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54 **Non-woven articles comprised of thermotropic liquid crystal polymer fibers and method of production thereof.**

57 **Non-woven articles comprised of thermotropic liquid polymer fibres made of fibres of a polymer which is capable of forming an anisotropic melt phase, said fibres being bonded together either autogeneously or by means of an adhesive composition.**

The polymer is a wholly aromatic polymer, preferably a wholly aromatic polyester.

A method for forming these non-woven articles comprises spray-spinning said polymer in the melt phase and collecting the multitude of discontinuous fibres in web form on a screen.

Such non-woven articles exhibit good thermal stability and chemical and solvent resistance.

A heat treatment in a non-oxidizing, moisture-free atmosphere can be effected to increase the melting temperature of the non-woven articles.

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NON-WOVEN ARTICLES COMPRISED OF
THERMOTROPIC LIQUID CRYSTAL POLY-
MER FIBERS AND METHOD OF
PRODUCTION THEREOF

BACKGROUND OF THE INVENTION

The present invention relates to non-woven articles comprised of thermotropic liquid crystal polymer fibers.

Various conventional non-woven articles comprised of polymeric materials have been employed for many purposes. For example, non-woven articles have been employed as filters, electrical insulation and reinforcement for resins. However, such non-woven articles have frequently been found to not be appropriate for use in a high temperature environment (e.g., in excess of about 200°C.) or in an environment where the structure will come into contact with solvents or corrosive chemicals. It is therefore desirable to provide non-woven articles comprised of a

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polymeric material which is resistant to solvents or corrosive chemicals and also suitable for use at high temperatures.

It is known to those skilled in the art that fibers comprised of lyotropic liquid crystal polymers have been employed in the production of non-woven scrim sheets in conjunction with polyester fibers which are not capable of forming an anisotropic melt phase wherein the polyester fibers are thermally bonded to the lyotropic liquid crystal polymer fibers.

It is also known to those skilled in the art that the heat treatment of shaped articles of liquid crystal polymers increases the melting temperature, molecular weight and mechanical properties of the polymer. See, for example, U.S. Patent Nos. 3,975,487; 4,183,895; and 4,247,514.

OBJECTS AND SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide non-woven articles which are resistant to thermal degradation.

It is also an object of the present invention to provide non-woven articles which are resistant to solvent and chemical degradation.

It is further an object of the present invention to provide non-woven articles which exhibit desirable multi-dimensional tensile strength and modulus.

In accordance with one aspect of the present invention, there is thus provided a non-woven article which exhibits desirable thermal stability and chemical and solvent resistance comprised of fibers of a polymer which is capable of forming an anisotropic melt phase, said fibers being bonded together to an extent sufficient to impart structural integrity to said article.

In accordance with another aspect of the present invention, there is thus provided a method for forming a non-woven article in the form of a web or sheet which exhibits desirable thermal stability and chemical and solvent resistance comprised of fibers of a polymer which is capable of forming an anisotropic melt phase, said method comprising spray spinning said polymer in the melt phase to form a multitude of discontinuous fibers and collecting said fibers in the form of a web or sheet.

DETAILED DESCRIPTION OF THE INVENTION

Thermotropic liquid crystal polymers are polymers which are liquid crystalline (i.e., anisotropic) in the melt phase. These polymers have been described by various terms, including "liquid crystalline," "liquid crystal" and "anisotropic." Briefly, the polymers of this class are thought to involve a parallel ordering of the molecular chains. The state wherein the molecules are so ordered is often referred to either as the liquid crystal state or the nematic phase of the liquid crystalline material. These polymers are prepared from monomers which are generally long, flat and fairly rigid along the long axis of the molecule and commonly have chain-extending linkages that are either coaxial or parallel.

Such polymers readily form liquid crystals (i.e., exhibit anisotropic properties) in the melt phase. Such properties may be confirmed by conventional polarized light techniques whereby crossed polarizers are utilized. More specifically, the anisotropic melt phase may be confirmed by the use of a Leitz polarizing microscope at a magnification of 40X with the sample on a Leitz hot stage and under nitrogen atmosphere. The polymer



Preferably, the thermotropic liquid crystal polymers which are employed comprise not less than about 10 mole percent of recurring units which include a naphthalene moiety. Preferred naphthalene moieties include 6-oxy-2-naphthoyl, 2,6-dioxynaphthalene, and 2,6-dicarboxynaphthalene.

Specific examples of suitable aromatic-aliphatic polyesters are copolymers of polyethylene terephthalate and hydroxybenzoic acid as disclosed in Polyester X7G-A Self Reinforced Thermoplastic, by W.J. Jackson, Jr., H.F. Kuhfuss, and T.F. Gray, Jr., 30th Anniversary Technical Conference, 1975 Reinforced Plastics/Composites Institute, The Society of the Plastics Industry, Inc., Section 17-D, Pages 1-4. A further disclosure of such copolymers can be found in "Liquid Crystal Polymers: I. Preparation and Properties of p-Hydroxybenzoic Acid Copolymers," Journal of Polymer Science, Polymer Chemistry Edition, Vol. 14, pp. 2043-58 (1976), by W.J. Jackson, Jr. and H.F. Kuhfuss. The above-cited references are herein incorporated by reference in their entirety.

Aromatic polyazomethines and processes of preparing the same are disclosed in the U.S. Patent Nos. 3,493,522; 3,493,524; 3,503,739; 3,516,970; 3,516,971; 3,526,611; 4,048,148; and 4,122,070. Each of these patents is herein incorporated by reference in its entirety. Specific examples of such polymers include poly(nitrilo-2-methyl-1,4-phenyl-enenitriloethylidyne-1,4-phenyleneethylidyne); poly(nitrolo-2-methyl-1,4-phenylene-nitrilomethylidyne-1,4-phenylene-methylidyne); and poly(nitrilo-2-chloro-1,4-phenylenenitrilomethylidyne-1,4-phenylene-

methyldiynes).

Aromatic polyester-carbonates are disclosed in U.S. Patent No. 4,107,143, which is herein incorporated by reference in its entirety. Examples of such polymers include those consisting essentially of hydroxybenzoic acid units, hydroquinone units, carbonate units, and aromatic carboxylic acid units.

The liquid crystal polymers which are preferred for use in the present invention include thermotropic wholly aromatic polyesters. Recent publications disclosing such polyesters include (a) Belgian Pat. Nos. 828,935 and 828,936, (b) Dutch Pat. No. 7505551, (c) West German Pat. Nos. 2,520,819, 2,520,820, and 2,722,120, (d) Japanese Pat. Nos. 43-223, 2132-116, 3017-692, and 3021-293, (e) U.S. Pat. Nos. 3,991,013; 3,991,014; 4,057,597; 4,066,620; 4,075,262; 4,118,372; 4,146,702; 4,153,779; 4,156,070; 4,159,365; 4,169,933; 4,181,792; 4,188,476; 4,201,856; 4,226,970; 4,232,143; 4,232,144; 4,238,600; 4,245,082; 4,267,304; 4,424,496; and 4,269,965; and (f) U.K. Application No. 2,002,404.

