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ESCOBAR - URIBE ASOCIADOS

A B O G A D O S

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SUPERINDUSTRIA Y COMERCIO
Radicacion : 00316913 00000006 Folios: 2
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Tramite : 832 PATENTES D 1 REGISTRO/ 538 PETICION
Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

SUPERINTENDENCIA DE INDUSTRIA Y CO
DIVISIÓN DE NUEVAS CREACIONES
E. S. D.

Ref.: Expediente No. 00-016.913
Solicitud de Patente a nombre de
HUMATRO CORPORATION

Yo, JIMENA ESCOBAR URIBE, identificada como aparece al pie de mi firma, domiciliada en Bogotá, en la Carrera 11 A No. 94-76 Of. 305, obrando como apoderada de la sociedad HUMATRO CORPORATION., domiciliada en Nueva York, Nueva York, Estados Unidos de América, solicitante de la patente de la referencia, pido a usted que se proceda a examinar si la invención, cuya patente se tramita en el expediente de la referencia, es patentable.

Adjunto al presente memorial el recibo No. 02 - 42,148 de junio 26, 2002, por la suma de $318.000.oo, con lo cual queda cubierta la tasa oficial correspondiente a dicho estudio.

Señor Superintendente,

JIMENA ESCOBAR URIBE
C.C. 39.779.452 de usaquén
T.P. 68.228
Cod. 5376

JEU/ra.

2320

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NIT : 800176089-2

RECIBO OFICIAL DE CAJA : 02 - 42,148
FECHA : JUNIO 26 DE 2002

***** C O N S I G N A C I O N *****

DEPO	NTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PGO	Vr. PAGO
ESCOBAR URIBE ASOCIADOS		CONSIGNACION	BANCO POPULAR	050-00110-6	4797064	26/06/2002	3,844,000.00

***** C O N C E P T O *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	005-01-01 SOLICITUDES	85 EXAMEN DE PATENTABILIDAD DE INVEN	318,000.00
		TOTAL : $	318,000.00

SON: TRESCIENTOS DIEZ Y OCHO MIL PESOS

RESPONSABLE : _____

RECIBO DE CAJA APLICADO AL EXPEDIENTE No._____

272

375
2005-06-02

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISIÓN DE NUEVAS CREACIONES

2020
Bogotá D.C., Mayo 17 de 2005

Doctor
JIMENA ESCOBAR URIBE
Apoderado **HUMATRO CORPORATION**

ASUNTO

Radicación	00-16913
Trámite	002
Evento	001
Actuación	430
Oficio	
Folios	018

12911

Como resultado del examen de fondo, realizado con fundamento en el artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le comunica:

1. Documentos estudiados:

A. Para el presente estudio se tuvo en cuenta el capítulo descriptivo, comprendido en los folios 3 a 139 del expediente correspondiente a la solicitud en estudio, tal como fue radicado al inicio del trámite; y correcciones en los folios 227 a 243.

B. El capítulo reivindicatorio tomado en cuenta para el presente estudio comprende 10 reivindicaciones y se encuentra en los folios 225 a 226, el cual reemplazó al capítulo reivindicatorio radicado al inicio del trámite.

C. Conforme lo establecen los artículos 9, 10 y 11 de la Decisión 486 de la Comisión de la Comunidad Andina, la presente solicitud en estudio fue presentada el 08 de marzo de 2000, en el momento de la radicación se reclamó prioridad. La copia certificada de la solicitud cuya prioridad fue reivindicada (US 09/264401 del 08 de marzo de 1999) aparece junto con la traducción de sus reivindicaciones en los folios 165 a 213.

2. Objeto de la invención:

A. Las reivindicaciones 1 a 10 de la solicitud en estudio se refieren a: una estructura flexible, absorbente, caracterizada porque comprende fibras de almidón, seudo-termoplásticas.

B. El objeto de la solicitud se puede clasificar según la clasificación internacional como A 61 L 15/28.

3. Claridad de la Solicitud:

A. El artículo 28 de la Decisión 486 de la Comisión de la Comunidad Andina establece "la descripción deberá divulgar la invención de una manera suficientemente clara y completa para su comprensión y para que una persona capacitada en la materia técnica correspondiente pueda ejecutarla"

No es claro qué puede significar "tracción en húmedo decaída". En castellano "decaído" significa "que se halla en decadencia; abatido, débil" (ver Diccionario de la

Real Academia de la Lengua). Luego, partiendo de dicha definición no es posible entender a qué se refiere el solicitante.

De acuerdo con lo anterior, la descripción no cumple con el requisito de claridad según lo establecido en el artículo 28 de la Decisión 486.

B. En el artículo 30 de la decisión 486 de la Comisión de la Comunidad Andina se establece: "Las reivindicaciones definirán la materia que se desea proteger mediante la patente. Deben ser claras y concisas y estar enteramente sustentadas por la descripción. Las reivindicaciones podrán ser independientes o dependientes. Una reivindicación será independiente cuando defina la materia que se desea proteger sin referencia a otra reivindicación anterior. Una reivindicación será dependiente cuando defina la materia que se desea proteger refiriéndose a una reivindicación anterior. Una reivindicación que se refiera a dos o más reivindicaciones anteriores se considerará una reivindicación dependiente múltiple." En el artículo 51 se establece además: "El alcance de la protección conferida por la patente estará determinado por el tenor de las reivindicaciones."

i. Las reivindicaciones deben ser claras, precisas y concisas ***por sí solas***. Por este motivo no se consideran claras cuando en ellas se hace referencia a marcas comerciales, como resinas Caldas o CoBond , porque bajo un mismo nombre comercial se puede suministrar un producto diferente; porque no todas las marcas comerciales se encuentran en todos los países; porque dependiendo del país de donde sea originaria la marca, puede tratarse de productos diferentes.

ii. Las abreviaturas Tg, GMDT y GMWT deben ser descifradas en las reivindicaciones, aún si ya han sido descifradas y explicadas en la descripción, por la misma razón enunciada en el párrafo anterior.

iii. En las reivindicaciones 3, 4, 7, 8, 9 y 10 se caracteriza el objeto de la solicitud por el resultado de mediciones hechas sobre él mismo, es decir por los resultados obtenidos. Esto no es permitido porque se está caracterizando el objeto de la solicitud por su desempeño, por la solución buscada. De esta manera, el alcance de la protección incluiría no sólo la solución propuesta por el solicitante, sino todas las alternativas presentes o futuras que lleguen a ese resultado.

De acuerdo con lo anterior, el capítulo reivindicatorio no cumple con el requisito de claridad según lo establecido en el artículo 30 de la Decisión 486. El solicitante deberá anexar un nuevo capítulo reivindicatorio con todas las correcciones aquí requeridas.

4. Determinación del estado de la técnica:

El artículo 16 de la Decisión 486 de la Comisión establece que: "El estado de la técnica comprenderá todo lo que haya sido accesible al público por una descripción escrita u oral, utilización, comercialización o cualquier otro medio antes de la fecha de presentación de la solicitud de patente o, en su caso, de la prioridad reconocida."

"Solo para el efecto de la determinación de la novedad, también se considerará dentro del estado de la técnica el contenido de una solicitud de patente en trámite

ante la oficina nacional competente, cuya fecha de presentación o de prioridad fuese anterior a la fecha de presentación o de prioridad de la solicitud de patente que se estuviese examinando, siempre que dicho contenido esté incluido en la solicitud de fecha anterior cuando ella se publique o hubiese transcurrido el plazo previsto en el artículo 40"

La fecha para determinar el estado de la técnica es el 08 de marzo de 1999, tomando en cuenta la prioridad reivindicada.

Consultadas las bases de datos y los archivos con que cuenta la entidad, especialmente bajo las clasificaciones A 61 L 15/28, se encontró que antes del 8 de marzo de 1999 habían sido publicados los documentos enumerados en la siguiente tabla.

No.	Documento	Título	Fecha de publicación
D1	US 5,346,936	Starch/polymer mixture, process for the preparation thereof, and products obtainable therefrom	1994-09-13
D2	US 5,516,815	Starch-containing fibers, process for their production and products made therefrom	1996-05-14
D3	US 5,679,145	Starch-based compositions having uniformly dispersed fibers used to manufacture high strength articles having a fiber reinforced, starch-bound cellular matrix.	1997-10-21
D4	US 5,444,113	End use applications of biodegradable polymers	1995-08-22

5. Evaluación de los requisitos de patentabilidad:

El artículo 14 de la Decisión 486 de la Comunidad Andina establece que: "*Los Países Miembros otorgarán patentes para las invenciones, sean de producto o de procedimiento en todos los campos de la tecnología, siempre que sean nuevas, tengan nivel inventivo y sean susceptibles de aplicación industrial*".

En cumplimiento del artículo 14 de la Decisión 486, se procedió a evaluar los requisitos de novedad, nivel inventivo y aplicación industrial con el fin de establecer la patentabilidad del objeto de la solicitud reivindicado en la solicitud en estudio.

A. Evaluación de la Novedad:

El artículo 16 de la decisión 486 de la Comisión de la Comunidad Andina establece:

"Una invención se considerará nueva cuando no esté comprendida en el estado de la técnica." "El estado de la técnica comprenderá todo lo que haya sido accesible al público por una descripción escrita u oral, utilización, comercialización o cualquier otro medio antes de la fecha de presentación de la solicitud de patente o, en su caso, de la prioridad reconocida."

