

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
18 April 2002 (18.04.2002)

PCT

(10) International Publication Number  
**WO 02/31037 A1**

(51) International Patent Classification<sup>7</sup>: **C08K 5/15**,  
5/00, C08L 67/04, 67/00

(21) International Application Number: PCT/US01/12476

(22) International Filing Date: 17 April 2001 (17.04.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
60/239,495 11 October 2000 (11.10.2000) US

(81) Designated States (*national*): AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

(71) Applicant (*for all designated States except US*): **UNION CARBIDE CHEMICALS & PLASTICS TECHNOLOGY CORPORATION** [US/US]; 39 Old Ridgebury Road, Danbury, CT 06817-0001 (US).

**Declarations under Rule 4.17:**

- *of inventorship (Rule 4.17(iv)) for US only*
- *of inventorship (Rule 4.17(iv)) for US only*

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **KUPPERBLATT, Sandra, Ann** [US/US]; 4 Duncan Court, Belle Mead, NJ 08502 (US). **GOLDBERG, Daniel** [US/US]; 25 Cargy Drive, Bordentown, NJ 08505 (US).

**Published:**

- *with international search report*

(74) Agent: **VOLLES, Warren, K.**; Union Carbide Chemicals & Plastics Technology Corporation, 39 Old Ridgebury Road, Danbury, CT 06817-0001 (US).

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: COMPOSITIONS COMPRISING CRYSTALLINE CONDENSATION POLYMERS AND NUCLEATING AGENTS

(57) Abstract: Compositions comprising crystalline condensation polymers, e.g., polycaprolactone, and nucleating agents are disclosed. The compositions are suitable for use, for example, in preparing extruded or molded articles, such as, biodegradable films, implantable medical devices, sheets, planting containers and fibers. Preferably, the nucleating agents are compounds having a heterocyclic group containing about 4-6 carbon atoms. Vitamin E is disclosed as being particularly useful as a nucleating agents.



WO 02/31037 A1

- 1 -

COMPOSITIONS COMPRISING CRYSTALLINE  
CONDENSATION POLYMERS AND NUCLEATING AGENTS

**Field of the Invention**

The present invention relates to compositions comprising crystalline condensation polymers, e.g., polyesters, and nucleating agents.

**Background of the Invention**

Current environmental concerns have generated interest in the use of biodegradable plastics for disposable items such as, for example, trash bags, packaging materials, eating utensils, and the like. A variety of biodegradable polymers have been proposed for such uses. Typical of such polymers are condensation polymers, such as, for example, polyesters, polyester amides, polymers formed by ring open polymerization, e.g., lactone, lactide and lactam polymerizations, polyhydroxyalkanoates, polylactic acid and naturally occurring polymers, such as, polysaccharides, e.g., cellulosic, starch, and soy derivatives.

Although many polymers, such as those described above, are highly effective in terms of their biodegradability, they often suffer from inferior mechanical performance which has hindered their commercial viability. More specifically, when converted to film by blown film extrusion, for example, biodegradable polymers often do not have good machine direction ("MD") Elmendorf Tear Strength as measured by ASTM D-1922, transverse direction ("TD") Tensile Impact as measured by ASTM D-1822, Falling Dart Impact Resistance as measured by ASTM D-1709, MD and TD Secant Modulus as measured

- 2 -

by ASTM D-882, and Puncture Resistance as measured by Union Carbide Test Method WC-68-L. On the other hand, when biodegradable polymers are modified to enhance their mechanical properties, their biodegradability often suffers.

Often, condensation polymers suitable for use as biodegradable materials are semi-crystalline in form, e.g., greater than about 30 wt.%, often greater than about 50 wt. % and more often greater than about 70 wt. % crystalline. Complete crystallization of polymers is often a slow process requiring minutes, hours or days to fully accomplish. When crystallization is desired, the temperature is held above the glass transition temperature ("T<sub>g</sub>") and below the crystalline melting point for a time sufficient to allow the molecules of the polymer to order themselves into crystal lattices. This process is also referred to in the art as "annealing". If the crystallinity of the polymer becomes too high, the molded article from the polymer may not have sufficient toughness to be viable in a typical end use like trash bags, mulch film, molded parts and the like.

Nucleating agents have been used in combination with a variety of polymeric materials in order to improve the performance of the polymers. Effective nucleating agents increase the nucleation density which in turn increases the overall rate of crystallization leading to smaller diameter crystals (also referred to in the art as "spherulites"). Also, increased crystallization rates often lead to reduced cycle time in processing steps such as in injection molding and reduced time to complete crystallization in blown film processes. Illustrative compositions are disclosed, for example, in British Patent 1,139,528 published January 8, 1969 which discloses compositions comprising one or more crystalline linear polyesters obtained by the

- 3 -

polymerization of  $\beta$ -lactones and one or more compounds of the following categories:

- (a) alkali metal chlorides, bromides or iodides or boron nitride, and
- (b) salts of mono-, bi- and trivalent metals and aromatic carboxylic, sulphonic or phosphinic acids.

However, the nucleating agents disclosed in British Patent 1,139,528, e.g., the alkali metal halides, boron nitride and metal salts, are often undesirable components in finished articles that may come in contact with humans, animals or the environment.

Accordingly, improved compositions comprising crystalline condensation polymers and nucleating agents which are non-toxic and safe for the environment are desired.

### **Summary of the Invention**

In accordance with the present invention, compositions comprising crystalline condensation polymers and nucleating agents are provided. The nucleating agents of the present invention are compounds having heterocyclic groups containing about 4 to 6 carbon atoms. Preferably, the heterocyclic groups contain oxygen in the ring. Quite surprisingly, in accordance with the present invention it has been found that alicyclic nucleating agents such as, for example, tocopherol or derivatives thereof, e.g., Vitamin E, are effective nucleating agents for crystalline condensation polymers.

By virtue of the present invention, it is now possible to provide compositions suitable for use in manufacturing articles, such as, for example, molded products, biodegradable film and the like, which have a desirable combination of excellent processing properties, e.g., high

- 4 -

crystallization rates, improved mechanical properties, e.g., Elmendorf tear strength and dart impact strength, and excellent environmental compatability.

### **Brief Description of the Drawings**

Figure 1 sets forth a micrograph of a crystalline condensation polymer without a nucleating agent.