Wholly aromatic polymers which are preferred for use in the present invention include wholly aromatic polyesters and poly(ester-amide)s which are disclosed in commonly-assigned U.S. Patent Nos. 4,067,852; 4,083,829; 4,130,545; 4,161,470; 4,184,996; 4,219,461; 4,238,599; 4,256,624 and 4,279,803; and in commonly-assigned U.S. Application Serial Nos. 91,003, filed November 5, 1979; 128,759, filed March 10, 1980; and 214,557, filed December 9, 1980. The disclosures of all of the above-identified commonly-assigned U.S. patents and applications are herein incorporated by reference in their entirety. The wholly aromatic polymers disclosed therein typically are capable of forming an anisotropic melt phase at a temperature below approxi-

mately 400°C., and preferably below approximately 350°C.

The wholly aromatic polymers including wholly aromatic polyesters and poly(ester-amide)s which are suitable for use in the present invention may be formed by a variety of ester-forming techniques whereby organic monomer compounds possessing functional groups which, upon condensation, form the requisite recurring moieties are reacted. For instance, the functional groups of the organic monomer compounds may be carboxylic acid groups, hydroxyl groups, ester groups, acyloxy groups, acid halides, amine groups, etc. The organic monomer compounds may be reacted in the absence of a heat exchange fluid via a melt acidolysis procedure. They, accordingly, may be heated initially to form a melt solution of the reactants with the reaction continuing as the polymer particles are suspended therein. A vacuum may be applied to facilitate removal of volatiles formed during the final stage of the condensation (e.g., acetic acid or water).

Commonly-assigned U.S. Patent No. 4,083,829, entitled "Melt Processable Thermotropic Wholly Aromatic Polyester," describes a slurry polymerization process which may be employed to form the wholly aromatic polyesters which are preferred for use in the present invention. According to such a process, the solid product is suspended in a heat exchange medium. The disclosure of this patent has previously been incorporated herein by reference in its entirety.

When employing either the melt acidolysis procedure or the slurry procedure of U.S. Patent No. 4,083,829, the organic monomer reactants from which the wholly aromatic polyesters are derived may be initially provided in a modified form whereby the usual hydroxy groups of such monomers are esterified (i.e., they

are provided as lower acyl esters). The lower acyl groups preferably have from about two to about four carbon atoms. Preferably, the acetate esters of organic monomer reactants are provided.

Representative catalysts which optionally may be employed in either the melt acidolysis procedure or in the slurry procedure of U.S. Patent No. 4,083,829 include dialkyl tin oxide (e.g., dibutyl tin oxide), diaryl tin oxide, titanium dioxide, antimony trioxide, alkoxy titanium silicates, titanium alkoxides, alkali and alkaline earth metal salts of carboxylic acids (e.g., zinc acetate), the gaseous acid catalysts such as Lewis acids (e.g., BF_3), hydrogen halides (e.g., HCl), etc. The quantity of catalyst utilized typically is about 0.001 to 1 percent by weight based upon the total monomer weight, and most commonly about 0.01 to 0.2 percent by weight.

The wholly aromatic polymers suitable for use in the present invention tend to be substantially insoluble in common solvents and accordingly are not susceptible to solution processing. As discussed previously, they can be readily processed by common melt processing techniques. Most suitable wholly aromatic polymers are soluble in pentafluorophenol to a limited degree.

The wholly aromatic polyesters which are preferred for use in the present invention commonly exhibit a weight average molecular weight of about 2,000 to 200,000, and preferably about 10,000 to 50,000, and most preferably about 20,000 to 25,000. The wholly aromatic poly(ester-amide)s which are preferred commonly exhibit a molecular weight of about 5000 to 50,000 and preferably about 10,000 to 30,000; e.g., 15,000 to 17,000. Such molecular weight may be determined by gel permeation chromato-

graphy as well as by standard techniques not involving the solutioning of the polymer, e.g., by end group determination via infrared spectroscopy on compression molded films. Alternatively, light scattering techniques in a pentafluorophenol solution may be employed to determine the molecular weight.

The wholly aromatic polyesters and poly(ester-amide)s additionally commonly exhibit an inherent viscosity (i.e., I.V.) of at least approximately 2.0 dl./g., e.g., approximately 2.0 to 10.0 dl./g., when dissolved in a concentration of 0.1 percent by weight in pentafluorophenol at 60°C.

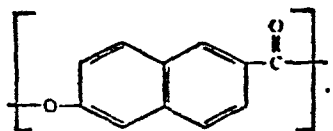
Especially preferred wholly aromatic polymers are those which are disclosed in above-noted U.S. Patent Nos. 4,161,470, 4,184,996, 4,219,461, 4,238,599 and 4,256,624 and Application Serial No. 214,557.

For the purposes of the present invention, the aromatic rings which are included in the polymer backbones of the polymer components employed in the present invention may include substitution of at least some of the hydrogen atoms present upon an aromatic ring. Such substituents include alkyl groups of up to four carbon atoms; alkoxy groups having up to four carbon atoms; halogens; and additional aromatic rings, such as phenyl or substituted phenyl. Preferred halogens include fluorine, chlorine, and bromine. Although bromine atoms tend to be released from organic compounds at high temperatures, bromine is more stable on aromatic rings than on aliphatic chains, and therefore is suitable for inclusion as a possible substituent on the aromatic rings.

The wholly aromatic polyester which is disclosed in U.S. Patent No. 4,161,470 is a melt processable wholly aromatic

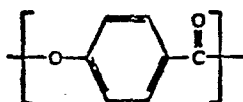
polyester capable of forming an anisotropic melt phase at a temperature below approximately 350°C. The polyester consists essentially of the recurring moieties I and II wherein:

I is



, and

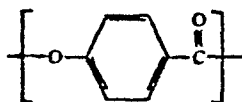
II is



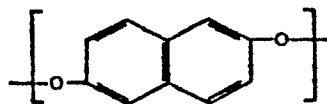
The polyester comprises approximately 10 to 90 mole percent of moiety I, and approximately 10 to 90 mole percent of moiety II. In one embodiment, moiety II is present in a concentration of approximately 65 to 85 mole percent, and preferably in a concentration of approximately 70 to 80 mole percent, e.g., approximately 75 mole percent. In another embodiment, moiety II is present in a lesser proportion of approximately 15 to 35 mole percent, and preferably in a concentration of approximately 20 to 30 mole percent. In addition, at least some of the hydrogen atoms present upon the rings optionally may be replaced by substitution selected from the group consisting of an alkyl group of 1 to 4 carbon atoms, an alkoxy group of 1 to 4 carbon atoms, halogen, phenyl, substituted phenyl, and mixtures thereof.

