



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification ⁶ : C09J 167/02, A61L 15/58, B32B 27/36</p>	<p>A1</p>	<p>(11) International Publication Number: WO 99/23187 (43) International Publication Date: 14 May 1999 (14.05.99)</p>
<p>(21) International Application Number: PCT/US98/22893 (22) International Filing Date: 28 October 1998 (28.10.98)</p> <p>(30) Priority Data: 60/063,801 31 October 1997 (31.10.97) US 09/179,334 27 October 1998 (27.10.98) US</p> <p>(71) Applicant: EASTMAN CHEMICAL COMPANY [US/US]; 100 North Eastman Road, Kingsport, TN 37660 (US).</p> <p>(72) Inventor: FOSTER, Bruce, William; 617 Ruthlynn Drive, Longview, TX 75605 (US).</p> <p>(74) Agent: ALLEN, Rose, M.; P.O. Box 511, Kingsport, TN 37662-5075 (US).</p>		<p>(81) Designated States: European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
<p>(54) Title: ALIPHATIC-AROMATIC COPOLYESTERS AS ADHESIVE TIE-LAYERS IN EXTRUSION COATINGS</p>		
<p>(57) Abstract</p> <p>An adhesive tie-layer comprising a biodegradable aliphatic-aromatic copolyesters is described. The aliphatic-aromatic copolyesters are useful for a biodegradable and/or a breathable film or extrusion coating. These materials can be used in co-extrusions for bonding polyester and cellulosic plastics to various substrates. Desirably, the substrate has a surface energy of less than about 50 dynes/cm.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

5

ALIPHATIC-AROMATIC COPOLYESTERS AS
ADHESIVE TIE-LAYERS IN EXTRUSION COATINGS

RELATED APPLICATION

10

This application claims benefit to the U.S. provisional patent application having Serial No. 60/063,801 filed October 31, 1997, the entire disclosure of which is incorporated herein by reference.

FIELD OF THE INVENTION

15

This invention relates to the use of biodegradable copolyesters and copolyester blends as adhesives and particularly the use of aliphatic-aromatic copolyesters and blends thereof as an adhesive tie-layer. The aliphatic-aromatic copolyesters and blends thereof are useful in providing an adhesive tie-layer for dissimilar materials and particularly for materials having a surface energy of less than about 50
20 dynes/centimeter (cm).

BACKGROUND OF THE INVENTION

25

In the area of disposable wearable articles, both absorbent and non-absorbent, and particularly in the area of articles to be worn adjacent to the skin of the wearer, it is important that the article present a dry surface feel to the wearer to improve comfort and to minimize the potential for the development of undesirable skin conditions. Generally, such articles are formed from a nonwoven fabric. For instance, garments
30 used in the medical field require a comfortable material, such as a nonwoven web or fabric that feels comfortable against the wearer's skin. As used herein, the term

“nonwoven web” refers to a web structure composed of individual fibers or threads which are, typically, randomly interlaid and are bonded or intertwined without weaving or knitting. Conventionally, nonwoven fabrics have been widely used for garments, carpets, 5 diapers, sanitary articles, and industrial materials, such as wipers or towels. Fibrous materials which have been used in the formation of nonwoven fabrics include polyolefins, such as, polypropylene, aromatic polyesters, such as PET and polybutylene terephthalate (PBT), polyamides such as nylon and cellulose such rayon. Nonwoven fabrics can be made using a variety of known methods and processes, such as 10 meltblowing, spunbonding and carded web process.

It is also known that such materials may not be ideally situated for a specific application, having only a few certain desired properties. Very often it is desirable to coat a substrate having one set of properties to impart new properties to the composite. Using a disposable medical scrub gown as an example, the material must be 15 comfortable to the wearer and preferably is biodegradable. However, most nonwoven materials are fluid permeable. Thus, the fabric would not prevent body fluids from contacting the wearer. The nonwoven material must be coated or covered with a material that prevents fluids from entering the garment and desirably, is still breathable so as not to detract from the comfort of the wearer. An ideal material that provides 20 such barrier properties is cellulose acetate propionate (CAP). Unfortunately, it is difficult to get CAP to adhere to a non-woven fabric. Therefore, one or more tie-layers must be used between CAP layer and the non-woven fabric to get the proper adherence.

Numerous tie-layers are available in the prior art for adhering one layer to another. However, this becomes more difficult when the layers tied together are 25 dissimilar in properties. This problem becomes even more difficult when the tie-layer must not interfere with the desirable properties of the various but dissimilar layers. Again, using medical garments as an example, the tie-layer must not interfere with the favorable barrier properties of the external layer (i.e., CAP) or the wearability of the internal layer (i.e., non-woven fabric).

30 A further problem is that in many applications a composite comprising two or more layers having a tie-layer in between one or more of the layers must be

“environmentally-friendly”, e.g., it must be readily disposable and desirably is biodegradable. This is particularly true in medical garments, since used medical garments are often likely to be contaminated with potentially hazardous body fluids, such as blood. Disposable medical garments which are worn once and then disposed of
5 have become the standard and are often mandated for use. Thus, any tie-layer used in such composites must also be readily disposable.

Accordingly, it would be desirable to provide a material that is useful as an adhesive tie-layer, for similar or dissimilar layers, that does not detract from the favorable properties of the materials. More particularly, it would be desirable to retain
10 the comfort, moisture vapor transmissibility or breathability, and strength of a nonwoven material while improving its liquid barrier properties, as well as biodegradable.

SUMMARY OF THE INVENTION

15

It has been unexpectedly discovered that biodegradable aliphatic-aromatic copolyesters can successfully be used as an adhesive tie-layer for bonding a variety of dissimilar materials. The tie-layer can be formed into a contiguous film providing an impermeable barrier to liquids, and possibly other environmental health hazards such as
20 fungus, pollen, and microbial viruses and bacteria, and yet having a high moisture vapor transmission rate (MVTR) so that, when used in a composite garment, the garment can have good wearability.

It was further unexpectedly discovered that a blend of an aliphatic-aromatic copolyester and a cellulose ester can be successfully be used as an adhesive tie-layer for
25 bonding a variety of dissimilar materials.