Figure 2 sets forth a micrograph of a crystalline condensation polymer and a nucleating agent in accordance with the present invention.

### **Detailed Description of the Invention**

As used herein, the term "biodegradable" means degradable polymers as defined in ASTM D-883 in which the degradation results from the action of micro-organisms occurring naturally such as, for example, bacteria, fungi, and algae. The biodegradability may be evidenced, for example, by the production of CO<sub>2</sub> and associated reduction in mechanical properties, such as tensile strength and percent elongation at break. Further details are known to those skilled in the art.

As used herein, the terms "condensation polymerization" and "polycondensation" mean: (i) a polymerization reaction in which two or more molecules are combined with the generation of water, alcohol or other simple substances as by-products; and (ii) polymerization of monomers, e.g., ester and amide monomers, formed by ring opening polymerization, e.g., lactones, lactides and lactams, which do not generate water, alcohol or other simple substances as by-products.

- 5 -

As used herein, the term "crystalline linear condensation polymers" means those condensation polymers, which as shown by x-ray analysis have a degree of crystallinity of at least 60 percent, preferably at least 30 percent. The degree of crystallinity can be measured by any means known to those skilled in the art, such as, for example, by X-ray Diffraction ("XRD") or Differential Scanning Calorimetry ("DSC").

The condensation polymers in accordance with the present invention can be polymerized to form aliphatic or aromatic polyesters or polyester amides or other condensation polymers, such as, for example, by ring opening polymerization. As used herein, the term "polymer" is intended to include copolymers, terpolymers and other polymers polymerized from one or more monomers.

The monomers for these polymers can be comprised of a single molecular unit, an oligomer or a prepolymer. The monomers can have functional groups selected from the group consisting of esters, ethers, alcohols, acids, amines, amides, acid halides, isocyanates and mixtures thereof as may be determined by those skilled in the art. They can be ethylenically unsaturated or alternatively can have no ethylenic unsaturation. The molecular structure of the monomers can be straight, e.g., normal, alkyl or branched, cyclic or aromatic. The monomers have a molecular weight of typically from about 62 to 12,000 grams per gram mole ("g/gmol"), more typically, from about 62 to 10,000 g/gmol.

Unless otherwise indicated, as used herein, the term "molecular weight" means number average molecular weight. Techniques for determining number average molecular weight are known to those skilled in the art. One such technique is gel permeation chromatography ("GPC").

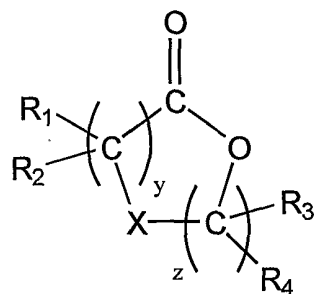
- 6 -

In one aspect of the present invention, the monomers comprise one or more compounds which can be polymerized or copolymerized to form aliphatic or aromatic polyesters or polyester amides or other condensation polymers. Examples of such polymers include, for example, polyesters prepared from the reaction of C<sub>2</sub>-C<sub>6</sub> diols, e.g., ethylene glycol, diethylene glycol, butanediol, neopentyl glycol, hexanediol with dicarboxylic acids, such as but not limited to, succinic, glutaric or adipic acid; copolyesters of terephthalic acid based polymers with dicarboxylic acids and diols; and polyester/amides from the reaction of caprolactam with dicarboxylic acids and diols. Suitable hydroxy acids include, for example,  $\alpha$ -hydroxybutyric acid,  $\alpha$ -hydroxyisobutyric acid,  $\alpha$ -hydroxyvaleric acid,  $\alpha$ -hydroxyisovaleric acid,  $\alpha$ -hydroxycaproic acid,  $\alpha$ -hydroxyisocaproic acid,  $\alpha$ -hydroxy- $\alpha$ -ethylbutyric acid,  $\alpha$ -hydroxy- $\beta$ -methylvaleric acid,  $\alpha$ -hydroxyheptanoic acid,  $\alpha$ -hydroxyoctanoic acid,  $\alpha$ -hydroxydecanoic acid,  $\alpha$ -hydroxymyristic acid and  $\alpha$ -hydroxystearic acid or their intermolecular cyclic esters or combinations thereof.

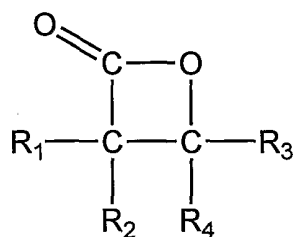
In another aspect of the present invention, the monomers comprise cyclic monomers which are polymerized by ring opening polymerization. Typical of such monomers are cyclic esters, such as, for example, glycolides, lactides, lactones and cyclic carbonates.

In one aspect of the present invention, the cyclic monomers include those having the formulas:

- 7 -



where X=nil, -O-, or -O-C=O; Z=1-3; Y=1-4; R<sub>1</sub>-R<sub>4</sub>= H-, -CH<sub>3</sub>, C<sub>2</sub>-C<sub>16</sub> alkyl group, -C(CH<sub>3</sub>)<sub>3</sub>, or HOCH<sub>2</sub>-, and where all R's are independent on each y or z carbon unit and independent of each other; or



where R<sub>1</sub>-R<sub>4</sub>= H-, -CH<sub>3</sub>, C<sub>2</sub>-C<sub>16</sub> alkyl group, or HOCH<sub>2</sub>-, and where all R's are independent of each other.

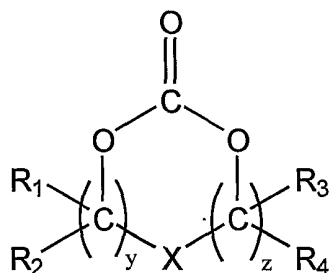
Examples of the lactones described above are, but not limited to,  $\epsilon$ -caprolactone, t-butyl caprolactone, zeta-enantholactone, deltavalerolactones, the monoalkyl-delta-valerolactones, e.g. the monomethyl-, monoethyl-, monohexyl-deltavalerolactones, and the like; the nonalkyl, dialkyl, and trialkyl-epsilon-caprolactones, e.g. the monomethyl-, monoethyl-, monohexyl-, dimethyl-, di-n-propyl-, di-n-hexyl-, trimethyl-, triethyl-, tri-n-epsilon-caprolactones, 5-nonyl-oxepan-2-one, 4,4,6- or 4,6,6-trimethyl-oxepan-2-one, 5-hydroxymethyl-oxepan-2-one, and the like; beta-lactones, e.g., beta-propiolactone, beta-butyrolactone gamma-lactones, e.g., gammabutyrolactone or



- 8 -

pivalolactone, glycolides, e.g., tetramethyl glycolides, and the like, ketodioxanones, e.g. 1,4-dioxan-2-one, 1,5-dioxepan-2-one, and the like. The lactones can consist of the optically pure isomers or two or more optically different isomers or can consist of mixtures of isomers.