The wholly aromatic polyester which is disclosed in U.S. Patent No. 4,184,996 is a melt processable wholly aromatic polyester capable of forming an anisotropic melt phase at a temperature below approximately 325°C. The polyester consists essentially of the recurring moieties I, II, and III wherein:

I is

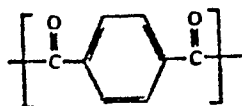


II is



, and

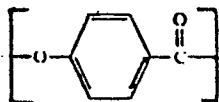
III is



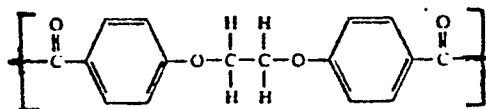
The polyester comprises approximately 30 to 70 mole percent of moiety I. The polyester preferably comprises approximately 40 to 60 mole percent of moiety I, approximately 20 to 30 mole percent of moiety II, and approximately 20 to 30 mole percent of moiety III. In addition, at least some of the hydrogen atoms present upon the rings optionally may be replaced by substitution selected from the group consisting of an alkyl group of 1 to 4 carbon atoms, an alkoxy group of 1 to 4 carbon atoms, halogen, phenyl, substituted phenyl, and mixtures thereof.

The wholly aromatic polyester which is disclosed in U.S. Patent No. 4,238,599 is a melt processable polyester capable of forming an anisotropic melt phrase at a temperature no higher than approximately 320°C. consisting essentially of the recurring moieties I, II, III and IV wherein:

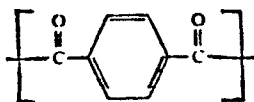
I is



II is

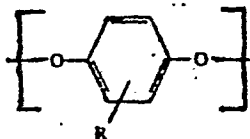


III is



, and

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IV is

, where

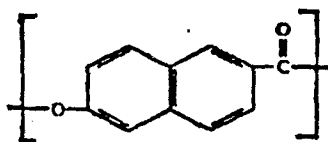
R is methyl, chloro, bromo, or mixtures thereof, and is substituted for a hydrogen atom present upon the aromatic ring,

and wherein said polyester comprises approximately 20 to 60 mole percent of moiety I, approximately 5 to 18 mole percent of moiety II, approximately 5 to 35 mole percent of moiety III, and approximately 20 to 40 mole percent of moiety IV. The polyester preferably comprises approximately 35 to 45 mole percent of moiety I, approximately 10 to 15 mole percent of moiety II, approximately 15 to 25 mole percent of moiety III, and approximately 25 to 35 mole percent of moiety IV, with the proviso that the total molar concentration of moieties II and III is substantially identical to that of moiety IV. In addition, at least some of the hydrogen atoms present upon the rings optionally may be replaced by substitution selected from the group consisting of an alkyl group of 1 to 4 carbon atoms, an alkoxy group of 1 to 4 carbon atoms, halogen, phenyl, substituted phenyl, and mixtures thereof. This wholly aromatic polyester commonly exhibits an inherent viscosity of at least 2.0 dl./g., e.g., 2.0 to 10.0 dl./g., when dissolved in a concentration of 0.1 weight/volume percent in pentafluorophenol at 60°C.

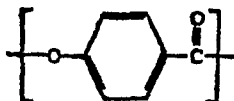
The polyester disclosed in U.S. Patent No. 4,219,461 is a melt processable wholly aromatic polyester which is capable of forming an anisotropic melt phase at a temperature below approximately 320°C. The polyester consists essentially of the recurring moieties I, II, III, and IV wherein:

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I is



II is



III is a dioxy aryl moiety of the formula $\{O-Ar-O\}$

wherein Ar is a divalent radical comprising at least one aromatic ring, and

IV is a dicarboxy aryl moiety of the formula $\{C(=O)-Ar'-C(=O)\}$

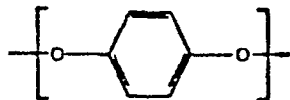
where Ar' is a divalent radical comprising at least one aromatic ring, and

wherein the polyester comprises approximately 20 to 40 mole percent of moiety I, in excess of 10 up to about 50 mole percent of moiety II, in excess of 5 up to about 30 mole percent of moiety III, and in excess of 5 up to about 30 mole percent of moiety IV. The polyester preferably comprises approximately 20 to 30 (e.g., approximately 25) mole percent of moiety I, approximately 25 to 40 (e.g., approximately 35) mole percent of moiety II, approximately 15 to 25 (e.g. approximately 20) mole percent of moiety III, and approximately 15 to 25 (e.g., approximately 20) mole percent of moiety IV. In addition, at least some of the hydrogen atoms present upon the rings optionally may be replaced by substitution selected from the group consisting of an alkyl group of 1 to 4 carbon atoms, an alkoxy group of 1 to 4 carbon atoms, halogen, phenyl, substituted phenyl, and mixtures thereof.

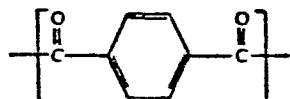
Moieties III and IV are preferably symmetrical in the sense that the divalent bonds which join these moieties to other

moieties in the main polymer chain are symmetrically disposed on one or more aromatic rings (e.g., are para to each other or diagonally disposed when present on a naphthalene ring). However, non-symmetrical moieties, such as those derived from resorcinol and isophthalic acid, may also be used.

Preferred moieties III and IV are set forth in above-noted U.S. Patent No. 4,219,461. The preferred dioxy aryl moiety III is:

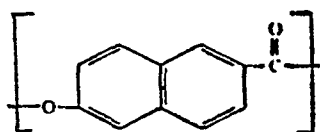


and the preferred dicarboxy aryl moiety IV is:



The polyester disclosed in U.S. Patent No. 4,256,624 is a melt processable wholly aromatic polyester which is capable of forming an anisotropic melt phase at a temperature below approximately 400°C. The polyester consists essentially of the recurring moieties I, II, and III wherein:

I is



II is a dioxy aryl moiety of the formula {O-Ar-O} where

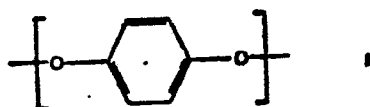
Ar is a divalent radical comprising at least one aromatic ring, and

III is a dicarboxy aryl moiety of the formula $\text{f}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{Ar}'-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{f}$ where Ar' is a divalent radical comprising at least one aromatic ring, and

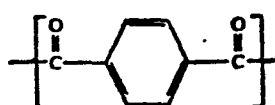
wherein the polyester comprises approximately 10 to 90 mole percent of moiety I, approximately 5 to 45 mole percent of moiety II, and approximately 5 to 45 mole percent of moiety III. The polyester preferably comprises approximately 20 to 80 mole percent of moiety I, approximately 10 to 40 mole percent of moiety II, and approximately 10 to 40 mole percent of moiety III. The polyester more preferably comprises approximately 60 to 80 mole percent of moiety I, approximately 10 to 20 mole percent of moiety II, and approximately 10 to 20 mole percent of moiety III. In addition, at least some of the hydrogen atoms present upon the rings optionally may be replaced by substitution selected from the group consisting of an alkyl group of 1 to 4 carbon atoms, an alkoxy group of 1 to 4 carbon atoms, halogen, phenyl, substituted phenyl, and mixtures thereof.

