

SEÑORES

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

DIVISIÓN DE NUEVAS CREACIONES

E. _____ S. _____ D. _____

Ref.: Expediente N°. 05-102.552

**Solicitud de Patente de Invención Titulada: "MATERIAL TERMOPLASTICO DE
REFUERZO PARA LA PRODUCCION DE CALZADO Y PROCESO RELACIONADO
CON EL MISMO"**

Solicitante: BK GIULINI GMBH.**RESPUESTA AL OFICIO N°. 10419 NOTIFICADO****POR FIJACION EN LISTA No. 438, DE FECHA 4 DE NOVIEMBRE DE 2005,****(EXAMEN DE FORMA)**

CARLOS R. OLARTE, mayor de edad y vecino de Bogotá, identificado tal como aparece al pie de mi firma, en mi carácter de apoderado de la sociedad en referencia, me permito dar respuesta al auto proferido por ese Despacho, dentro del término de prórroga solicitado en mi memorial de fecha 20 de diciembre de 2005, en los siguientes términos:

1. En respuesta a la primera observación del Examinador, me permito aclarar al despacho que la presente solicitud entra en Fase Nacional Capítulo I y no Capítulo II como inicialmente se presentó. Por lo tanto una copia de los anexos no será presentada ya que no fue solicitado el Examen Preliminar Internacional.
2. En respuesta a la segunda observación del Examinador, me permito aportar junto al presente memorial, el documento de cesión debidamente legalizado, junto con su correspondiente traducción, según lo previsto en el Art. 26- k de la Decisión 486.

OLARTE RAISBECK
OLARTE RAISBECK & FRIER, LTDA.

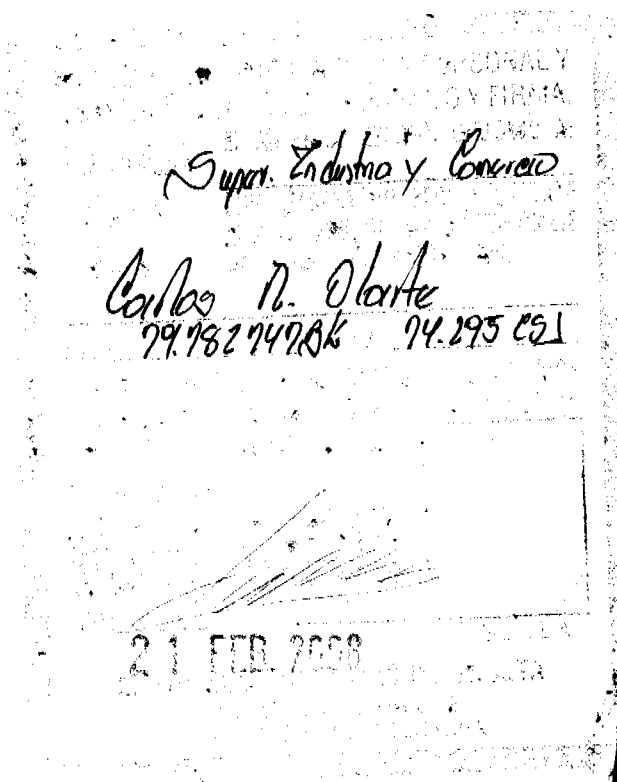
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En respuesta a la tercera observación del Examinador, me permito adjuntar copia auténtica del poder a mi conferido por mi representada según lo previsto en los Artículos 63 y subsiguientes del Código de Procedimiento Civil.

Atentamente,

CARLOS R. OLARTE
C.C. No. 79.782.747 de Bogotá
T.P. 74.295

Anexo: Documento de Cesión
Poder



BOGOTA D.C. FEBRERO 02, 2006

TRADUCCION CONTENIDOS EN INGLES AL IDIOMA CASTELLANO (FOTOCOPIA)

COLOMBIA

(DOCUMENTO DE CESION, Contenido en Castellano)

(Hoja Anexa en Inglés)

U.R. NR. 2635/2005

Yo, Ludwig Draxel-Fischer, Notario Público en Ludwigshafe/Rhine, Republica Federal de Alemania, con el presente certifico y confirmo que las siguientes formas de

1. Sr. Emil Siegfried Wilding, nacido Diciembre 1, 1944, Técnico Textil, residente en SudetenstraBe 1, 67134 Birkenheide, República Federal de Alemania personalmente conocido para mi,
2. Químico Graduado Dr. Markis Wolfgang Fath, nacido en Diciembre 13, 1964, Químico, residente el Karlrader-Str. 7, República Federal de Alemania, pesonalmente conocido para mi,
3. Sr. Stefan Frey, nacido Agosto 05, 1967, Químico-Técnico, residente en HSH-Str 8, 67310, Hetteleidelberg, República Federal de Alemania personalmente conocido para mi,

son auténticas y válidas

Ludwigshafen/Rhine, Hoy octubre 20, 2005.

(FIRMADO) Notario Público.

(Anexa Apostilla N. 91 Eb -1247/05, de Noviembre 16, 2005, en Idioma Alemán.

Fidel Murcia
FIDEL ANTONIO MURCIA MURCIA
Traductor e Intérprete Oficial
Resolución Nr. 488/94 Ministerio de Justicia



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A P O S T I L L E

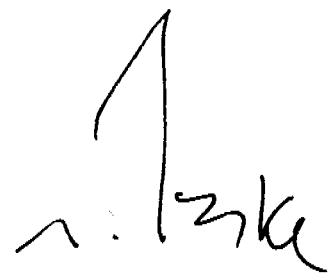
(Convention de la Haye du 5 octobre 1961)

1. País: República Federal de Alemania
El presente documento público
2. ha sido firmado por el notario Draxel - Fischer
3. actuando en calidad de: Notario público
4. lleva el sello/estampilla del Notario Ludwig Draxel-Fischer en
Ludwigshafen am Rhein

C e r t i f i c a d o

- | | |
|--|---|
| 5. en: Frankenthal | 6. el: 16 de noviembre de 2005 |
| 7. por: el Presidente del Tribunal Regional | |
| 8. bajo el No.: 91Eb - 1247/2005 | |
| 9. Sello / Estampilla
(Sello del Presidente del Tribunal
Regional) | 10. Firmado
Christian Köneke
Juez del Tribunal Regional |

Costos notariales por valor de 13,50 Euros



ADOLF WATZKE
Traductor Oficial
Res. 2433 Minjusticia

**DOCUMENTO DE CESIÓN
ASSIGNMENT DOCUMENT**

Los suscritos,
(We the undersigned)

- 1) EMIL WILDING
con domicilio en Birkenheide, Alemania
(domiciled in)
- 2) MARKUS FATH
con domicilio en Limburgerhof, Alemania
(domiciled in)
- 3) STEFAN FREY
con domicilio en Hettenleidelheim, Alemania
(domiciled in)

declaramos que somos los inventores de la invención que lleva el título
(declare that we are the inventors of the invention titled)

**THERMOPLASTIC STIFFERING MATERIAL USED FOR MANUFACTURING SHOES AND
A METHOD FOR THE PRODUCTION THEREOF**

**MATERIAL TERMOPLÁSTICO DE REFUERZO PARA LA PRODUCCIÓN DE CALZADO Y
PROCESO RELACIONADO CON EL MISMO**

y que hemos cedido el derecho sobre esta invención en Colombia, junto con los privilegios
(and that we have assigned our rights over this invention in Colombia, together with its
privileges)

y anexidades a favor de
(and attachments, to)

BK GIULINI GMBH LUDWIGSHAFEN.

1)

3)

2)

LUDWIGSHAFEN, den 12.10.2005

U.R.Nr. 2635/2005

I, Ludwig Draxel-Fischer, notary public at Ludwigshafen/Rhine, Federal Republic of Germany, hereby testify and confirm that the foregoing signatures of

1. Mr. Emil Siegfried **Wilding**, born on December 1, 1944, textile-technician, residing at Sudetenstraße 1, 67134 Birkenheide, Federal Republic of Germany, personally known to me,
2. graduate chemist Dr. Markus Wolfgang **Fath**, born on December 13, 1964, chemist, residing at Karl-Räder-Str. 7, Federal Republic of Germany, personally known to me,
3. Mr. Stefan **Frey**, born on August 5, 1967, chemotechnician, residing at HSH-Str. 8, 67310 Hettenleidelheim, Federal Republic of Germany, personally known to me,

are true and valid.

Ludwigshafen/Rhine, this 20th day of October, 2005


notary public

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APOSTILLE

(Convention de La Haye du 5 octobre 1961)

1. Land : Bundesrepublik Deutschland
Diese öffentliche Urkunde
2. ist unterschrieben von Notar
D r a x e l - F i s c h e r
3. in seiner Eigenschaft als
öffentlicher Notar
4. sie ist versehen mit dem Siegel/Stempel
des Notars Ludwig Draxel-Fischer
in Ludwigshafen am Rhein

Bestätigt

5. in Frankenthal (Pfalz)
6. am 16. November 2005
7. durch den Präsidenten des Landgerichts
8. unter Nr. 91 Eb - 1247/05

9. Siegel/Stempel:
10. Unterschrift
Im Auftrag

.....
(Christian Köneke)
Richter am Landgericht

Kostenvermerk:
Gebühr 13,50 €

Handwritten signature or mark.



ACTUACION NOTARIAL



N 005700801

FOLIO 579.- PRIMERA COPIA.- ESCRITURA NUMERO: CIENTO CUARENTA Y NUEVE.- SUSTITUCIÓN PARCIAL DE PODER: MESSERER, Dagmar a favor de OLARTE, Carlos Reinaldo y otro del poder otorgado por BK GIULINI GmbH.- En la Ciudad Autónoma de Buenos Aires, Capital de la República Argentina, el día VEINTE de DICIEMBRE del año DOS MIL CINCO, ante mí María Silvina LASARTE, Escribana Autorizante, titular del Registro Notarial número 1788, COMPARECE: Dagmar MESSERER, argentina, nacida el 28 de mayo de 1.968, hija de Walter Messerer y Elsa Onelia Romanelli, soltera, titular del Documento Nacional de Identidad Número 20.383.892, Clave Única de Identificación Tributaria número 27-20383892-7, domiciliada legalmente en la Avenida Leandro N. Alem 1.134, Piso 10º, de esta Ciudad, persona capaz y de mi conocimiento personal, doy fe.- INTERVIENE: por su propio derecho.- Y la compareciente EXPRESA: PRIMERO: Que la Sociedad "BK GIULINI GmbH", con domicilio Giulini Strasse 2, 67065 Ludwigshafen, Alemania, le otorgó en dicho país, un Poder, el cual mediante escritura número 146, de fecha 19 de diciembre del corriente año, otorgada ante mí, al folio 567, protocolo corriente, de este Registro Notarial Número 1788 a mi cargo, fue incorporado y transcripto a dicho protocolo, cuya primera copia tengo para este acto a la vista, doy fe y en lo pertinente transcribiré en la presente.- SEGUNDO: Manifiesta bajo juramento que el referido poder se encuentra plenamente vigente en virtud de no haberle sido revocado, suspendido ni limitado en ninguna de sus partes.- TERCERO: En consecuencia DICE: Que en uso de la facultad conferida SUSTITUYE PARCIALMENTE el poder mencionado a favor de Carlos Reinaldo OLARTE y/o James Ian RAISBECK al solo y único objeto de que en nombre y representación de la Sociedad "BK GIULINI GmbH", y actuando en forma individual y/o alternadamente, se presenten exclusivamente ante las autoridades de COLOMBIA

CECBA - LEY 404 GCBA
LEGALIZACION

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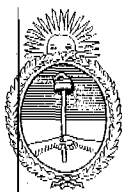
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CECBA - LEY 404 GCBA
APOSTILLA

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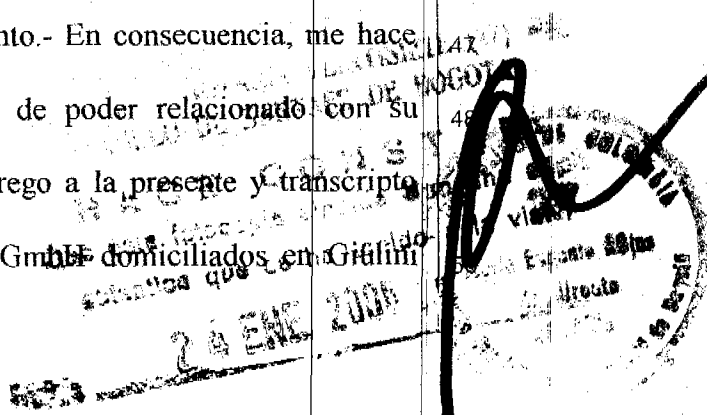
N 005700801

que correspondan, y realicen a tal efecto los actos enumerados en el citado poder y con las facultades que surgen del mismo el que transcripto en lo pertinente dice: "...

ESCRITURA NÚMERO: CIENTO CUARENTA Y SEIS.- ... En la Ciudad Autónoma de Buenos Aires, ..., el día DIECINUEVE de DICIEMBRE del año DOS MIL CINCO, ante mí ... COMPARECE: Dagmar MESSERER, argentina, nacida el 28 de mayo de 1.968, hija de Walter Messerer y Elsa Onelia Romanelli, soltera, titular del Documento Nacional de Identidad Número 20.383.892, Clave Única de Identificación Tributaria número 27-20383892-7, domiciliada legalmente en la Avenida Leandro N. Alem 1.134, Piso 10º, de esta Ciudad de Buenos Aires.- La compareciente es mayor de edad y de mi conocimiento personal, doy fe.-

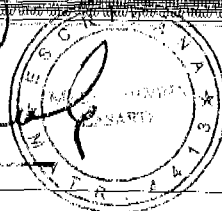
INTERVIENE: por su propio derecho y la compareciente, EXPRESA: Que a los efectos que hubiere lugar, solicita de mí, la Autorizante, LA INCORPORACIÓN y TRANSCRIPCIÓN en este protocolo del PODER que le fuera conferido el 20 de octubre de 2005, por la Sociedad "BK GIULINI GmbH", con domicilio en Giulini Strasse 2, 67065 Ludwigshafen, Alemania, sobre cuya plena vigencia responde la requirente bajo juramento.- Yo, la Autorizante, hago constar: a) Que el instrumento de poder cuya incorporación y transcripción a este protocolo solicita la compareciente, se encuentra extendido en idioma castellano e inglés, certificadas las firmas por notario en idioma inglés, legalizado en idioma alemán (Sello de Apostilla de la Convención de La Haya del 5 de octubre de 1961) y traducido en lo pertinente al idioma nacional por la Traductora Pública Laura Thieberger.- b) Que la compareciente en virtud de lo manifestado tiene interés legítimo en su requerimiento.- En consecuencia, me hace

entrega en este acto del original del instrumento de poder relacionado con su respectiva traducción al idioma nacional, el que agrego a la presente y transcripto dice: "PODER Los abajo firmante/s BK GIULINI GmbH domiciliados en Giulini