In addition, cyclic carbonates of the formula:



where X=nil, -O-; Z=1-3; Y=1-3; R<sub>1</sub>-R<sub>4</sub>= H-, -CH<sub>3</sub>, C<sub>2</sub>-C<sub>16</sub> alkyl group, or HOCH<sub>2</sub>-, and where all R's are independent on each y or z carbon unit and independent of each other, can be used as a comonomer with the lactones of this invention.

Examples of suitable cyclic carbonates are ethylene carbonate, 3-ethyl-3-hydroxymethyl trimethylene carbonate, propylene carbonate, trimethylene carbonate, trimethylolpropane monocarbonate, 4,6-dimethyl-1,3-propylene carbonate, 2,2-dimethyl trimethylene carbonate, and 1,3-dioxepan-2-one.

$\epsilon$ -caprolactone and its derivatives and other seven membered ring lactones are especially preferred for use as monomers in accordance with the present invention.

Examples of typical cyclic ester polymers and their (co)polymers resulting from the polymerization of the above-mentioned monomers include: poly(glycolide); poly(trimethylenecarbonate); poly(epsilon-caprolactone); poly(L-lactide-co-glycolide); poly(L-lactide-co-

- 9 -

trimethylenecarbonate); poly(L-lactide-co-epsilon-caprolactone); poly(D,L-lactide-co-glycolide); poly(D,L-lactide-co-trimethylenecarbonate); poly(D,L-lactide-co-epsilon-caprolactone); poly(meso-lactide-co-glycolide); poly(meso-lactide-co-trimethylenecarbonate); poly(meso-lactide-co-epsilon-caprolactone); poly(glycolide-co-trimethylenecarbonate); poly(glycolide-co-epsilon-caprolactone) and poly(ethylene terephthalate).

In one aspect of the invention, the amount of lactone monomer used in preparing the polymers of the present invention is from about 40 to 100 wt. %, often from about 50 to 99 wt. %, preferably from about 60 to 98 wt. % and more preferably from about 85 to 95 wt. %, based on the total weight of the monomers in the polymer.

The amount of the initiator suitable for use in preparing the polymers of the present invention is from about 0.01 to 50 wt. %, preferably from about 0.05 to 35 wt. % and more preferably from about 0.1 to 20 wt. % based on the total weight of the monomers used to make the polymer. The optimal level of the initiator will depend on the specific structure of the monomer and can be determined by those skilled in the art.

Typically, the compositions of the present invention comprise from about 75 to greater than 99.9 wt. % of the condensation polymer based on the total weight of the nucleating agent and the condensation polymer. Often, the compositions will comprise from about 90 to greater than 99.9 wt. % and more often, from about 95 to greater than 99.9 wt. % of the condensation polymer. The particular concentration of the condensation polymer will depend on the particular use intended which concentration can be determined by those skilled in the art.

- 10 -

Further details of the condensation polymers suitable for use in accordance with the present invention are known to those skilled in the art. Such condensation polymers and the monomers useful for manufacturing such condensation polymers are readily commercially available.

The processes used to prepare the polymers of the present invention are not critical. The polymers of the present invention can be prepared by bulk polymerization, suspension polymerization, extruder or solution polymerization. The polymerization can be carried out, for example, in the presence of an inert normally-liquid organic vehicle such as, for example, aromatic hydrocarbons, e.g., benzene, toluene, xylene, ethylbenzene and the like; oxygenated organic compounds such as anisole, dimethyl, and diethyl esters of ethylene glycol; normally-liquid hydrocarbons including open chain, cyclic and alkyl-substituted cyclic saturated hydrocarbons such as hexane, heptane, cyclohexane, decahydronaphthalene and the like.

The polymerization process can be conducted in a batch, semi-continuous, or continuous manner. The monomers and catalysts can be admixed in any order according to known polymerization techniques. Thus, the catalyst can be added to one comonomeric reactant. Thereafter, the catalyst-containing comonomer can be admixed with another comonomer. In the alternative, comonomeric reactants can be admixed with each other. The catalyst can then be added to the reactant mixture. If desired, the catalyst can be dissolved or suspended in an inert normally-liquid organic vehicle. If desired, the monomeric reactants either as a solution or a suspension in an inert organic vehicle can be added to the catalyst, catalyst solution or catalyst suspension. Still further, the catalyst and comonomeric

- 11 -

reactants can be added to a reaction vessel simultaneously. The reaction vessel can be equipped with a conventional heat exchanger and/or mixing device. The reaction vessel can be any equipment normally employed in the art of making polymers. One suitable vessel, for example, is a stainless steel vessel. A plasticizer, if used, or a solvent can be blended into the polymer to aid in removal of the polymer material from the reactor vessel.

Typically, the polymerization reactions are conducted at a temperature of from about 70 to 250°C, preferably from about 100 to 220°C, over a reaction time of from about 3 minutes to 24 hours preferably from about 5 to 10 hours. The reaction pressure is not critical to the present invention. The particular catalyst used in the polymerization is not critical and can be determined by those skilled in the art.

In addition to the monomers, other ingredients may be added, such as plasticizers, e.g. epoxidized soybean oil, epoxidized linseed oil, citrate esters such as, for example, trialkyl citrates, e.g., triethyl citrate, acetyltriethyl citrate, tri-n-butyl citrate, acetyltri-n-butyl citrate, acetyltri-n-hexyl citrate, glycerin, diethylphthalate, dioctylphthalate; slip/antiblocks, e.g. stearamide, behenamide, oleoamide, erucamide, stearyl erucamide, erucyl erucamide, oleyl palmitamide, steryl stearamide, erucyl stearamide, N,N'-ethylenebisstearamide, N,N'-ethylenebisoleamide, talc, calcium carbonate, kaolin clays, molecular sieves and other particulate materials, stabilizers, compatibilizers, pigments, etc. Typically, the total amount of such other ingredients ranges from about 0.01 to 10 weight percent, based on the total weight of the copolymer

- 12 -

composition. Further details concerning the selection and amount of such additives are known to those skilled in the art.