As with moieties III and IV of the polyester disclosed in U.S. Patent No. 4,219,461, moieties II and III of the polyester described immediately above may be symmetrical or nonsymmetrical, but are preferably symmetrical.

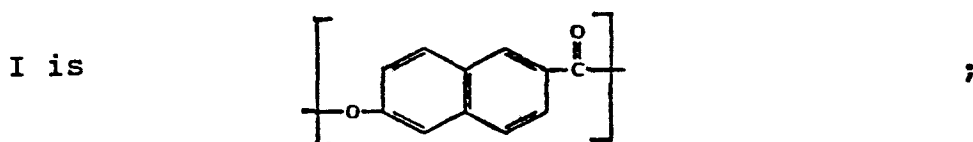
Preferred moieties II and III are set forth in above-noted U.S. Patent No. 4,256,624. The preferred dioxy aryl moiety II is:



and the preferred dicarboxy aryl moiety III is:



U.S. Application Serial No. 214,557, filed December 9, 1980, discloses a melt processable poly(ester-amide) which is capable of forming an anisotropic melt phase at a temperature below approximately 400°C. The poly(ester-amide) consists essentially of the recurring moieties I, II, III and optionally IV wherein:



II is $\left\{ \overset{\text{O}}{\parallel} \text{C} - \text{A} - \overset{\text{O}}{\parallel} \text{C} \right\}$, where A is a divalent radical comprising at least one aromatic ring or a divalent trans-cyclohexane radical;

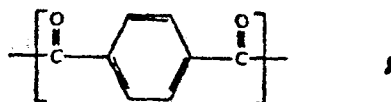
III is $\{ \text{Y} - \text{Ar} - \text{Z} \}$, where Ar is a divalent radical comprising at least one aromatic ring, Y is O, NH, or NR, and Z is NH or NR, where R is an alkyl group of 1 to

6 carbon atoms or an aryl group; and

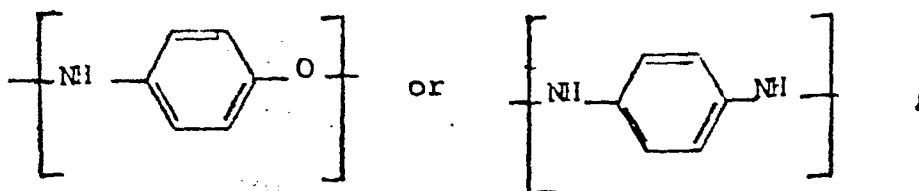
IV is $\{O-Ar'-O\}$, where Ar' is a divalent radical comprising at least one aromatic ring;

and wherein said poly(ester-amide) comprises approximately 10 to 90 mole percent of moiety I, approximately 5 to 45 mole percent of moiety II, approximately 5 to 45 mole percent of moiety III, and approximately 0 to 40 mole percent of moiety IV. In addition, at least some of the hydrogen atoms present upon the rings optionally may be replaced by substitution selected from the group consisting of an alkyl group of 1 to 4 carbon atoms, an alkoxy group of 1 to 4 carbon atoms, halogen, phenyl, substituted phenyl, and mixtures thereof.

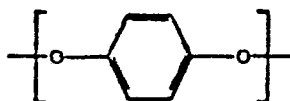
Preferred moieties II, III and IV are set forth in above-noted U.S. Application Serial No. 214,557. The preferred dicarboxy aryl moiety II is:



the preferred moiety III is:



and the preferred dioxy aryl moiety IV is:



The non-woven articles of the present invention are comprised of fibers of thermotropic liquid crystal polymers and may be produced in a variety of ways. For example, a thermotropic liquid crystal polymer may be spray spun onto a web or screen to provide a random array of polymeric fibers. In the alternative, melt spun fibers of a thermotropic liquid crystal polymer cut to appropriately short lengths can be slurried with a liquid which is a non-solvent for the polymer (e.g., water) and subsequently filtered (or wet-laid) onto a web or screen to provide a random (i.e., multi-dimensional) array of fibers.

The thus-produced random array may then be subjected to a suitable thermal bonding or heat pressing step at a suitable temperature to bond the fibers together and impart the desired structural integrity thereto. That is, the article at a minimum will support its own weight and preferably can be pulled apart only with difficulty. In such a process the fibers are heated and pressed together for a period of time and at a pressure sufficient to at least bond the fibers together at the cross-over points. Such fusion bonding does not result in any significant loss of orientation (and accordingly, loss of strength) since the polymer of which the fibers is comprised forms an anisotropic melt phase. Such a characteristic is in direct contrast to conventional thermoplastic polymers which do not form an anisotropic melt phase and which readily lose their orientation upon being

heated to temperatures in excess of their melting temperature.

This is also in contrast to lyotropic liquid crystal polymers which cannot be fusion bonded.

It should be noted that if the spray spun fibers are not allowed to cool sufficiently prior to being deposited on the web, the fibers will become bonded together as they collect upon the web or screen and a formal heat pressing step will not be required. Polymers which are capable of forming an anisotropic melt phase are particularly suited for use in such a method since the polymer retains its orientation upon being spun and collected in the form of a web or sheet. The spray-spun fibers can thus be thermally bonded together to form a non-woven article having the desired degree of structural integrity without exhibiting a significant loss of orientation (and strength) as a result of being bonded together in the melt phase.

The above-described spray spinning and slurry filtering production processes are conventional processes for the production of non-woven articles and are well within the knowledge of one skilled in the art.

The fibers may also be bonded together by means of adhesives such as thermoplastic or thermosetting resins, epoxies, water soluble adhesives such as casein, guar gum, or polyacrylic acid, solvent-based adhesives, and emulsion or latex based adhesives such as styrene/butyl/acrylic copolymer systems. The adhesives may be coated onto the web or array of thermotropic liquid crystal fibers by use of kiss rolls. In the alternative, the adhesives may be sprayed upon or deposited upon the web by known emulsion techniques (for use with wet laid paper). The use of adhesives in such methods is known and will not be discussed

in greater detail herein.

The non-woven articles of the present invention possess many advantageous characteristics due to the presence of thermotropic liquid crystal polymers therein. That is, since liquid crystal polymers are fully drawn and highly oriented as spun, the fibers which comprise the non-woven articles of the present invention possess relatively high tensile strength and modulus. Accordingly, non-woven articles comprised of such fibers similarly exhibit relatively high tenacity and modulus.