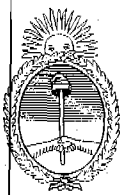


ACTUACION NOTARIAL



N 005700802

1 Strasse 2, 67065 Ludwigshafen, Alemania declaran por el presente otorgar a Dagmar
2 MESSERER indistintamente poder general amplio y suficiente para recabar de las
3 autoridades ..., sud y centroamericanas ... que correspondan, la obtención de patentes
4 de invención, el registro y la renovación de marcas y modelos y/o derechos de
5 propiedad intelectual y/o nombres de dominio, a cuyo efecto los faculta/n para llevar a
6 cabo ante dichas autoridades todas las gestiones necesarias al objeto indicado,
7 presentar solicitudes, formular descripciones, oposiciones, protestos, declaraciones,
8 apelaciones y reclamos, oblar impuestos, justificar explotaciones, solicitar
9 testimonios, aceptar transferencias, recibir documentos y valores, percibir y hacer
10 cuanto fuere necesario ante las autoridades administrativas de cualquier orden. Por
11 otra parte, les confieren mandato para que en su nombre y representación puedan
12 iniciar y proseguir cualquier juicio que actualmente los que suscriben tengan o en el
13 futuro tuvieran en ... Sudamérica, Centroamérica ..., con motivo de su nombre, marcas
14 de fábrica o de comercio, patentes de invención y modelos y/o de sus derechos de
15 propiedad intelectual que actualmente posean o adquieran en lo sucesivo, promover
16 juicios de cualquier jurisdicción, criminales, correccionales, civiles o comerciales,
17 contra los falsificadores, usurpadores o imitadores y contra los tenedores de artículos
18 que infrinjan su nombre, marcas o patentes de invención, seguir los juicios por
19 oposición u otros en que fueran parte como actores o demandados, defender el
20 nombre, las marcas, patentes y modelos y/o de derechos de propiedad intelectual y/o
21 nombres de dominio, haciendo las protestas del caso o diciendo de nulo el efecto
22 podrán presentarse con escritos, querellas, pedidos, y lo que fuere necesario ante
23 cualquier autoridad judicial, presentar testigos, documentos y demás justificativos,
24 rendir pruebas de cualquier especie, pedir nombramientos de peritos, pedir y absolver
25 posiciones, asistir a juicios verbales, declarar y prorrogar de jurisdicción, tachar,



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recusar, apelar, transar, someter a arbitraje o mediación, hacer renunciaciones, exigir y dar
cauciones, pedir embargos preventivos, definitivos o inhibiciones y su levantamiento,
pedir la venta de los bienes de los deudores, solicitar y obtener el cumplimiento de
sentencias, prestar juramentos, decir de nulidad, desistir, percibir, otorgar recibos y en
general practicar todos los actos y diligencias que sean precisos al desempeño de este
mandato. Podrán asimismo substituir el presente poder en todo o en parte. Dado y
firmado en Ludwigshafen, den 20.10.2005.- Sigue una firma ilegible ppa. Emil
Wilding. Sigue otra firma ilegible ppa. Harmut Bergmann".- ES COPIA FIEL, doy
fe.- En hojas adjuntas consta: a) La certificación notarial de las firmas obrantes en el
poder, en idioma inglés, efectuada por el Escribano Público de Ludwigshafen del Rin
Ludwig Draxel – Fischer; b) La legalización de la firma y sello del notario, en idioma
alemán, efectuada por el Presidente del Tribunal Regional de Frankenthal (Palatinado)
Christian Köneke – Juez del Tribunal Regional, Alemania (Sello de Apostilla de la
Convención de la Haya del 5 de octubre de 1961); c) La certificación notarial de
vigencia de la Sociedad, en idioma inglés, efectuada por el Escribano Público de
Ludwigshafen/Rin Ludwig Draxel – Fischer; y d) La legalización de la firma y sello
del notario, en idioma alemán, efectuada por el Presidente del Tribunal Regional de
Frankenthal (Palatinado) Christian Köneke – Juez del Tribunal Regional, Alemania
(Sello de Apostilla de la Convención de la Haya del 5 de octubre de 1961), doy fe.- En
hojas adjuntas siguen las referidas traducciones al idioma nacional las que transcritas
textualmente por su orden dicen: "TRADUCCIÓN PUBLICA (A continuación de un
PODER otorgado por la Sociedad "BK GIULINI GmbH", de Ludwigshafen,
Alemania figuran los siguientes textos que traducidos dicen:) La versión en inglés es
para su información únicamente. Reg. de Actas N° 2634/2005. El 20 de octubre de
2004, ante mí, comparecieron personalmente las siguientes personas de m

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ACTUACIÓN NOTARIAL



N 005700803

1 conocimiento: Emil Wilding, técnico textil, domiciliado en Ludwigshafen/Rin,
2 Hartmut Bergmann, graduado en administración de empresas, Gerente de la
3 contabilidad financiera, domiciliado en Ludwigshafen/Rin. Certifico y confirmo por el
4 presente que las firmas antepuestas de los mencionados arriba son verídicas y
5 auténticas. Después de haber controlado en el día de la fecha el Registro de Comercio
6 competente, confirmo por el presente que el Sr. Emil Wilding, y el graduado en
7 Administración de Empresa Hartmut Bergmann son Directores autorizados a
8 representar en forma conjunto a la Sociedad "BK Giulini GmbH", de
9 Ludwigshafen/Rin. Certifico que esta empresa es una persona jurídica debidamente
10 fundada según las leyes de la República Federal de Alemania y que está registrada en
11 el Tribunal de Distrito de Ludwigshafen/Alemania (HR B 1782) Ludwigshafen/Rin,
12 20 de octubre de 2005. (Hay un sello notarial en oblea sobre precinto).- APOSTILLA
13 - (Convención de La Haya del 5 de octubre de 1961).- País: República Federal de
14 Alemania.- Este instrumento público fue firmado por el Escribano Draxel - Fischer,
15 en su carácter de Escribano Público y está provisto del sello del Escribano Ludwig
16 Draxel - Fischer de Ludwigshafen del Rin. Certificado en Frankenthal (Palatinado), el
17 16 de noviembre de 2005, por el Presidente del Tribunal Regional con el N° 91 Eb-
18 1248/05 - Sello (Hay un sello en oblea sobre precinto:) El Presidente del Tribunal
19 Regional de Frankenthal (Palatinado) - Firma - El Funcionario autorizado (Firmado y
20 aclarado:) Christian Köneke) - Juez del Tribunal Regional - Derechos: 13,50 €. ES
21 TRADUCCIÓN FIEL de las partes pertinentes del documento de referencia, que en
22 los idiomas inglés y alemán, he tenido a la vista y he vertido al idioma español, en
23 Buenos Aires, el 5 de diciembre de 2005.- Hay una firma ilegible y un sello que dice:
24 "LAURA THIEBERGER - MATRICULA DE TRADUCTORES - ALEMAN -
25 FRANCES - Tomo II Folio 254 (Cap.) Tomo III - 98 - (La Plata) - INGLES - Tomo



N 005700803

III: Folio 14 (Cap.) – Tomo III Folio 329 (La Plata) – COLEGIO TRADUCTORES PUBLICOS N° 173”.- ES COPIA FIEL, doy fe.- A continuación hay un sello que dice: “COLEGIO DE TRADUCTORES PÚBLICOS DE LA CIUDAD DE BUENOS AIRES Corresponde a la Legalización N° T4-21701/05. Sigue una firma ilegible: GUSTAVO ADRIÁN SIGALOFF”.- ES COPIA FIEL, doy fe.- En el margen superior derecho hay un sello timbrador- ES COPIA FIEL, doy fe.- A continuación sigue la legalización de la firma de la nombrada traductora, ..., que dice: “N° 00868313... LEGALIZACIÓN Por la presente, el COLEGIO DE TRADUCTORES PÚBLICOS DE LA CIUDAD DE BUENOS AIRES, en virtud de la facultad que le confiere el artículo 10, inc. d) de la Ley 20.305, certifica únicamente que la firma y sello que aparecen en la traducción adjunta, concuerdan con los correspondientes al Traductor Público THIEBERGER, LAURA que obran en los registros de esta institución en el folio tomo ALEMÁN 254 - 2 - INGLÉS 14 - 3. Buenos Aires, Legalización Número: 21701 / 2005 / T4 Fecha 07/12/05. Hay una firma ilegible. Hay un sello que dice: “Marcelo F. Sigaloff ...”.- ES COPIA FIEL, doy fe.- “TRADUCCIÓN PÚBLICA. CERTIFICACIÓN NOTARIAL DE LA SOCIEDAD. Yo, Ludwig Draxel –Fischer, Escribano Público de Ludwigshafen/Rin, certifico por el presente en virtud de los documentos que han sido presentados por la Sociedad “BK GIULINI GmbH”, es una sociedad en existencia y fundada de acuerdo con las leyes de la República Federal de Alemania, con sede en Giuliani Strasse 2, 67065, Ludwigshafen, Alemania, y, que esta sociedad en la fecha de firma de este certificado está en vigencia. Declaro por el presente que lo que figura más arriba es verdadero y exacto de acuerdo con la ley. Firmado en Ludwigshafen, el 20 de mayo de 2005 – (Sello:) Ludwig Draxel – Fischer – Escribano de Ludwigshafen del Rin – (Sigue la firma ilegible del Escribano Público) - APOSTILLA – (Convenión de La Haya del 5

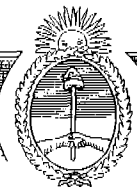
COLEGIO DE TRADUCTORES PUBLICOS N° 173
LEGALIZACIÓN N° T4-21701/05
FOLIO 14 (Cap.)

COLEGIO DE TRADUCTORES PUBLICOS N° 173
LEGALIZACIÓN N° T4-21701/05
FOLIO 14 (Cap.)

COLEGIO DE TRADUCTORES PUBLICOS N° 173
LEGALIZACIÓN N° T4-21701/05
FOLIO 14 (Cap.)

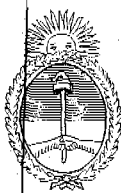


ACTUACION NOTARIAL
LEY 404



N 005700804

1 de octubre de 1961). País: República Federal de Alemania. Este instrumento público
2 fue firmado por el Escribano Draxel - Fischer, en su carácter de Escribano Público y
3 está provisto del sello del Escribano Ludwig Draxel - Fischer de Ludwigshafen del
4 Rin. Certificado en Frankenthal (Palatinado), el 16 de noviembre de 2005, por el
5 Presidente del Tribunal Regional con el N° 91 Eb-1246/05 - Sello (Hay un sello en
6 oblea sobre precinto:) El Presidente del Tribunal Regional de Frankenthal (Palatinado)
7 - Firma - El Funcionario autorizado (Firmado y aclarado:) Christian Köneke) - Juez
8 del Tribunal Regional - Derechos: 10,00 €. ES TRADUCCIÓN FIEL de las partes
9 pertinentes del documento de referencia, que en los idiomas inglés y alemán, he tenido
10 a la vista y he vertido al idioma nacional, en Buenos Aires, el 5 de diciembre de
11 2005.- Hay una firma ilegible y un sello que dice: "LAURA THIEBERGER -
12 MATRICULA DE TRADUCTORES - ALEMÁN - FRANCÉS - Tomo II Folio 254
13 (Cap.) Tomo III - 98 - (La Plata) - INGLES - Tomo III: Folio 14 (Cap.) - Tomo III
14 Folio 329 (La Plata) - COLEGIO TRADUCTORES PÚBLICOS N° 173".- ES
15 COPIA FIEL, doy fe.- A continuación hay un sello que dice: "...COLEGIO DE
16 TRADUCTORES PÚBLICOS DE LA CIUDAD DE BUENOS AIRES Corresponde a
17 la Legalización N° T4-21700/05. Sigue una firma ilegible: GUSTAVO ADRIÁN
18 SIGALOFF".- ES COPIA FIEL, doy fe.- En el margen superior derecho hay un sello
19 timbrador ...".- ES COPIA FIEL, doy fe.- A continuación sigue la legalización de la
20 firma de la nombrada traductora, ..., que dice: "N° 00868312 ... LEGALIZACIÓN Por
21 la presente, el COLEGIO DE TRADUCTORES PÚBLICOS DE LA CIUDAD DE
22 BUENOS AIRES, en virtud de la facultad que le confiere el artículo 10, inciso 1º de la
23 Ley 20.305, certifica únicamente que la firma y sello que aparece en la traducción
24 adjunta, concuerdan con los correspondientes al Traductor Público THIEBERGER,
25 LAURA que obran en los registros de esta institución en el folio tomo ALEMÁN



N 005700804

254- 2 - INGLÉS 14 - 3. Buenos Aires, Legalización Número: 21700 / 2005 / T4

Fecha 07/12/05. Hay una firma ilegible. Hay un sello que dice: "Marcelo F.

Sigaloff...".- ES COPIA FIEL, doy fe.- En este estado la compareciente DICE: que en

la forma expresada deja INCORPORADO y TRANSCRIPTO en este Protocolo el

Poder que agrego a la presente, solicitando de mí, la Escribana Autorizante, expida

primera copia de la presente para la nombrada apoderada ... - LEO esta escritura a la

compareciente, quien así la otorga y en prueba de conformidad, la firma ante mí, doy

fe.- Dagmar MESSERER. Ante mí: MARIA SILVINA LASARTE. Escribana. Está

mi sello. CONCUERDA con su escritura matriz que pasó ante mí, al folio 567 del

Registro Notarial número 1788, a mi cargo. PARA LA APODERADA expido la

presente PRIMERA COPIA en cuatro (4) sellos de actuación notarial numerados

correlativamente desde el número N 005558117 al presente inclusive, que sello y

firmo en la fecha y lugar de su otorgamiento, doy fe."- **ES COPIA FIEL**, doy fe.-

CUARTO: Finalmente la compareciente DICE: a) Que el presente otorgamiento no

significa renunciar al ejercicio de las facultades sustituidas y; b) Que los nombrados

apoderados sustitutos no podrán sustituir el presente poder en ninguna de sus partes.-

Yo, la Escribana Autorizante impongo y advierto a la compareciente, a tenor de lo

dispuesto en el artículo 77 inciso h) de la Ley Orgánica Notarial Número 404,

respecto de los alcances y consecuencias de las cláusulas contenidas en la presente

escritura y del derecho de leer por sí este instrumento.- **LEO** esta escritura a la

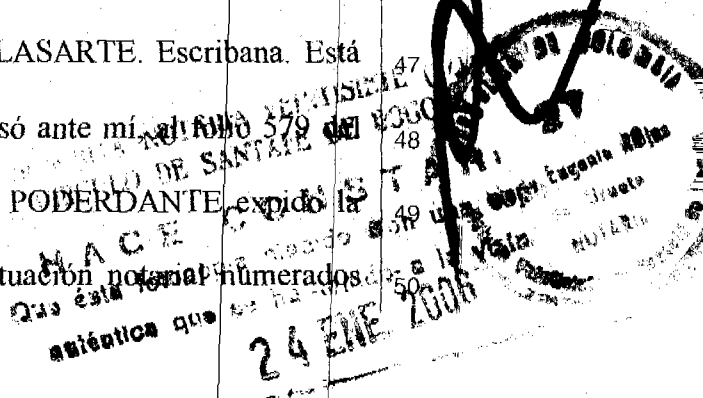
compareciente, quien así la otorga y en prueba de conformidad la firma ante mí, doy

fe.- Dagmar MESSERER. Ante mí: MARIA SILVINA LASARTE. Escribana. Está

mi sello. **CONCUERDA** con su escritura matriz que pasó ante mí, al folio 579 del

Registro Notarial número 1788, a mi cargo. PARA LA PODERANTE expido la

presente **PRIMERA COPIA** en cinco (5) sellos de actuación notarial numerados



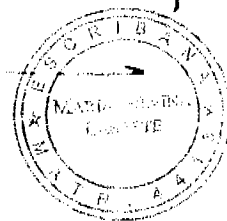


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N 005700805

1 correlativamente desde el número N 005700801 al presente inclusive, que sello y
2 firmo en la fecha y lugar de su otorgamiento, doy fe.-

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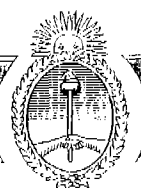
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LEGALIZACION
LEY 404



COLEGIO DE ESCRIBANOS

L 006815932

EL COLEGIO DE ESCRIBANOS de la Ciudad de Buenos Aires, Capital Federal de la República Argentina, en virtud de las facultades que le confiere la ley vigente, LEGALIZA la firma y sello del escribano MARIA SILVINA LASARTE obrantes en el documento anexo, presentado en el día de la fecha bajo el N° 051222495766/1 La presente legalización no juzga sobre el contenido y forma del documento.



