 (b) recurring units formed from a polyamide.
- 35 24. The melt-blown nonwoven web of claim 23, wherein the amine-ended polyethylene oxide has the general formula



wherein the sum of a plus c ranges from about 2 to about 20, and b is from about 5 to about 500.

- 45 25. The melt-blown nonwoven web of claim 23, wherein the amine-ended polyethylene oxide has a molecular weight of from about 600 to about 2000.
26. The melt-blown nonwoven web of claim 23, wherein the amine-ended polyethylene oxide has a molecular weight of from about 700 to about 1000.
- 50 27. The melt-blown nonwoven web of claim 23, wherein the amine-ended polyethylene oxide has a molecular weight of from about 800 to about 900.
- 55 28. The melt-blown nonwoven web of claim 23, wherein the block copolymer comprises from about 5% to about 30% by weight of the recurring units formed from an amine-ended polyethylene oxide based on the weight of the copolymer.

29. The melt-blown nonwoven web of claim 28, wherein the block copolymer comprises from about 10% to about 15% by weight of the recurring units formed from an amine-ended polyethylene oxide based on the weight of the copolymer.

5 30. The melt-blown nonwoven web of claim 28, wherein the block copolymer comprises from about 40% to about 95% by weight of the recurring units formed from a polyamide based on the weight of the copolymer.

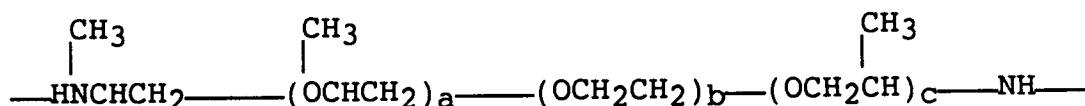
10 31. The melt-blown nonwoven web of claim 28, wherein the polyamide is selected from the group consisting of nylon 4,6; nylon 6,10; nylon 6; nylon 11; nylon 12; nylon 66; MXD-6; PACM-9; PACM-10; and PACM-12.

32. The melt-blown nonwoven web of claim 23, wherein the polyamide is a nylon.

15 33. The melt-blown nonwoven web of claim 32, wherein the nylon is nylon 6.

34. The melt-blown nonwoven web of claim 23, wherein
(a) the amine-ended polyethylene oxide has the general formula

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wherein the sum of a plus c varies from about 2 to about 20, and b is from about 5 to about 500, and

(b) the polyamide is nylon 6.

30 35. The melt-blown nonwoven web of claim 23, wherein
(a) the composition further comprises at least one additive agent selected from the group consisting of delustrants, antioxidants, plasticizers, and flame retardants;

(b) the block copolymer further comprises at least one additive agent selected from the group consisting of delustrants, antioxidants, plasticizers, and flame retardants; or

35 (c) both of the conditions (a) and (b) exist.

36. The melt-blown nonwoven web of claim 23, wherein the block copolymer has a number average molecular weight of from about 5,000 to about 50,000.

40 37. The melt-blown nonwoven web of claim 23, wherein the block copolymer has a relative viscosity at 10% w/v in 90% formic acid of less than about 50.

38. A hydrophilic wipe comprising the melt-blown nonwoven web of claim 24.

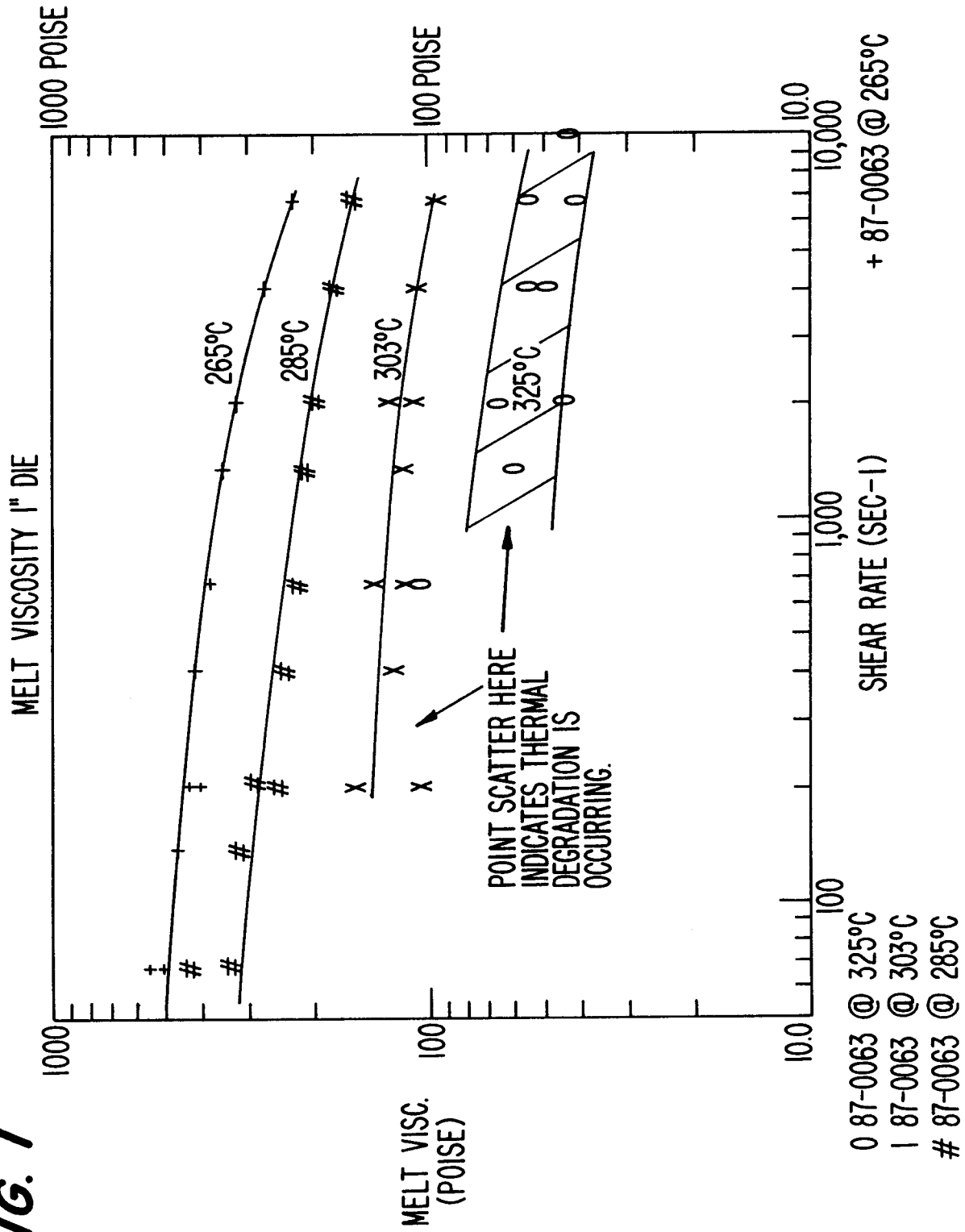
45 39. An absorptive liner for a garment, dressing, or personal care item, the liner comprising the melt-blown nonwoven web of claim 24.

40. A filter comprising the melt-blown web of claim 24.

50 41. A battery separator comprising the melt-blown nonwoven web of claim 24.

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FIG. 1





European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 11 9017

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	GB-A-2 214 201 (THE PROCTER & GAMBLE COMPANY) * the whole document * -----	1-41	D04H1/42 D01F6/80 D01D5/098
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			D04H D01F D01D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 12 FEBRUARY 1992	Examiner TARRIDA TORRELL J. B.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			