Broadly, the present invention provides a method for adhesively securing at least two materials together, and advantageously, materials of dissimilar properties to form a laminated web. Particularly, the present invention provides a method for adhesively securing two materials together wherein the adhesive includes an aliphatic-
30 aromatic copolyester.

Another aspect of the invention is for a method for adhesively securing two materials together wherein the adhesive includes a binary and/or ternary blend of an aliphatic-aromatic copolyester and a cellulose ester.

It is another aspect of the invention to provide a laminated composite having a tie layer adhesively securing at least two layers of a material together wherein the tie layer includes an aliphatic-aromatic copolyester.

It is another aspect of the invention to provide a laminated composite having a tie layer adhesively securing at least two layers of a material together wherein the tie layer includes a blend of a cellulose ester and an aliphatic-aromatic copolyester.

It is an object of the invention to provide a method for adhesively securing at least two materials together wherein the adhesive is biodegradable.

It is another object of the invention to a method for securing together at least two materials having different surface energies using a biodegradable adhesive.

It is another object of the invention to provide a multi-layer laminate having a biodegradable tie-layer. The laminate is capable of being used in diverse composites such as medical garments, coated papers, and wet or dry packaging applications.

It is yet another object of the invention to provide a material that can be extruded into films and can be coextruded with a second extrusion coating material.

BRIEF DESCRIPTION OF THE DRAWING

The figure illustrates a schematic representation of an exemplary process for forming a laminated composite of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In accordance with the present invention, it has been unexpectedly discovered that biodegradable aliphatic-aromatic copolyesters can be used as an adhesive tie layer for bonding a variety of materials, and particularly dissimilar materials, and more particularly materials having a surface energy of less than about 50 dynes/cm.

In forming a laminated composite of at least two materials, a portion of at least one of the layers to be positioned in a facing relationship relative to the other layer, is coated with a co-compatible adhesive material having an aliphatic-aromatic copolyester and/or a blend of a cellulose ester and an aliphatic-aromatic copolyester. In a particularly preferred embodiment, the laminate, if to be used as a fabric for a disposable garment, has a surface energy gradient from low to high relative to the layer positioned adjacent to or in contact with the wearer's skin.

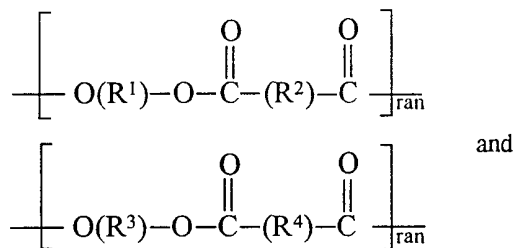
With particular reference to the drawing, the laminated composite of the invention is formed from a first layer material 10 which is typically unwound from a supply roll 12 and travels in the direction as indicated. A tie layer composition 14 is coated onto the surface 16 of first layer material 10, which is adapted to be positioned in a facing relationship with a second material 18. The coated first layer is then mated to the second material, preferably CAP or CAB, which then passed through the nip rolls 20.

Materials suitable for use in forming the layers of the laminate include natural and synthetic materials with synthetic materials being preferred. Non-limiting examples of suitable materials include nonwoven webs of synthetic fibers. The webs can be made using extrusion processes well known to those skilled in the nonwoven art, such as meltblowing, spunbonding, and carded web. Typically, nonwoven webs have discontinuous, spaced regions that impart fluid mobility through the web. The nonwoven web may be a single layer or a multi-layered material. The nonwoven web may be elastic or extensible, in that the material is capable of being stretched in at least one direction when a biasing force is applied and then substantially returns to its pre-stretched shape or configuration. As used herein "substantially returns" means the nonwoven web has less than about 5 percent permanent deformation, as measured 24 hours after the biasing force has been removed from the nonwoven web.

The nonwoven web may also be a composite made up of a mixture of two or more different fibers and particles. Such mixtures may be formed by adding fibers and particles to the gas stream in which the meltblown fibers are carried resulting in an intimate intermingling of meltblown fibers and other materials.

Desirably, the materials have a surface energy of less than about 50 dynes/cm, preferably, less than about 45 dynes/cm and most preferably less than about 30 dynes/cm.

The preferred tie layer composition includes a biodegradable copolyester and
 5 desirably, includes one or more, including blends thereof, of the biodegradable aliphatic-aromatic copolyesters, (AAPE), described in U.S. Patent Nos. 5,661,193; 5,599,858; 5,580,911; and 5,446,079 the entire disclosures of each being incorporated herein by reference. More specifically, the aliphatic-aromatic copolyesters useful in the present invention can be linear random copolymers preferably having repeating units
 10 of:



wherein R^1 and R^3 are the same and are selected from the groups consisting of C_2 - C_8 alkylene or oxyalkylene; R^2 is selected from one or more of the groups consisting of C_0 - C_8 alkylene or C_2 - C_4 oxyalkylene, and the mole % of R^2 is from about
 15 95-35%; R^4 is selected from the group of C_6 - C_{10} aryl, and the mole % of R^4 is from about 5-65%. More preferred AAPE are those wherein R^1 and R^3 are the same and are selected from C_2 - C_4 alkylene; R^2 is selected from one or more of the groups consisting of C_2 - C_6 alkylene or C_2 oxyalkylene, and the mole % of R^2 is from about 95-40%; R^4 is 1,4-disubstituted- C_6 aryl, and the mole % of R^4 is from about 5-60%. The most
 20 preferred compositions for these AAPE are those prepared from the following diols and diacids (or polyester forming derivatives thereof) in the following mole %, based on 100 mole percent acid and 100 mole percent diol:

(1) Glutaric acid (30-65%); diglycolic acid (0-10 mol %); terephthalic acid (25-60%); 1,4-butanediol (100 mole %).

(2) Succinic acid (30-85%); diglycolic acid (0-10%); terephthalic acid (5-60%); 1,4-butanediol (100 mole %).

(3) Adipic acid (30-65%); diglycolic acid (0-10%); terephthalic acid (25-60%); 1,4-butanediol (100 mole %).