Buenos Aires, Jueves 22 de Diciembre de 2005

ESC. ALBA ROSA MUÑOZ DE LEON
COLEGIO DE ESCRIBANOS
CONSEJERA

COLEGIO DE ESCRIBANOS
CIUDAD DE BUENOS AIRES
CAPITAL FEDERAL - REPUBLICA ARGENTINA
24 DE DICIEMBRE DE 2005

APOSTILLE

REPUBLICA
ARGENTINA

(Convention de La Haye du 5 octobre 1961)

A 00060028

1. PAÍS: REPUBLICA ARGENTINA

El presente documento público

2. Ha sido firmado por ALBA ROSA MUÑOZ DE LEON

3. Quien actúa en calidad de CONSEJERA

4. Lleva el sello / timbre de COLEGIO DE ESCRIBANOS DE LA CIUDAD DE BUENOS
AIRES

5. En LA CIUDAD DE BUENOS AIRES 6. El día 22/12/2005

7. Por EL COLEGIO DE ESCRIBANOS DE LA CIUDAD DE BUENOS AIRES

MINISTERIO DE RELACIONES EXTERIORES, COMERCIO INTERNACIONAL Y CULTO
(Convenio 02/09/2003)

8. Bajo el número: 051222041218

9. Sello / Timbre



10. Firma

ESC. MIGUEL ERNESTO CHAMIE
COLEGIO DE ESCRIBANOS
(BUENOS AIRES)

COLEGIO DE ESCRIBANOS
LA CIUDAD DE BUENOS AIRES
24 de Diciembre de 2005
Esc. Miguel Ernesto Chamie
Esc. Miguel Ernesto Chamie

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REPUBLICA DE COLOMBIA
SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

Folio ~~59~~

2020
Bogotá D.C.,

Doctor(a)
OLARTE GARCIA CARLOS REINALDO
Apoderado(a) y/o Representante de
BK GIULINI GMBH

REFERENCIA	Radicación No.	05 102552
	Solicitud internacional	EP2004/003300
	Fecha inicio fase nacional	11/11/2005
	Trámite	11
	Evento	379
	Actuación	416
	Oficio No.	2231
	Folios	1

Teniendo en cuenta que la solicitud de privilegio de patente que se tramita bajo el expediente indicado en la referencia, reúne los requisitos de forma establecidos en la Decisión 486 de la Comisión de la Comunidad Andina, el Tratado de Cooperación en Materia de Patentes (PCT), el Reglamento y la Circular Única de la Superintendencia de Industria y Comercio, se envía el extracto de la solicitud a la Oficina de Comunicaciones para efecto de su publicación en la Gaceta de Propiedad Industrial.

Cúmplase
Dado en Bogotá DC,

20 DIC. 2006

ALIX CARMENZA CESPEDES DE VERGEL
Jefe de la división de Nuevas Creaciones

adpa10

DIVISIÓN DE NUEVAS CREACIONES

RADICACIÓN EXPEDIENTE No. 05-102552

EL EXTRACTO DE LA PRESENTE SOLICITUD DE **PATENTE DE INVENCION**

FUE PUBLICADO EN LA GACETA DE PROPIEDAD INDUSTRIAL No **576** DE

FECHA **31 DE MAYO DE 2007** EL TÉRMINO HÁBIL SEÑALADO POR LA LEY

EXPIRA EL **31 DE AGOSTO DEL 2007**

NOTA: Dentro del plazo de los seis (6) meses siguientes a partir de la fecha de publicación en la gaceta de Propiedad Industrial, deberá solicitar y cancelar el examen de patentabilidad so pena de que la solicitud caiga en abandono, de acuerdo con lo establecido en el Artículo 44 de la Decisión 486/2000.

SE PRESENTARON OPOSICIONES POR PARTE DE TERCEROS.

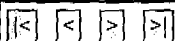
SI _____

NO ☒ _____

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO SISTEMA DE TRAMITES-CONSULTA DE TRÁMITES*

Lunes 9 de Junio de 2008

6264



Datos del Trámite (PENDIENTE)

Radicación: Año: 2005 * Número: 102552 * Ctrl: * Cons Rad: 4 * Secu Even: 0 *

Tipo Trámite: 11 PCT-PATENTE DE INVENCION CAPITULOS I Y II *

Tipo Evento: 378. FASE NACIONAL INCLUIDO CAPITULO I *

Tipo Actuación: 538. PETICION DE EXAMEN *

Dependencia Origen: *

Dependencia Destino: 2020. DIVISION DE NUEVAS CREACIONES *

Solicitante/Destinatario: J. IAN RAISBECK * Tipo: Contenida

Identificación CC. CEDULA DE CIUDADANIA Número: 79376996.0

Dirección: CALLE 100 NO 8A-37 TORRE A PISO 10 WORLD TRADE CENTER BOGOTA D.C.

Punto de Radicación: EN. ENTRADA * Folios: 3

Fecha de Radicación: Día: 8 Mes: Agosto Año: 2007 16:28:08 Entrega: VENTANILLA

Guía: fecha:

Observaciones:

Otros Datos

[Documentos] [Recibos]

Nueva Consulta

[Cerrar Sesión]

Registro : 5 / 5

Información adicional en la Oficina de Sistemas

Año	Número	Ctrl	Cons Rad	Sec Eve	Trámite	Evento	Actuación	Tipo	Fecha	Solicitante	Asignacion/ Estado- Correspondencia
5	102552		0	0	PCT-PATENTE DE INVENCION CAPITULOS I Y II	FASE NACIONAL INCLUIDO CAPITULO I	PRESENTACION	EN	2005-10-07 16:57:33	CARLOS R OLARTE	e
5	102552		1	0	PCT-PATENTE DE INVENCION CAPITULOS I Y II	FASE NACIONAL INCLUIDO CAPITULO I	REQUERIMIENTO DE INFORMACION	SA	2005-11-03 14:35:19	PARA MIGRACION TRAMITES SOLICITANTE DESTINATARIO NO IDENTIFICADO	e
5	102552		2	0	PCT-PATENTE DE INVENCION CAPITULOS I Y II	FASE NACIONAL INCLUIDO CAPITULO I	SOLICITUD PRORROGA	EN	2005-12-20 09:16:59	CARLOS R OLARTE	e
5	102552		3	0	PCT-PATENTE DE INVENCION CAPITULOS I Y II	FASE NACIONAL INCLUIDO CAPITULO I	REPUESTA A REQUERIMIENTO DE INFORMACION	EN	2006-02-21 14:58:56	CARLOS R OLARTE	e
					PCT-	FASE					

**SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
SISTEMA DE TRAMITES-CONSULTA DE RECIBOS**

Miercoles 11 de Junio de 2008

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Recibos de pago del Expediente Año : 5 Número: 102552 Ctrl: Cons Rad: 4

[Salir](#)

Número de Recibo	Fecha	Rentistico	Concepto	Tipo	Número	Cuenta	Cantidad	Valor	Estado
7	60717	26/07/2007	SOLICITUDES	PTC CAP-II EXAMEN DE PATENTIBILIDAD DE INVERSION	CONSIGNACION 67532137	050-00110-6	1	202000.0	U
7	60718	26/07/2007	SOLICITUDES	PTC CAP-II EXAMEN DE PATENTIBILIDAD DE INVERSION	CONSIGNACION 67532137	050-00110-6	1	202000.0	U

Información adicional en la Oficina de Sistemas

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**SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISIÓN DE NUEVAS CREACIONES**

2020

Bogotá, D. C., 11 de junio de 2008

Doctor

CARLOS OLARTE

Representante **BK GIULINI GMBH**

ASUNTO

Radicación **05-102552**

Trámite 002

Evento 001

Actuación **430** 8362

Oficio

Folios **021**

Patente de Invención

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Patente de Modelo de Utilidad

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Vía Nacional

☐

Vía PCT (fase nacional)

☒

Cap. I

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Cap. II

☐

No. Sol. Internacional

PCT/EP2004/003300

Fecha de Presentación Internal.

27 de marzo de 2004

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

1.1. Descripción: Folios: 20 a 35 tal como se radicó inicialmente

1.2. Reivindicaciones: Folios 1 a 12 tal como se radicó inicialmente

1.3. Prioridad:
Fecha 11 de abril de 2003
País Alemania
Número (¿?) 1031617.3

2. Análisis de la Prioridad

El solicitante deberá aclarar la no coincidencia del número relacionado en los documentos entregados por la WIPO con la prioridad original. Al parecer se trata de un error mecanográfico que olvidó un número intermedio. Deberá llegar copia de la prioridad original donde se demuestre el número correcto.

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3. Objeto de la invención

- Título de la solicitud (folio 1) *MATERIAL TERMOPLÁSTICO DE REFUERZO PARA LA PRODUCCIÓN DE CALZADO Y PROCESO RELACIONADO CON EL MISMO*
- Las reivindicaciones 1 a 12 de la solicitud en estudio se refieren a
 - *un material termoplástico de refuerzo para la fabricación de calzado mediante un compuesto de material termofundible/material de carga, caracterizado por el hecho de que consiste en:*
 - *a. uno o más adhesivos termofundibles en una cantidad entre 50 y 95% en peso, donde su valor MMFR (medido a 100°C, 21,6kg de acuerdo con la norma DIN ISO 1133) es de entre 2 y 300, preferiblemente entre 10 y 20cm³/10 minutos y*
 - *b. una o más cargas en una cantidad entre 50 y 5% en peso, insolubles en el material termofundible, donde el compuesto de material termofundible/material de carga que satisface de manera concurrente los siguientes parámetros:*
 - 1. Valor MMFR entre 2 y 6, preferiblemente entre 3 y 5cm³/10 minutos
 - 2.- Adherencia superficial medida de acuerdo con la norma DIN EN 14610 a 65°C de por lo menos 10N, hasta un máximo de 60N, preferiblemente 15N, aquí en particular 30N.
 - 3.- Resistencia de adherencia contra la superficie de los materiales de por lo menos 30N/5cm medida adoptando la norma alemana DIN 53357.
 - *El uso del material*
 - *Un calzado fabricado con dicho material.*
- El anterior producto busca mejorar la calidad de refuerzos de zapatos.
- La Clasificación Internacional de Patentes (IPC) para esta solicitud es C09J167/04.

4. Reivindicaciones relativas a un uso o a un segundo uso (artículos 14 y 21 D 486)

La solicitud de patente, en lo referente a los usos, NO cumple con el artículo 14 de la Decisión 486 de la Comisión de la Comunidad Andina de Naciones dado que:

- Las reivindicaciones 11 y 12 explícitamente solicitan protección sobre el uso del material de las primeras reivindicaciones. La legislación andina es clara en la no protege de los usos. Por tanto, dichas reivindicaciones deberán eliminarse.

De lo anterior la(s) reivindicación(es) 11 y 12 no pueden ser consideradas invenciones patentables

5. Determinación del Estado de la Técnica

- La fecha que se ha tenido en cuenta para determinar el estado de la técnica es 11 de abril de 2003
- Teniendo en cuenta la fecha indicada se realizó la búsqueda en el estado de la técnica de documentos relacionados con la solicitud encontrándose los siguientes documentos más relevantes:

Nº	Documento	Título	Fecha de publicación*
D1	US 4 717 496	Stiffening material with melt adhesive properties	05.01.1988
D2	US 4 820 769	Hot melt adhesive composition	11.04.1989
D3	US 2002/0091176	Stiffener material with self adhesive properties	11.07.2002
D4	WO 94 03211	Orthopaedic splinting casting material	17.02.1994

6. Análisis de patentabilidad (artículo 14 D486)

El solicitante pretende que se le proteja un material termoplástico caracterizado porque consiste en uno o más adhesivos termofundibles y una o más cargas insolubles en el material termofundible.

El documento D1, US 4717496, refiere también composiciones que son materiales termoplásticos y contienen adhesivos termofundibles y una o varias cargas que resultan insolubles en el material termofundible, como carbonato de calcio o madera. De la misma forma, los restantes documentos relacionan los mismos componentes de la solicitud colombiana. Las diferencias se encuentran en los parámetros establecidos para cada componente. Sin embargo, podría pensarse que se podría derivar de las anterioridades señaladas.

7. Conclusión:

Los requisitos de patentabilidad de la presente solicitud se encuentran afectados así:

Nº	Documento	Reivindicaciones afectadas	Requisito que afecta
D1	US 4 717 496	1 – 12	Nivel inventivo
D2	US 4 820 769	1 – 12	Nivel inventivo
D3	US 2002/0091176	1 – 12	Nivel inventivo
D4	WO 94 03211	1 – 12	Nivel inventivo

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 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 N° 10 de 2001.

ALIX CARMENZA CÉSPEDES DE VERGEL
Jefe de División de Nuevas Creaciones

El anterior requerimiento fue notificado por fijación en lista, de fecha

CONCEPTO TÉCNICO	EXAMINADOR
No.	TÉCNICO
1652	Código No. 202003

United States Patent [19]

Brehmer et al.