1. El documento D2 trata de composiciones que contienen fibras de almidón que pueden ser hiladas y son seudo termo – plásticas, además de usarse en artículos absorbentes. Esto coincide con lo reivindicado en la primera reivindicación de la solicitud estudiada. Por lo tanto, se ve afectada la novedad del objeto de la primera reivindicación.

B. Evaluación del nivel inventivo:

El artículo 18 de la Decisión 486 de la Comisión de la Comunidad Andina dispone que: "Se considerará que una invención tiene nivel inventivo, si para una persona del oficio normalmente versada en la materia técnica correspondiente, esa invención no hubiese resultado obvia ni se hubiese derivado de manera evidente del estado de la técnica".

Las estructuras de las composiciones que contienen almidón descritas en D1, al igual que las reivindicadas, también constan de polioles, en calidad de plastificadores, y de poliamidas. Dichas composiciones se extruyen para formar películas. El documento D2 revela, además, la posibilidad de hilar las dichas composiciones usándolas como fibras absorbentes.

De la misma manera, D3 y D4 divulgan composiciones absorbentes a base de almidón, las cuales sugieren directamente cómo un técnico de nivel medio en la materia habría podido derivar de manera evidente el objeto reivindicado. Efectivamente, allí se indican múltiples formas de lograr las estructuras fibrosas a base de almidón que está reclamando el solicitante, incluidas la presencia de plastificadores y reticulantes. En D3 se indica el nivel de amilasa que debe tener el almidón para poder ser usado en las composiciones sugeridas. En D4 se indica el tipo de almidón que puede ser usado.

Así las cosas, la solicitud en estudio no cumple con el requisito de nivel inventivo establecido por el artículo 18 de la Decisión 486.

C. Resumen

En conclusión los requisitos de patentabilidad de la presente solicitud podrían encontrarse afectados así:

No.	Documento	Reivindicaciones afectadas	Requisito afectado
D1	US 5,346,936	1 a 10	Nivel inventivo
D2	US 5,516,815	1 a 10	Novedad y nivel inventivo
D3	US 5,679,145	1 a 10	Nivel inventivo
D4	US 5,444,113	1 a 10	Nivel inventivo

Se anexa copia de las anterioridades mencionadas.

6. Notificación

En cumplimiento del artículo 45 de la decisión 486 de la Comisión de la comunidad Andina, se le indica que debe dar respuesta dentro del término de sesenta días contados a partir de la fecha de la notificación de la presente comunicación. En caso de no dar respuesta al presente requerimiento, o si a pesar de la respuesta subsistieran los impedimentos para la concesión, se denegará la patente.

Notifíquese el presente oficio conforme a lo dispuesto en el numeral 5.2, literal e) del capítulo quinto del título primero de la circular única No. 10 de 2001.

ALIX CÉSPEDES DE VERGEL
Jefe de la División de Nuevas Creaciones

El anterior requerimiento fue notificado por fijación en lista, de fecha 02 JUN. 2005

CONCEPTO TÉCNICO Número: 702	**EXAMINADOR TÉCNICO** Código: 202043

US005346936A

United States Patent [19]

Buehler et al.

[11] **Patent Number: 5,346,936**

[45] **Date of Patent: Sep. 13, 1994**

[54] **STARCH/POLYMER MIXTURE, PROCESS FOR THE PREPARATION THEREOF, AND PRODUCTS OBTAINABLE THEREFROM**

[75] Inventors: **Friedrich S. Buehler**, Thusis; **Eduard Schmid**, Bonaduz; **Hans-Joachim Schultze**, Chur, all of Switzerland

[73] Assignee: **EMS-Inventa AG**, Switzerland

[21] Appl. No.: **898,132**

[22] Filed: **Jun. 15, 1992**

[30] **Foreign Application Priority Data**

Jun. 17, 1991 [DE] Fed. Rep. of Germany 4119915

[51] **Int. Cl.**[5] **C08L 3/04**; C08L 101/00; C08K 5/21; C08K 5/05

[52] **U.S. Cl.** **524/47**; 524/50; 524/51; 524/52

[58] **Field of Search** 524/47, 50, 51, 52

[56] **References Cited**

U.S. PATENT DOCUMENTS

4,673,438	6/1987	Wittwer et al.	106/126
4,983,651	1/1991	Griffin	524/47
5,094,054	3/1992	Lay et al.	524/47
5,108,807	4/1992	Tucker	524/47

FOREIGN PATENT DOCUMENTS

0118240	9/1984	European Pat. Off. .
0327505	8/1989	European Pat. Off. .
0409781	1/1991	European Pat. Off. .
0409782	1/1991	European Pat. Off. .
14938	12/1990	PCT Int'l Appl. .
2214918	9/1989	United Kingdom .

Primary Examiner—Nathan M. Nutter
Attorney, Agent, or Firm—Jordan B. Bierman

[57] **ABSTRACT**

A biodegradable, single-phase starch/polymer mixture comprising

(a) 10 to 99 parts of a starch molding composition comprising

(i) 95 to 45 parts of at least one chemically modified starch, and

(ii) 5 to 55 parts of at least one emulsifier, plasticizer or destructurizing agent, the parts of (i) and (ii) adding up to 100; and

(b) 90 to 1 parts of at least one linear polymer, the parts by weight of components (a) and (b) adding up to 100. In addition, 0 to 20 parts of additives which are customary in this area are included. A method of preparation, and the use thereof for thermoplastically molded parts, in particular films, is also disclosed.

27 Claims, No Drawings

STARCH/POLYMER MIXTURE, PROCESS FOR THE PREPARATION THEREOF, AND PRODUCTS OBTAINABLE THEREFROM

This application claims the priority of German Application P 41 19 915, filed Jun. 17, 1991.

The invention relates to a biodegradable and single-phase starch/polymer mixture comprising a selected linear polymer and a starch molding composition. Preferably, it is prepared from chemically modified starch, plasticizer, emulsifier, and urea or derivatives thereof. A process for the preparation of this single-phase starch/polymer mixture is also disclosed. Still further, the invention is directed to thermoplastically molded parts, in particular films, produced from the mixture by injection molding, extrusion, coextrusion, blow molding, injection stamping, and thermoforming, and the like.

BACKGROUND OF THE INVENTION

Since starch is a vegetable carbohydrate, efforts are being made to use it as a "natural plastic" in a wide variety of areas using existing methods of processing plastics. Due to their granular structure, however, natural starches must first be broken down or destructurized, before they become thermoplastically processable. Although they are biodegradable and have then the characteristics of thermoplastic plastics, the starches do not have their desired good properties. In order to achieve these properties, thermoplastic starch compositions of this type must be further improved. However, this frequently causes them to lose their full biodegradability.

EP 344 118 A2 relates to a polymer blend material comprising a melt of at least one water-containing destructurized hydrophilic polymer and at least one synthetic, essentially water-insoluble thermoplastic polymer. Examples are blends based on gelatin and cellulose derivatives, and polyethylene, polystyrene, polyvinyl ether, polyoxymethylene, and ethylene-acrylic acid copolymers which show an improvement in dimensional stability resulting from the addition of the water-insoluble polymer. However, the reference made therein to a possible biodegradability, namely the loss of this additional stability after several days, is instead something of a disadvantage for products molded from the blends, without actually saying anything regarding biodegradability itself.

EP-A 327 505 A2 describes a melt-mixed polymer blend material comprising destructurized, - but chemically unmodified-starch and at least one water-insoluble, synthetic thermoplastic polymer.

In the same way, EP-A 409 789 A2, EP-A 409 788 A2, EP-A 409 783 A2, EP-A 409 782 A2, EP-A 409 781 A2, EP-A 408 503 A2, EP-A 408 502 A2, EP-A 408 501 A2, EP-A 407 350 A2, EP-A 404 728 A2, EP-A 404 723 A2, and EP-A 404 727 A2 disclose polymer blend compositions comprising destructurized, but chemically unmodified, starch and a functionalized polymer. Each of these compositions may additionally contain a water-insoluble, thermoplastic polymer. The functionalized polymer then acts as a compatibility enhancer between the chemically unmodified starch and the additional third thermoplastic polymer.

SUMMARY OF THE PRESENT INVENTION

The object of the present invention is to provide a biodegradable, single-phase (compatible) starch/polymer mixture for thermoplastic processing which contains no polymeric compatibility promoters, and a process for the preparation of this mixture. The mixture should also have a long shelf life in granular form; i.e., it should be resistant to moisture, and suitable for the production of thermoplastically molded parts, in particular highly extensible, weldable films which are resistant to cold water. Such mixtures should have a particular application in the production of coextrusion films with further polymers the without the addition of a primer.

Surprisingly, it has been found that a single-phase starch/polymer mixture for thermoplastic processing can be prepared without polymeric compatibility promoters if (1) the starch employed is chemically modified and contains certain additives, and (2) the polymer employed is a linear polymer preferably having a melting or softening point of 50° to 160° C. All parts and percentages referred to in the specification and claims are by weight.

DETAILED DESCRIPTION OF THE INVENTION

The biodegradable, single-phase starch/polymer mixture according to the invention comprises

(a) from 10 to 99 parts of a starch molding composition comprising
  (i) 95 to 45 parts of a chemically modified starch, and
  (ii) 5 to 55 parts of plasticizers and/or destructurizing agents, the parts of (i) and (ii) adding up to 100; and

(b) 90 to 1 parts of at least one linear polymer,

the parts of components (a) and (b) adding up to 100. Up to 20 parts of customary additives may also be included. The chemically modified starch to be employed according to the invention should have a natural water content of from 5% to 16%.