The polymers produced in accordance with the present invention typically have a melting point of from about 50 to 240°C, preferably from about 52 to 120°C, and a T<sub>g</sub> of from about -120 to 120°C and preferably from about -60 to 60°C. The polymers typically have a Melt Flow of from about 0.1 to 7, preferably from about 0.2 to 2.5 and more preferably from about 0.5 to 2. As used herein, the term "Melt Flow" means grams of material that flow through a die in ten minutes at 125°C/2.16 kilograms ("Kg") as described in ASTM D-1238.

The density of the polymers typically ranges from about 1.00 to 1.50 grams per cubic centimeter ("g/cc") and preferably from about 1.05 to 1.20 g/cc.

Typically, the polymers of the present invention have a weight average molecular weight (M<sub>w</sub>) of from about 500 to 800,000 grams/gram mole, and preferably from about 50,000 to 500,000 grams/gram mole. Typically, the number average molecular weight (M<sub>n</sub>) ranges from about 500 to 700,000 grams/gram mole, preferably from about 30,000 to 500,000 grams/gram mole. The Polydispersity Index (M<sub>w</sub>/M<sub>n</sub>) typically ranges from about 1.3 to 10.

Typically, the nucleating agents suitable for use in accordance with the present invention are effective to provide an increase in the crystallization temperature of at least 2°C compared to a composition comprising the condensation polymer without the nucleating agent. More preferably, the increase in crystallization temperature will be at least about 4°C.

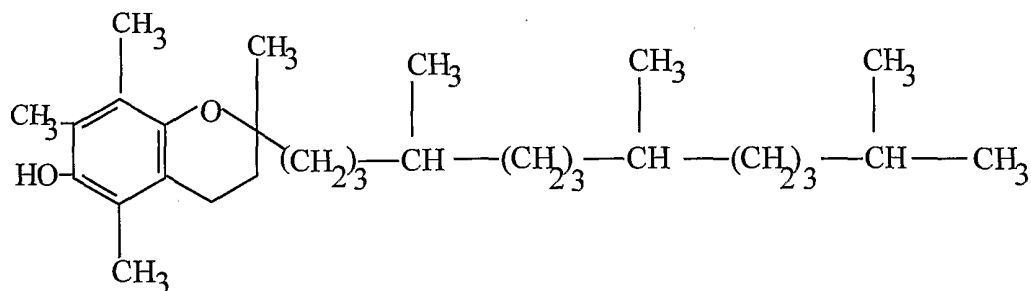
Preferably the nucleating agents are substantially non-polar. As used herein, the term "substantially non-polar" means the chemical

- 13 -

structure is predominantly carbon and hydrogen with few heteroatoms, i.e., less than about 5 wt. % based on the total weight of the nucleating agent.

Preferably the nucleating agents are non-toxic and environmentally friendly. More preferably, the nucleating agents contain a substantial absence of alkali metal halides, boron nitride or salts of metals or aromatic carboxylic, sulfonic or phosphinic acids. As used herein, the term "substantial absence" means less than about 5 wt. %, preferably less than about 2 wt. %, more preferably less than about 1 wt. % and most preferably less than about 100 ppmw, based on the total weight of the nucleating agent.

In one aspect of the invention, the nucleating agents are compounds having a heterocyclic group containing about 4 to 6 carbon atoms. The compounds may be polymerizable or not polymerizable and may, for example, be monomers, oligomers or polymers. Preferably, the heterocyclic group contains an oxygen atom. Other possible non-carbon substituents in the heterocyclic ring include, for example, sulfur or nitrogen. Preferably, the nucleating agent is alicyclic. In a preferred aspect of the invention, the nucleating agent is tocopherol or a derivative thereof. Tocopherol generally comprises any of a group of related substances which constitute Vitamin E. A preferred form of tocopherol is dl- $\alpha$ -tocopherol (also known as dl-2,5,7,8-tetramethyl-2-(4', 8', 12'-trimethyltridecyl)-6-chromanol). The structure can be represented by:



Tocopherol is available from a variety of commercial sources including for example, Irganox™ E17 (with additives) and Irganox™ E-201 available from Ciba Specialty Chemicals.

Preferably, the nucleating agents are organic in nature and have a melting point lower than the melting point at which the composition will be processed. For example, polycaprolactone has a melting point of about 60°C. Typically, polycaprolactone is processed, e.g., extruded, at temperatures of from about 110 to 150°C. Preferably, the nucleating agent will have a melt temperature in the range of about -100 to 125°C in order to be most effective. Although nucleating agents with higher melting points may be suitable in terms of providing appropriate mechanical properties such high melting materials may tend to cause haziness in extruded films and other molded articles. Some or all of the nucleating agent can be introduced during polymerization of the condensation polymer or after polymerization is conducted.

Typically, the compositions of the present invention comprise from about 100 ppmw to 25 wt. % of the nucleating agent based on the total weight of the nucleating agent and the condensation polymer. Often, the compositions comprise from about 100 ppmw to 10 wt. % and more often, from about 500 ppmw to 5 wt. % of the nucleating

- 15 -

agent. The determination of the appropriate amount of nucleating agents in the compositions of the present invention can be determined by those skilled in the art.

One or more crystalline condensation polymers can be utilized in accordance with the present invention. One or more nucleating agents can be used in accordance with the present invention.

The compositions of the present invention can be provided in any form desired, typically the compositions are provided as a physical blend of the polymer and the nucleating agent either in solid liquid or a combined solid/liquid form. In many cases, it is desired to prepare a masterbatch of the composition comprising the nucleating agents in a concentration which is higher than would typically be used in the preparation of the desired article, e.g., film. In such cases, the masterbatch would be diluted with additional amounts of the condensation polymer or other polymers prior to molding or extrusion. Still alternatively, the condensation polymer can be polymerized in the presence of the nucleating agent. In a preferred aspect of the invention, the polymer is transported directly after polymerization in its molten state to a pelletizer extruder or molding machine and combined with the nucleating agent either in a neat form or combined with a masterbatch prior to producing the desired product.