[11] Patent Number: 4,717,496

[45] Date of Patent: Jan. 5, 1988

- [54] **STIFFENING MATERIAL WITH MELT-ADHESIVE PROPERTIES**
- [75] Inventors: **Harald Brehmer, Neuhofen; Emil Wilding, Birkenheide**, both of Fed. Rep. of Germany
- [73] Assignee: **Glulini Chemie GmbH, Ludwigshafen**, Fed. Rep. of Germany

- [21] Appl. No.: 708,059
- [22] Filed: Mar. 4, 1985

Related U.S. Application Data

- [63] Continuation-in-part of Ser. No. 677,296, Dec. 3, 1984, abandoned.
- [51] Int. Cl. C08K 9/10; C08L 23/08; C08L 67/04; C08L 75/04
- [52] U.S. Cl. 525/129; 523/167; 523/201; 523/206; 525/127; 525/130; 525/131; 525/186; 525/222; 525/233; 525/239; 525/240
- [58] Field of Search 523/167, 209, 206, 201; 525/186, 131, 129, 127, 130, 222, 233, 239, 240; 524/904; 428/407, 402, 403

References Cited

U.S. PATENT DOCUMENTS

- 3,518,221 6/1970 Kenyon et al. 523/209
- 3,764,456 10/1973 Woodhams 523/209
- 3,773,708 11/1973 Takahashi et al. 523/209

- 3,778,251 12/1973 Trask 117/68
- 3,956,230 5/1976 Grayford 523/206
- 4,124,562 11/1978 Yoi et al. 523/209
- 4,151,155 4/1979 Chapnick 523/167
- 4,211,691 7/1980 Fitzgerald et al. 524/904
- 4,273,919 6/1981 Feldman et al. 524/904
- 4,433,073 2/1984 Sano et al. 523/106
- 4,478,963 10/1984 McGarry 523/206
- 4,480,057 10/1984 Sano 523/206

FOREIGN PATENT DOCUMENTS

- 1027838 3/1978 Canada 154/140
- 2621193 11/1977 Fed. Rep. of Germany

OTHER PUBLICATIONS

Kunststoff-Lexikon, Beck et al, eds., definition of "Polyphenylenoxid", p. 303, Carl Hauser Verlag, Munich (1973).

Primary Examiner—Allan M. Lieberman
Attorney, Agent, or Firm—Spencer & Frank

ABSTRACT

A stiffening material composed of 30 to 80 weight percent filler particles and 70 to 20 weight percent binder which is thermoplastically deformable and has melt-adhesive properties in the temperature range of 50° to 80° C., wherein the filler particles are plastic particles or particles having plastic surfaces with a particle size distribution of 50 to 500 microns.

11 Claims, No Drawings

STIFFENING MATERIAL WITH MELT-ADHESIVE PROPERTIES

This application is a continuation-in-part application of co-pending U.S. Ser. No. 677,296, filed Dec. 3, 1984) now abandoned.

BACKGROUND OF THE INVENTION

The present invention relates to a novel stiffening material having melt-adhesive properties, particularly for shoe parts, and to a method for producing such a material.

Thermoplastic stiffening materials are known; they have been used in the shoe industry for a long time. Advisably they are produced in sheet forms and are used in pieces cut therefrom to stiffen the heel region and possibly also the toe region of shoes. The cut pieces can be deformed under the influence of heat, with the stiffening material having to have such properties that, after deformation and cooling, the molded piece will assuredly retain its shape and have good flexibility.

Moreover, the stiffening materials may be coated on one or both sides with thermoplastic adhesives to that during or after deformation they may also be heat sealed to the upper and/or lining material of the shoe.

As is known, thermoplastic stiffening materials may be produced in various ways, e.g. by spreading the coating materials in the form of a dispersion, solution or melt onto woven or knitted or nonwoven textile fabrics. Stiffening sheets may also be produced by laminating thin sheets onto fabric substrates, and most recently also by extrusion of suitable thermoplastic materials.

German Pat. No. 2,621,195 discloses stiffening materials which are produced by melting powdered mixtures of plastics (binders) and fillers onto woven or nonwoven textile fabrics. It is significant for the production process that the powdered fillers are present in a particle size distribution which is comparable to the particle size distribution of the plastic powder, with the particle size distributions in each case lying between 50 and 500 microns, preferably between 100 and 400 microns. If these parameters are maintained, the filler may be used in quantities up to 100 volume percent with respect to the volume of the plastic powder, without this making the melting together of the plastic particles more difficult or impossible.

Although stiffening materials according to German Pat. No. 2,621,195 can still be deformed in a temperature range from 50° to 80° C., they cannot be heat sealed to the upper or lining material without first being provided on one or both sides with an adhesive layer, for example a hot melting adhesive, which today is considered to be a drawback.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a stiffening material which is deformable and can be heat sealed directly in the processing range, which in the shoe industry lies at about 50° to 80° C.

Surprisingly, this can be accomplished with a stiffening material composed of 30 to 80 weight percent filler and 70 to 20 weight percent binder, wherein the filler particles are plastic particles or, at least, particles having plastic surfaces, with a particle size distribution of 50 to 500 microns, preferably 100 to 400 microns, and the binder is thermoplastically deformable in a temperature range of about 50° to 80° C. and has melt-adhesive

4,717,496

properties. According to a particularly advantageous embodiment of the invention, the filler component is present in the mixture in an amount of 40 to 60 weight percent and the binder component is present in an amount of 60 to 40 weight percent.

DETAILED DESCRIPTION OF THE EMBODIMENTS

Only those materials are used as binders which are thermally deformable in a temperature range of about 50° to 80° C. and are also melt-adhesives. Such binders are commercially available but have so far not been used as stiffening materials in the shoe industry. Preferred materials are polymerizates and copolymerizates of cyclic esters as well as mixtures of these polymerizates. Polymerizates of cyclic esters are disclosed, inter alia, in U.S. Pat. No. 3,778,251 and in Canadian Pat. No. 1,027,838. In both patents, the substances are used on one or both sides as adhesive films on customary stiffening materials, for example on such materials made of styrene-butadiene copolymerizates and of copolymerizates of vinyl chloride and an alpha-olefin, and they may be modified with viscosity enhancers, fillers and other additives.

The deformation temperature of the binders used according to the present invention likewise is in a temperature range of 50° to 80° C. For polyepsilon caprolactone, for example, the deformation temperature is 60° C.

Other suitable binders are elastomer polyurethanes as well as modified polyolefins, e.g. polyethylene vinyl acetate. Ionomers can also be used as binders.

The binder which causes adhesion of the filler particles during manufacture of the stiffening material as well as the later adhesion to the shoe parts, is preferably polyepsilon caprolactone, which can be used in powder form as well as in granulated form. If it is used in powder form, then it should have a particle size distribution between 50 and 500 microns, particularly between 100 and 400 microns, i.e. a distribution comparable to the particle size distribution of the filler powder.

In the novel stiffening material, the filler particles are made of plastic, particularly waste plastic. For example, high impact rigid PVC particles and copolymerizates of vinyl chloride and an alpha olefin or of styrene and butadiene or acrylonitril, butadiene and styrene, are particularly suitable.

In summary, it can be stated at this point, that the plastics used as fillers according to the present invention are essentially those which, due to their melting properties, cannot be processed alone, or only with difficulty, according to processes of the powder technology to form areal structures.

Conventional inorganic fillers may also be used, if they are coated with a plastic layer according to the above definition. Such inorganic or organic fillers may be, for example: calcium carbonate, kaolin, quartz meal, wood or cork meal. In addition to these fillers, the composition may include dye pigments, anti-static agents, adjuvants and other conventional additives.

The novel stiffening material may be produced according to various methods, e.g. according to methods known in the powder processing art, by casting, screen printing, molding resp. flow-molding or extrusion. The powder mixture may also be melted onto one or both sides of a substrate material, for example onto woven or nonwoven textile fabrics or onto shoe parts. Adhesion to the substrate material may be conducted during ex-

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trusion. The powder mixture can be heated by any energy known in the art, e.g. by radiant heat, infrared heating, high-frequency heating (radio heat), microwave-heating and magnetic induction-heating.

One absolute prerequisite of the present invention is that the filler particles must not dissolve in the binder during the melting process, but remain in the form of essentially discrete bodies, as do the inorganic fillers. Only then can the favorable characteristics of the binder be retained. Moreover, the binder must firmly adhere to the filler. Slight surface dissolution or softening of the filler particles in the melt, however, will not be avoidable in every case, and will not detract from the overall characteristics of the invention.

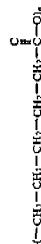
The advantage of the novel stiffening material is seen primarily in the fact that it adheres to any desired cut surface, since it is composed of a multitude of particles which are covered by a melt-adhesive. Accordingly, each particle acts as a unitary stiffening material with a surface having melt-adhesive properties. The processing process is thus simplified considerably, e.g., it is no longer necessary to subsequently provide a mechanically thinned (stiffened) stiffening material with an adhesive.

Type, shape and quantity of the filler particles can greatly influence the characteristics of the end product, particularly its stiffness and its viscosity when heated. By adding the filler particles, viscosity and stiffness of the end product can be greatly increased so that the binder will be prevented from flowing during thermal plastic deformation. The physical characteristics of the end product, however, are greatly influenced by the shape of the particles as well as by the quantity of the filler. For example, it has been found that plate-shaped (flat) particles are particularly effective in increasing viscosity.

The present invention will now be described in greater detail with the aid of the following examples.

EXAMPLE 1

Waste pieces of thin sheets of an high impact rigid PVC were ground in a suitable comminution system, and processed and classified such that the edge lengths of the selected particles were between 100 and 400 microns. High molecular weight polyacrylonitrile of the formula



and having a molecular weight of 40,000 [Union Carbide PCL 700] was similarly comminuted to a particle size of 100 to 400 microns.

500 parts by weight PCL 700 were then mixed with 500 parts by weight hard PVC powder in a suitable powder mixer. On a roller spreader, a plain weave (1:1) cotton fabric weighing 60 g/m² was then covered with 700 g/m² of the powder mixture. A subsequent heat treatment was conducted in an infrared field, in which the powder mixture was heated to about 130° C. The fabric panel remained in the infrared apparatus until the PCL 700 was completely melted. In the plastic state, the panel was then brought through a cold smoothing calender and, after cooling, was rolled onto a reel.

EXAMPLE b 2

Regenerated acrylonitril-butadiene-styrene copolymerized granules [Novodur KL 1-520 made by

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Bayer AG] were ground in a comminution system to a particle size distribution between 100 and 500 microns (0.1 to 0.5 m). This powder was mixed, as in Example 1, with ground PCL 700, but instead of 50 weight percent, 60 weight percent PCL 700 was used.

A negative silicone mold provided for the manufacture of heel reinforcements in shoes was filled with the mixture. The silicone mold was of such configuration that heel reinforcements were formed which tapered toward the lateral and upper edges to almost 0.01 mm. The mold filled with the powder was heated under pressure for 20 seconds with the aid of a high frequency generator (40,000 MHz/40 KW/h) and then cooled for 20 seconds. After cooling, the ready-for-use shoe stiffener was removed from the silicone mold.

EXAMPLE 3

In an extrusion system, the powder mixture of Example 1 was plasticized in such a manner that only the PCL 700 was liquefied. Upon leaving the sheet die, the temperature of the melt was about 100° C., and the sheet had a thickness of 0.9 mm. After cooling, the sheet was rolled onto a reel.

EXAMPLE 4

On a continuously operating kneading machine, suitable for the addition of a plurality of components in different process stages, PCL 700 was introduced in its supplied form (granulate) as the first component. After heating, the PCL melted at 140° C. Shortly before reaching the extrusion tool, in the last kneading zone, the melt was carefully mixed with 40 weight percent ground acrylonitril-butadiene-styrene copolymerized without the filler being dissolved or further comminuted. The particle size distribution of the filler was between 100 and 500 microns (0.1 to 0.5 mm). Then the melt was extruded as in Example 3 and rolled onto a reel.

EXAMPLE 5

As in Example 4, a mixture of PCL 700 and acrylonitril-butadiene styrene copolymerizable was produced, but the melt was discharged in charges and, in a still deformable state, was pressed into a cooled mold or a plurality of molds. At the end, the molded body was taken out of the mold.

EXAMPLE 6

A melt-adhesive, composed of 65 weight percent PCL 700, 21 weight percent phenol resin (SP-560, made by Schenck Chemical Inc.) having a melting point of 150° C. and a density of 1.10 at 25° C. 10 weight percent EVA [ethylene vinyl acetate] and 4 weight percent microcrystalline wax were ground in a comminuting system to a particle size of from 100 to 400 microns. Thereafter, 500 parts by weight of the melt-adhesive (binder) and 500 parts by weight hard PVC powder having a particle size of from 100 to 400 microns were mixed in a powder mixer. The powder mixture was processed further, as in Example 1, on a roller spreader machine.

EXAMPLE 7

Regenerated acrylonitril-butadiene-styrene copolymerized granules (Novodur KL 1-5202 made by Bayer AG) were ground in a comminution system to a particle size distribution between 100 and 500 microns

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(0.1 to 0.5 mm). This powder was mixed, as in Example 1, with ground PCL 700, but instead of 50 weight percent, 60 weight percent PCL 700 was used. A silicone mold, provided for the manufacture of heel reinforcements in shoes was filled with the mixture using screen printing technology. The silicone mold was of such configuration that heel reinforcements were formed which tapered toward the lateral and upper edges to almost 0.01 mm.

The mold filled with the powder was heated for 20 seconds with the aid of a high frequency generator (40,000 MHz/40 KW/h) and then cooled for 20 seconds. After cooling, the ready-for-use shoe stiffener was removed from the silicone mold.

It will be understood that the above description of the present invention is susceptible to various modifications, changes and adaptations, and the same are intended to be comprehended within the meaning and scope of equivalents of the appended claims.

We claim:

1. A stiffening material composed of filler and binder and produced by melting the binder, shaping a composition which includes filler and binder, and then cooling the shaped composition, said stiffening material comprising 30 to 80 weight percent filler and 70 to 20 weight percent binder, wherein the filler consists of at least one type of particle selected from the group consisting of plastic particles, organic filler particles coated with at least one plastic surface layer, and inorganic filler particles coated with at least one plastic surface layer, said particles being present in a particle size distribution of from 50 to 500 microns, the plastic comprising the plastic particles or the surface layer of the coated

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filler particles being selected such that it will not dissolve in the binder at temperatures of about 50° C. to 80° C. but the particles remain in the form of essentially discrete bodies, wherein the binder firmly adheres to the filler particles; and wherein the binder is thermoplastically deformable in a temperature range of about 50° C. to 80° C. and has melt-adhesive characteristics.

2. The stiffening material of claim 1, wherein the filler particles are present in a particle size distribution of from 100 to 400 microns.

3. The stiffening material of claim 1, wherein the binder is a polymer of a cyclic ester or a copolymer of a cyclic ester.

4. The stiffening material of claim 3, wherein the binder is polycaprolactone.

5. The stiffening material of claim 1, wherein the binder is an elastomeric polyurethane.

6. The stiffening material of claim 1, wherein the binder is an olefin copolymer.

7. The stiffening material of claim 6, wherein the binder is an ethylene-vinyl acetate copolymer.

8. The stiffening material of claim 1, wherein the filler is high impact rigid PVC.

9. The stiffening material of claim 1, wherein the filler is a copolymer of acrylonitril, butadiene and styrene.

10. The stiffening material of claim 1, wherein the filler is a copolymer of vinyl chloride and an alpha olefin.

11. The stiffening material of claim 1, wherein the filler is present in the amount of 40 to 60 weight percent and the binder is present in the amount of 60 to 40 weight percent.

* * * * *

United States Patent [19]

Gaku et al.

[11] Patent Number: 4,820,769

[45] Date of Patent: Apr. 11, 1989

[54] HOT MELT ADHESIVE COMPOSITION

[75] Inventors: Morio Gaku, Saitama; Hidenori Kinbara, Tokyo, both of Japan

[73] Assignee: Mitsubishi Gas Chemical Company, Inc., Tokyo, Japan

[21] Appl. No.: 118,910

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Related U.S. Application Data

[63] Continuation of Ser. No. 914,976, Oct. 3, 1986, abandoned.