5 Such compositions are commercially available from Eastman Chemical Company, Kingsport, TN.

 Specific examples of preferred AAPE include poly(tetramethylene glutarate-co-terephthalate-co-diglycolate) [50/45/5], poly(tetramethylene glutarate-co-terephthalate) [50/50], poly-(tetramethylene glutarate-co-terephthalate) [60/40], poly-(tetramethylene
10 glutarate-co-terephthalate) [40/60], poly(tetramethylene succinate-co-terephthalate) [85/15], poly(ethylene succinate-co-terephthalate) [70/30], poly(tetramethylene adipate-co-terephthalate) [85/15], and poly(tetramethylene succinate-co-terephthalate) [70/30].

 Alternatively, the aliphatic-aromatic copolyester can be blended, preferably
15 with cellulose esters, to form binary and ternary blends. The cellulose esters useful in formulating the blend can be a cellulose triester or a secondary cellulose ester. Examples of cellulose triesters include cellulose triacetate, cellulose tripropionate, or cellulose tributyrate. Examples of secondary cellulose esters include cellulose acetate, cellulose acetate propionate, and cellulose acetate butyrate. These cellulose esters are
20 described in U.S. Pat. Nos. 1,698,049; 1,683,347; 1,880,808; 1,880,560; 1,984,147, 2,129,052; and 3,617,201, incorporated herein by reference in their entirety.

 The cellulose esters useful in the present invention can be prepared using techniques known in the art or are commercially available, e.g., from Eastman
Chemical Company, Inc., Kingsport, Tenn., U.S.A.

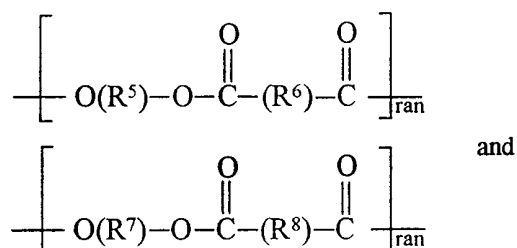
25 The cellulose esters useful in the present invention have at least 2 anhydroglucose rings and typically have between 2 and 5,000 anhydroglucose rings; also, such polymers typically have an inherent viscosity (IV) of about 0.2 to about 3.0 deciliters/gram, preferably about 1 to about 1.5, as measured at a temperature of 25° C. for a 0.5 gram sample in 100 ml of a 60/40 by weight solution of
30 phenol/tetrachloroethane. In addition, the DS/AGU of the cellulose esters useful herein ranges from about 1.7 to about 3.0. Preferred esters of cellulose include cellulose

acetate (CA), cellulose propionate (CP), cellulose butyrate (CB), cellulose acetate propionate (CAP), cellulose acetate butyrate (CAB), cellulose propionate butyrate (CPB), and the like. CAP and CAB are more preferred cellulose esters. The most preferred ester of cellulose is CAP.

5 For binary blends, the preferred esters of cellulose for blending with aliphatic-aromatic copolyesters are CAP and CAB. The preferred ester of cellulose is CAP having a DS/AGU of 2.1 to 2.85 wherein the DS/AGU of acetyl ester is 1% to 50% of the total ester content. The most preferred CAPs have a DS/AGU of 2.5 to 2.75 wherein the DS/AGU of acetyl ester is 4% to 30 % of the total ester content.

10 For ternary blends, the preferred esters of cellulose for blending with aliphatic-aromatic copolyesters and/or polymeric compounds, biodegradable additives, or hydrophobic agents are CAP and CAB. The preferred ester of cellulose is CAP having a DS/AGU of 1.7-3.0 wherein the DS/AGU of acetyl ester is 1% to 50% of the total ester content. The most preferred CAP's have a DS/AGU of 2.5-2.75 wherein the
15 DS/AGU of acetyl ester is 4%-30% of the total ester content.

The aliphatic-aromatic copolyesters that are useful in such blends in the present invention are random copolymers and preferably comprises repeating units of:



20

R^5 and R^7 are independently selected from one or more of the following groups consisting of C_2 - C_{12} alkylene or oxyalkylene; C_2 and C_{12} alkylene or oxyalkylene substituted with one to four substituents independently selected from the group consisting of halo, C_6 - C_{10} aryl, and C_1 - C_4 alkoxy; C_5 - C_{10} cycloalkylene; C_5 - C_{10}

cycloalkylene substituted with one to four substituents independently selected from the group consisting of halo, C₆-C₁₀ aryl, and C₁-C₄ alkoxy.

R⁶ is selected from one or more of the following groups consisting of C₀-C₁₂ alkylene or oxyalkylene; C₁-C₁₂ alkylene or oxyalkylene substituted with one to four substituents independently selected from the group consisting of halo, C₆-C₁₀ aryl, and C₁-C₄ alkoxy; C₅-C₁₀ cycloalkylene; and C₅-C₁₀ cycloalkylene substituted with one to four substituents independently selected from the group consisting of halo, C₆-C₁₀ aryl, and C₁-C₄ alkoxy.

R⁸ is selected from one or more of the following groups consisting of C₆-C₁₀ aryl, C₆-C₁₀ aryl substituted with substituted with one to four substituents independently selected from the group consisting of halo, C₁-C₄ alkyl, and C₁-C₄ alkoxy.

Desirably, the aliphatic-aromatic copolyester has from about 10 to about 1,000 repeating units and preferably, from about 15 to about 600 repeating units.

In the present invention, the mole % of R⁶ in the copolymer can range from 30 to 95%, and the mole % of R⁸ can range from 5 to 70%. A more preferred range is when the mole % of R⁶ is from about 45 to 85% and the mole % of R⁸ is from about 15-55 mole %. The most preferred ranges, in general, depend upon the needed level of miscibility of the copolyester with the cellulose esters and the physical properties desired. The most preferred ranges for miscible blends is when R⁶ is glutaric and the mole % of R⁶ in the copolyester ranges from 70 to 85% and the mole % of R⁸ range from 15-30 mole %. The most preferred ranges for partially miscible blends is when R⁶ is glutaric and the mole % of R⁶ in the copolyester ranges from 45 to 60% and the mole % of R⁸ ranges from 40-55 mol %. The range of miscibility of a particular blend can change as the molecular weight of a blend component is changed. In general, an aliphatic-aromatic polyester having a lower molecular weight or inherent viscosity will be more miscible with a given cellulose ester relative to the higher molecular weight polyester.

It is preferred that the aliphatic-aromatic copolyester has an inherent viscosity of about 0.4 to about 1.2 as measured at a temperature of 25° C. for a 0.5 gram sample in 100 ml of a 60/40 by weight solution of phenol/tetrachloroethane.