In addition, the article exhibits such tensile strength and modulus in a multi-dimensional manner due to the multi-dimensional orientation of the fibers within the structure.

The non-woven articles also benefit from other physical characteristics of thermotropic liquid crystal polymers such as resistance to chemical corrosion or solvation and high temperature stability due to the high melting temperatures of the fibers. For instance, the melting temperature of the polymer is preferably in excess of 200°C. and most preferably in excess of 400°C. Such articles thus are well suited for use as filters in high temperature and/or otherwise destructive environments which would tend to degrade conventional filters such as treatment of stack gases from electrical generating plants. The articles can also be used to filter a variety of liquids without dissolving or being subject to corrosion or other degradative chemical processes.

A particularly interesting use for such non-woven articles is as the matrix material in ballistics protection wearing apparel. Due to the high tenacity and modulus exhibited by the liquid crystal polymers which comprise the non-woven

articles, such articles are readily adaptable to such a use. In order to take full advantage of the properties of the fibers of thermotropic liquid crystal polymers, it is preferred that the non-woven article comprise at least a major portion (e.g., at least about 50 percent by weight) of the fibers and preferably consists essentially of such fibers. In a most preferred embodiment the article consists entirely of fibers of liquid crystal polymers.

The mechanical properties of the non-woven articles produced in accordance with the present invention can be improved by subjecting the articles to a heat treatment following formation thereof. The heat treatment improves the properties of the article by increasing the molecular weight of the liquid crystalline polymer which comprises the fibers present within the article and increasing the degree of crystallinity thereof while also increasing the melting temperature of the polymer. Such heat treatment can also serve to bond the fibers together.

The articles may be thermally treated in an inert atmosphere (e.g., nitrogen, carbon dioxide, argon, helium) or alternatively, in a flowing oxygen-containing atmosphere (e.g., air). The use of a non-oxidizing substantially moisture-free atmosphere is preferred to avoid the possibility of thermal degradation. For instance, the article may be brought to a temperature approximately 10 to 30 centigrade degrees below the melting temperature of the liquid crystal polymer, at which temperature the fibers remain a solid object. It is preferable for the temperature of the heat treatment to be as high as possible without equaling or exceeding the melting temperature of the polymer. It is most preferable to gradually increase the tem-

perature of heat treatment in accordance with the increase of the melting temperature of the polymer during heat treatment.

The duration of the heat treatment will commonly range from a few minutes to a number of days, e.g., from 0.5 to 200 hours, or more. Preferably, the heat treatment is conducted for a time of 1 to 48 hours and typically from about 5 to 30 hours.

Generally, the duration of heat treatment varies depending upon the heat treatment temperature; that is, a shorter treatment time is required as a higher treatment temperature is used. Thus, the duration of the heat treatment can be shortened for higher melting polymers, since higher heat treatment temperatures can be applied without melting the polymer.

Preferably, the heat treatment is conducted under conditions sufficient to increase the melting temperature of the polymer at least 10 centigrade degrees. Most preferably, the melting temperature of the liquid crystal polymer is increased from between about 20 to about 50 centigrade degrees as a result of the heat treatment. The amount of increase which is obtained is dependent upon the temperature used in the heat treatment, with higher heat treatment temperatures giving greater increases.

Similar advantages can also be obtained by heat treatment of the fibers prior to their incorporation into the non-woven structure. It is, however, preferable to heat treat the structure subsequent to its formation since the thermal bonding and heat treatment steps can then be combined.

It should be noted at this time that reference herein to a temperature below which a specific polymer may exhibit anisotropic properties in the melt phase is intended to refer to the temperature below which the polymer exhibits such properties

prior to any heat treatment thereof.

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The chemical resistance of the polymer also increases with heat treatment and the solubility into pentafluorophenol, one of the rare solvents for thermotropic liquid crystal polymers, continuously decreases with increasing heat treatment time and eventually the material will not dissolve even minimally (such as in amounts of 0.1 percent by weight). Accordingly, reference herein to solution characteristics of specific polymers is intended to refer to such characteristics prior to any heat treatment of the polymer.

The invention is additionally illustrated in connection with the following Examples which are to be considered as illustrative of the present invention. It should be understood, however, that the invention is not limited to the specific details of the Examples.

EXAMPLE 1

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As-spun fibers comprised of a thermotropic liquid crystal polymer consisting of 40 mole percent of a p-oxybenzoyl moiety and 60 mole percent of a 6-oxy-2-naphthoyl moiety are provided having a denier per filament ranging from about 7 to 10. The fibers are chopped into microfibers ranging in length from about 1/4 to 3/8 inch in length and admixed with water to form a slurry. The slurry is well stirred to achieve a uniform dispersal of the chopped fibers in the slurry.

The slurry admixture is poured into a tall Buchner filter funnel containing a disk of filter paper. The water is drained off with the aid of a vacuum leaving a random mat of chopped fibers upon the filter paper. The web is carefully removed from contact with the filter paper and dried. The dried web of fibers demonstrates weak structural integrity (i.e., it barely supports its own weight and is easily pulled apart).

The fibers are bound together by pressing the web between two heated plates whereupon the web is heated to approximately 275°C. The web is sandwiched between Kapton release films to prevent the web from sticking to the plates. The web subsequent to hot pressing exhibits substantial structural integrity and is pulled apart only with difficulty while also exhibiting textile-like draping characteristics.

EXAMPLE 2

Pellets comprised of a thermotropic liquid crystal polymer consisting of 40 mole percent of a p-oxybenzoyl moiety

and 60 mole percent of a 6-oxy-2-naphthoyl moiety are dried for 24 hours in a warm vacuum oven. The pellets are then introduced into the hopper of a spray spinning unit with the temperature of the polymer subsequently being raised to 360°C within the extruder section of the unit to provide a polymer melt. The melt is then spun from a 0.16 mill jet into an air attenuation section of the spray spinning unit where the melt is exposed to the air drag of three impinging unheated air jets and reduced to a fiber of about 50 denier per filament. The spun fiber is collected as a non-bonded mat upon a wire screen located approximately 30 inches from the jet.

Air heated to between about 200-500°C. is also employed to attenuate the melt which results in the production of a mat of fibers which are bonded together at their cross-over points. This bonded mat is formed by collecting the fibers on a screen located approximately 12 to 16 inches from the jet.

The principles, preferred embodiments and modes of operation of the present invention have been described in the foregoing specification. The invention which is intended to be protected herein, however, is not to be construed as limited to the particular forms disclosed, since these are to be regarded as illustrative rather than restrictive. Variations and changes may be made by those skilled in the art without departing from the spirit of the invention.