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525/148; 525/185; 525/186; 525/330.5;
525/437

[58] Field of Search 525/185, 186, 330.5,
525/113, 148, 132

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Macpeak, and Seas

[57] ABSTRACT

A hot melt adhesive composition comprising (A) 99 to 80 wt % of a thermoplastic resin selected from the group consisting of a substantially amorphous thermoplastic saturated polyester resin, an ethylene-vinyl acetate copolymer and an ethylene-ethyl acrylate copolymer and (B) from 1 to 20 wt % of a monofunctional or polyfunctional cyanate ester compound having at least one cyanate group in the molecule is disclosed. The hot melt adhesive composition can further contain a comonomer, a monofunctional or polyfunctional maleimide compound or a cross-linking catalyst for the thermoplastic resin (A). This composition has improved adhesive force, mechanical characteristics and heat resistance.

5 Claims, No Drawings

HOT MELT ADHESIVE COMPOSITION

This is a continuation of application Ser. No. 914,976, filed Oct. 3, 1986, now abandoned.

FIELD OF THE INVENTION

The present invention relates to a hot melt adhesive composition having an improved adhesive strength, and more particularly to a hot melt adhesive comprising a thermoplastic resin selected from the group consisting of a substantially amorphous or low-crystalline thermoplastic saturated polyester resin, an ethylene-ethyl acrylate copolymer and an ethylene-vinyl acetate copolymer, and cyanate ester compounds blended therewith. The hot melt adhesive composition has improved mechanical characteristics and heat resistance, and is used by applying it to a material to be adhered, in the form of a molded article, tape, melting adhesive, an adhesive sheet or a solution.

BACKGROUND OF THE INVENTION

A substantially amorphous thermoplastic saturated polyester resin (hereinafter referred to as "LPES" for brevity), an ethylene-ethyl acrylate copolymer (hereinafter referred to as "EEA" for brevity) and an ethylene-vinyl acetate copolymer (hereinafter referred to as "EVA" for brevity) are thermoplastic resins having excellent flexibility, rubber elasticity and low temperature characteristics and are widely used as a material to be blended with a wax, a base resin for hot melt adhesives and a molded product.

Hot melt adhesives prepared by mixing EEA or EVA with adhesives such as resins, turpentine oil, polyisobutylene and paraffin, and waxes do not always have a sufficient adhesive force, and have the disadvantage that an adhesive force at high temperatures is poor. Hot melt adhesive composition comprising a substantially non-crystalline thermoplastic saturated polyester resin alone or a mixture of the substantially non-crystalline thermoplastic saturated polyester resin and an epoxy resin are known. This adhesive has practically acceptable properties such as adhesive properties and flexibility, but in many cases its adhesive force is poor.

Methods for preparing a composition having excellent adhesive properties by compounding a butadiene-acrylonitrile copolymer, polyvinyl acetate, dimeric acid-based polyamide, thermoplastic polyurethane, amorphous thermoplastic polyester and so forth to a thermosetting resin composition containing as a main component polyfunctional cyanate ester compounds which are the component (B) of the present invention are described in, for example, U.S. Pat. Nos. 4,396,745 and 4,404,330, and U.S. patent application Ser. No. 711,291, filed on Mar. 13, 1985, now U.S. Pat. No. 4,645,805. However, the object of those methods is to obtain a thermosetting composition containing the component (B) of the present invention as the main component. Although this composition exhibits excellent characteristics, it has the disadvantages that since a curing reaction of the component (B) is essential, a relatively long time is required for heat curing; since the composition is thermosetting, the storage stability over a long period of time is poor; and the cost is expensive.

As a result of extensive investigations on utilization of the unique properties of a cyanate group of a compound having a cyanate group ($-O-C\equiv N$), it has been found that the adhesive properties can be greatly im-

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proved by adding the compound having a cyanate group to resins for hot melt adhesive such as EVA, EEA and LPES.

SUMMARY OF THE INVENTION

Accordingly, an object of the present invention is to provide a hot melt adhesive composition comprising

(A) from 99 to 80 wt % of a thermosetting resin selected from the group consisting of a substantially amorphous thermoplastic saturated polyester resin, an ethylene-vinyl acetate copolymer and an ethylene-ethyl acrylate copolymer and

(B) from 1 to 20 wt % of a monofunctional or polyfunctional cyanate ester compound having at least one cyanate group in the molecule compounded therewith.

In a preferred embodiment, a monofunctional or polyfunctional maleimide compound or a crosslinking catalyst of the thermoplastic resin (A) is used as a comonomer in an amount of from 0.1 to 5% by weight based on the weight of the hot melt adhesive composition, and the substantially amorphous thermoplastic saturated polyester resin having a number average molecular weight calculated from the number of terminal functional groups of from 5,000 to 22,000 and a softening point of from 40° to 140° C. is used.

DETAILED DESCRIPTION OF THE INVENTION

The ethylene-vinyl acetate copolymer (EVA) which can be used in the present invention is conventional ethylene-vinyl acetate copolymers having the vinyl acetate content of from 8 to 50 wt% and preferably from 25 to 40 wt%.

The ethylene-ethyl acrylate copolymer (EEA) which can be used in the present invention is conventional random copolymers prepared by copolymerizing ethylene and ethyl acrylate, and in which the ethyl acrylate content is 8 to 36 wt%.

The substantially amorphous thermoplastic polyester resin (LPES) which can be used in the present invention is prepared by polycondensing an aromatic or aliphatic di- or polycarboxylic acid and an aliphatic or alicyclic di- or polyol or its prepolymer, particularly an acid component containing terephthalic acid as a main component and a diol component containing ethylene glycol, propylene glycol or butanediol as a main component, in combination with other acids or diols while controlling the melting point, flowability characteristics, degree of crystallinity and so forth of the desired product. The softening point of the resin is generally 150° C. or less, preferably from 140° to 40° C. and more preferably from 120° to 50° C., and the degree of crystallinity determined by the X-ray method is generally 15% or less and more preferably 0%. In the present invention, the number average molecular weight calculated from the number of terminal functional groups is preferably from 1,500 to 25,000 and more preferably from 5,000 to 22,000 from standpoint of compatibility and the like. The number of free hydroxyl groups or carboxyl groups in LPES is preferred to be as small as possible because if an excess of free hydroxyl groups or carboxyl groups are present in LPES, these groups gradually react with the cyanate group of the component (B) even at room temperature, thereby deteriorating the storage stability of the hot melt adhesive composition.

Examples of the above aromatic or aliphatic di- or polycarboxylic acid are terephthalic acid, isophthalic

3 acid, maleic acid, succinic acid, adipic acid, pimelic acid, sebacic acid, azelaic acid, their lower alkyl esters and acid anhydrides, and low molecular weight thermal decomposition products of a carboxyl group-terminated unsaturated polyester resin.

Examples of the aliphatic or alicyclic di- or polyol or its prepolymer are ethylene glycol, propylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, neopentyl glycol, diethylene glycol, triethylene glycol, polyethylene glycol, polypropylene glycol, polybutylene glycol, polycaprolactonediol, 2,2-dimethylpropanediol, 2,2-bis(4-hydroxycyclohexyl)propane, 1,4-dihydroxymethylcyclohexane, trimethylolpropane, 1,2,3-trihydroxypropane and tetramethylmethane. Low molecular weight compounds are preferably used to obtain low crystalline or non-crystalline resins.

Preferred examples of LPES are "POLYESTER" produced by Nippon Gosei Kagaku Kogyo Co., Ltd., "PES SERIES" produced by Toa Gosei Chemical Industry Co., Ltd., "VYLON" produced by Toyo Boseki Co., Ltd., "KODAR PET" produced by Eastman Chemical Co., Ltd. and so forth which are commercially available.

As the component (A) of the present invention, a mixture of each LPES, EVA and EEA can be used if desired. In addition, conventional plastics such as vinyl chloride, polyethylene, polypropylene, an ethylene-propylene rubber and polycarbonate; conventional adhesives and waxes for hot melt adhesives, such as rosin, hydrogenated rosin, hydrogenated rosin ester, coumarone-indene resin, polyterpene, alkyd resin, petroleum hydrocarbon resin, xylene resin, phenolic resin, epoxy resin, paraffin, phthalic acid ester, phosphoric acid ester, chlorinated diphenyl, neoprene rubber and nitrile rubber; inorganic fillers such as calcium carbonate, aluminum hydroxide, calcium hydroxide, magnesium hydroxide, talc, clay, mica and wollastonite; powders, fibers or flakes of metals such as copper, iron, cobalt, nickel, chromium, aluminum and manganese, or their alloys; powders, fibers or flakes of copper oxide, iron oxide, lead oxide and so on; organic metal compound pigments such as copper phthalocyanine (phthalocyanine blue); inorganic pigments such as chrome yellow, mineral violet, carbon black, iron oxide, ultramarine, cobalt blue, cobalt violet and titan white; and additives such as plasticizers, flame retardants, ultraviolet absorbers and stabilizers can be added to the component (A) of the present invention.

Referred monofunctional or polyfunctional cyanate ester compounds which can be used as the component (B) of the present invention are compounds represented by the formula



wherein m is an integer of 1 or more, and preferably from 1 to 5, R is an aromatic organic group, and the cyanato group is bonded to the aromatic ring of the organic group.

Representative examples of the compounds represented by the above formula are monocyanatobenzene, 1,3- or 1,4-dicyanatobenzene, 1,3,5-tricyanatobenzene, 1,3-, 1,4-, 1,6-, 1,8-, 2,6- or 2,7-dicyanatophthalene, 1,3,6-tricyanatophthalene, 4,4'-dicyanatobiphenyl, bis(4-dicyanophenyl)methane, 2,2-bis(4-cyanatophenyl)propane, 2,2-bis(3,5-dichloro-4-cyanatophenyl)propane, 2,2-bis(3,5-dibromo-4-cyanatophenyl)propane, bis(4-cyanatophenyl)ether, bis(4-cyanatophenyl)-

thioether, bis(4-cyanatophenyl)sulfone, tris(4-cyanatophenyl)phosphite, tris(4-cyanatophenyl)phosphate, cyanate esters obtained by the reaction of novolak and cyanogen halide (U.S. Pat. Nos. 4,002,755 and 3,448,079), and cyanate esters obtained by the reaction of hydroxy group-terminated polycarbonate oligomers and cyanogen halide (U.S. Pat. No. 4,026,913). In addition, cyanate esters as described in Japanese Patent Publication Nos. 1928/66, 18468/68, 4791/69, 11712/70, 41112/71, 26853/72, Japanese Patent Application (OPI) No. 63149/76 (the term "OPI" as used herein means a "published unexamined patent application"), U.S. Pat. Nos. 3,553,244, 3,755,403, 3,740,348, 3,595,900, 3,694,410 and 4,116,949, which are incorporated herein by reference, can also be used.

The above monofunctional or polyfunctional cyanate ester compound can be used alone or they can be used as prepolymers which are obtained by adding co-modifiers as described hereinafter to the ester compounds and pre-reacting the mixture upon heating in the presence or absence of conventional catalysts. These prepolymers contain, as well as unreacted —OCN groups, a sym-triazine ring formed by trimerization of a cyan group, and have the number average molecular weight of from 300 to 6,000 and preferably 3,000 or less.

The hot melt adhesive composition of the present invention contains the above-described components (A) and (B) as essential components. A co-modifier, particularly a cross-linking catalyst to cross-link the component (A) of the present invention or the monofunctional or polyfunctional maleimide compound can be added in an amount of from 0.1 to 5% by weight based on the weight of the hot melt adhesive composition to improve its adhesive properties or impart other properties thereto.

Examples of the cross-linking catalysts to cross-link the component (A) are conventional catalysts such as organic peroxides, e.g., dicumyl peroxide, benzoyl peroxide, lauroyl peroxide, capryl peroxide, acetyl peroxide, p-chlorobenzoyl peroxide and di-tert-butylperphthalate, and sulfur. Further examples thereof are organometallic salts such as lead naphthenate, lead stearate, zinc naphthenate, zinc octoate, tin oleate, dibutyl tin maleate, manganese naphthenate, cobalt naphthenate and metal chelates, such as iron acetylacetonate which are co-catalyst for the above cross-linking catalysts.

The monofunctional or polyfunctional maleimide compounds are compounds having at least one N-maleimide group in the molecular. Representative examples thereof are phenyl maleimide, bis(4-maleimidophenyl)methane, bis(4-maleimidophenyl)ether, 1,1-bis(4-maleimidophenyl)cyclohexane, 2,2-bis(4-maleimido-3-chlorophenyl)propane, 2,2-bis(4-maleimido-3,5-dibromophenyl)propane, 1,1-bis(4-maleimidophenyl)-1-phenylethane, and polymaleimides obtained by reacting polyamine which is prepared by reacting aniline and formalin so as to bond benzene rings through a methylene bond, and maleic anhydride.

Examples of other co-modifiers which can be used in the present invention are bisphenol A-type, phenol novolak-type, cresol novolak-type and other type epoxy resins; poly(meth)acrylates such as (meth)acrylate, polyfunctional (meth)acrylate, alkyl(meth)acrylate, and epoxy(meth)acrylate; polyallyl compounds and their prepolymers, such as diallyl phthalate, divinylbenzene, diallylbenzene, and trialkenyl isocyanurate;

dicyclopentadiene and its prepolymers; a phenol resin; and the like.

The proportions of the components (A) and (B) in the hot melt adhesive composition are such that the amount of the component (A) is from 99 to 80 wt%, preferably from 95 to 85 wt%, based on the weight of the component (A) and the component (B), and the amount of the component (B) is from 1 to 20 wt% and preferably from 5 to 15 wt%, based on the weight of the component (A) and the component (B). If the amount of the component (B) is more than 20 wt%, a curing reaction is essential and a cured product tends to become hard. On the other hand, if the amount of the component (B) is less than 1 wt%, the improvement effect of the adhesive force is insufficient.

A method for mixing the component (A) of the present invention with the cyanate ester compound as the component (B) of the present invention, or further with a cross-linking catalyst as a co-modifier thereof, or a monofunctional or polyfunctional maleimide compound, is not particularly limited, and any method can be employed so long as those components are uniformly dispersed. Any conventional methods such as a method of mixing the above components with e.g., a blender, and using an extruder; a method of solution mixing and drying; a method of mixing with e.g., a kneader or a Herschel mixer, and using the mixture as such or after extrusion; a method in which an inorganic filler, a metal, a metal oxide or a pigment, and other additives are previously mixed with the co-modifiers of the present invention, and the resulting mixture is mixed with the component (A) and extruded; and a master batch method in which high concentration master batches are produced and those are mixed, can be used. In addition, a method in which the components (A) and (B) are dissolved in an organic solvent capable of dissolving the components (A) and (B), such as toluene and xylene, at room temperature or while heating to form a solution in a relatively emulsified condition is suitable. In this method, as mixing conditions, extrusion conditions of the component (A) can be used as such in the case of using an extruder. This mixing is carried out at room temperature or under heating.