As used herein the terms "alkyl" and "alkylene" refer to either straight or branched chain moieties such as $-\text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2-$ and $-\text{CH}_2\text{CH}(\text{X}) - \text{CH}_2 -$. Also, all of the carbon atoms of the cycloalkyl and cycloalkylene moieties are not necessarily in the ring structure, e.g., a C_8 cycloalkyl group can be cyclooctyl or dimethylcyclohexyl. The term "oxyalkylene" refers to alkylene chains containing from 1 to 4 ether oxygen groups.

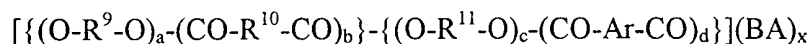
The preparation of polyesters and copolyesters is well known in the art (U.S. Pat. No 2,012,267, incorporated herein by reference in its entirety.) Such reactions are usually carried out at temperatures from 150°C . to 300°C . in the presence of polycondensation catalysts such as titanium tetrachloride, manganese diacetate, antimony oxide, dibutyl tin diacetate, zinc chloride, or combinations thereof. The catalysts are typically employed in amounts between 10 to 1000 ppm, based on total weight of the reactants. For the purpose of the present invention, a representative aliphatic polyester is the polycondensation product of dimethylglutarate and 1,6-hexanediol. This polyester, poly(hexamethylene glutarate), is produced when dimethylglutarate and 1,6-hexanediol are heated at approximately 210°C . for 4 hours and then at 260°C . for 1.5 hours under vacuum in the presence of 100 ppm of Ti. A representative aliphatic-aromatic copolyester is poly(tetramethylene glutarate-coterephthalate) containing 30 mole per cent terephthalate. This polyester is produced when dimethylglutarate, dimethyl terephthalate, and 1,4-butanediol are heated at 200°C . for 1 hour then at 245°C . for 0.9 hour under vacuum in the presence of 100 ppm of Ti present initially as $\text{Ti}(\text{O}^i\text{Pr})_4$.

It is preferred that the aliphatic-aromatic copolyester for use in blending is prepared from any polyester forming combination of dicarboxylic acids or derivatives thereof, and diols. Dicarboxylic acids may be selected from the group consisting of the following diacids; malonic, succinic, glutaric, adipic, pimelic, azelaic, sebacic, fumaric, 2,2-dimethyl glutaric, suberic, diglycolic, itaconic, 1,3-cyclopentanedicarboxylic, 1,4-cyclohexanedicarboxylic, meleic, 1,3-cyclohexanedicarboxylic, 2,5-norbornanedicarboxylic, 1,4-terephthalic, 1,3-terephthalic, 2,6-naphthoic, 1,5-naphthoic, and ester forming derivatives thereof, and combinations thereof; and said diols are selected from the group consisting of ethylene glycol, diethylene glycol,

propylene glycol, 1,3-propanediol, 2,2-dimethyl-1,3-propanediol, 1,3-butanediol, 1,3-butanediol, 1,5-pentanediol, 1,6-hexanediol, 2,2,4-trimethyl-1,6-hexanediol, thiodiethanol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 2,2,4-trimethyl-1,6-hexanediol, thiodiethanol, 1,3-cyclohexanedimethanol,
 5 1,4-cyclohexanedimethanol, 2,2,4,4-tetramethyl-1,3-cyclobutanediol, triethylene glycol, tetraethylene glycol, and combinations thereof.

Specific examples of preferred aliphatic-aromatic copolyesters for blending include poly(tetramethylene glutarate-co-terephthalate-co-diglycolate) [50/45/5], poly(tetramethylene glutarate-co-terephthalate) [50/50], poly(tetramethylene glutarate-co-terephthalate) [60/40], poly(tetramethylene glutarate-co-terephthalate) [70/30],
 10 poly(tetramethylene glutarate-co-terephthalate) [85/15], poly(tetramethylene glutarate-co-terephthalate) [70/30], poly(tetramethylene adipate-co-terephthalate) [85/15], poly(tetramethylene succinate-co-terephthalate) [85/15], poly(tetramethylene-co-ethylene glutarate-co-terephthalate) [50/50] [70/30].

15 The aliphatic-aromatic copolyester of the present invention may also be a branched copolymer having repeating units of:



20 The aliphatic acid residue, $-CO-R^{10}-CO-$, is present in an amount "b" ranging from 30 to 95 mol percent, preferably 55 to 60 mol percent, and contains 3 to 40 carbon atoms, preferably 3 to 12 carbon atoms. The aromatic acid residue, $-CO-Ar-CO-$, is present in an amount "d" ranging from 5 to 70 mol percent, preferably 40 to 45 mol percent, and contains from 8 to 40 carbon atoms, preferably 8 to 14 carbon atoms. The
 25 diol residues, $-O-R^9-$ and $-O-R^{11}-O-$, which contain from 2 to 20 carbon atoms are present in an amount a of 0 to 100 mol percent and in an amount "c" of 100 to 0 mol percent, respectively. The mole percent of the acid components and diol components are each based on 100 mole percent.

30 The aliphatic acid components are preferably selected from the group consisting of malonic, succinic, glutaric, adipic, pimelic, azelaic, sebacic, fumaric, 2,2-dimethyl glutaric, suberic, 1,3-cyclopentane-dicarboxylic, 1,4-cyclohexanedicarboxylic, 1,3-

cyclohexanedicarboxylic, diglycolic, itaconic, maleic and 2,5-norbornanedicarboxylic. Hydroxy acids such as 4-(hydroxymethyl) cyclohexanecarboxylic acid, hydroxypivalic acid, 6-hydroxyhexanoic acid, glycolic acid, lactic acid and ester forming derivations thereof may also be used as aliphatic acid components to make these co-polyesters.

5 The aromatic acid components are preferably selected from the group consisting of ethylene glycol, diethylene glycol, propylene glycol, 1,3-propanediol, 2,2-dimethyl 1,3-propanediol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 2,2,4-trimethyl-1,6-hexanediol, thiodiethanol, 1,3-cyclohexanedimethanol, 1,4-cyclohexanedimethanol, 2,2,4,4,-tetramethyl-1,2-cyclobutanediol, triethylene glycol, 10 tetraethylene glycol, and combinations thereof. The diol components may be the same of different.