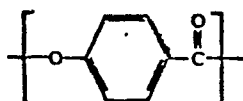
CLAIMS

1. A non-woven article which exhibits desirable thermal stability and chemical and solvent resistance comprised of fibers of a polymer which is capable of forming an anisotropic melt phase, said fibers being bonded together to an extent sufficient to impart structural integrity to said article.
5
2. The article of claim 1 wherein said polymer is a wholly aromatic polymer.
3. The article of claim 1 wherein said polymer is a wholly aromatic polyester.
4. The article of claim 1 wherein said polymer exhibits an inherent viscosity of at least 2.0 dl./g. when dissolved in a concentration of 0.1 percent by weight in pentafluorophenol at 60°C.
5. The article of claim 1 wherein said polymer comprises not less than about 10 mole percent of recurring units which include a naphthalene moiety.
6. The article of claim 5 wherein said naphthalene moiety of said wholly aromatic polymer is selected from the group consisting of a 6-oxy-2-naphthoyl moiety, a 2,6-dioxynaphthalene moiety, and a 2,6-dicarboxynaphthalene moiety.
7. The article of claim 1 wherein said polymer is capable of forming an anisotropic melt phase at a temperature below approximately 400°C.

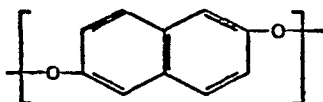
8. The article of claim 1 wherein said polymer comprises a melt processable wholly aromatic polyester which is capable of forming an anisotropic melt phase and consists essentially of the recurring moieties I, II, and III wherein:

5

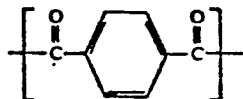
I is



II is



III is



, and

, and

10

wherein said polyester comprises approximately 30 to 70 mole percent of moiety I and wherein at least some of the hydrogen atoms present upon the rings optionally may be replaced by substitution selected from the group consisting of an alkyl group of 1 to 4 carbon atoms, an alkoxy group of 1 to 4 carbon atoms, halogen, phenyl, substituted phenyl, and mixtures thereof.

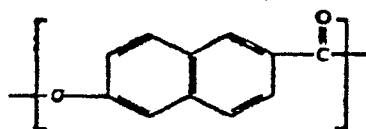
15

9. The article of claim 8 wherein said polyester comprises approximately 40 to 60 mole percent of moiety I, approximately 20 to 30 mole percent of moiety II, and approximately 20 to 30 mole percent of moiety III.

10. The article of claim 1 wherein said polymer comprises a melt processable wholly aromatic polyester which is capable of forming an anisotropic melt phase and consists essentially of the recurring moieties I and II wherein:

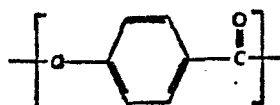
5

I is



, and

II is



10

wherein said polyester comprises approximately 10 to 90 mole percent of moiety I, and approximately 10 to 90 mole percent of moiety II and wherein at least some of the hydrogen atoms present upon the rings optionally may be replaced by substitution selected from the group consisting of an alkyl group of 1 to 4 carbon atoms, an alkoxy group of 1 to 4 carbon atoms, halogen, phenyl, substituted phenyl, and mixtures thereof.

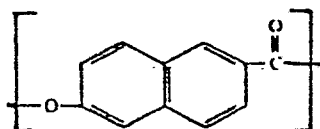
11. The article of claim 10 wherein said polyester comprises approximately 65 to 85 mole percent of moiety II.

12. The article of claim 10 wherein said polyester comprises approximately 15 to 35 mole percent of moiety II.

13. The article of claim 1 wherein said polymer comprises a melt processable wholly aromatic polyester which is capable of forming an anisotropic melt phase and consists essentially of the recurring moieties I, II, and III wherein:

5

I is



II is a dioxy aryl moiety of the formula $\{\text{O}-\text{Ar}-\text{O}\}$ where Ar is a divalent radical comprising at least one aromatic ring, and

III is a dicarboxy aryl moiety of the formula $\{ \overset{\text{O}}{\parallel} \text{C} - \text{Ar}' - \overset{\text{O}}{\parallel} \text{C} \}$

10 where Ar' is a divalent radical comprising at least one aromatic ring, and

wherein said polyester comprises approximately 10 to 90 mole percent of moiety I, approximately 5 to 45 mole percent of moiety II, and approximately 5 to 45 mole percent of moiety III and

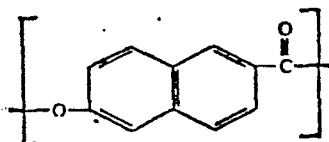
15 wherein at least some of the hydrogen atoms present upon the rings optionally may be replaced by substitution selected from the group consisting of an alkyl group of 1 to 4 carbon atoms, an alkoxy group of 1 to 4 carbon atoms, halogen, phenyl, substituted phenyl, and mixtures thereof.

14. The article of claim 13 wherein said polyester comprises approximately 20 to 80 mole percent of moiety I, approximately 10 to 40 mole percent of moiety II, and approximately 10 to 40 mole percent of moiety III.

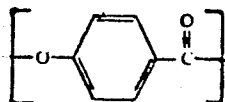
15. The article of claim 1 wherein said polymer comprises a melt processable wholly aromatic polyester which is capable of forming an anisotropic melt phase and consists essentially of the recurring moieties I, II, III and IV wherein:

5

I is



II is



III is a dioxy aryl moiety of the formula $\{ \text{O} - \text{Ar} - \text{O} \}$ wherein Ar is a divalent radical comprising at least one aromatic ring, and

10 IV is a dicarboxy aryl moiety of the formula $\text{+}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{-Ar}'\text{-}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{+}$
 where Ar' is a divalent radical comprising at least one
 aromatic ring, and

wherein the polyester comprises approximately 20 to 40 mole
 percent of moiety I, in excess of 10 up to about 50 mole percent
 15 of moiety II, in excess of 5 up to about 30 mole percent of
 moiety III, and in excess of 5 up to about 30 mole percent of
 moiety IV and wherein at least some of the hydrogen atoms present
 upon the rings optionally may be replaced by substitution
 selected from the group consisting of an alkyl group of 1 to 4
 20 carbon atoms, an alkoxy group of 1 to 4 carbon atoms, halogen,
 phenyl, substituted phenyl, and mixtures thereof.

16. The article of claim 15 wherein said polyester
 comprises approximately 20 to 30 mole percent of moiety I,
 approximately 25 to 40 mole percent of moiety II, approximately
 15 to 25 mole percent of moiety III and approximately 15 to 25
 5 mole percent of moiety IV.