The hot melt adhesive composition of the present invention prepared by the above method is molded into molded articles such as plates, pellets, sheets, films, rods or the like by a method such as press molding, extrusion molding and injection molding, and is used to form an adhesive layer or a film for bonding, using a solution of mixture with solvent.

Bonding conditions using the hot melt adhesive composition of the present invention vary depending upon the type of the composition components used or the

like, but are generally at temperatures of from 90° to 250° C. for from 5 seconds to 30 minutes. It is preferred to apply a pressure at the time of bonding. The pressure applied is generally from 0.1 to 500 kg/cm² and preferably from 5 to 150 kg/cm².

The present invention is described in greater detail by reference to the following examples and comparative examples. All parts are by weight unless otherwise indicated.

EXAMPLE 1

As the thermoplastic resin (A) for a hot melt adhesive composition, three types of LPES ("PES 110H" and "PES 170", produced by Toa Gosei Chemical Industry Co., Ltd., "LP 035" (number average molecular weight: 16,000, hydroxyl value: 6 mg.KOH/g), produced by Nippon Gosei Kagaku Co., Ltd.; hereinafter referred to as "110H", "170" and "LP 035", respectively) were used; as the cyanate ester compound (B), a product having a weight average molecular weight of about 300 (hereinafter referred to as "BT 1003") prepared by pre-mixing 90 parts of 2,2-bis(4-cyanatophenyl)propane (hereinafter referred to as "BPACN") and 10 parts of bis(4-maleimidophenyl)methane (hereinafter referred to as "BMT") at 130° C. for 30 minutes, and a product having a weight average molecular weight of about 2,000 (hereinafter referred to as "BT 2020") prepared by pre-reacting 80 parts of 1,4-dicyanatobenzene and BMT at 150° C. for 3 hours were used; and as a co-modifier, dicumyl peroxide (hereinafter referred to as "DCPO") and rosin were used.

These components were used as shown in Table 1 below and mixed in a kneader under conditions of 80° C. and 30 minutes in the tests other than Test Nos. 13 to 15 and under conditions of 100° C. and 30 minutes in Test Nos. 13 to 15 to produce hot melt adhesive compositions.

The above produced hot melt adhesive compositions and LPES alone for the sake of comparison were measured for adhesive strength.

In measurement of the shear adhesive strength (σ_T , kg/cm²), an adhesive layer was formed on a 15 mm long end portion of a soft iron plate having a thickness of 2 mm and a width of 25 mm in a thickness of 100 μ m and bonded under conditions of 180° C., 3 minutes and 5 kg/cm² to produce a test piece.

In measurement of the peel strength (σ_S , kg/cm), an adhesive layer was formed in a thickness of 150 μ m between 100 μ m thick aluminum foils and the composite was bonded under conditions of 160° C., 30 minutes and 5 kg/cm² to produce a test piece. Using this test piece, both ends of the bonded foils were peeled off.

The results obtained are shown in Table 1 below.

TABLE 1

Test No.	LPES		Co-Modifier		Aids		σ_T (kg/cm ²)	σ_S (kg/cm)
	Type	Parts	Type	Parts	Type	Parts		
1	110H	100	BPACN	5			65	
2	"	"	"	10			98	
3	"	"	"	20			140	
4	"	"	BT1003	5			70	
5	"	"	"	10			105	
6	"	"	"	20			169	
7	"	"	BT2020	5			98	
8	"	"	"	10			136	
9	"	"	"	20			185	
10	"	"	BT1003	5	DCPO	1	69	
11	"	"	"	10	"	1	122	
12	"	"	"	20	"	1	175	
13	170	"	"	5			79	

TABLE 1-continued

Test No.	LPES		Co-Modifier		Aids		σT (kg/cm ²)	σS (kg/cm)
	Type	Parts	Type	Parts	Type	Parts		
14	"	"	"	"	"	10	116	
15	"	"	"	"	"	20	182	
16	LP035	"	"	"	"	5	72	2.0
17	"	"	"	"	"	10	104	2.5
18	"	"	"	"	"	20	169	2.7
19	110H	"	"	"	"	"	44	
20	"	"	"	"	Rosin	5	46	
21	"	"	"	"	"	20	0	
22	035	"	"	"	"	"	38	0.5

Test Nos. 1-18: Invention
Test Nos. 19-22: Comparison

EXAMPLE 2

EVA (produced by Mitsui Polychemical Co., Ltd., trade name, "EVAFLEX #250", vinyl acetate content: 28%, melt index (=MFR, ASTM D1238 method): 15 g/10 min) was mixed with a roll maintained at 90° C. BPACN, BMI, DCPO, rosin, or solid paraffin (produced by Nippon Seirou Co., Ltd., 145° F. paraffin wax) was added to 100 parts of EVA in an amount as shown in Table 2 and then kneaded with a roll for 10 minutes. The resulting mixture was press molded under conditions of 100° C., 30 kg/cm² and 1 minute to produce a sheet having a thickness of 0.3 mm.

This sheet was interposed between 100 μ m thick polyethylene terephthalate (hereinafter referred to as "PET") films and the laminate was bonded by press molding under conditions of 30 kg/cm², 180° C. and 3 minutes.

The peel strength (σS , 180, kg/25 mm) between the above bonded PET films at a 180° C. angle was measured, and the results obtained are shown in Table 2 below.

TABLE 2

	Test Nos.							
	1	2	3	4	5	6	7	8
BPACN	10	9	9	16				30
BMI	1	1	1	2				
DCPO	1	1	1	1				1
Rosin					20			
Paraffin			10					30
σS , 180 (kg/25 mm)	12	17	8	8	3	0	1	0

Test Nos. 1-6: Invention
Test Nos. 7-8: Comparison

EXAMPLE 3

To 100 parts of EVA (produced by Mitsui Polychemical Co., Ltd., trade name, "EVAFLEX #40", vinyl acetate content: 40%, MFR: 55 g/10 min) were added a prepolymer having a weight average molecular weight of 1,500 (hereinafter referred to as "BT1015") prepared by pre-reacting 9 parts of BPACN and 10 parts of BMI as shown in Table 3 at 140° C. for 2 hours, and DCPO. The resulting mixture was kneaded with 60 rolls maintained at 80° C. for 10 minutes and then press molded for 1 minute at 5 kg/cm² with a press maintained at 80° C. to produce a film having a thickness of 150 μ m.

The above produced film was interposed between 65 100 μ m thick PET films, and the laminate was bonded by press molding under conditions of 5 kg/cm², 180° C. and 3 minutes. The peel strength of the film bonded

surface was measured in the same manner as in Example 2.

The results obtained are shown in Table 3 below.

TABLE 3

	Test Nos.			
	1	2	3	4
EVA	100	100	100	100
BT1015	9	10	18	18
DCPO	0	1	0	1
σS , 180 (kg/25 mm)	15	17	10	12

Test Nos. 1-4: Invention

A roll kneaded composition obtained in the same manner as in Test No. 2 was dissolved in toluene at 80° C. to prepare a solution having a solid concentration of 25%.

This solution was coated on one surface of a 100 μ m thick aluminum foil and dried at 130° C. for 5 minutes to form a 60 μ m thick coating. A 100 μ m thick aluminum foil was placed on the coating side of the above aluminum foil and pressed at 160° C. and a pressure of 5 kg/cm² for 15 minutes. The peel strength was measured in the same manner as above and was 11 kg/25 mm.

EXAMPLE 4

BT1015, DCPO, rosin and solid paraffin were added as shown in Table 4 to EVA (produced by Mitsui Polychemical Co., Ltd.; trade name, "EVAFLEX #220", vinyl acetate content: 28%; MFR: 150 g/10 min) and kneaded for 10 minutes with rolls maintained at 70° C. The resulting mixture was extruded from a T die maintained at 180° C. in a thickness of 60 μ m and placed on a 50 μ m thick iron foil to form a layer having a thickness of 60 μ m. Immediately a 50 μ m thick iron foil was superposed on the layer. The resulting laminate was passed between rolls of 180° C. and 25 kg/cm at a speed of 1 m/min and then allowed to stand at room temperature.

The peel strength was measured in the same manner as in Example 2. The results obtained are shown in Table 4 below.

TABLE 4

	Test Nos.						
	1	2	3	4	5	6	7
EVA	40	40	40	40	40	40	40
BT1015	0	0	0	5	10	10	10
DCPO	0	1	1	1	2	1	1
Rosin	40	40	40	40	40	40	40
Paraffin	20	20	0	0	0	0	5
σS , 180	2	1	3	11	10	12	6

TABLE 4-continued

	Test Nos.						
	1	2	3	4	5	6	7
(kg/25 mm)							
Test Nos. 1-3: Comparison							
Test Nos. 4-7: Invention							

EXAMPLE 5

To 100 parts of EVA (trade name, "EVAFLEX" #150) were added a prepolymer having a weight average molecular weight of 2,000 (hereinafter referred to as "BT1020") prepared by pre-reacting 90 parts of BPACN and 10 parts of BMI at 140° C. for 4 hours as shown in Table 5 and benzoyl peroxide (hereinafter referred to as "BPO"). The resulting mixture was kneaded with rolls maintained at 80° C. for 8 minutes and then press molded for 1 minute at 20 kg/cm² using a press maintained at 80° C. to produce a film having a thickness of 150 μ m.

The above produced film was interposed between a 100 μ m thick aluminum foil, a 50 μ m thick copper foil, a polycarbonate film, a polysulfone film and a polyimide film, and the laminate was then bonded by press molding under conditions of 20 kg/cm², 160° C. and 3 minutes.

The peel strength was measured in the same manner as in Example 2. The results obtained are shown in Table 5 below.

TABLE 5

	Test Nos.		
	1	2	3
Composition:	EVA	100	100
	BT1020	3	6
	BPO	1	1
	Al foil	3	10
	Cu foil	6	9
	Polycarbonate film	3	5
	Polysulfone film	3	5
	Polyimide film	4	6
σS , 180 (kg/25 mm)			

Test Nos. 1-3: Invention

EXAMPLE 6

EEA (produced by Mitsui Dupont Polychemical Co., Ltd.; trade name, "EVAFLEX-EEA, 709A", ethyl acrylate content: 35%; random copolymer, hereinafter referred to as "EEA709") was kneaded using rolls maintained at 80° C. To 100 parts of EEA 709 were added, as shown in Table 6, a prepolymer having a weight average molecular weight of 2,000 (hereinafter referred to as "BPAC20") prepared by pre-reacting BPACN and BPACN at 140° C. for 8 hours, BT1015, and rosin or DCPO. The mixture was then kneaded at 80° C. for 10 minutes using rolls, and molded into a 200 μ m thick film using rolls maintained at 80° C.

This film was interposed between 100 μ m thick PET films and bonded therebetween by press molding under conditions of 5 kg/cm², 180° C. and 3 minutes.

The peel strength was measured in the same manner as in Example 2. The results obtained are shown in Table 6 below.

TABLE 6

	Test Nos.										
	1	2	3	4	5	6	7	8	9	10	11
Modifier (parts)											
BPACN											

TABLE 6-continued

	Test Nos.										
	1	2	3	4	5	6	7	8	9	10	11
BPAC20											
BT1015											
co-modifier											
Rosin											
DCPO											
σS , 180 (kg/25 mm)											

Test Nos. 1-3 and 10: Comparison
Test Nos. 4-9 and 11: Invention

EXAMPLE 7

A 200 μ m thick film was produced using the components shown in Table 7 in the same manner as in Example 6. This film was interposed between 100 μ m thick aluminum foils, between 50 μ m thick copper foils, between polysulfone films, between polyetherimide films, or between polyetheretherketone films and bonded by press molding under conditions of 20 kg/cm², 190° C. and 1 minute.

The peel strength was measured in the same manner as in Example 2. The results obtained are shown in Table 7 below.

TABLE 7

	Test Nos.		
	1	2	3
Components (parts)			
EEA709	100	100	100
BPACN	10		
BT1015		10	10
Arakun P-100*			10
DCPO		1	1
σS , 180 (kg/25 mm)			
Al foils		10	11
Cu foils		10	11
Polysulfone film		5	6
Polyetherimide film		5	5
Polyetheretherketone film		5	5

Note:
*Alcyclic hydrocarbon resin, produced by Arakawa Resin Kagaku Co., Ltd., trade name, "ARUKON P-100"

EXAMPLE 8

The same EEA resin as used in Example 6 was kneaded with rolls maintained at 80° C. The components shown in Table 8 were then added to 100 parts of EEA and kneaded at 100° C. for 10 minutes using rolls.

The resulting mixture was press molded under conditions of 170° C. and 30 minutes to produce a 3 mm thick plate at a test piece.

The test results obtained are shown in Table 8 below.

TABLE 8

	Test Nos.				
	1	2	3	4	5
Components (parts)					
EEA709	100	100	100	100	100
BT1015					
DCPO					
Iron acetylacetone					
Tensile Strength (kg/mm ²)					
Elongation 100%	0.16	0.17	0.17	0.19	0.20
Elongation 300%	0.20	0.30	0.16	0.42	0.46
At break	0.32	0.58	0.55	0.60	0.66

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TABLE 8-continued

	Test Nos.				
	1	2	3	4	5
Tensile Elongation	720	540	530	430	430
at Break %					

Test Nos. 1 and 2: Comparison
Test Nos. 3-5: Invention

While the invention has been described in detail and with reference to specific examples thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

What is claimed is:

1. A hot melt adhesive composition consisting essentially of
(A) 99 to 80 wt% of an ethylene-vinyl acetate copolymer and

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(B) 1 to 20 wt% of a monofunctional or polyfunctional cyanate ester compound having at least one cyanate group in the molecule.

2. The composition as claimed in claim 1, wherein the amount of the ethylene-vinyl acetate copolymer is 95 to 85 wt%.
3. The composition as claimed in claim 1, wherein the ethylene-vinyl acetate copolymer has a vinyl acetate content of 8 to 50 wt%.
4. The composition as claimed in claim 3, wherein the vinyl acetate content is 25 to 40 wt%.
5. The composition as claimed in claim 1, wherein the monofunctional or polyfunctional cyanate ester compound having at least one cyanate group in the molecule is represented by the formula



wherein m is an integer of 1 or more, R is an aromatic organic group, and the cyanate group is bonded to an aromatic ring of the aromatic organic group.

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ADHESIVE PROPERTIES

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(57) ABSTRACT

A process of making a fabric based stiffener material having thermal adhesive properties on its top and bottom surfaces which is based on (a) contacting a non-woven fabric with a latex forming resin and a finely divided powder adhesive polymer to form a latex saturated non-woven fabric; and (b) removing the excess latex from the non-woven fabric formed in step (a); and (c) drying the product of step (b).

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STIFFENER MATERIAL WITH SELF ADHESIVE
PROPERTIES[0001] This application is a divisional of U.S. patent
application Ser. No. 09/631,503 filed Aug. 3, 2000.

BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] The present invention is concerned with stiffener
materials for use in the fabrication of shoes and for making
other articles.