The preferred chemically modified starch according to the invention is prepared by a special process described in U.S. application Ser. No. 890,563, filed Nov. 6, 1992, incorporated herein by reference. In this process, 95 to 53.2 parts of chemically modified starch are destructurized with 4.8 to 39.8 parts of at least one plasticizer, 0.1 to parts of urea and/or urea derivatives, and 0.1 to 2 parts of at least one emulsifier at elevated temperatures and pressures in an extruder. The mixture is extruded as a melt.

The preferred chemically modified starch has a natural water content of 5% to 16%, preferably 6% to 12%, most preferably from 6 to 8%. In general, the final water content of the starch/polymer mixture is 2% to 8%, preferably 2% to 5%. The preferred starch has been modified by reaction of its OH groups with alkylene oxides or other substances which form ethers, esters, urethanes, carbamates, and/or isocyanates. Particular preference is given to hydroxy alkyl having 2 to 6 carbon atoms, acetyl, and carbamate starches or mixtures thereof.

The degree of substitution of the desirable chemically modified starch is 0.01 to 0.2, and the amylose content is 20% to 100%, preferably 50% to 100%, especially 65% to 100%.

The plasticizers of (a)(ii) are organic compounds containing at least one hydroxyl group, preferably a polyol. Particularly preferable are glycerol, sorbitol, mannitol, D-glucose, ethylene glycol, polyethylene glycol, propylene glycol, and mixtures thereof. They are usefully employed in amounts of 4.8 to 39.8 parts, preferably 9.8 to 39.8 parts, most preferably 15 to 30 parts. The urea and/or urea derivatives of (a)(ii) are advantageously added in amounts of 0.1 to 5 parts, preferably from 0.1 to 2 parts, most preferably about 2 parts.

The emulsifier desirably has a hydrophilic-lipophilic balance value (HLB) of 0 to 20, preferably 10 to 20; and is employed in amounts of 0.1 to 2 parts, preferably 0.1 to 2 parts, especially about 0.2 parts, per 100 parts of component (a). Suitable emulsifiers are metal stearates, glycerol monostearates, polyoxyethylene (20) sorbitan monolaurate, polyoxyethylenemonopalmitate, polyoxyethylene (40) stearate, polyoxyethylene (100) stearate, and mixtures thereof.

In a preferred embodiment, component (a) comprises 70 parts of hydroxyethyl- and/or hydroxypropylstarch, having a degree of substitution of 0.06 and an amylose content of 50%, 15 parts of glycerol, 12.8 parts of sorbitol, 2 parts of urea, and 0.2 parts of magnesium stearate.

Component (b) is at least one linear polymer having a melting or softening point of 50° to 160° C., preferably 60° to 150° C. Particularly suitable are polyamides and/or polyesters. From the polyamide class, preference is given to homopolyamides and/or copolyamides made from ω-aminocaproic acid, ω-aminoenanthic acid, ω-aminocaprylic acid, ω-aminopelargonic acid, ω-aminocapric acid, ω-aminoundecanoic acid, 107 -aminolauric acid, caprolactam, lactam-7, lactam-8, lactam-9, lactam-10, lactam-11, and/or laurolactam. Particularly preferred are those polyamides made from caprolactam, laurolactam, ωaminolauric acid, and/or ωaminocaproic acid.

Suitable polyamides can also be made, for example, from dimethylenediamine, trimethylenediamine, tetramethylenediamine, pentamethylenediamine, hexamethylenediamine, polyetherdiamine, and mixtures thereof, on the one hand; and oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, nonanedicarboxylic acid, decanedicarboxylic acid, undecanedioic acid, dodecanedioic acid, dimerised fatty acids, and mixtures thereof, on the other hand. Of particular value are hexamethylenediamine, polyetherdiamine, adipic acid, dimerised fatty acids, and mixtures thereof.

From the class of the polyesters, preference is given to homopolyesters and/or copolyesters made from ω-hydroxyacetic acid, ω-hydroxypropionic acid, ω-hydroxybutyric acid, ω-hydroxyvaleric acid, ω-hydroxycaproic acid, ω-hydroxyenanthic acid, ω-hydroxycaprylic acid, ω-hydroxypelargonic acid, ω-hydroxycapric acid, ω-hydroxyundecanoic acid, ω-hydroxylauric acid, caprolactone, lactone-7, lactone-8, lactone-9, lactone-10, lactone-11, and/or laurolactone.

Also useful for this purpose are ethylene glycol, propanediol, butanediol, pentanediol, hexanediol, an aliphatic diol mixture having 2 to 18 carbon atoms, on the one hand; and oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, nonanedicarboxylic acid, decanedicarboxylic acid, undecanedioic acid, dodecanedioic acid, terephthalic acid, isophthalic acid, anhydrides and/or chlorides of the foregoing, and/or esters thereof.

Particularly preferred as sources of polyesters are aliphatic diol mixtures having 2 to 18 carbon atoms, ω-hydroxycaproic acid, butane-1,4-diol, adipic acid, terephthalic acid, isophthalic acid, and mixtures thereof. Homopolyesters and/or copolyesters made from aliphatic dicarboxylic acids having 2 to 12 carbon atoms and aliphatic diols having 2 to 6 carbon atoms are especially suitable. In practice, the above-mentioned copolyamides and copolyesters or mixtures thereof have proven particularly successful as component (b), it being possible to replace some or all of these by the above-mentioned homopolymers.

Customary additives are optical brighteners, stabilizers, antioxidants, flameproofing agents, dyes, fillers, and processing aids; one or more of these can additionally be employed in amounts of from 0 to 20 parts per 100 parts of the starch/polymer mixture.

In a preferred embodiment, the inventive mixture contains 50 to 95 parts of component (a) and 50 to 5 parts of component (b). Most preferably, 70 to 80 parts of component (a) and 30 to 20 parts of component (b) are used.

The process for the preparation of the single-phase starch/polymer mixture according to the invention comprises jointly melting components (a) and (b) in a ratio of from 10:90 to 99:1 in an extruder or in an injection-molding machine at temperatures at least 10° C. below the decomposition point of the starch and a maximum of 30° C., preferably 20° C., above the melting or softening point of the polymer. By adjusting the processing temperature, an optimum ratio between the viscosity of the polymer and the viscosity of the starch (the latter can be modified only slightly by temperature variations) can be determined by means of simple preliminary experiments, it being possible to homogeneously mix the melts by applying strong shear forces to the components. The customary additives may either be metered in during the preparation of the starch/polymer mixture or, preferably, are previously added to components (a) and/or (b).

The starch/polymer mixture according to the invention can be used for the production of thermoplastically molded parts, it being preferred first to produce a granulate which is then employed for the production of moldings. These can be formed, for example, by injection molding, blow molding, extrusion, coextrusion, injection stamping, or thermoforming. Particular preference is given here to the production of films by monoextrusion or coextrusion; these films may be formed as flat or blown films.

Advantages of the starch/polymer mixture according to the invention are:

1. Single-phase without addition of a polymeric compatibility promoter/compatibilizer.
2. Surprising biodegradability of the polymer component.
3. Good tear strength and elongation at break.
4. Ability to be converted to storage-stable granulate due to the low tendency to absorb moisture.
5. Simple processing without any tendency toward blocking and without any tack problems to produce films.

In the production of coextruded films from the inventive single-phase starch/polymer mixture and further polymers, the latter should have a melting or softening point of 50° to 180° C. Polymers which are suitable for

this purpose are copolyamides, copolyesters, and/or polyolefins. Preference is given here to polyolefins selected from polyethylene, polypropylene, polybutylene, and their derivatives. Particular preference is given to polyethylene and/or its derivatives.

In a specific embodiment, the single-phase starch/polymer mixture forms the middle layer, and the further polymer(s) form the inner and outer layers of the coextruded film. If the film has more than three layers, the layers thus alternate, the outer layer being selected on the basis of the desired application for the film. All films can be produced in a thickness of from 20 to 500 μm, preferably from 50 to 100 μm.

Advantages of the films according to the invention are:

1. Good adhesion of the coextruded film layers without addition of a primer
2. The film layer made from the starch/polymer mixture has, in the dry state, a barrier action against O_2, N_2, and CO2
3. Biodegradability of the monofilms
4. Improved moisture resistance
5. Low-temperature stretchability of the monofilms
6. High extensibility of the monofilms, in some cases greater than 400%
7. Welding possible using conventional heat-sealing equipment, fully transparent seal welds being obtained for monofilms.
8. Antistatic behavior of monofilms
9. Printing of monofilms with water-soluble inks
10. Paper-like hand of the monofilms in the highly stretched state
11. Smooth surfaces of the monofilms.

The monofilms are suitable, for example, for the production of carrier bags, refuse sacks, agricultural sheeting, diaper outer films, and biodegradable sheeting and film of all types. In addition, all films can be subjected to a thermoplastic forming process, such as deep drawing (thermoforming).

Table 1 shows the parameters for the preparation of single-phase starch/polymer mixtures and Table 2 shows the properties thereof. Table 3 shows the extrusion parameters and the properties of the monofilms and coextruded films.