 The branching agent is represented by "(BA)_x", wherein "x" is the weight percent of the branching agent. The weight percent ranges from 0.01 to 10 percent, preferably 0.1 to 1.0 weight percent.

15 The branching agent preferably has a weight average molecular weight of about 50-5000, more preferably 92-3000, and a functionality of about 3-6. The branching agent may be a polyol having 3-6 hydroxyl groups, a polycarboxylic acid having 3 or 4 carboxyl groups or a hydroxy acid having a total of 3-6 hydroxyl and carboxyl groups.

 Representative low molecular weight polyols that function as branching agents 20 include glycerol, trimethylolpropane, 1,2,4-butanetriol, pentaerythritol, 1,2,6-hexanetriol, sorbitol, 1,1,4,4,-tetrakis (hydroxymethyl) cyclohexane, tris(2-hydroxyethyl) isocyanurate, and dipentaerythritol. Particular branching agent examples of higher molecular weight polyols (MW 400-3000) are triols derived by condensing alkylene oxides having 2-3 carbons, such as ethylene oxide and propylene oxide with 25 polyol initiators.

 Representative polycarboxylic acids that may be used as branching agents include hemimellitic acid, trimellitic acid, trimesic acid, pyromellitic acid, benzene tetracarboxylic acid, benzophenone tetracarboxylic acid, 1,1,2,2,-ethanetetracarboxylic acid, 1,1,2-ethanetricarboxylic acid, 1,3,5-pentanetricarboxylic acid, and 1,2,3,4- 30 cyclopentanetetra-carboxylic acid. Although the acids may be used as such, preferably

they are used in the form of their lower alkyl esters or their cyclic anhydrides in those instances where cyclic anhydrides can be formed.

Representative hydroxy acids as branching agents include malic acid, citric acid, tartaric acid, 3-hydroxyglutaric acid, mucic acid, trihydroxyglutaric acid, and 4-
5 (beta-hydroxyethyl)phthalic acid. Such hydroxy acids contain a combination of 3 or more hydroxyl and carboxyl groups.

Especially preferred branching agents include trimellitic acid, trimesic acid, pentaerythritol, trimethylol propane and 1,2,4-butanetriol.

The preparation of polyesters and copolyesters is well known in the art, such as
10 disclosed in U.S. Pat. No. 2,012,267. Such reactions are typically operated at temperatures from 150° C. to 300° C. in the presence of polycondensation catalysts such as titanium isopropoxide, manganese diacetate, antimony oxide, dibutyl tin diacetate, zinc chloride, or combinations thereof. The catalysts are typically employed in amounts between 10 to 1000 parts per million (ppm), based on total weight of the
15 reactants.

A branched random aliphatic-aromatic copolyester of the present invention is poly(tetramethylene adipate-co-terephthalate) branched with 0.5 weight percent pentaerythritol and containing 43 mole percent terephthalate. This copolyester is produced when dimethyladipate, dimethyl terephthalate, pentaerythritol and 1,4-
20 butanediol are heated at 190° C. for 1 hour, 200° C. for 2 hours, 210° C. for 1 hour, then at 250° C. for 1.5 hours under vacuum in the presence of 100 ppm of Ti present initially as $Ti(O^iPr)_4$. The copolyester is typically pelletized after formation for use in extrusion foaming.

Another branched random copolyester of the present invention is
25 poly(tetramethylene adipate-co-terephthalate) branched with 0.3 weight percent pyromellitic dianhydride and containing 43 mole percent terephthalate. This copolyester is produced via reactive extrusion of linear poly (tetramethylene adipate-co-terephthalate) with pyromellitic dianhydride using an extruder.

The aliphatic-aromatic copolyester compositions can be applied and used as an
30 adhesive between two substrates using techniques known to those skilled in the adhesive art. Advantageously, an adhesive tie-layer can be formed by extruding the

- 14 -

compositions as a film and even more advantageously the aliphatic-aromatic copolyester is coextruded with a second film-forming material, such as CAP. Film extrusion and coextrusion methods are well-known to the skilled artisan.

The present invention is illustrated in greater detail by the specific examples presented below. It is to be understood that these examples are illustrative
5 embodiments and are not intended to be limiting of the invention, but rather are to be construed broadly within the scope and content of the appended claims.

Examples 1-4

10

A laboratory extrusion coating and laminating line, manufactured by ErWePa Machineinfabrik (now, Egan/Davis-Standard) consisted of three extruders- Extruder A is a 2.5" diameter, 24:1 L/D, single-flighted design, with a compression ratio of 3:1. Extruders B and C were 2 inches in diameter, with screws comparable to that in
15 Extruder A. The three extruders feed into a mixing block, of ErWePa design, that allows the operator to extrude multi-layer coatings onto a moving web. These coatings can have the following structures:

Substrate / A

Substrate / A / B

20

Substrate / B / A

Substrate / C / B / A

Substrate / A / B / C

Substrate A / B / C / B / A

These variations are accomplished using techniques known to those skilled in
25 the art of co-extrusion coating and laminating.

The laminator section of the line included an unwind station, flame and corona discharge pre-treating stations, a nip, or lamination station with a chilled metal roll and rubber nip roll, a secondary unwind station (for laminating), and a rewind station. The line was 42" (107 cm) wide, and was capable of running up to speeds of 2000 feet per
30 minute (610 meters per minute).

MISSING AT THE TIME OF PUBLICATION

Table 2

Example	1	2	3	4
Substrate	Adhesion Quality or Strength			
a	0	0	tore substrate	tore substrate
b	0	0	19 g/in	534 g/in
c	0	0	Poor	Fair
d	0	0	tore substrate	tore substrate

The foil adhesion numbers were for 1 inch strips separated on a tensile tester according to ASTM D-92. Values are the average of 5 specimens.

5 In the first example, the CAP is coated onto a polyester nonwoven because it provides a desirable combination of barrier to body fluids and a high moisture transmission rate, thereby providing a breathable, comfortable material.

In a second example, the CAP is extrusion coated directly onto aluminum foil. In packaging applications, the plastic layer would generally provide a heat seal medium and barrier to hold in the contents, while the foil will protect the contents from
 10 atmospheric oxygen and hence spoilage. Extruded directly onto the aluminum foil, the copolyester exhibits no measurable adhesion to the foil.