The products made from the compositions of the present invention can be produced in any form known to those skilled in the art. The products comprising the polymer compositions of the present invention can be converted into cast or blown film, sheet, blow molded, injection molded, or spun into fibers using any process or equipment known to those skilled in the art. Typically, the films have a thickness of from about 0.5 to 2 mils, preferably from about 0.6 to 1.7 mils, and



- 16 -

more preferably from about 0.7 to 1.5 mils. The mechanical properties recited herein are based on a film thickness of 1.0 to 1.3 mils.

Typically, the films have a MD tensile strength of from about 3000 to 10000 psi, preferably from about 4000 to 9500 psi, as measured by ASTM D-882. Typically, the films have a TD tensile strength from about 2000 to 9000 psi, preferably from about 4000 to 8000 psi. The dart drop impact properties of the films typically range from about 20 to 200 grams per 1/1000 inch ("g/mil"), preferably at least 40 g/mil and more preferably range from about 40 to 150 g/mil. The MD Elmendorf tear properties of the films typically range from about 5 to 200 g/mil and preferably range from about 10 to 150 g/mil. The TD Elmendorf tear properties of the films typically range from 100 to 700 g/mil and preferably range from about 100 to 500 g/mil. The MD tensile impact properties of the films typically range from 400 to 2500 ft-lb/cu in and preferably range from about 1000 to 2200 ft-lb/cu in. The TD tensile impact properties of the films typically range from 100 to 2500 ft-lb/cu in and preferably range from about 200 to 2400 ft-lb/cu in. The puncture resistance properties of the films typically range from 3 to 50 in-lbs/mil and preferably range from about 5 to 30 in-lbs/mil.

Preferably in accordance with the present invention, the nucleating agent is effective to provide a reduction in spherulite size of at least about 30%, preferably at least about 50% based on the visual inspection of micrographs of cryo-microtomed (-100°C to -130°C) films made from the compositions of the present invention compared to films made from an identical composition without the nucleating agent. Typical micrographs can be taken for example, using a Olympus VANOX-T AH2 optical light microscope under polarized light at a

- 17 -

magnification level of from about 300X to 1500X. Preferably in such a comparison, the film thickness should be about 1 micrometer ("μm") to 5 μm and the process conditions, both for polymerization and film production should be identical or nearly identical for a meaningful comparison.

The polymers of the present invention can be used in the fabrication of a wide variety of products including, for example, sheets, i.e. greater than 10 mil thick, 10 mil thick or less, e.g. trash bags, fibers, e.g. sutures, fishing line, non-woven fabrics, molded articles, e.g., containers, tools and medical devices, e.g. staples, clips, pins, prostheses, etc. One particularly preferred end use in accordance with the present invention is to provide compostable film for use as a trash bag. As defined in ASTM D-883, a compostable plastic is a plastic that undergoes biological degradation during composting to yield carbon dioxide, water, inorganic compounds, and biomass at a rate consistent with other known compostable materials and leaves no visually distinguishable or toxic residues.

### Examples

The following Examples are provided for illustrative purposes and are not intended to limit the scope of the claims which follow.

The following test procedures were used in the Examples.

#### GPC Test Procedure

GPC was conducted on a Waters 590 HPLC unit having a LC-241 Autosampler, Waters Styragel columns HR-1, HR-3, HR-4, HR-4E, HR-5E, a ERMA ERC-7510 Differential Refractometer Detector connected to a VG Data System, using tetrahydrofuran (stabilized with BHT) as the solvent, 0.45μ PTFE disposable filters (for sample

- 18 -

preparation) and a 0.45u Nylon 66 filter (for mobile phase degassing). The unit was calibrated using polystyrene standards in the molecular weight range of 162 to 1,800,000. The operating parameters were:

Flow	1.0 milliliter per minute ("ml/min").
Run Time	65 minutes
Injection Size	200 microliter ("ml") $\mu$ l
Temperatures	
Detector	35°C
Columns	Ambient
Injector	Ambient

The sample concentration was 0.5 percent weight/volume.

#### Film Properties

Except for puncture resistance, the film properties were measured using the appropriate ASTM test procedure, e.g. ASTM D-1709 for Falling Dart Impact Resistance (also referred to herein as "dart drop"). Puncture resistance of film was measured using Union Carbide Corporation's procedure WC-68-L, and is a test procedure known to those skilled in the art (also referred to herein as "puncture resistance"). Puncture resistance is defined as the force required to rupture a test specimen and the energy absorbed by the film during rupture. Unlike the falling dart method, which measures high speed impact, the puncture resistance employs a slowly moving plunger moving at a crosshead speed of 20 inch/minute. An Instron Tensile Tester, compression cell CC (model G-03-2), integrator, film holder and plunger, calibration weights, and micrometer are used. Five 6 inch x 6 inch samples of each film are prepared and conditioned for 40 hours at

- 19 -

23±2°C and 50±5% relative humidity. The thickness of each film is measured in the center to the nearest 0.0001 inch and is mounted on the compression cell so that the plunger will puncture the center of the film. The plunger is positioned 8 inch above the compression cell and will have a downward travel of 6 inch. The load in pounds required to rupture the samples is recorded and the results are reported as in-lbs/mil.

#### Differential Scanning Calorimetry (DSC)

DSC for polymers were measured in a helium atmosphere from 100°C to 85°C at a rate of 10°C/minute. The effect of crystalline suppression by addition of an amorphous block or short chain branching was determined using DSC. The effect is shown with a depression of the temperature of crystallization ( $T_c$ ), and on second heat depression of the melting point ( $T_m2$ ) and a decrease in crystallinity as measured by a reduction in the heat of fusion ( $\Delta H_f$ ).

#### Biodegradability

ASTM D-5338, which is a standard test method for Determining Aerobic Biodegradation of Plastic Materials Under Controlled Composting Conditions, was used to determine the biodegradability of copolymer.

The following ingredients were used in the Examples.

TONE™ Polymer P-787 - a polymer of 80,000 Mn available from Union Carbide Corporation, Danbury, CT.

- 20 -

Polypropylene ESD47 - polypropylene available from Union Carbide Corporation, Danbury, CT

HS-7028 - a linear low-density polyethylene available from Union Carbide Corporation, Danbury, CT.