FIG. 1 shows the Differential Scanning Calorimetry (DSC) curves for the starch/polymer mixtures of Examples 2 to 5. These show that only one melting point exists in each case, which proves that the starch/polymer mixtures according to the invention have a single phase.

The following examples illustrate the invention but do not limit it.

EXAMPLE 1

Preparation of the biodegradable starch molding composition

Component (a)

A starch molding composition is prepared by the process described in U.S. application Ser. No. 890,563, filed Nov. 6, 1992 from 70 parts of hydroxypropyl maize starch (having a degree of substitution of 0.06 and an amylose content of 50%), 15 parts of glycerol, 12.8 parts of sorbitol, 2 parts of urea, and 0.2 parts of magnesium stearate. The composition is subsequently granulated.

EXAMPLES 2 to 19

Preparation of the biodegradable, single-phase starch molding mixture

The starch granulate of Example 1 is mixed with granulate of the linear polymer of component (b) and the mixture is metered into the metering zone of a ZSK-30 twin-screw extruder (Werner & Pfleiderer) having 6 heating zones. The rotational speed and throughput are 100 rpm and 8–10 kg/h, respectively. The polymer type, polymer melting point, proportion by weight of the polymer, extrusion temperatures, and granulate properties are shown in Table 1. The material properties of the resultant single-phase starch/polymer mixtures are shown in Table 2.

The final water contents of the single-phase starch/polymer mixtures are determined by the method of Karl Fischer in accordance with DIN 53 714, and the melting point is determined by DSC in the dry state at a heating rate of 20° C./min in a Du Pont thermal analyzer type 1091B. The melt viscosity is measured by the melt flow index method at 160° C. and a load of 236.4N. The mechanical properties are determined on injection-molded test bars in accordance with DIN 53 457 (modulus of elasticity in tension) and DIN 53 455 (tear strength and elongation at break).

In experiments to determine the biodegradability it was observed, surprisingly, that the single phase starch/polymer-mixture according to the invention and the blown films produced therefrom have a more rapid oxygen consumption than the pure polymer (component (b) of the starch-polymer-mixture). It is well known that linear polyesters or polyamides are predestined for biological decomposition as, structurally, they are closely related to peptides. The actual resistance is caused by their unfavorable wetability with water in which the decomposition bacteria are contained. A possible explanation for this surprising effect is that the starch component greatly increases the otherwise low wetability of the polymer with water and in addition synergistic effects occur.

Comparative Examples 7 and 9 to 12 show that, if the three temperature conditions, namely (1) the melting point of the polymer of between 50° to 160° C., (2) the processing temperature of a maximum of 30° C. above the melting point of the polymer, and (3) the processing temperature at least 10° C. below the decomposition point of the starch, are not observed, a brown coloration results. The decomposition point of the preferred modified starch is 190° C.

EXAMPLES 20 to 22

Production of coextruded films

A three-extruder coextrusion unit according to the prior art is used to produce three-layer blown films from the granulated single-phase starch/polymer mixture and Lucalen (BASF). Extruder 1 produces the Lucalen inner layer, extruder 2 produces the middle layer of the single-phase starch/polymer mixture, and extruder 3 produces the Lucalen outer layer. The extrusion parameters and the properties of the films are shown in Table 3. Although no primer is added, the individual film layers adhere to one another very well.

EXAMPLES 23 to 27

Production of monofilms

On the same extrusion unit as in Examples 20 to 22, but with only one extruder, blown films are produced

US005516815A

United States Patent [19]

Buehler et al.

[11] **Patent Number: 5,516,815**

[45] **Date of Patent: May 14, 1996**

[54] **STARCH-CONTAINING FIBERS, PROCESS FOR THEIR PRODUCTION AND PRODUCTS MADE THEREFROM**

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[21] Appl. No.: **390,165**

[22] Filed: **Feb. 17, 1995**

Related U.S. Application Data

[62] Division of Ser. No. 973,055, Nov. 6, 1992, abandoned.

[30] **Foreign Application Priority Data**

Nov. 7, 1991 [DE] Germany 41 36 694.8

[51] **Int. Cl.**[6] **C08L 3/00**; C08L 67/02; C08L 77/02

[52] **U.S. Cl.** **523/128**; 523/124; 524/47; 525/54.24

[58] **Field of Search** 524/47, 50, 52, 524/54, 48; 428/364, 395; 523/124, 128; 525/54.24, 54.31

[56] **References Cited**

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[57] **ABSTRACT**

A starch fiber produced by a spinning process and comprising:

A A first amount of 1 to 100 parts of a starch melt-spinnable composition comprising
1. a second amount of 56 to 96 parts of at least one modified and/or unmodified starch,
2. a third amount of 4 to 40 parts of at least one destructuring agent,
3. a fourth amount of 0 to 4 parts of at least one additive, selected from urea, urea derivatives, emulsifiers, lubricants, and proteins and their alkali salts,

components 1, 2 and 3 totaling 100 parts; and

B a fifth amount of 99 to 0 parts of at least one melt-spinnable polymer,

ingredients A and B totaling 100 parts.

In addition, there may also be included 0 to 20 parts of conventional additives for melt spinning compositions.

The invention further relates to a process for the production of these starch fibers from this melt spinning composition, and to uses for fibers which, by modification with the starch melt-spinnable composition, have special properties.

21 Claims, 1 Drawing Sheet

STARCH-CONTAINING FIBERS, PROCESS FOR THEIR PRODUCTION AND PRODUCTS MADE THEREFROM

PRIOR APPLICATION

This application is a division of U.S. patent application Ser. No. 973,055 filed Nov. 6, 1992, now abandoned.

This application claims the priority of German Application 41 36 694.8, filed Nov. 7, 1991.

The present invention is directed to starch fibers produced from certain melt spinning compositions, their use as ingredients of other fibers, methods of producing them, and products made therefrom.

BACKGROUND OF THE INVENTION

There have been numerous attempts to make use of starch (a plant carbohydrate) as a "natural plastic" in a number of areas. It is important to commercial development that the starches be processible on standard equipment and use existing technology. However, natural starches are relatively grainy and, if they are to be suitably processed, they must first be destructured.

It has long been recognized that amylose, an important component of starch, is soluble in formaldehyde-containing aqueous solutions and alkaline aqueous solutions. In either case, the ultimate solutions obtained are relatively viscous and their stability is based primarily on the concentration of alkali or formaldehyde. Both solutions are suitable for the production of fibers, filaments, or foils.

The production of fibers, filaments, or foils from amylose has been carried out from solution in precipitation baths; i.e. wet spinning. This is set forth in, for example, DE-PS 10 63 325. However, there is no mention in this patent of any thermoplastic method.

In DE-OS 23 62 991, pharmaceutical preparations with delayed release of active ingredients for direct introduction into body cavities, are described. A mixture of the active ingredient and the polymer, including starch among other materials, is processed by melt spinning and extruded; the extrusion is then cut into pellets. These pellets are put into the usual melt spinning apparatus to produce fine fibers. The fibers are cut to a suitable length and carded dry to form "cotton" wads. The melt spinning process is mentioned very generally, but neither the process nor apparatus are not specifically described; only the use of hydroxypropyl cellulose and the extrusion are set forth. This melt spinning process is today the simplest and most widely used method for the production of synthetic filaments.

BRIEF DESCRIPTION OF THE INVENTION

It is, therefore, an object of the invention to provide novel starch or starch-modified fibers with special properties which can be produced from a biodegradable melt spinning composition, said composition to be spun by the current melt spinning processes and equipment. It is also an object of the invention to permit the use of the fibers thus produced, endowed with special properties, in a variety of applications.

It has now been found that the starch melt-spinnable compositions can be processed with polyamides, polyesters, and other polymers by thermoplastic methods to form fibers. For special applications, depending on the degree to which the starch or starch derivative is hydrophilic, portions soluble in cold water, soluble in hot water, or insoluble in water can be built into the synthetic fiber. For example, when

such fibers, containing small amounts of starch melt-spinnable compositions insoluble in hot water, are treated with hot water, porous fibers are obtained. If the fiber contains more than 50% starch molding composition, the treatment with hot water produces a fine powder precipitate of the fiber polymer, which sinks if its density is greater than that of water. The starch-laden waste water is completely biodegradable, and the polymer precipitate can be filtered and regenerated.

Surprisingly, it has been found that, in homogeneous starch melt-spinnable compositions with polyesters, polyethers, or linear aliphatic polyamides, the thermoplastic, finely-dispersed, polymer component itself is also amenable to biodegradation. The more homogeneous the polymer component is with the starch molding composition, the faster the biodegradation takes place. Further, the rate of degradation depends on the length of the carbon chain between hydrolyzable groups. If this starch molding composition is used without the polymer component, an unusually quick biodegradation in less than 20 days is observed.

The invention also relates to starch fibers which can be spun by known methods thermoplastically from a starch molding composition. This melt-spinnable composition is notable for its easy processibility and can produce fibers, which are useful for biodegradable fabrics, nonwovens, knits, etc., and can serve as modifiers of traditional fibers; in particular, for filters, household fabrics, sanitary nonwovens, and the like. Fabrics and nonwovens made of these materials are usable for bags, cloths, nets, and especially for packing agricultural products of all kinds. Additional areas of use are root packings of plants, trees, flowers, and the like.