These examples show that the aliphatic-aromatic copolyester of the present invention imparts excellent adhesion to materials having different surface energies as well as composed of normally incompatible materials. The examples further show that
 15 the aliphatic-aromatic copolyester of the present invention imparts excellent adhesion to polymers, cellulose and foils. The examples also show that the aliphatic-aromatic copolyester of the present invention imparts excellent adhesion to bleached board and polyester nonwoven, when co-extruded with CAP at a thickness of 3 to 7 microns, and
 20 excellent adhesion to aluminum foil at a thickness greater than about 3 microns.

Examples 5-8

The same procedure as described for Examples 1-4 above was used with the
 25 following exceptions:

Extruder A: 70 rpm (175 lbs/hr output copolyester, measured by weighing)

Extruder B: 20 rpm (50 lbs/hr output AAPE, also measured by weighing)

The line speed and layer thicknesses are given in Table 3 below:

Table 3

Example	5	6	7	8
Line Speed, fpm:	100	200	100	200
Ext. A (gsm):	57	28	57	52
Ext. B(gsm):	0	0	16	8
Layer A, microns:	48	24	48	24
Layer B, microns:	0	0	14	7

5

The CAP and aliphatic-aromatic copolyester were coated onto the following substrates: a) unprimed aluminum foil; b) woven polyethylene fabric; and c) 350 gsm bleached carton stock, or paperboard. The adhesion results are summarized in Table 4 below:

Table 4

Example	5	6	7	8
Substrate	Adhesion Quality or Strength			
a	0	0	tore substrate	tore substrate
b	0	0	Poor	0
c	0	0	tore substrate	tore substrate

10

These examples show that an aliphatic-aromatic copolyester, when co-extruded between a typical co-polyester and aluminum foil or a copolyester and bleached board, at thicknesses greater than about 7 microns, provides excellent bonding. However, the aliphatic-aromatic copolyester is less than satisfactory in the case of the woven polyethylene fabric.

15

Examples 9-21

The feasibility of blending various polymers with the aliphatic-aromatic copolyester was evaluated for the effects on adhesion and on processability. For ease of study, these experiments were carried out in a monolayer coating. In the examples, the various blends were extrusion coated onto two substrates – natural kraft paper, and a high-density woven polyethylene fabric at the conditions shown in Table 5 below:

Table 5

Example	Modifier	% Modifier	Line Speed, fpm	Melt Temp.
9	LDPE	95	150	550
10	LDPE	80	150	550
11	LDPE	60	150	440
12	LDPE	40	150	440
13	LDPE	20	150	440
14	LDPE	10	150	440
15	EMA (24)	20	150	425
16	E-BA-MA ¹	20	500	455
17	E-BA-MA ²	25	0	430 – 540
18	E-BA-MA ¹	25	700	501
19	E-BA-MA ¹	35	350	500
20	E-BA-MA ¹	60	0	519
21	E-BA-MA ¹	80	0	519

LDPE: 4.2 melt flow, 0.924 density polyethylene

EMA (24) – 24% methyl-acrylate ethylene copolymer

E-BA-MA¹ - 5.5% butyl-acrylate, 3.5% maleic acid terpolymer

E-BA-MA² - 16.5% butyl-acrylate, 3.5% maleic acid terpolymer

These results indicate the unexpected broad compatibility of the aliphatic-aromatic copolyester with low-density polyethylene, as indicated by the fact that a moderate line speed of 150 fpm was possible with these materials.

Furthermore, compatibility with the 24% methacrylate EMA copolymer was acceptable at 20% EMA. However, when blended with E-BA-MA terpolymers, there

was no compatibility with a 16.5% BA material, Example 17, and poor compatibility with a 5.5% BA terpolymer, when the E-BA-MA material constituted 60 to 80% of the blend, Examples 20 and 21. Surprisingly, when the 5.5% BA terpolymer was blended from 20 – 25%, a material with superior processability resulted. These particular
 5 blends also exhibit improved adhesion to polyethylene fabrics and paper substrates, as show in Table 6 below:

Table 6

Example	Melt Appearance	Adhesion to HDPE fabric	Adhesion to kraft paper	MVTR (g/mil/day)
9	Good	Excellent	Excellent	<1.0
10	Good	Excellent	Excellent	<1.0
11	Good	Fair	Excellent	2-4
12	Good	Fair	Excellent	10-12
13	Good	Poor	Excellent	20-30
14	Good	Poor	Excellent	40-50
15	Good	Fair	Excellent	60
16	Good	Fair	Excellent	75
17	Streaky/surging	N/A	N/A	
18	Good	Fair	Excellent	50
19	Good	Good	Excellent	35
20	Streaky/surging	N/A	N/A	
21	Streaky/surging	N/A	N/A	

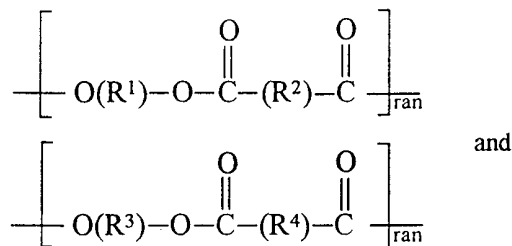
These results show that the use of blends of an aliphatic-aromatic copolyester with LDPE or with the preferred E-BA-MA terpolymer at a level of 20 – 35% and a
 10 concentration of 0.01 weight % to about 14 weight % butyl-acrylate can be used in a monolayer or coextrusion operations, and provide excellent adhesion to paper substrates and, in some cases, to a high density polyethylene fabric. Such fabric is commonly used to make tarpaulins and the like, and the higher MVTR over that of pure
 15 polyethylenes will be useful in lessening condensation that would otherwise occur beneath such coverings.

- 20 -

It has been shown that aliphatic-aromatic copolyesters according to the present invention are useful as adhesive materials in various diverse applications to bond dissimilar materials. It will be recognized by those of skill in the art in possession of the present invention that these bonding materials will bond together one or more
5 materials such as paper, metals, plastics, fabrics, and the like. These adhesive materials are particularly useful as tie-layers in such applications as paper coating for water-based inks, and as a packaging material to protect foil linings from corrosive contents. The aliphatic-aromatic copolyesters are also useful as films when used in co-extrusions with, for instance, extrusion coating grades of polyester and with cellulosic plastics to
10 various substrates. While the particular embodiments of the present invention have been described, it would be within those skilled in the art to make obvious changes and modifications without departing from the spirit and scope of the present invention. Accordingly, it is intended that the appended claims cover such changes and modifications without departing from the scope of this invention.