17. The article of claim 1 wherein said polymer
 comprises a melt processable poly(ester-amide) which is capable
 of forming an anisotropic melt phase and consists essentially of
 the recurring moieties I, II, III and optionally IV wherein:



II is $\text{+}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{-A-}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{+}$, where A is a divalent radical comprising
 at least one aromatic ring or a divalent trans-

cyclohexane radical;

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10 III is {Y-Ar-Z}, where Ar is a divalent radical
 comprising at least one aromatic ring, Y is O, NH,
 or NR, and Z is NH or NR, where R is an alkyl group
 of 1 to 6 carbon atoms or an aryl group; and

 IV is {O-Ar'-O}, where Ar' is a divalent radical
 comprising at least one aromatic ring;
15 and wherein said poly(ester-amide) comprises approximately 10 to
 90 mole percent of moiety I, approximately 5 to 45 mole percent
 of moiety II, approximately 5 to 45 mole percent of moiety III,
 and approximately 0 to 40 mole percent of moiety IV and wherein
 at least some of the hydrogen atoms present upon the rings
20 optionally may be replaced by substitution selected from the
 group consisting of an alkyl group of 1 to 4 carbon atoms, an
 alkoxy group of 1 to 4 carbon atoms, halogen, phenyl, substituted
 phenyl, and mixtures thereof.

18. The article of claim 1 wherein said polymer has
been subjected to a heat treatment for a period of time and at a
temperature sufficient to increase the melting temperature of the
polymer between about 20 to 50 centigrade degrees.

19. The article of claim 18 wherein said polymer has
been subjected to a heat treatment after formation of said
article.

20. The article of claim 18 wherein said heat treat-

ment temperature ranges from about 10 to about 30 centigrade degrees below the melting temperature of the polymer.

21. The article of claim 20 wherein said period of time ranges from about 0.5 to about 200 hours.

22. The article of claim 21 wherein said period of time ranges from about 1 to about 48 hours.

23. The article of claim 22 wherein said period of time ranges from about 5 to about 30 hours.

24. The article of claim 18 wherein said heat treatment occurs in a non-oxidizing atmosphere.

25. The article of claim 24 wherein said atmosphere is substantially moisture-free.

26. The article of claim 24 wherein said heat treatment occurs in a nitrogen atmosphere.

27. The article of claim 1 which is in the form of a sheet.

28. The article of claim 1 which consists essentially of fibers of a polymer which is capable of forming an anisotropic melt phase.

29. The article of claim 1 wherein said polymer has a

melting temperature in excess of about 200°C.

30. The article of claim 29 wherein said polymer has a melting temperature in excess of about 400°C.

31. The article of claim 1 wherein said fibers are thermally bonded together.

32. The article of claim 1 wherein said fibers are bonded together by means of an adhesive.

33. A method for forming a non-woven article in the form of a web or sheet which exhibits desirable thermal stability and chemical and solvent resistance comprised of fibers of a polymer which is capable of forming an anisotropic melt phase,
5 said method comprising spray spinning said polymer in the melt phase to form a multitude of discontinuous fibers and collecting said fibers in the form of a web or sheet.

34. The method of claim 33 wherein said fibers are collected on a screen.

35. The method of claim 33 wherein said fibers become thermally bonded together as they are collected.

36. The method of claim 33 wherein said fibers are adhesively bonded together subsequent to being collected.

37. The method of claim 33 wherein said polymer is a

wholly aromatic polymer.

38. The method of claim 33 wherein said polymer is a wholly aromatic polyester.

39. The method of claim 33 wherein said polymer exhibits an inherent viscosity of at least 2.0 dl./g. when dissolved in a concentration of 0.1 percent by weight in pentafluorophenol at 60°C.

40. The method of claim 33 wherein said polymer comprises not less than about 10 mole percent of recurring units which include a naphthalene moiety.

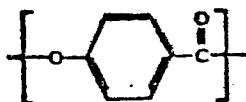
41. The method of claim 40 wherein said naphthalene moiety of said wholly aromatic polymer is selected from the group consisting of a 6-oxy-2-naphthoyl moiety, a 2,6-dioxynaphthalene moiety, and a 2,6-dicarboxynaphthalene moiety.

42. The method of claim 33 wherein said polymer is capable of forming an anisotropic melt phase at a temperature below approximately 400°C.

43. The method of claim 33 wherein said polymer comprises a melt processable wholly aromatic polyester which is capable of forming an anisotropic melt phase and consists essentially of the recurring moieties I, II, and III wherein:

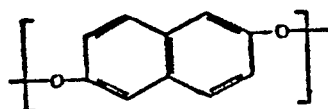
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I is



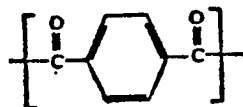
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II is



, and

III is



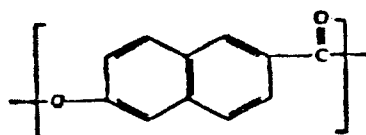
, and

wherein said polyester comprises approximately 30 to 70 mole percent of moiety I and wherein at least some of the hydrogen atoms present upon the rings optionally may be replaced by substitution selected from the group consisting of an alkyl group of 1 to 4 carbon atoms, an alkoxy group of 1 to 4 carbon atoms, halogen, phenyl, substituted phenyl, and mixtures thereof.

44. The method of claim 43 wherein said polyester comprises approximately 40 to 60 mole percent of moiety I, approximately 20 to 30 mole percent of moiety II, and approximately 20 to 30 mole percent of moiety III.

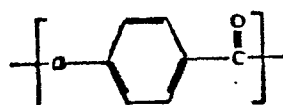
45. The method of claim 33 wherein said polymer comprises a melt processable wholly aromatic polyester which is capable of forming an anisotropic melt phase and consists essentially of the recurring moieties I and II wherein:

I is



, and

II is



,

wherein said polyester comprises approximately 10 to 90 mole

percent of moiety I, and approximately 10 to 90 mole percent of moiety II and wherein at least some of the hydrogen atoms present upon the rings optionally may be replaced by substitution selected from the group consisting of an alkyl group of 1 to 4 carbon atoms, an alkoxy group of 1 to 4 carbon atoms, halogen, phenyl, substituted phenyl, and mixtures thereof.

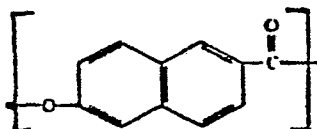
46. The method of claim 45 wherein said polyester comprises approximately 65 to 85 mole percent of moiety II.