Further, the invention relates to areas of use for fibers which are given special properties by modification with the starch melt-spinnable composition. By the addition of starch, the disadvantage of the synthetic textile fibers with respect to the low moisture absorption can be eliminated and wearing comfort comparable to cotton fabrics achieved. Moreover, the high density of the starch melt-spinnable compositions provides higher weights and offers particular advantages where heavy fibers are required.

Especially advantageous is the use of fast biodegradable fibers as cigarette filters. Further, biodegradable fibers are also desirable for sanitary nonwovens, fabrics, operating room textiles, diapers, absorbent "cotton" and wound dressing materials.

In conjunction with starch, the properties of resorbable materials such as polyhydrobutyric acid, polyhydrovaleric acid, polylactides, polyglycolides, as well as their copolymers and blends, can be modified and processed to provide resorbable filaments and fabrics.

In the case of bi- or multi-component fibers containing starch melt-spinnable compositions, due to the hydrophilic nature of selectable starches, the starch melt-spinnable compositions, which are stable to cold water in the cooling bath, can be dissolved out in hot water, thereby obtaining porous fibers. This method can be used also for the production of hollow fibers, through the formation of a coextruded starch core. The fibers of the present invention can, of course, be produced in all shapes; e.g. round, star-shaped, and angular. The cores may be incorporated continuously or intermittently, and can subsequently be dissolved out wholly or partially.

The starch melt-spinnable composition can be used as matrix material in production of superfine fibers. After spinning the superfine fibers in the matrix, the matrix can be dissolved away with hot water in an ecologically friendly

and economical manner and can either be reused or disposed of by biodegradation. These fibers can be used, for example, for the production of imitation suede or extremely fine-pored filter nonwoven materials.

The inventive melt-spinnable composition is also capable of giving synthetic fibers an antistatic finish. In addition, if the starch melt-spinnable composition contains residual water, it is suitable for flameproof finishing and reduces drip problems in synthetic fibers in a manner similar to metal hydroxide finishes in plastics.

Starch-modified fibers can serve for the production of separating yarns destroyable with hot water. They are useful as temporary or permanent adhesive fibers, depending on their water solubility, allowing temporary bondings, e.g. in nonwovens, to be separated again by steam treatment. Thus recyclable composite nonwovens of different materials can be produced.

For the production of permanent bondings, these fibers can be finished with reactive systems such as isocyanates; hindered isocyanates; formaldehydes; epoxides; hindered epoxides; anhydrides; and ester-, amide-, and carbamate-forming materials; and crosslinked immediately or subsequently.

Starch-modified fibers can be used in composite fiber technology as hot-water soluble fabric layers in order to keep different fiber materials separated. Later, after separation by hot water treatment, recycling of the pure material is possible.

Nowadays, synthetic fibers are used for paper reinforcement and for wet fiber finishing. However, they have the disadvantage that, when the paper is disposed of, these fibers are non-biodegradable. With the aid of starch-modified fibers, reinforced papers can be produced which are fully biodegradable. Papers with high starch fiber content are especially suitable as release papers, and insulating materials, as well as papers having improved sliding properties and printability, which are particularly suitable for use in photocopiers. On recycling, starch-modified paper reinforcement fibers break down into the water-soluble starch component, which remains in the pulp, and a pulverized polymer component which sinks, not being water-soluble and having a density higher than water, and which can thus be separated from the pulp for reutilization.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a schematic view of a twin-screw extruder useful in the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The starch fibers according to the invention are made from a melt spinning composition comprising the following components. Throughout the specification and claims, all parts and percentages are by weight:

A. 1 to 100 parts of a starch melt-spinnable composition comprising
   1. 56 to 96 parts of at least one modified and/or unmodified starch,
   2. 4 to 10 parts of at least one destructuring agent,
   3. 0 to 4 parts of at least one additive, selected from the group consisting of urea, urea derivatives, emulsifiers, lubricants, proteins and their alkali salts, and mixtures thereof,

the parts of components 1, 2, and 3 totaling 100; and

B. 99 to 0 parts of at least one melt-spinnable polymer, the parts by weight of components (A) and (B) adding up to 100.

In addition to the foregoing there may also be present 0 to 20 parts of materials of the prior art customarily added to melt spinning compositions.

Preferably, the additive consists of at least one of 0.1 to 2 parts of urea and/or urea derivatives, and 0.1 to 2 parts of at least one emulsifier. Preferably, the melt spinning composition consists of 20 to 95 parts, especially 20 to 80 parts, and most particularly 50 to 60 parts, of component A and of 80 to 5, preferably 80 to 20, more particularly 50 to 20, parts of component B. Component A advantageously contains the destructuring agent in quantities of 9 to 40 parts, more desirably 10 to 30 parts.

In a preferred embodiment, the starch fiber according to the invention is produced by a melt spinning process and which consists of the following components:

A. 10 to 100, preferably 30 to 100, parts of a starch melt-spinnable composition comprising
   1. 66 to 90 parts of at least one modified and/or unmodified starch,
   2. 10 to 30 parts of at least one destructuring agent,
   3. 0 to 4 parts of at least one additive selected from the group consisting of urea, urea derivatives, emulsifiers, and lubricants,

the parts of components 1, 2, and 3 adding up to 100; and

B. 90 to 0 parts, preferably 70 to 0 parts, of at least one melt-spinnable polymer,

the parts of components A and B adding up to 100.

In addition, there may also be present 0 to 10 parts of materials of the prior art customarily added to melt spinning compositions.

A particularly preferred form of the melt spinning composition according to the invention contains component A in an amount of from 20 to 95, more particularly 20 to 80, parts and component B in an amount of from 80 to 5, more particularly 80 to 20, parts, 50 to 80 parts of component A and 50 to 20 parts of component B being most preferred.

The chemically modified or unmodified starch to be used according to the invention advantageously has a natural water content of 5% to 16%, preferably 5% to 12%, more particularly 6% to 8% by weight. The preferred starch melt-spinnable composition can be produced by the process described in U.S. patent application Ser. No. 890,563, filed May 28, 1991, now U.S. Pat. No. 5,316,578. The starch having a natural water content, in the presence of at least one plasticizer, urea or urea derivative, and at least one emulsifier, is broken down at suitable elevated temperatures and pressures in an extruder and extruded as a melt.

In the present process, this starch is then chemically modified by reaction of its OH groups with alkylene oxides or other ether-, ester-, urethane-, carbamate- and/or isocyanate-forming substances. Preferred are hydroxy-, C_2- to C_6 alkyl-, acetyl- or carbamate-starches or mixtures thereof.

The degree of substitution of the chemically modified starch is 0.01 to 3.0, preferably 0.05 to 1.0. The amylose content of the modified or unmodified starch used is 20% to 100%, preferably 50% to 100%, and most preferably 65% to 100%. For water-resistant starch fibers, hydrophobic starch derivatives of a degree of substitution of 2 to 3 are particularly useful.

The plasticizer is advantageously an organic compound having at least one hydroxyl group, preferably a polyol. Sorbitol, mannitol, D-glucose, ethylene glycol, polyethylene glycol, propylene glycol, and mixtures thereof have been found to be especially suitable.

US005679145A

United States Patent [19]

Andersen et al.

[11] Patent Number: 5,679,145

[45] Date of Patent: Oct. 21, 1997

[54] **STARCH-BASED COMPOSITIONS HAVING UNIFORMLY DISPERSED FIBERS USED TO MANUFACTURE HIGH STRENGTH ARTICLES HAVING A FIBER-REINFORCED, STARCH-BOUND CELLULAR MATRIX**

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[73] Assignee: **E. Khashoggi Industries**, Santa Barbara, Calif.

[21] Appl. No.: **353,783**

[22] Filed: **Dec. 9, 1994**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 327,524, Oct. 21, 1994, Ser. No. 288,667, Aug. 9, 1994, Ser. No. 218,971, Mar. 25, 1994, Ser. No. 109,100, Aug. 18, 1993, abandoned, Ser. No. 95,662, Jul. 21, 1993, Pat. No. 5,385,764, Ser. No. 982,383, Nov. 25, 1992, abandoned, and Ser. No. 929,898, Aug. 11, 1992, abandoned.

[51] **Int. Cl.**[6] **C04B 14/38**; C08L 3/02

[52] **U.S. Cl.** **106/162.5**; 106/162.51; 106/162.9; 106/164.01; 106/205.01; 106/206.1; 106/217.01; 106/287.35; 106/400; 536/102

[58] **Field of Search** 521/68, 84.1; 524/442, 524/445, 449, 493; 536/102; 106/162.5, 162.51, 162.9, 164.01, 205.01, 206.1, 217.01, 287.35, 400

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[57] **ABSTRACT**

Compositions, methods, and systems for manufacturing articles, particularly containers and packaging materials, having a starch-bound cellular matrix reinforced with substantially uniformly dispersed fibers. High strength articles that have adequate flexibility and toughness immediately or very shortly after being demolded without the need for subsequent conditioning are molded from compositions having a starch-based binder and fibers that are uniformly dispersed by means of a high yield stress fluid fraction within the starch-based composition. In a two-step mixing process, a preblended mixture is formed by gelating a portion of the starch-based binder or other thickening agent in water to form a liquid phase having high yield stress into which the fibers are substantially uniformly dispersed. The fibers preferably have an average length of at least about 2 mm and an aspect ratio of at least about 25:1. The remaining starch-based binder, water, and other desired admixtures, such as mold-release agents, inorganic fillers, rheology-modifying agents, plasticizers, integral coating or sealing materials, and dispersants, are added to the preblended mixture to form a moldable starch-based composition, which is molded between heated molds to produce form-stable articles having a desired shape and a selectively controlled foamed structural matrix. Such articles can replace articles presently made from conventional materials like paper, paperboard, polystyrene, plastic, or other organic-based materials and have especial utility in the mass-production of containers, particularly food and beverage containers.