DMDH-6400 - a high-density polyethylene resin available from Union Carbide Corporation, Danbury, CT.

Irganox™ E217 - 2H-1-Benzopyran-6-ol, 3,4,-dihydro-2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)- (35%), available from Ciba Specialty Chemicals Additives, Tarrytown, NY.

Citroflex™ 2 - Triethylcitrate, available from Morflex, Inc., Greensboro, N.C.

Irganox™ E17 - available from Ciba Specialty Chemicals Additives, Tarrytown, NY

Irganox™ E201 - available from Ciba Specialty Chemicals Additives, Tarrytown, NY

Irganox™ E201 - 6-chroman-2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)-2H-1-benzopyran-6-ol,3,4-dihydro-2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)-, available from Ciba Specialty Chemicals Additives, Tarrytown, NY.

- 21 -

Millad™ 3905 - dibenzylidene sorbitol, available from Milliken Chemical, Inman, SC.

Millad™ 3988 - Bis(p-methylbenzylidene) sorbitol, available from Milliken Chemical, Inman, SC.

Arkon™ P-125, a fully saturated alicyclic hydrocarbon available from Mitsui, Houston, Texas.

Arkon™ P-140, a fully saturated alicyclic hydrocarbon available from Mitsui, Houston, Texas.

Irganox™ 1425 - Phosphoric acid, [[3,5-bis-(1,1-dimethylethyl)-4-hydroxyphenyl]methyl]-, monoethyl ester, calcium salt (2:1) or FDA designation is Calcium bis[monoethyl(3,5-di-tert-butyl-4-hydroxybenzyl)phosphonate], available from Ciba Specialty Chemicals Additives, Tarrytown, NY.

Irganox™ 1425WL - 1 part Irganox 1425 and 1 part polyethylene wax, available from Ciba Specialty Chemicals Additives, Tarrytown, NY.

Carbowax™ 1450 - Polyethylene Glycol 1450, available from Union Carbide Corporation, Danbury, CT.

Carbowax™ 4600 - Polyethylene Glycol 4600, available from Union Carbide Corporation, Danbury, CT.

- 22 -

Boron Nitride - available from Aldrich, Milwaukee, WI.

HM-10™ - 75% calcium carbonate 25% LLDPE, available from Heritage Plastics, Inc., Picayune, MS.

### **EXAMPLE 1**

#### **PREPARATION OF PCL MASTERBATCH WITH NUCLEATING AGENTS**

Preparation of a 10% masterbatch of Irganox E201 in polycaprolactone ("PCL") was performed by first dry mixing 100 grams ("g") of Irganox and 900 g of TONE® P787 together and then compounding on a brabender twin screw extruder. The brabender twin screw extruder contained a screw diameter of 42 millimeters ("mm"), a barrel length of 276 mm, and counterrotating intermeshing screws. The resultant polymer blend was pelletized.

### **EXAMPLE 2**

#### **PREPARATION OF COMPOSITIONS CONTAINING PCL AND NUCLEATING AGENTS**

The pellets from Example 1 were then diluted with TONE® P787. An amount of 4.54 g of the masterbatch from Example 1 and 449.46 g of TONE® P787 were first dry mixed and then were compounded on the same brabender twin screw extruder used in Example 1. The final concentration of the Irganox™ E201 in the sample was approximately 1000 ppmw. Table 1 below shows a variety of nucleating agents at various concentrations.

TABLE 1

Sample	Nucleating Agent	Additive Level, wt%
1	Millad 3905	0.2
2	Arkox P-125	5.0
3	Arkox P-140	5.0
4	Irganox E17	0.2
5	Irganox E201	0.05
6	Irganox E201	0.1
7	Irganox E201	0.2
8	Irganox 1425	0.2
9	Irganox 1425WL	0.2
10	Carbowax 1450	1.0
11	Carbowax 4600	1.0
12	Boron Nitride	0.2
13	Boron Nitride	1.0

**EXAMPLE 3****MEASUREMENT OF CRYSTALLIZATION TEMPERATURE**

The compounded materials from Example 2 were pressed into plaques and were analyzed by DSC at a specific heating and cooling rate. This DSC profile was as follows: Equilibrate equipment at -25.0°C.

Isothermal at -25.0°C for 5 minutes, increase 10°C/min to 230°C, hold isothermal for 5 minutes, decrease temperature at 10°C/min to -25°C, hold isothermal for 5 minutes, increase temperature at 10°C/min to 230°C.



If a molten polymer is cooled at a constant rate, an exotherm may be produced as the polymer crystallizes. The temperature range over which the crystallization occurs, the area of the peak and the peak sharpness give an indication of the crystallization behavior of the material. The addition of an effective nucleating agent generally causes an increase in the crystallization peak temperature,  $T_c$  and/or the peak area, i.e. the heat of crystallization,  $\Delta H_c$ . The data from the DSC analyses are set forth in Table 2.

**TABLE 2**

Sample	Nucleating Agent	Amount of additive in P787, wt %	$T_c, ^\circ\text{C}$	$\Delta H_c$ , cal/g
A (Control)	P787 base resin, no additive	0	25.9	13.1
1	Millad 3905	0.2	31.2	14.1
2	Arkon P-125	5.0	29.9	13.4
3	Arkon P-140	5.0	29.9	12.0
4	Irganox E17	0.2	37.1	31.3
5	Irganox E201	0.05	30.0	12.0
6	Irganox E201	0.1	32.3	13.3
7	Irganox E201	0.2	30.9	11.2
8	Irganox 1425	0.2	32.5	14.4

**TABLE 2 (Continued)**

Sample	Nucleating Agent	Amount of additive in P787, wt %	Peak crystallization temperature, °C	Peak Area, cal/g
9	Irganox 1425WL	0.2	32.3	14.1
10	Carbowax 1450	1.0	29.8	15.0
11	Carbowax 4600	1.0	29.3	14.7
12	Boron Nitride	0.2	31.9	14.6
13	Boron Nitride	1.0	34.2	15.9
14	HDPE, DMDH-6400	5.0	35.6	13.4

**EXAMPLE 4****PREPARATION OF FILM**

Film samples were produced by extruding the resins of Example 2 on a brabender film line. The brabender film line used was a ¾ inch extruder equipped with a 2 inch annular die, a single lip air ring, and a 20 mil die gap. The pellets from the resins produced in Example 2 were extruded under the following conditions: barrel temperatures were set at 175°C, the die temperatures were set at 175°C, the output rate was approximately 3 pounds/hour, the film blow-up ratio ("BUR") was 1.35:1 and the film gauge was 1.35 mil.