47. The method of claim 45 wherein said polyester comprises approximately 15 to 35 mole percent of moiety II.

48. The method of claim 33 wherein said polymer comprises a melt processable wholly aromatic polyester which is capable of forming an anisotropic melt phase and consists essentially of the recurring moieties I, II, and III wherein:

5

I is



II is a dioxy aryl moiety of the formula $\{O-Ar-O\}$ where Ar is a divalent radical comprising at least one aromatic ring, and

10

III is a dicarboxy aryl moiety of the formula $\{C(=O)-Ar'-C(=O)\}$ where Ar' is a divalent radical comprising at least one aromatic ring, and

wherein said polyester comprises approximately 10 to 90 mole percent of moiety I, approximately 5 to 45 mole percent of moiety

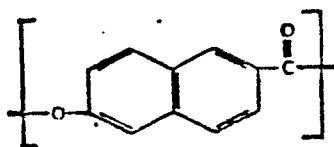
15 II, and approximately 5 to 45 mole percent of moiety III and wherein at least some of the hydrogen atoms present upon the rings optionally may be replaced by substitution selected from the group consisting of an alkyl group of 1 to 4 carbon atoms, an alkoxy group of 1 to 4 carbon atoms, halogen, phenyl, substituted phenyl, and mixtures thereof.

49. The method of claim 48 wherein said polyester comprises approximately 20 to 80 mole percent of moiety I, approximately 10 to 40 mole percent of moiety II, and approximately 10 to 40 mole percent of moiety III.

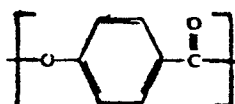
50. The method of claim 33 wherein said polymer comprises a melt processable wholly aromatic polyester which is capable of forming an anisotropic melt phase and consists essentially of the recurring moieties I, II, III and IV wherein:

5

I is



II is



III is a dioxy aryl moiety of the formula $\{O-Ar-O\}$ wherein Ar is a divalent radical comprising at least one aromatic ring, and

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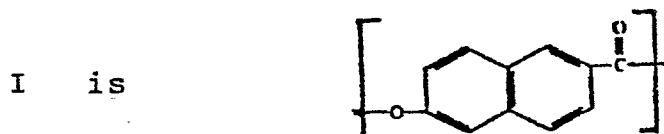
IV is a dicarboxy aryl moiety of the formula $\{C(=O)-Ar'-C(=O)\}$ where Ar' is a divalent radical comprising at least one aromatic ring, and

wherein the polyester comprises approximately 20 to 40 mole per-

cent of moiety I, in excess of 10 up to about 50 mole percent of moiety II, in excess of 5 up to about 30 mole percent of moiety III, and in excess of 5 up to about 30 mole percent of moiety IV and wherein at least some of the hydrogen atoms present upon the rings optionally may be replaced by substitution selected from the group consisting of an alkyl group of 1 to 4 carbon atoms, an alkoxy group of 1 to 4 carbon atoms, halogen, phenyl, substituted phenyl, and mixtures thereof.

51. The method of claim 50 wherein said polyester comprises approximately 20 to 30 mole percent of moiety I, approximately 25 to 40 mole percent of moiety II, approximately 15 to 25 mole percent of moiety III and approximately 15 to 25 mole percent of moiety IV.

52. The method of claim 33 wherein said polymer comprises a melt processable poly(ester-amide) which is capable of forming an anisotropic melt phase and consists essentially of the recurring moieties I, II, III and optionally IV wherein:



II is $\{-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{A}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\}$, where A is a divalent radical comprising at least one aromatic ring or a divalent trans-cyclohexane radical;

III is $\{-\text{Y}-\text{Ar}-\text{Z}-\}$, where Ar is a divalent radical comprising at least one aromatic ring, Y is O, NH, or NR, and Z is NH or NR, where R is an alkyl group of 1 to

6 carbon atoms or an aryl group; and

IV is {O-Ar'-O}, where Ar' is a divalent radical comprising at least one aromatic ring;

15 and wherein said poly(ester-amide) comprises approximately 10 to 90 mole percent of moiety I, approximately 5 to 45 mole percent of moiety II, approximately 5 to 45 mole percent of moiety III, and approximately 0 to 40 mole percent of moiety IV and wherein at least some of the hydrogen atoms present upon the rings
20 optionally may be replaced by substitution selected from the group consisting of an alkyl group of 1 to 4 carbon atoms, an alkoxy group of 1 to 4 carbon atoms, halogen, phenyl, substituted phenyl, and mixtures thereof.

53. The method of claim 33 wherein said polymer is subjected to a heat treatment for a period of time and at a temperature sufficient to increase the melting temperature of the polymer between about 20 to 50 centigrade degrees subsequent to
5 formation of said article.

54. The method of claim 53 wherein said heat treatment temperature ranges from about 10 to about 30 centigrade degrees below the melting temperature of the polymer.

55. The method of claim 54 wherein said period of time ranges from about 0.5 to about 200 hours.

56. The method of claim 55 wherein said period of time ranges from about 1 to about 48 hours.

57. The method of claim 56 wherein said period of time ranges from about 5 to about 30 hours.

58. The method of claim 53 wherein said heat treatment occurs in a non-oxidizing atmosphere.

59. The method of claim 58 wherein said atmosphere is substantially moisture-free.

60. The method of claim 58 wherein said heat treatment occurs in a nitrogen atmosphere.

61. The method of claim 33 wherein said polymer has a melting temperature in excess of about 200°C.

62. The method of claim 61 wherein said polymer has a melting temperature in excess of about 400°C.



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EUROPEAN SEARCH REPORT

0166830

Application number

EP 84 30 4572

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 4)
X	EP-A-0 103 371 (DU PONT DE NEMOURS) * Claims 1,6; page 7, lines 7-12 *	1-3	D 04 H 1/56 D 04 H 1/54 D 04 H 3/14
A, L	US-A-4 395 307 (CELANESE) * Claims 1,4,9; column 1, lines 12-15: citation of a former US-patent application Ser. No. 315.525, filed 09-11-1981, entitled: "Non-woven articles comprised of thermotropic liquid crystal polymer fibers" *	1	
A	TAPPI, vol. 56, no. 4, April 1973, pages 74-77, Atlanta, Georgia, US; R.R. BUNTIN et al.: "Melt blowing - a one-step web process for new nonwoven products" * Page 76: Polymers which can be melt-blown *	33	
			TECHNICAL FIELDS SEARCHED (Int Cl 4)
			D 04 H D 01 F
D, A	US-A-4 184 996 (CELANESE)		
D, A	US-A-4 219 461 (CELANESE)		
D, A	US-A-4 238 599 (FIBER INDUSTRIES)		
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 05-03-1985	Examiner CATTOIRE V.A.
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			



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EUROPEAN SEARCH REPORT

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Application number

EP 84 30 4572

Page 2

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. 4)
D, A	US-A-4 256 624 (CELANESE)		

D, A	US-A-4 330 457 (CELANESE)		

			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 05-03-1985	Examiner CATTOIRE V.A.
CATEGORY OF CITED DOCUMENTS			
X particularly relevant if taken alone		T theory or principle underlying the invention	
Y particularly relevant if combined with another document of the same category		E earlier patent document, but published on, or after the filing date	
A technological background		D document cited in the application	
O non-written disclosure		L document cited for other reasons	
P intermediate document		& member of the same patent family, corresponding document	