90 Claims, 34 Drawing Sheets

The present invention may be embodied in other specific forms without departing from its spirit or essential characteristics. The described embodiments are to be considered in all respects only as illustrated and not restrictive. The scope of the invention is, therefore, indicated by the appended claims rather than by the foregoing description. All changes which come within the meaning and range of equivalency of the claims are to be embraced within their scope.

What is claimed and desired to be secured by United States Letters Patent is:

1. A fiber-filled, starch-based composition for molding into a shaped article of manufacture having a cellular matrix, the composition comprising a starch-based binder, water, a thickening agent, and fibers having an average aspect ratio greater than about 25:1, wherein the starch-based binder comprises unmodified starch and remains substantially ungelatinized prior to molding, wherein the water and thickening agent comprise a fluid fraction having a yield stress in a range from about 10 Pa to about 5000 Pa such that the fibers are substantially uniformly dispersed throughout the starch-based composition, wherein the starch-based composition forms the cellular matrix during molding upon substantial gelation of the starch-based binder and subsequent removal of at least a portion of the water from the starch-based composition by evaporation.

2. A fiber-filled, starch-based composition as defined in claim **1**, wherein the fluid fraction has a yield stress in a range from about 20 Pa to about 2000 Pa.

3. A fiber-filled, starch-based composition as defined in claim **1**, wherein the fluid fraction has a yield stress in a range from about 50 Pa to about 1000 Pa.

4. A fiber-filled, starch-based composition as defined in claim **1**, wherein the fluid fraction has a yield stress in a range from about 100 Pa to about 500 Pa.

5. A fiber-filled, starch-based composition as defined in claim **1**, wherein the fluid fraction has an apparent viscosity measured at a shear rate of 5 s^{-1} in a range from about 5 Pa.s to about 1000 Pa.s.

6. A fiber-filled, starch-based composition as defined in claim **1**, wherein the fluid fraction has an apparent viscosity measured at a shear rate of 5 s^{-1} in a range from about 10 Pa.s to about 500 Pa.s.

7. A fiber-filled, starch-based composition as defined in claim **1**, wherein the fluid fraction has an apparent viscosity measured at a shear rate of 5 s^{-1} in a range from about 30 Pa.s to about 200 Pa.s.

8. A fiber-filled, starch-based composition as defined in claim **1**, wherein the starch-based composition has a yield stress in a range from about 250 Pa to about 4000 Pa.

9. A fiber-filled, starch-based composition as defined in claim **1**, wherein the starch-based composition has a yield stress in a range from about 500 Pa to about 3000 Pa.

10. A fiber-filled, starch-based composition as defined in claim **1**, wherein the starch-based composition has a yield stress in a range from about 1000 Pa to about 2000 Pa.

11. A fiber-filled, starch-based composition as defined in claim **1**, wherein the starch-based composition has an apparent viscosity measured at a shear rate of 5 s^{-1} in a range from about 50 Pa.s to about 2000 Pa.s.

12. A fiber-filled, starch-based composition as defined in claim **1**, wherein the starch-based composition has an apparent viscosity measured at a shear rate of 5 s^{-1} in a range from about 100 Pa.s to about 1000 Pa.s.

13. A fiber-filled, starch-based composition as defined in claim **1**, wherein the starch-based composition has an apparent viscosity measured at a shear rate of 5 s^{-1} in a range from about 300 Pa.s to about 600 Pa.s.

14. A fiber-filled, starch-based composition as defined in claim **1**, wherein the starch-based binder includes a potato starch or potato starch derivative.

15. A fiber-filled, starch-based composition as defined in claim **1**, wherein the starch-based binder includes a waxy corn starch or waxy corn starch derivative.

16. A fiber-filled, starch-based composition as defined in claim **1**, wherein the thickening agent includes a modified starch that provides a portion of the binder upon molding the composition into the article.

17. A fiber-filled, starch-based composition as defined in claim **16**, wherein the thickening agent includes a starch that has been modified by a process selected from the group consisting of esterification, etherification, oxidation, acid hydrolysis, cross-linking, and enzyme conversion.

18. A fiber-filled, starch-based composition as defined in claim **1**, wherein the starch-based binder has a concentration in a range from about 5% to about 50% by weight of the starch-based composition.

19. A fiber-filled, starch-based composition as defined in claim **1**, wherein the starch-based binder has a concentration in a range from about 10% to about 40% by weight of the starch-based composition.

20. A fiber-filled, starch-based composition as defined in claim **1**, wherein the starch-based binder has a concentration in a range from about 15% to about 30% by weight of the starch-based composition.

21. A fiber-filled, starch-based composition as defined in claim **1**, wherein the starch-based binder has a concentration in a range from about 10% to about 80% by weight of total solids in the starch-based composition.

22. A fiber-filled, starch-based composition as defined in claim **1**, wherein the starch-based binder has a concentration in a range from about 30% to about 70% by weight of total solids in the starch-based composition.

23. A fiber-filled, starch-based composition as defined in claim **1**, wherein the starch-based binder has a concentration in a range from about 40% to about 60% by weight of total solids in the starch-based composition.

24. A fiber-filled, starch-based composition as defined in claim **1**, wherein the starch-based binder has an amylose content of less than about 45%.

25. A fiber-filled, starch-based composition as defined in claim **1**, wherein the starch-based binder has an amylose content of less than about 35%.

26. A fiber-filled, starch-based composition as defined in claim **1**, wherein the starch-based binder has an amylose content of less than about 25%.

27. A fiber-filled, starch-based composition as defined in claim **1**, wherein the water has a concentration in a range from about 15% to about 80% by weight of the starch-based composition.

28. A fiber-filled, starch-based composition as defined in claim **1**, wherein the water has a concentration in a range from about 30% to about 70% by weight of the starch-based composition.

29. A fiber-filled, starch-based composition as defined in claim **1**, wherein the thickening agent comprises a gelatinized starch-based binder.

30. A fiber-filled, starch-based composition as defined in claim **1**, wherein the thickening agent comprises a cellulosic ether.

31. A fiber-filled, starch-based composition as defined in claim **30**, wherein the cellulosic ether is selected from the group consisting of methylhydroxyethylcellulose, hydroxymethylethylcellulose, carboxymethylcellulose, methylcellulose, ethylcellulose, hydroxyethylcellulose,

hydroxyethylpropylcellulose, hydroxypropylmethylcellulose, and mixtures or derivatives thereof.

32. A fiber-filled, starch-based composition as defined in claim 1, wherein the thickening agent comprises a polysaccharide or a polysaccharide derivative.

33. A fiber-filled, starch-based composition as defined in claim 32, wherein the polysaccharide or polysaccharide derivative is selected from the group consisting of alginic acid, phycocolloids, agar, gum arabic, guar gum, locust bean gum, gum karaya, xanthan gum, gum tragacanth, and mixtures or derivatives thereof.

34. A fiber-filled, starch-based composition as defined in claim 1, wherein the thickening agent is a protein or a protein derivative.

35. A fiber-filled, starch-based composition as defined in claim 34, wherein the protein or protein derivative is selected from the group consisting of a prolamine, collagen, gelatin, casein, and mixtures or derivatives thereof.

36. A fiber-filled, starch-based composition as defined in claim 1, wherein the thickening agent is a synthetic organic material.

37. A fiber-filled, starch-based composition as defined in claim 36, wherein the synthetic organic material is selected from the group consisting of polyvinyl pyrrolidone, polyethylene glycol, polyvinyl alcohol, polyvinylmethyl ether, polyacrylic acids, polyacrylic acid salts, polyvinyl acrylic acids, polyvinyl acrylic acid salts, polyacrylamides, ethylene oxide polymers, polylactic acid, latex, and mixtures or derivatives thereof.

38. A fiber-filled, starch-based composition as defined in claim 1, wherein the fibers include naturally occurring organic fibers.

39. A fiber-filled, starch-based composition as defined in claim 1, wherein the fibers include cellulosic fibers.

40. A fiber-filled, starch-based composition as defined in claim 1, wherein the fibers are derived from at least one fiber source selected from the group consisting of plant leaves, stems, husks, shells, and fruits.

41. A fiber-filled, starch-based composition as defined in claim 1, wherein the fibers are derived from a fiber source selected from the group consisting of hemp, cotton, sisal, abaca, and bagasse.

42. A fiber-filled, starch-based composition as defined in claim 1, wherein the fibers are derived from hardwood.

43. A fiber-filled, starch-based composition as defined in claim 1, wherein the fibers are derived from softwood.

44. A fiber-filled, starch-based composition as defined in claim 1, wherein the fibers include inorganic fibers.

45. A fiber-filled, starch-based composition as defined in claim 1, wherein the fibers are derived from a material selected from the group consisting of glass, graphite, silica, ceramic, and metal.