- 26 -

**EXAMPLE 5****SPHERULITE SIZE**

Figures 1 and 2 are light micrographs analyzed under polarized light at 750 magnification of TONE® P787 and TONE® P787 with 900 ppmw of Irganox™ E201, respectively. As can be seen, a marked reduction in spherulite size of approximately 90% was observed with the addition of the Irganox™ E201.

**EXAMPLE 6****FILM PROPERTIES**

The film properties of various samples were evaluated according to the procedure described above. The data are shown in Table 3.

D-18074-1-PC

**Table 3**  
**Brabender Film Properties of Screened Nucleating agents in P787**

Sample	Nucleating Agent	Amount of additive in P787, wt %	Elmendorf Tear, g/mil MD	Elmendorf Tear, g/mil TD	Tensile Impact, psi MD	Tensile Impact, psi TD
A	P787 base resin, no additive	0	7	232	1030	390
4	Irganox E17	0.2	7	350	1370	390
8	Irganox 1425	0.2	11	231	1420	410
9	Irganox 1425WL	0.2	8	214	1680	520
10	Carbowax 1450	1.0	8	265	1230	410
11	Carbowax 4600	1.0	8	275	1300	470
12	Boron Nitride	0.2	10	333	1290	315
13	Boron Nitride	1.0	9	363	1090	260

**Table 3 (continued)**  
**Brabender Film Properties of Screened Nucleating agents in P787**

15	Polypropylene ESD47	5	3	209	1180	50
15	LLDPE, HS- 7028	5	7	261	1210	270
16	HDPE DMDH-6400	5	3	135	1480	50
17	HM-10	5	10	307	1370	410

The results obtained with Irganox™ E17 (Sample 4) were interesting and were pursued further since this additive is comprised of three compounds, high density polyethylene, Vitamin E and polyethylene glycol. High density polyethylene and polyethylene glycol have been shown to improve film properties and act as nucleating agents. Accordingly, left to be analyzed for performance was Vitamin E, i.e., Irganox™ E201. The effect of Vitamin E at different levels was evaluated measuring by film properties on a brabender blown film extrusion line (See Table 4 ). The film data was generated on a ¾ inch brabender film extruder equipped with a 2 inch annular die, a single lip air ring, and a 20 mil die gap. The BUR for the films was 1.35:1 and the film gauge was 1.35 mil.

**Table 4**  
**Effect of Vitamin E, Irganox E201, on P787**  
**Brabender Film Properties**

Sample	Amount of Irganox E201 in P787, wt %	Elmendorf Tear, g/mil MD	Elmendorf Tear, g/mil TD	Tensile Impact, psi MD	Tensile Impact, psi TD	Puncture, in- lb/mil
A	0	12	337	1050	340	4
5	0.05	13	416	1520	420	5
6	0.1	14	381	900	420	10
7	0.2	13	360	1530	460	5

EXAMPLE 7EFFECT OF PLASTICIZER

The effect of addition of plasticizer and nucleating agents on film properties from film generated on a 11/2 inch Sterling film extruder was evaluated. The data are shown in Table 5 below. The Sterling blown film line was equipped with a 3 inch annular die, a 40 mil die gap and a dual lip air ring. The addition of 1000 ppmw of Irganox™ E201 was effective in increasing the MD Elmendorf tear strength, the dart impact strength slightly, the puncture resistance and the balance in MD/TD tensile strength. The addition of 5% Citroflex™ 2 was effective in increasing the dart impact strength and the tensile impact strength. Quite surprisingly, the addition of both nucleating agent and plasticizer lead to films with a further improvement in toughness properties suggesting a synergistic effect between the two additives. The MD tear strength and puncture resistance increase from the Irganox™ E201 was maintained, the tensile impact strength increase from the plasticizer was maintained and the dart impact strength was increased over the value with each individual additive. Additionally, the combination of the nucleating agent and the plasticizer did not adversely effect the tensile strength.



**Table 5**  
**Effect of Vitamin E and Plasticizer on PCL Film Properties**

Sample	6 (Control)	17	18	19
Composition	P787	P787 + 1000 ppm Irganox E201	P787 + 5% Citroflex 2	P787 + 1000ppm Irganox E201 + 5% Citroflex 2
Film Notebook #	20570-142-1	20570-144-1	20570-147-3	20570-144-4
Film gauge, mil	1.35	1.35	1.35	1.35
BUR	2.1:1	2.1:1	2.1:1	2.1:1
Elmendorf Tear	18	32	14	34
g/mil	122	155	112	137
Tensile Impact	1870	1050	2590	2530
Ft lb/cu in	960	850	2380	2400
Dart Drop, g/mil	all failures	42	59	72
Puncture, in lb/mil	9	24	11	24
Tensile Strength	MD 9560	9080	9190	9060
psi	TD 6950	8000	7510	6490

- 33 -

Although the invention has been described above with respect to specific aspects, those skilled in the art will recognize that other aspects are intended to be included within the scope of the claims which follow. For example, in addition to the specific condensation polymers described herein, other condensation polymers may be utilized. Moreover, in addition to the condensation copolymers other polymers may be blended with the copolymers. Furthermore, in addition to the specific articles described herein, other articles such as, for example, injection, compression or blow-molded molded plastic articles may be manufactured from the compositions of the present invention. Also nucleating agents or plasticizers other than those specifically disclosed herein may be employed.

**CLAIMS**

1. A composition comprising a crystalline condensation polymer and a nucleating agent, characterized in that the nucleating agent is a compound having a heterocyclic group containing about 4 to 6 carbon atoms.
2. The composition of claim 1 wherein the nucleating agent is effective to provide at least a 30% reduction in spherulite size in a film made from the composition compared to a film made from the condensation polymer without the nucleating agent.
3. The composition of claim 1 wherein the nucleating agent is effective to provide at least a 50% reduction in spherulite size in a film made from the composition compared to a film made from the condensation polymer without the nucleating agent.
4. The composition of claim 1 wherein the condensation polymer is polymerized from one or more monomers having a functional group selected from the group consisting of esters, ether, carbonates, acetals, alcohols, acids, amines, amides, acid halides, isocyanates and mixtures thereof.
5. The composition of claim 1 wherein the condensation polymer is polymerized from a monomer selected from the group consisting of lactones, lactides, lactams, polyols, urethanes, ureas, carbonates, acetals, and mixtures thereof.