[0004] 2. Description of the Related Art

[0005] Stiffener materials traditionally are used in the shoe industry to provide varying degrees of resilient, stiffness, and shape-retention to the heel and toe portions of shoes. These materials have been made of either a needle punched non-woven fabric which is saturated with a latex resin composition or a flexible thermoplastic resin that is extruded or powder coated onto a woven fabric or extruded into a sheet. If a non-woven fabric is employed, the typical material which is selected is a polyester mat made from fibers having a denier of between 3 and 6 deniers or mixtures of such fibers. The latex resin compositions may be based on resins selected from styrene resins, styrene-butadiene resins, vinyl acetate resins, vinyl chloride resins or acrylic resins. The extruded thermoplastic or powder coated thermoplastic materials may be selected from the group consisting of polyvinyl chloride, ionomers, high, medium or low density polyethylene, polypropylene, polyesters, polystyrene and copolymers and compatible blends of such polymers. After the initial coating of the woven or non-woven fabrics, a separate hot melt coating operation is carried out to provide a finished stiffener which has self adhesive properties which are sufficient to bond the stiffener to an inner layer and an outer layer of a manufactured article.

[0006] The powder-coated resins usually contain particles which measure from about 100 to about 500 microns which prevents the particles from passing through the woven fabrics during the coating operation.

[0007] A typical non-woven latex saturated stiffener is made with a polymer latex wherein the dispersed polymer particles have an average latex particle size of less than one micron and a filler such as calcium carbonate which has an average particle size of less than 10 microns. A continuous sheet of the non-woven fabric may be passed through a bath containing the latex composition to saturate the non-woven fabric prior to passing the saturated sheet through calendaring rolls, which are spaced apart with a filler gauge, in order to remove excess latex composition. The saturated non-woven fabric is then clipped onto a tenter frame and passed to a drying oven to remove the water from the latex composition. The dried non-woven fabric is then sized by passing the dried latex saturated non-woven fabric through calendaring rolls and wound on a beam. The product may be made heavier, thinner, stiffer or more flexible depending on the weight and thickness of the non-woven fabric, the amount of the latex applied and the formulation of the latex.

[0008] Since the dried non-woven fabric has no adhesive properties after the application of the latex and the oven drying, it is necessary to apply a hot melt adhesive, such as a ethylene vinylacetate hot melt adhesive. This results in a

product that can be heat activated to provide a finished stiffener which has self adhesive properties which are sufficient to bond the stiffener to an inner layer and an outer layer of a shoe.

[0009] U.S. Pat. No. 4,717,496 describes a method of making a stiffening material with non-latex powders. The disclosure of U.S. Pat. No. 4,717,496 is incorporated by reference.

SUMMARY OF THE INVENTION

[0010] The present invention provides a novel process that produces a novel stiffener material which is made by adding an effective amount of a finely divided thermally activatable powder adhesive to a latex composition which is used to saturate a non-woven fabric to make a stiffener material.

[0011] The process of the invention comprises a method of making a fabric based stiffener material having thermal adhesive properties on its top and bottom surfaces, said process comprising:

[0012] (a) preparing a coating composition which comprises a latex forming resin and a finely divided powdered adhesive polymer;

[0013] (b) contacting a non-woven fabric with the composition of step (a) to form a latex saturated non-woven fabric;

[0014] (c) removing the excess latex from the non-woven fabric; and

[0015] (d) drying the product of step(c).

[0016] Accordingly, it is a primary object of the invention to provide a process where a treating composition comprising a latex based stiffening resin and a heat activated adhesive resin is used to saturate a non-woven fabric to form a treated fabric and thereafter drying and sizing said treated fabric to make a heat activated adhesive stiffener having adhesive properties on both sides of the stiffener material.

[0017] It is also an object of the invention to provide a novel heat activated stiffener material which has adhesive material on the surface and on the interior of the stiffener material.

[0018] It is also an object of the invention to eliminate the need to carry out a separate adhesive coating operation whereby an adhesive is applied as a separate manufacturing step to a stiffener which is prepared by a latex coating a non-woven fabric.

[0019] It is also an object of the invention to provide a novel polyester containing latex composition which provides a stiffener having a good combination of stiffness, shape-retention, and resiliency.

[0020] These and other objects and features of the invention will become apparent from a review of the following detailed description.

DETAILED DESCRIPTION OF THE
INVENTION

[0021] While woven or non-woven fabrics may be used in the practice of the invention, it is preferred to employ a non-woven fabric that is made with fibers having a denier of about 6 to about 15 or fabrics made with a blend of such

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fibers. It is especially preferred to use a non-woven fabric made with fibers that are a 70/30 blend of 15 and 6 denier fibers. If fabrics are used that are made with deniers substantially different than the above described results, difficulty can arise when using the latex containing the adhesive and the polymer material.

[0022] The polyester containing latex composition is prepared by taking a conventional latex of a material such as styrene butadiene, an acrylic polymer, a vinyl acetate resin, a vinyl chloride resins or other suitable latex forming polymer and adding an amount of a polyester powder which is sufficient to impart good adhesive properties to the finished stiffener material. Saturated powdered polyesters such as polycaprolactone, azelaic, adipic, sebacic and copolymers of polyethylene terephthalate and the like may be employed as substantially pure resins or in the form of commercially formulated adhesive compositions with conventional dispersants, tackifiers, stabilizers, fillers and the like. If the polyester is employed as a pure resin, conventional dispersants such as non-ionic surfactants, gums, colloids or thickening agents may be added to stabilize the latex containing the polyester. In order to provide an adhesive which adheres to the non-woven fabric without "dropping out" or in other words separating as a discrete powder on the non-woven fabric, it is preferred to grind the powdered polyester to a finely divided state which will remain dispersed in a polymeric latex. Generally an average particle size of less than 150 microns and more preferably less than 100 microns will provide good results. The "dropping out" phenomenon is usually observed when the process of the invention is practiced on a full scale commercial apparatus as compared to a laboratory scale operation. Ammonium chloride or other acid forming ingredients may be employed as a catalyst to cross-link certain polymer latex resins. It is preferred to add an effective amount of an organic cross-linking agent to the polyester containing latex to improve resilience and prevent "washing out" of the latex. Melamine-formaldehyde condensates are preferred. Suitable examples of these materials are described in U.S. Pat. No. 2,871,213 and U.S. Pat. No. 3,215,647, which are incorporated by reference. If a cross-linker is used, a total of 1.0% to 2.0% by weight may be used. Compatible fillers such as finely calcium carbonate, and the like may be employed.

[0023] The novel stiffener may be evaluated to determine the adhesive bonding strength of the finished product by die cutting a piece of the stiffener to be tested and inserting the stiffener between two pieces of a non-woven lining material that is a 35% polyester blend having a thickness of 0.029 inches. The three pieces are held together and placed into a back part heel counter molding machine with the female mold at 180° F. and the male mold at 200° F. The mold is closed and held in position for 17 seconds. The mold is opened and the laminate is placed, at room temperature, in a laminate cooling station having the desired shape of the final product. The shaped heel counter is now rigid and the stiffener is bonded to the two pieces of non-woven lining material. The adhesive test requires that the three part laminate remain bonded together when unusual pressure is applied to pull the components apart. The resiliency test is based on making a thumb indent on the side of the heel counter and evaluating the degree which the indent bounces back. An acceptable bounce is when the indent bounces back immediately with a "ping-pong" sound.

[0024] The latex of the invention will comprise the following formulation:

latex forming polymer dry basis	15 wt % to 35 wt %
dispersant	0.4 wt % to 1.0 wt %
adhesive polymer	10 wt % to 31 wt %
water	35 wt % to 50 wt %
filler	0 wt % to 15 wt %

[0025] Generally the preferred latex formulations will comprise the following formulation:

latex forming polymer dry basis	25.5 wt % to 35 wt %
dispersant	.7 wt % to .9 wt %
adhesive polymer	15 wt % to 19 wt %
water	43 wt % to 44 wt %
filler	1.1 wt % to 11.8 wt %

[0026] The non-woven fabric should be saturated with an amount of the latex formulation that will result in a dry weight gain of between 300 to 1000 g/meter² of coated fabric and preferably between 400 to 900 g/meter² of based on the dry weight of the coated fabric after the coating and drying operation as compared to the dry weight of the uncoated fabric. The preferred drying conditions are a temperature of from 200 to 400° F. and preferably from 250° F. to 370° F. which are applied for a period of 5 to 15 minutes in a tenter frame equipped therewith controlled oven.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0027] The following examples are added to illustrate the invention. They are not to be construed as limitations on the scope of the invention.

EXAMPLE 1

[0028] A formulation was made by adding the ingredients in sequence using a laboratory propeller agitator:

Styrene-butadiene copolymer (Dow 242 SBR on resin - 45% solids; particle size 175-1 Argonome; Brookfield viscosity #2-50 rpm = 70; Tg 45° C.)	318.0 g
Melamine-formaldehyde condensate cross-linker (Cyex 433 CAS No. 88002-20-1)	8.0 g
Water	98.0 g
Oxazoline surfactant (Alkacerge T-IV wt % mol wt 545 CAS No. 95706-86-8) Polysiloxane-probucione-88 micron av. dia. (Tosol 767-MPT D1238-72 1.9 at 80° C., 44 psi, g/10 min. mp. 140° C.; shore hardness 55D)	3.0 g
Calcium carbonate (Median particle dia. 6.5µ; Onyacarb 6)	48 g
Aqueous Soln. Sod. polycrylate (Alogum 296; Brookfield viscosity 20 rpm, 25° C. 20,000-30,000 cps; 14.7-17.3% solids)	3 g
Ammonium chloride	14.5 g
Total mix Viscosity-Brookfield-Spinde-20 rpm-25° C.	2050 cps
% polyester based on total weight of solids - 25%	
% polyester based on total weight of resin - 30%	

[0029] This formulation applied to a non-woven fabric, 166 g/m², which was made from a 70/30 blend of 15 and 6 denier fibers. The fabric was provided on a continuous roll, 60" wide which was passed through a trough to saturate the fabric prior to passing the fabric through a set of steel rolls that were 76" wide and 9" in diameter with an opposing hydraulic pressure of 500-600 psi. After passing through the rolls, the fabric was dried in an oven 85 ft. long at a temperature of 130-200° C. and wound on a reel at a speed of 3.25 yards/minute. The product produced had good resiliency and a fair bond.

EXAMPLE 2

[0030] A formulation was made by adding the ingredients in sequence using a laboratory propeller agitator:

Styrene-butadiene copolymer (Dow 242 SBR on resin - 45% solids; particle size 175-1 Argonome; Brookfield viscosity #2-50 rpm = 70; Tg 45° C.)	260.0 g
Melamine-formaldehyde condensate cross-linker (Cyex 433 CAS No. 88002-20-1)	8.0 g
Water	75.0 g
Oxazoline surfactant (Alkacerge T-IV wt % mol wt 545 CAS No. 95706-86-8) Polysiloxane-probucione-88 micron av. dia. (Tosol 767-MPT D1238-72 1.9 at 80° C., 44 psi, g/10 min. mp. 140° C.; shore hardness 55D)	4.0 g
Calcium carbonate (Median particle dia. 6.5µ; Onyacarb 6)	0 g
Aqueous Soln. Sod. polycrylate (Alogum 296; Brookfield viscosity 20 rpm, 25° C. 20,000-30,000 cps; 14.7-17.3% solids)	22 g
Ammonium chloride	4 g
Total mix Viscosity-Brookfield-Spinde-20 rpm-25° C.	2100 cps
% polyester based on total weight of solids 37.4%	
% polyester based on total weight of resin 40%	

[0031] This formulation applied to a non-woven fabric, 166 g/m², which was made from a 70/30 blend of 15 and 6 denier fibers. The fabric was provided on a continuous roll, 60" wide which was passed through a trough to saturate the fabric prior to passing the fabric through a set of steel rolls that were 76" wide and 9" in diameter with an opposing hydraulic pressure of 500-600 psi. After passing through the rolls, the fabric was dried in an oven 85 ft. long at a temperature of 130-200° C. and wound on a reel at a speed of 3.25 yards/minute. The product produced has a very good bond and good resiliency.

EXAMPLE 3

[0032] A formulation was made by adding the ingredients in sequence using a laboratory propeller agitator:

Styrene-butadiene copolymer (Dow 242 SBR on resin - 45% solids; particle size 175-1 Argonome; Brookfield viscosity #2-50 rpm = 70; Tg 45° C.)	227.0 g
Melamine-formaldehyde condensate cross-linker (Cyex 433 CAS No. 88002-20-1)	7.0 g
Water	92.0 g
Oxazoline surfactant	4.0 g

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(Alkacerge T-IV wt % mol wt 545 CAS No. 95706-86-8) Polysiloxane-probucione-88 micron av. dia. (Tosol 767-MPT D1238-72 1.9 at 80° C., 44 psi, g/10 min. mp. 140° C.; shore hardness 55D)	91 g
Calcium carbonate (Median particle dia. 6.5µ; Onyacarb 6)	52 g
Aqueous Soln. Sod. polycrylate (Alogum 296; Brookfield viscosity 20 rpm, 25° C. 20,000-30,000 cps; 14.7-17.3% solids)	14 g
Total mix Viscosity-Brookfield-Spinde-20 rpm-25° C.	1850 cps
% polyester based on total weight of solids 34.5%	
% polyester based on total weight of resin 45%	

[0033] This formulation applied to a non-woven fabric at a level of 166 g/m². The non-woven fabric was made from a 70/30 blend of 15 and 6 denier fibers. The fabric was provided on a continuous roll, 60" wide which was passed through a trough to saturate the fabric prior to passing the fabric through a set of steel rolls that were 76" wide and 9" in diameter with an opposing hydraulic pressure of 500-600 psi. After passing through the rolls, the fabric was dried in an oven 85 ft. long at a temperature of 130-200° C. and wound on a reel at a speed of 3.25 yards/minute. The product produced had good resiliency and a good bond.

What is claimed is:

1. A latex composition for preparing a stiffened fabric, said latex composition comprising:

latex forming polymer	15 wt % to 35 wt %
dispersant	0.4 wt % to 1.0 wt %
adhesive polyester resin	10 wt % to 31 wt %
water	35 wt % to 50 wt %; and
filler	0 wt % to 15 wt %.

2. A latex composition as defined in claim 1, wherein the latex forming polymer is styrene butadiene and the adhesive polyester resin is poly-epsilon caprolactone.

3. A stiffener comprising a non-woven fabric saturated with a composition comprising:

latex forming polymer	15 wt % to 35 wt %
dispersant	0.4 wt % to 1.0 wt %
adhesive polyester resin	10 wt % to 31 wt %
water	35 wt % to 50 wt %; and
filler	0 wt % to 15 wt %.

4. A stiffener as defined in claim 2, wherein the latex forming polymer is styrene butadiene and the adhesive polyester resin is poly-epsilon caprolactone.

5. A stiffener as defined in claim 3, wherein the fabric is a non-woven fabric comprised of 15 denier fibers.

6. A stiffener as defined in claim 3, wherein the adhesive polyester resin is formed from a powder with a particle size less than 100 microns.