46. A fiber-filled, starch-based composition as defined in claim 1, wherein the fibers include recycled paper fibers.

47. A fiber-filled, starch-based composition as defined in claim 1, wherein the fibers have a concentration in a range from about 1% to about 40% by weight of the starch-based composition.

48. A fiber-filled, starch-based composition as defined in claim 1, wherein the fibers have a concentration in a range from about 2% to about 20% by weight of the starch-based composition.

49. A fiber-filled, starch-based composition as defined in claim 1, wherein the fibers have a concentration in a range from about 3% to about 10% by weight of the starch-based composition.

50. A fiber-filled, starch-based composition as defined in claim 1, wherein the fibers have a concentration in a range from about 2% to about 80% by weight of total solids within the starch-based composition.

51. A fiber-filled, starch-based composition as defined in claim 1, wherein the fibers have a concentration in a range from about 4% to about 40% by weight of total solids within the starch-based composition.

52. A fiber-filled, starch-based composition as defined in claim 1, wherein the fibers have a concentration in a range from about 5% to about 20% by weight of total solids within the starch-based composition.

53. A fiber-filled, starch-based composition as defined in claim 1, wherein the fibers have an aspect ratio of at least about 25:1.

54. A fiber-filled, starch-based composition as defined in claim 1, wherein the fibers have an aspect ratio of at least about 100:1.

55. A fiber-filled, starch-based composition as defined in claim 1, wherein the fibers have an aspect ratio of at least about 250:1.

56. A fiber-filled, starch-based composition as defined in claim 1, wherein the fibers have an average length in a range from about 0.3 mm to about 2 mm.

57. A fiber-filled, starch-based composition as defined in claim 1, wherein the fibers have an average length of at least about 2 mm.

58. A fiber-filled, starch-based composition as defined in claim 1, wherein the fibers have an average length of at least about 3.5 mm.

59. A fiber-filled, starch-based composition as defined in claim 1, wherein the fibers have an average length of at least about 6.5 mm.

60. A fiber-filled, starch-based composition as defined in claim 1, further comprising an inorganic aggregate filler.

61. A fiber-filled, starch-based composition as defined in claim 60, wherein the inorganic aggregate filler includes calcium carbonate.

62. A fiber-filled, starch-based composition as defined in claim 60, wherein the inorganic aggregate filler is selected from the group consisting of sand, gravel, rock, limestone, sandstone, glass beads, mica, clay, kaolin, synthetic clay, alumina, silica, fly ash, fused silica, tabular alumina, microspheres, calcium sulfate dihydrate, calcium aluminate, hydrated hydraulic cement particles, and unhydrated hydraulic cement particles.

63. A fiber-filled, starch-based composition as defined in claim 60, wherein the inorganic aggregate filler is selected from the group consisting of perlite, vermiculite, hollow glass spheres, aerogels, xerogels, porous ceramic spheres, xonotlite, lightweight expanded clays, pumice, and exfoliated rock.

64. A fiber-filled, starch-based composition as defined in claim 60, wherein the inorganic aggregate filler has a concentration in a range from about 20% to about 80% by weight of total solids in the starch-based composition.

65. A fiber-filled, starch-based composition as defined in claim 60, wherein the inorganic aggregate filler has a concentration in a range from about 30% to about 70% by weight of total solids in the starch-based composition.

66. A fiber-filled, starch-based composition as defined in claim 60, wherein the inorganic aggregate filler has a concentration in a range from about 40% to about 60% by weight of total solids in the starch-based composition.

67. A fiber-filled, starch-based composition as defined in claim 60, wherein the inorganic aggregate filler has a specific surface area in a range from about 0.1 m^2/g to about 400 m^2/g.

68. A fiber-filled, starch-based composition as defined in claim 60, wherein the inorganic aggregate filler has a specific surface area in a range from about 0.15 m^2/g to about 50 m^2/g.

69. A fiber-filled, starch-based composition as defined in claim 60, wherein the inorganic aggregate filler has a specific surface area in a range from about 0.2 m^2/g to about 2 m^2/g.

70. A fiber-filled, starch-based composition as defined in claim 60, wherein the inorganic aggregate filler has a natural packing density in a range from about 0.5 to about 0.9.

71. A fiber-filled, starch-based composition as defined in claim 60, wherein the inorganic aggregate filler has a natural packing density in a range from about 0.6 to about 0.8.

72. A fiber-filled, starch-based composition as defined in claim 1, further comprising a mold release agent.

73. A fiber-filled, starch-based composition as defined in claim 72, wherein the mold release agent includes a salt of a fatty acid.

74. A fiber-filled, starch-based composition as defined in claim 72, wherein the mold release agent includes magnesium stearate.

75. A fiber-filled, starch-based composition as defined in claim 1, further comprising a humectant.

76. A fiber-filled, starch-based composition as defined in claim 1, further comprising a dispersant.

77. A fiber-filled, starch-based composition as defined in claim 1, further comprising an enzyme to increase the rate of gelation of the starch-based binder.

78. A fiber-filled, starch-based composition as defined in claim 1, further comprising an integral coating material.

79. A fiber-filled, starch-based composition as defined in claim 78, wherein the integral coating material is capable of migrating to the surface of an article formed by molding the starch-based composition between heated molds.

80. A fiber-filled, starch-based composition as defined in claim 1, further comprising an integral sealing material.

81. A fiber-filled, starch-based composition as defined in claim 80, wherein the integral sealing material comprises polyvinyl alcohol.

82. A fiber-filled, starch-based composition as defined in claim 1, further comprising a plasticizer.

83. A fiber-filled, starch-based composition for molding a shaped article of manufacture having a cellular matrix, the composition comprising a first starch-based binder component in a substantially gelatinized state, a second starch-based binder component including unmodified starch in a substantially ungelatinized state, water, and fibers having an average aspect ratio of at least about 25:1 and a concentration in a range from about 2% to about 80% by weight of the starch-based composition, the water and first starch-based binder component comprising a fluid fraction having a yield stress in a range from about 10 Pa to about 5000 Pa such that the fibers are substantially uniformly dispersed throughout the starch-based composition, wherein the starch-based composition forms the cellular matrix during molding upon substantial gelation of the second starch-based binder component and subsequent removal of at least a portion of the water from the starch-based composition by evaporation.

84. A fiber-filled, starch-based composition for molding a shaped article of manufacture having a cellular matrix, the composition comprising a starch-based binder including unmodified starch that is substantially ungelatinized prior to molding, water, a thickening agent, an inorganic filler having a concentration in a range from about 20% to about 80% by weight of solids within the starch-based composition, and fibers having an average aspect ratio of at least about 25:1 and a concentration in a range from 2% to about 80% by weight of solids within the starch-based composition, the water and thickening agent comprising a fluid fraction having a yield stress such that the fibers are substantially uniformly dispersed throughout the starch-based composition, the composition forming the cellular matrix during molding upon substantial gelation of the starch-based binder and subsequent removal of at least a portion of the water from the starch-based composition by evaporation.

85. A fiber-filled, starch-based composition as defined in claim 84, wherein the thickening agent includes a substantially gelatinized starch-based binder.

86. A fiber-filled, starch-based composition for molding a shaped article of manufacture having a cellular matrix, the composition comprising a fluid fraction prior to molding and solids dispersed therein, the fluid fraction comprising water, a mold releasing agent, and a substantially gelatinized starch-based binder in a concentration such that the fluid fraction has a yield stress greater than about 100 Pa, the solids comprising a substantially ungelatinized starch-based binder including unmodified starch, an inorganic aggregate filler having a concentration in a range from about 5% to about 50% by weight of the starch-based composition, and fibers having an average aspect ratio of at least 25:1, an average length of at least about 2 mm, and a concentration in a range from about 2% to about 40% by weight of the starch-based composition, the substantially gelatinized starch-based binder and the substantially ungelatinized starch-based binder together having a combined concentration in a range from about 5% to about 50% by weight of the starch-based composition, the fluid fraction having a yield stress such that the fibers are substantially uniformly dispersed throughout the starch-based composition, the composition forming the cellular matrix during molding upon substantial gelation of the ungelatinized starch-based binder and subsequent removal of at least a portion of the water from the starch-based composition by evaporation.

87. A fiber-filled, starch-based composition for molding into a shaped article of manufacturing having a cellular matrix, the composition comprising a starch-based binder including unmodified starch that is substantially ungelated prior to molding, water having a concentration greater than about 30% by weight of the starch-based composition, a thickening agent, and fibers having an average length greater than 1.5 mm and an average aspect ratio greater than about 25:1, the water and thickening agent comprising a fluid fraction having a yield stress such that the fibers are substantially uniformly dispersed throughout the starch-based composition, the composition forming the cellular matrix during molding upon substantial gelation of the starch-based binder and subsequent removal of at least a portion or the water from the starch-based composition by evaporation.

88. A fiber-filled, starch-based composition as defined in claim 87, wherein the water has a concentration greater than about 50% by weight of the starch-based composition.

89. A fiber-filled, starch-based composition for molding into a shaped article of manufacture having a cellular matrix, the composition comprising a starch-based binder including unmodified starch having an amylose content less than about 45% and that is substantially ungelated prior to molding, water, a thickening agent, and fibers having an average length greater than 1.5 mm and an average aspect ratio greater than about 25:1, the water and thickening agent comprising a fluid fraction having a yield stress such that the fibers are substantially uniformly dispersed throughout the starch-based composition, the composition forming the cellular matrix during molding upon substantial gelation of the

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United States Patent [19]

Sinclair et al.