- 35 -

6. The composition of claim 1 wherein the condensation polymer is polymerized from a monomer selected from the group consisting of caprolactone and derivatives thereof.

7. The composition of claim 1 wherein the nucleating agent has an oxygen atom in the heterocyclic ring.

8. The composition of claim 1 wherein the nucleating agent is alicyclic.

9. The composition of claim 8 wherein the nucleating agent is tocopherol or a derivative thereof.

10. The composition of claim 1 comprising from about 100 ppmw to 25 wt. % of the nucleating agent based on the total weight of the nucleating agent and the condensation polymer.

11. The composition of claim 10 comprising from about 100 ppmw to 10 wt. % of the nucleating agent based on the total weight of the nucleating agent and the condensation polymer.

12. The composition of claim 11 comprising from about 500 ppmw to 5 wt. % of the nucleating agent based on the total weight of the nucleating agent and the condensation polymer.

13. The composition of claim 1 comprising from about 75 to greater than 99.9 wt. % of the condensation polymer, based on the total weight of the nucleating agent and the condensation polymer.

14. The composition of claim 1 further comprising at least one polymer other than the condensation polymer.

15. The composition of claim 1 wherein the nucleating agent is effective to provide an increase in the crystallization temperature of at least about 2°C compared to a composition comprising the condensation polymer without the nucleating agent.

16. The composition of claim 15 wherein the nucleating agent is effective to provide an increase in the crystallization temperature of at least about 4°C compared to a composition comprising the condensation polymer without the nucleating agent.

17. The composition of claim 1 further comprising a plasticizer.

18. The composition of claim 17 wherein the plasticizer is a citrate ester.

19. The composition of claim 18 wherein the citrate ester is a trialkyl citrate.

20. A film made from the composition of claim 1.

21. The film of claim 20 having a puncture resistance of from about 3 to 50 in-lbs/mil.

22. The film of claim 20 having a dart drop of at least 50 g/mil.

- 37 -

23. A method of enhancing the toughness of a film, said method comprising forming the film from the polymer of claim 1.

## INTERNATIONAL SEARCH REPORT

Inter 1al Application No

PC17US 01/12476

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08K5/15 C08K5/00 C08L67/04 C08L67/00

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 7 C08K C08L

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)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE CHEMABS 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; KAWAGUCHI, TATSUYA ET AL: "Polyester resin compositions comprising sorbitol derivatives and crystalline moldings therefrom" retrieved from STN Database accession no. 129:109670 XP002177345 abstract & JP 10 158369 A (MITSUI TOATSU CHEMICALS, INC., JAPAN) 16 June 1998 (1998-06-16) abstract	1,4,5,7, 8,10-14, 20
X	US 5 258 422 A (CHANG PETER I ET AL) 2 November 1993 (1993-11-02) claims 1,7,13,15-20 --- -/--	1,4-12, 14,17,20

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

## ° Special categories of cited documents :

\*A\* document defining the general state of the art which is not considered to be of particular relevance

\*E\* earlier document but published on or after the international filing date

\*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)

\*O\* document referring to an oral disclosure, use, exhibition or other means

\*P\* document published prior to the international filing date but later than the priority date claimed

\*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

\*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

\*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.

\*&amp;\* document member of the same patent family

Date of the actual completion of the international search

9 October 2001

Date of mailing of the international search report

26/10/2001

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

Rose, E

## INTERNATIONAL SEARCH REPORT

Inter national Application No  
PC17US 01/12476

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 918 057 A (MILLIKEN RES CORP) 26 May 1999 (1999-05-26)  claims 1,8,17 ----	1,4,7,8, 10-14, 17,20
X	GB 2 261 667 A (SANDOZ LTD) 26 May 1993 (1993-05-26) claims 1,4,7 ----	1,4,7,8, 10-14,20
A	US 5 919 487 A (SIMONNET JEAN-THIERRY ET AL) 6 July 1999 (1999-07-06) example 1 claims 1,8,12,15 ----	1-23
A	EP 0 962 459 A (NEW JAPAN CHEM CO LTD) 8 December 1999 (1999-12-08) claims 1,38 ----	1-23
A	US 5 518 730 A (FUISZ RICHARD C) 21 May 1996 (1996-05-21) claims 1,2,5 ----	1-23
A	US 5 973 100 A (PIERRE JEAN R ET AL) 26 October 1999 (1999-10-26) examples 1,3 -----	1-23



# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PC1/JS 01/12476

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
JP 10158369	A	16-06-1998	NONE	
US 5258422	A	02-11-1993	NONE	
EP 0918057	A	26-05-1999	US 5973043 A BR 9805042 A CN 1226556 A EP 0918057 A1 JP 11236385 A	26-10-1999 01-02-2000 25-08-1999 26-05-1999 31-08-1999
GB 2261667	A	26-05-1993	NONE	
US 5919487	A	06-07-1999	FR 2742677 A1 DE 69600758 D1 DE 69600758 T2 EP 0780115 A1 ES 2125703 T3 JP 3001821 B2 JP 9175931 A	27-06-1997 12-11-1998 04-03-1999 25-06-1997 01-03-1999 24-01-2000 08-07-1997
EP 0962459	A	08-12-1999	AU 7938498 A BR 9806259 A EP 0962459 A1 NO 992670 A US 6245843 B1 WO 9918108 A1	27-04-1999 25-01-2000 08-12-1999 02-08-1999 12-06-2001 15-04-1999
US 5518730	A	21-05-1996	AU 665844 B2 AU 4405893 A CA 2137268 A1 EP 0746342 A1 JP 7507548 T WO 9324154 A1	18-01-1996 30-12-1993 09-12-1993 11-12-1996 24-08-1995 09-12-1993
US 5973100	A	26-10-1999	AU 8758498 A EP 0996671 A1 WO 9905208 A1	16-02-1999 03-05-2000 04-02-1999