I claim:

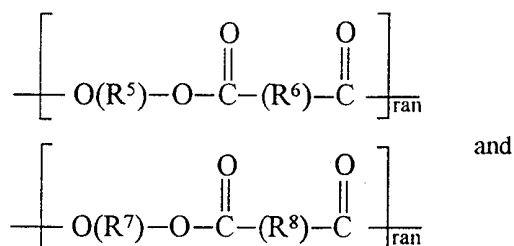
1. A composite comprising two materials secured together with a third material,
 wherein said third material comprises an aliphatic-aromatic copolyester comprising
 5 repeating units of :



- wherein R^1 and R^3 are the same and are selected from the groups consisting of $\text{C}_2\text{-C}_8$
 alkylene or oxyalkylene;
 R^2 is selected from one or more of the groups consisting of $\text{C}_0\text{-C}_8$ alkylene or $\text{C}_2\text{-C}_4$
 10 oxyalkylene; and
 R^4 is selected from the group of $\text{C}_6\text{-C}_{10}$ aryl.
2. The composite of claim 1 wherein R^2 is from about 95-35 mole % and R^4 is from about
 5-65 mole %.
- 15
3. The composite of claim 1 wherein said aliphatic-aromatic copolyester is selected from
 the group consisting of :
- a. from about 30-65% glutaric acid, from about 0-10 mole % diglycolic acid,
 from about 25-60 mole % terephthalic acid, and 100 mole % 1,4-butanediol;
 - 20 b. from about 30-85 mole % succinic acid, from about 0-10 mole % diglycolic
 acid, from about 60 mole % terephthalic acid, and 100 mole % 1,4-butanediol; and
 - c. from about 30-65 mole % adipic acid, from about 0-10 mole % diglycolic acid,
 from about 25%-60% terephthalic acid, and 100 mole% 1,4-butanediol, wherein the
 mole % is based on 100 mole percent acid and 100 mole percent diol.

25

4. The composite of claim 1 wherein said aliphatic-aromatic copolyester is a blend comprising repeating units of:



wherein, R^5 and R^7 are independently selected from one or more of the groups consisting of C_2 - C_{12} alkylene or oxyalkylene; C_2 and C_{12} alkylene or oxyalkylene substituted with one to four substituents independently selected from the group consisting of halo, C_6 - C_{10} aryl, and C_1 - C_4 alkoxy; C_5 - C_{10} cycloalkylene; C_5 - C_{10} cycloalkylene substituted with one to four substituents independently selected from the group consisting of halo, C_6 - C_{10} aryl, and C_1 - C_4 alkoxy;

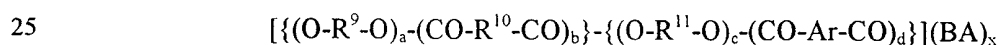
R^6 is selected from one or more of the groups consisting of C_0 - C_{12} alkylene or oxyalkylene; C_1 - C_{12} alkylene or oxyalkylene substituted with one to four substituents independently selected from the group consisting of halo, C_6 - C_{10} aryl, and C_1 - C_4 alkoxy; C_5 - C_{10} cycloalkylene; and C_5 - C_{10} cycloalkylene substituted with one to four substituents independently selected from the group consisting of halo, C_6 - C_{10} aryl, and C_1 - C_4 alkoxy;

R^8 is selected from one or more of the groups consisting of C_6 - C_{10} aryl, C_6 - C_{10} aryl substituted with substituted with one to four substituents independently selected from the group consisting of halo, C_1 - C_4 alkyl, and C_1 - C_4 alkoxy; and

a cellulose ester selected from the group consisting of CAP and CAB.

5. The composite of claim 7 wherein R^6 is from about 30 to 95 mole % and R^8 is from about 5 to 70 mole %.

6. The composite of claim 1 wherein said aliphatic-aromatic copolyester comprises repeating units of:



wherein said aliphatic acid residue, $-\text{CO}-\text{R}^{10}-\text{CO}-$, is present in an amount "b" ranging from about 30 to 95 mole %, said aromatic acid residue, $-\text{CO}-\text{Ar}-\text{CO}-$, is present in an amount

“d” ranging from about 5 to 70 mole %; diol components “a” are present in an amount of from 0 to 100 mole % and “c” is present in an amount of from about 100 to 0 mole %, based on 100 mole % acid and 100 mole % diol and said branching agent is present in an amount “x” ranging from about 0.01 to about 10 weight percent based on the total weight of the constituents.

5

7. A composite comprising a first and a second material adhesively secured together by a third material comprising an aliphatic-aromatic copolyesters selected from the group consisting of an aliphatic-aromatic copolyester of claim 1, 4, 6 and blends thereof.