[11] Patent Number: 5,444,113

[45] Date of Patent: * Aug. 22, 1995

[54] END USE APPLICATIONS OF BIODEGRADABLE POLYMERS

[75] Inventors: **Richard G. Sinclair**, Columbus; **Edward S. Lipinsky**, Worthington; **James D. Browning; Donald Bigg**, both of Columbus, all of Ohio; **Thomas A. Rogers**, Golden, Colo.

[73] Assignee: **Ecopol, LLC**, Golden, Colo.

[*] Notice: The portion of the term of this patent subsequent to Jan. 19, 2010 has been disclaimed.

[21] Appl. No.: **128,520**

[22] Filed: **Sep. 29, 1993**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 950,854, Sep. 22, 1992, which is a continuation-in-part of Ser. No. 579,000, Sep. 6, 1990, Pat. No. 5,216,050, Ser. No. 579,005, Sep. 6, 1990, Pat. No. 5,180,765, Ser. No. 579,460, Sep. 6, 1990, Pat. No. 5,252,642, and Ser. No. 579,465, Sep. 6, 1990, which is a continuation-in-part of Ser. No. 387,670, Jul. 31, 1989, abandoned, which is a continuation-in-part of Ser. No. 229,939, Aug. 8, 1988, abandoned, said Ser. No. 579,000, is a continuation-in-part of Ser. No. 387,676, Jul. 31, 1989, abandoned, which is a continuation-in-part of Ser. No. 229,894, Aug. 8, 1988, abandoned, said Ser. No. 579,005, is a continuation-in-part of Ser. No. 387,678, Jul. 31, 1989, abandoned, which is a continuation-in-part of Ser. No. 229,896, Aug. 8, 1988, abandoned, said Ser. No. 579,460, is a continuation-in-part of Ser. No. 386,844, Jul. 31, 1989, abandoned, which is a continuation-in-part of Ser. No. 317,391, Mar. 1, 1989, abandoned.

[51] **Int. Cl.**[6] **C08K 5/10**

[52] **U.S. Cl.** **524/306**; 524/310; 524/315; 524/317; 524/320; 523/124; 528/354; 528/361

[58] **Field of Search** 524/306, 310, 315, 317, 524/320; 523/124; 528/354, 361

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(List continued on next page.)

Primary Examiner—Paul R. Michl
Assistant Examiner—Edward J. Cain
Attorney, Agent, or Firm—Sheridan Ross & McIntosh

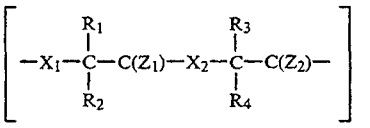
[57] **ABSTRACT**

Disclosed are products made of degradable materials which include a hydrolytically degradable polymer. The degradable materials can be internally or externally modified. The internally modified polymer composition has polymers modified by the use of comonomers having a relatively high molecular weight. The externally modified polymer composition includes a modifier, wherein the modifier is compatible with the polymer and the modifier is nontoxic, nonvolatile and nonfugitive. The various degradable materials include films, fibers, extruded and molded products, laminates, foams, powders, nonwovens, adhesives and coatings. The disclosed materials are particularly useful for the production of a variety of products in high volumes which are suitable for recycling after use or which are discarded into the environment in large volumes.

22 Claims, No Drawings

(a) a backbone chain;

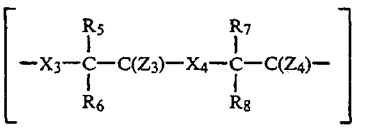
(b) first repeating units of the formula



where, independently for each such first repeating unit:

X_1 and X_2 are independently O or NR' and R' is independently H, hydrocarbyl, substituted hydrocarbyl or a hydrocarbyl derivative; R_1, R_2 and Z_1 combined have at most one carbon atom; R_3, R_4 and Z_2 combined have at most one carbon atom; Z_1 and Z_2 are each independently one or more constituent group extending from the backbone chain and being covalently bonded to an associated carbon atom in the backbone chain, at least one of Z_2 and Z_2 being oxygen which forms a carbonyl group with the associated carbon atom in the backbone chain; and the molecular weight of such a first repeating unit is less than about 145; and

(c) from about 1 weight percent to about 50 weight percent, based on the total weight of said polymer, of second repeating units of the formula

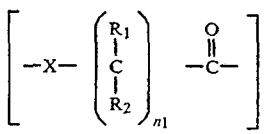


where, independently for each such second repeating unit:

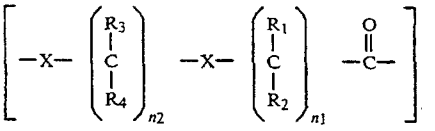
X_3 and X_4 are independently O or NR' and R' is independently H, hydrocarbyl, substituted hydrocarbyl or a hydrocarbyl derivative; R_5, R_6, R_7 and R_8 combined have at least four carbon atoms; Z_3 and Z_4 are each independently one or more constituent group extending from the backbone chain and being covalently bonded to an associated carbon atom in the backbone chain, at least one of Z_3 and Z_4 being oxygen which forms a carbonyl group with the associated carbon atom in the backbone chain.

10. A clothing product comprising a hydrolytically degradable polymer and a modifier, wherein said modifier is compatible with said polymer and is non-volatile and non-fugitive and wherein said polymer comprises repeating monomer or comonomer units selected from the group consisting of:

i)



ii)



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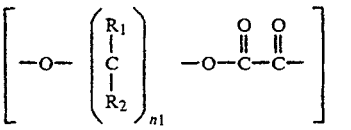
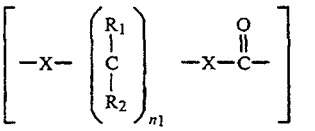
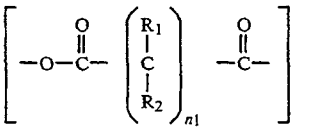
iii)



iv)



v)

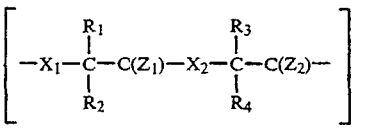


wherein X is the same or different and is O or NR' with R' being the same or different and being hydrocarbyl, or substituted hydrocarbyl; R_1, R_2, R_3 and R_4 can be the same or different and are hydrogen, hydrocarbyl containing 1 to 24 carbon atoms, or substituted hydrocarbyl containing 1 to 24 carbon atoms, and where n_1 and n_2 can be the same or different and are an integer of from 1–12.

11. A clothing product comprising a hydrolytically degradable polymer, said polymer comprising:

(a) a backbone chain;

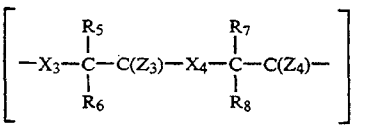
(b) first repeating units of the formula



where, independently for each such first repeating unit:

X_1 and X_2 are independently O or NR' and R' is independently H, hydrocarbyl, substituted hydrocarbyl or a hydrocarbyl derivative; R_1, R_2 and Z_1 combined have at most one carbon atom; R_3, R_4 and Z_2 combined have at most one carbon atom; Z_1 and Z_2 are each independently one or more constituent group extending from the backbone chain and being covalently bonded to an associated carbon atom in the backbone chain, at least one of Z_1 and Z_2 being oxygen which forms a carbonyl group with the associated carbon atom in the backbone chain; and the molecular weight of such a first repeating unit is less than about 145; and

(c) from about 1 weight percent to about 50 weight percent, based on the total weight of said polymer, of second repeating units of the formula



where, independently for each such second repeating unit:

X_3 and X_4 are independently O or NR' and R' is independently H, hydrocarbyl, substituted hydro-

290

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

RADICACIÓN: **0-16913** EDICTO No. **12998**

LA SECRETARÍA GENERAL AD-HOC
HACE SABER:

Que esta Superintendencia profirió **Resolución** No. **22974** de **19-SEP-2005**. Que el contenido de la parte resolutiva es como sigue: El Superintendente de Industria y Comercio.

RESUELVE

ARTICULO PRIMERO: Negar el privilegio de patente de invención para la solicitud correspondiente a "ESTRUCTURA ABSORBENTE, FLEXIBLE QUE COMPRENDE FIBRAS DE ALMIDON".

ARTICULO SEGUNDO: Notificar personalmente el contenido de la presente resolución a la doctora Jimena Escobar Uribe, o a quien haga sus veces, en su calidad de apoderada de Humatro Corporation., entregándole copia de la misma, advirtiéndole que contra ella procede el recurso de reposición interpuesto ante el Superintendente de Industria y Comercio, al momento de la notificación o dentro de los 5 días hábiles siguientes a ella.

NOTIFÍQUESE Y CUMPLASE
Dada en Bogotá, D.C., a los 19 SET. 2005

EL SUPERINTENDENTE DE INDUSTRIA Y COMERCIO,

JAIRO RUBIO ESCOBAR

Para notificar a los interesados, se fija el presente EDICTO en lugar visible al público en la SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO, por el término de (10) diez días hábiles contados a partir de las 8:30 a.m. de hoy.

Secretaría General Ad-Hoc **04-OCT-2005** Este edicto se desfija hoy **18-OCT-2005** a las cinco (5:00 p.m.)
Secretaría General Ad-Hoc
EDICTO No. **12998**