10

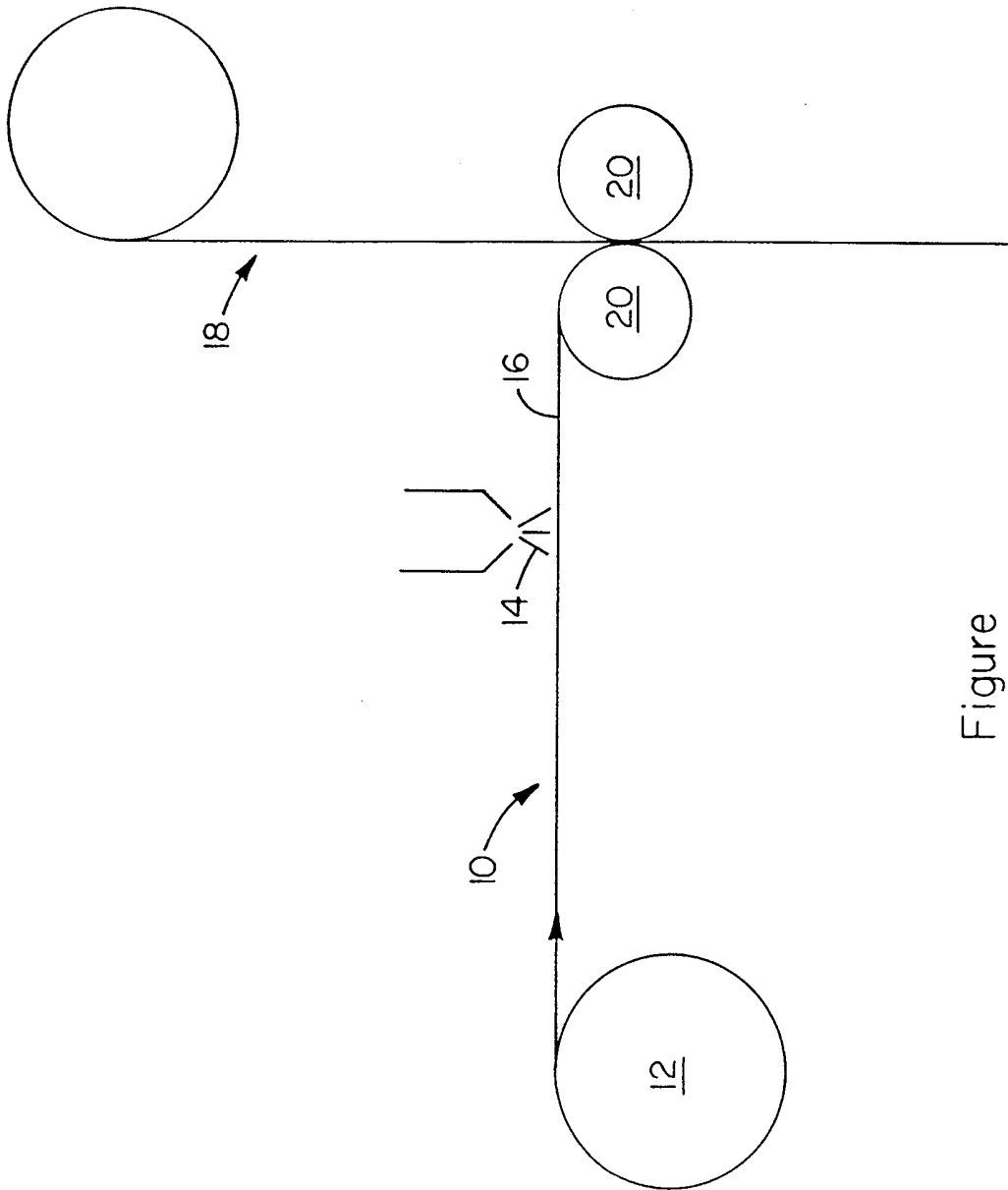
8. The composite of claim 7 wherein said aliphatic-aromatic copolyester further includes from about 5 weight percent to about 95 weight percent of a modifier selected from the group consisting of a polyolefin, methyl-acrylate ethylene copolymer and butyl-acrylate/maleic acid terpolymer.

15

9. The composite of claim 8 wherein said aliphatic-aromatic copolyester includes from about 5 weight percent to about 35 weight percent of said butyl-acrylate/maleic acid terpolymer and said terpolymer includes from about 0.01 weight percent to about 14 weight percent butyl-acrylate and about 0.1 to about 5 weight percent maleic acid.

20

10. A method of forming a laminated composite from at least two materials comprising contacting at least one of said materials with a third material selected from the group consisting of an aliphatic-aromatic copolyester of claim 1, 4, 6 and blends thereof, and bonding said at least two materials together.



Figure

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 98/22893

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 C09J167/02 A61L15/58 B32B27/36

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
 Minimum documentation searched (classification system followed by classification symbols)
 IPC 6 A61L C09J B32B C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 83 02621 A (EASTMAN KODAK COMPANY) 4 August 1983 see claims 1-9 ---	1,2,7,10
X	US T100504 I (SUBLETT BOBBY J) 7 April 1981 see the whole document ---	1,7
X	EP 0 261 669 A (AUSIMONT S.P.A.) 30 March 1988 see page 2, column 1, line 1 - line 14; claims 1-14; example 1 ---	1,8,9
A	EP 0 481 109 A (KUFNER TEXTILWERKE GMBH) 22 April 1992 see claim 1 ---	8
	-/--	

Further documents are listed in the continuation of box C. Patent family members are listed in annex.

* Special categories of cited documents :

<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>
--	--

Date of the actual completion of the international search 19 February 1999	Date of mailing of the international search report 02/03/1999
--	---

Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Decocker, L
--	--

INTERNATIONAL SEARCH REPORT

Intern. Patent Application No

PCT/US 98/22893

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 391 423 A (WNUK ET AL.) 21 February 1995 see claims 1-11 -----	1-10

INTERNATIONAL SEARCH REPORT

information on patent family members

Interr. 1al Application No

PCT/US 98/22893

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 8302621 A	04-08-1983	US 4419507 A CA 1191299 A EP 0099394 A	06-12-1983 30-07-1985 01-02-1983
US T100504 I	07-04-1981	US 8100504 I	07-04-1981
EP 261669 A	30-03-1988	CA 1317045 A DE 3788262 D DE 3788262 T JP 63152684 A US 5057561 A	27-04-1993 05-01-1994 17-03-1994 25-06-1988 15-10-1991
EP 481109 A	22-04-1992	AT 108817 T CA 2041997 A CN 1060862 A DE 59006526 D JP 2582486 B JP 5059340 A MX 172654 B RU 2051938 C US 5153064 A	15-08-1994 17-04-1992 06-05-1992 25-08-1994 19-02-1997 09-03-1993 05-01-1994 10-01-1996 06-10-1992
US 5391423 A	21-02-1995	AT 163883 T AU 681589 B AU 4533993 A CA 2138120 A CN 1085493 A DE 69317423 D DE 69317423 T DK 647184 T EG 20102 A EP 0647184 A ES 2113542 T FI 946071 A GR 3026335 T JP 8500062 T MX 9303853 A NO 944985 A WO 9400293 A	15-03-1998 04-09-1997 24-01-1994 06-01-1994 20-04-1994 16-04-1998 09-07-1998 27-04-1998 31-07-1997 12-04-1995 01-05-1998 23-12-1994 30-06-1998 09-01-1996 31-05-1994 24-02-1995 06-01-1994