* * * * *

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(54) Title: ORTHOPAEDIC SPLINTING/CASTING MATERIAL.		
(57) Abstract An orthopaedic splinting/casting material comprises a high molecular weight polyester in combination with a cellulosic filler, the material is mouldable at a temperature in the range of 55 to 70 °C and has a self-adherent characteristic at such temperature, its weight is in the range 0.75 to 4.0 kg/m ² , its density in the range 900 to 1200 kg/m ³ , and its modulus, at ambient temperature, not less than 350 mPa. Preferably the polyester is a polyhexamethylene adipate or a polyepsilon-caprolactone. The cellulosic filler may be one or a combination of ground almond shell, ground olive stones and wood flour. Preferably the polyester is in powder form, in which case the polyester and the filler are both generally of the same or closely similar grain size distribution. If desired a fabric layer, e.g. a lightweight polyester fabric, may be incorporated at or adjacent at least one surface of the polyester/filler material.		

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CS	Czechoslovakia	MC	Monaco	TG	Togo
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ES	Spain			VN	Viet Nam
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ORTHOPAEDIC SPLINTING/CASTING MATERIALTECHNICAL FIELD

This invention is concerned with orthopaedic splinting/casting materials.

BACKGROUND ART

There are described in GB-A-1 366 091 various formable orthopaedic cast materials in the form of a bandage, web, film, tape or sheet for use in the treatment of both human and animal bodies, in particular in the case of broken limbs and sprains. In the case of each of the various materials there described it is proposed to use high molecular weight poly-epsilon-caprolactone, either as a component of a blend or as a sole polymeric constituent. Poly-epsilon-caprolactone had the advantage of being easily and rapidly applicable to the affected body part when heated to a moulding temperature, while forming a rigid, non-irritating, strong, durable, water-resistant, close-fitting splint or cast when at temperatures below the softening temperature, which splint or cast was nevertheless easily removable when no longer required without risk of injury or irritation to the patient and indeed without serious damage to the material itself, which could therefore be sterilised and re-used, if desired. Because the splint or cast could be custom-made from sheet or the like, furthermore, it was not necessary to stock different sizes or styles of splint or cast. Moreover, splints or casts made from poly-epsilon-caprolactone are relatively light in weight and do not have the disadvantages of being bulky, as was the case with previously used plaster of Paris, for example. Moreover, the softening

temperature of poly-epsilon-caprolactone is in the range 55 to 70°C, which, especially bearing in mind the low thermal conductivity of the material, would not cause discomfort to the patient whose body part is brought into contact with the thus softened material.

Problems have, however, been perceived in the use of poly-epsilon-caprolactone and various proposals have been made for modifying it, and in particular for blending it with other polymeric materials, in order to achieve physical characteristics which are considered to be desired: see e.g. US-A-4,144,223, GB-A-2 015 004 and WO 83/02898.

It is of course well known that the physical characteristics of a polymer can be significantly varied by the use of fillers, which also of course in general render the cost of the material cheaper. Thus, in GB-A-1 366 091 it is proposed that up to 25% by weight filler can be used. Moreover, the proposed fillers in this case include magnesium or calcium carbonate, finely divided silica, clay, asbestos and alpha cellulose, the filler particles in each case being in a size range of 3 to 4 microns. In other proposals made, fillers having a particle size up to 50 microns have been proposed, again however of the same filler types as referred to in GB-A-1 366 091.

It is also known to provide a material for use in reinforcing/stiffening shoes, which material comprises a polyester having a molecular weight of not less than 10,000 and a viscosity measured at 100°C of at least 30 Pa.s in combination with a filler, said material being mouldable at a temperature in the range 55 to 70°C, having a weight in the range 0.75 to 1.25 kg/m², a density in the range 900 to 1200 kg/m³, and a modulus, at ambient temperature, in the order of 350 to 700 mPa. One such material is described in our co-pending

1 EP-A-0 448 294, which material comprises a
polyhexamethylene adipate of the type described, along
with its manner of manufacture, in EP-A-0 448 079. In
5 addition, there are described in EP-A-0 349 140 and
EP-A-0 183 912 respectively shoe reinforcing/stiffening
materials comprising a polycaprolactone.

In the last mentioned specification it is
proposed to use a filler which is made wholly of or at
least a surface of which is coated with a synthetic
10 material, one preferred embodiment comprising hard PVC.
In EP-A-0 349 140, on the other hand, a filler is
proposed in the form of pulverised fuel ash, while in
EP-A-0 448 294, in addition to the two fillers already
referred to, a proposal is made to utilise almond shell
15 grain, olive stone grain or wood flour.

In contrast with the relatively low grain size
distribution of the materials disclosed in
GB-A-1 366 091, the grain size distribution in each of
the three EP Specifications referred to is substantially
20 greater, being in the order of 50 to 500, preferably 100
to 400 (in the case of 0 183 912), 350 microns (in the
case of 0 349 140), and up to 600 microns (in the case of
0 448 294). Thus, in the case of the reinforcing/
stiffening materials for shoes, a substantially higher
25 grain size distribution of the filler is encountered than
in the previous cases relating to splinting/casting
materials.

In using a splinting or casting material based
upon poly-epsilon-caprolactone, or indeed any other
30 splinting or casting material, it is highly desirable,
especially in the case of the smaller body parts, for the
moulding of the material to follow closely the shape of
the body part to which the splint or cast is to be
applied. In addition, it is highly desirable that the
35 "feel" of the contacting surface of the material is

1 comfortable to the patient. In the case of larger limbs
it may be that a suitable sheet material can be
interposed between the casting or splinting material on
the one hand and the skin on the other, but, in
5 particular in the case of smaller body parts, such an
interlining would be detrimental to the accuracy of the
moulding to the shape of the body part in question. It
is thus very desirable for the surface of the material
itself to have the desired "feel".

10 A further feature which has been found
desirable, and which is closely related to the
comfortable "feel" referred to above, is to ensure that
sufficient ventilation is provided to the region of the
skin encased by the cast or splint material. In e.g.
15 US-A-4,240,415, therefore, it is proposed to perforate
the material over the whole of its area.

OBJECT OF THE INVENTION

20 It is thus an object of the present invention
to provide an improved orthopaedic splinting/casting
material which is moisture-permeable and which has a
comfortable "feel" when applied to a body part.

SUMMARY OF THE INVENTION

25 It has now been established that, surprisingly,
the shoe reinforcing/stiffening materials are in certain
circumstances, and with selected fillers, appropriate in
30 resolving the object of the present invention. More
particularly, the solution in accordance with the present
invention resides in the use, as an orthopaedic splinting
or casting material, of a material in sheet or strip form
comprising not less than 50% by weight of a polyester
35 having a molecular weight of not less than 10,000 and a

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- 1 viscosity measured at 100°C of at least 30 Pa.s, and up
to 50% by weight of a cellulosic filler, said material
being mouldable at a temperature in the range 55 to 70°C,
being self-adherent at such moulding temperature, and
5 having
- a weight in the range 0.75 to 4.0 kg/m²,
 - a density in the range 900 to 1200 kg/m³, and
 - a modulus, at ambient temperature, of not less than
350 mPa.
- 10 It has been found that the use of such a material affords
comfort to the wearer in terms both of the surface "feel"
of the material and also by reason of the material being
moisture-permeable. (Tests have shown that vapour
transmission rates through the material are in the order
15 of not less than 300 mg/m²/hour.) The reason for the
moisture-permeability is not wholly understood, but it is
believed that the presence of relatively large particles
of cellulosic filler, constituting up to 50% of the total
weight of the polyester/filler composition, allows paths
20 through the thickness of the material by the
juxtaposition of moisture-absorbent filler particles.
Moreover, it may be presumed that, based on the
difference in density between the constituent parts and
the overall density of the material, the material is in
25 fact also microporous.
- The stiffness of the material, which is of
course a function of the thickness and modulus, depends
largely upon the requirements for the particular body
part to be treated. Thus, in the case of, say, a
30 fractured limb, a heavy gauge material will be required
in order totally to immobilise the limb in question. In
the case of a moderate sprain, on the other hand, a much
less thick (and thus a much less stiff) material will be
adequate. It is likely, therefore, that materials having
35 a thickness in the range 1 to 4mm will be adequate for

- 1 most purposes in accordance with the invention.
- Suitable polyesters for use in a material as
referred to above are preferably aliphatic polyesters,
e.g. poly-epsilon-caprolactone (which is a polymer formed
5 of a cyclic ester) and polyhexamethylene adipate of a
type having high molecular weight, as disclosed in
EP-A-0 448 079. Moreover, preferably the polyester has a
molecular weight of at least 30,000 and a viscosity
measured at 100°C of at least 600 Pa.s.
- 10 Preferably the material comprises not less than
55% by weight polyester; more preferably the
polyester:filler ratio is in the order of 60:40.
- Preferably the material incorporates a fabric
layer at or adjacent at least one surface. The fabric
15 layer is preferably a non-woven synthetic material, e.g.
viscose or polyester, having a melt temperature higher
than that of the polyester, in which case there is little
or no tendency for the non-woven layer to soften when the
polyester/filler composition is softened. Preferably,
20 furthermore, the or each fabric layer has a weight not
exceeding about 0.025 kg/m². When the material is in
use, and especially when pressure is applied to the
material in its softened state, sufficient of the
polyester/filler material passes through the fabric layer
25 to provide an adhesive surface, but the fabric layer does
not become wholly embedded in the polyester/filler
composition. Thus, by the provision of such a layer or
layers, when the material has been heated to soften it,
the effect of the layer(s) is to render the hot material
30 more readily capable of being handled comfortably not
only from the point of view of the heat in the
composition, but also in reducing the tendency of the
material to stick to the hands of the person handling it.
Similarly, the fabric layer has the same effect in
35 relation to the skin of the patient. Moreover, by

1 providing what is essentially a non-flat surface, by
 arranging the fabric layer(s) at or adjacent the surface
 of the material, an air gap is created between the
 material and the skin of the patient, and this air gap is
 5 believed to contribute to the comfortable "feel" of the
 material when in use. A further advantage of the use of
 a fabric layer in this manner is that it can be utilised
 to alter the tensile properties of the finished product;
 where, for example a non-woven layer is used which has
 10 been produced by carding and then bonding fibres, it
 significantly restrains elongation of the finished
 product in the "machine" direction, i.e. the direction in
 which the fibres are laid. In the case of e.g. spun-
 bonded or hydro-entangled non-woven fabrics, on the other
 15 hand, the tendency of the composition to stretch when
 softened can be restrained in all directions.

The cellulosic filler is preferably selected
 from one or a combination of the following:

- ground almond shell having a grain size distribution
 20 of 150 to 400 microns,
- ground olive stones having a grain size distribution
 of 150 to 400 microns, and
- wood flour having a grain size distribution of up to
 a maximum of 600 microns.

25 It will of course be appreciated by the
 selection of different fillers, the stiffness of the
 finished product can be varied. The selection of a
 particular cellulosic filler to be used will be
 determined largely according to the desired weight and
 30 stiffness of the finished product.

One significant advantage of the material
 referred to above has been found to be that it is
 substantially transparent to X-rays. Thus it is possible,
 while a splint made of said material remains in situ for
 35 the limb to be X-rayed without any significant increase

1 in the level of radiation.

A preferred manner of manufacturing the
 material for use as referred to above is by a powder
 deposition process in which the polyester in powder form
 5 is first mixed with the filler; it should of course be
 understood that the grain size distribution of the
 polyester powder should be the same as or closely similar
 to that of the filler in order to ensure proper mixing
 and to prevent separating out during dispensing of the
 10 powder. The thus mixed powder is then deposited in a
 measured layer on a band of non-woven fabric which passes
 beneath the dispensing hopper and is supported on a
 suitable belt and thereafter preferably a second layer of
 non-woven fabric is laid over the thus deposited layer
 15 and the "sandwich" is passed through a double-band press,
 e.g. of the type described in EP-A-0 322 145. This press
 serves by heating and subsequent cooling to fuse and
 consolidate the powder into a continuous material; if
 desired, a pre-heating step may be included prior to the
 20 second non-woven layer being introduced, this pre-heating
 step serving to cause an initial fusion of the powder
 materials. After the consolidated material has left the
 belts of the press, and while it is in a still mouldable
 state, it is passed between rollers by which the final
 25 thickness (gauge) of the material is determined.
 Thereafter the material is either formed into rolls or
 cut into sheets and stacked. In a different method of
 production, still utilising a powder deposition process,
 the press may be replaced by an oven, in which case the
 30 second non-woven layer may be dispensed with, while in
 yet another method of production two plies of material
 are used, one comprising two layers of a non-woven fabric
 with a polyester layer therebetween, as referred to
 above, and the other comprising a layer of polyester
 35 having a layer of non-woven fabric on one side only

1 thereof, the two lies being placed in face-to-face
 contact, with the fabric surface of the second ply
 exposed, and being passed through a double-band press as
 aforesaid. In such a material, it will be appreciated,
 5 one layer of non-woven fabric is thus located between the
 two polyester layers. Moreover, it will also be
 appreciated, other material than a polyester non-woven
 fabric may be selected for this intermediate layer
 according to any particular characteristic desired for
 10 the material as a whole, bearing in mind of course the
 overall need to retain sufficient flexibility to ensure
 that the material will nevertheless be mouldable to the
 shape of the limb to be supported thereby.

In using the material, firstly it is necessary
 15 to soften it by the application of heat. In one
 preferred use this is effected by immersing the material
 in a bath of hot water at, say, 70°C; alternatively, if
 available an oven may be used for the same purpose.
 Where the material is in sheet form it will normally have
 20 been cut to an appropriate size and shape prior to
 immersion or other form of heating, while if in the form
 of a strip, e.g. a bandage, it will have been cut to
 length prior to immersion or other heating. When the
 material has reached the desired temperature it is then
 25 removed from the heat source and applied to the body part
 of the patient. At this stage although the substance of
 the material has been heated to a relatively high
 temperature, in terms of what is tolerable by the
 patient, because of the relatively low thermal
 30 conductivity of the material, it is unlikely that
 significant discomfort will be caused to the patient by
 bringing the material into skin contact. Depending upon
 the particular composition of the material, the material
 will remain mouldable for a known period, likely to be
 35 between one minute and, say, five minutes, thus giving a

1 "window" for the moulding of the material to the affected
 body part of the patient. Moreover, depending upon the
 degree to which the material is heated, and also
 depending upon to what extent the temperature reached
 5 approximates to the crystalline temperature of the
 material, the material will be self-adherent for at least
 the initial part of the "window", so that it is possible
 for the person treating the patient to mould the material
 to the desired shape and to cause it to adhere to itself,
 10 as least as a temporary fixing. In the case of splints
 for minor sprains, the fixing by self-adherence may be
 adequate; in the case of casts for fractured limbs, on
 the other hand, it may be desirable to provide further
 straps, which may be of the same material, applied
 15 subsequently, e.g. by heating locally with a heat gun.

When it is desired to remove the splint or
 cast, moreover, this may be achieved by again heating to
 soften the material and then to unwrap it.

20 MODES FOR CARRYING OUT THE INVENTION

The manufacture of various materials suitable
 for use in carrying out the invention will now be further
 described with reference to the following specific
 25 examples.

EXAMPLE I

A polyhexamethylene adipate in powder form
 having a molecular weight calculated at approximately
 30 30,000, a viscosity of approximately 800 Pa.s at 100°C
 and a particle size range of 0 to 600 microns, which is
 available from Bostik Limited under the designation
 Bostik HM5189AE ("Bostik" is a registered trade mark) was
 mixed in a ratio of 60:40 parts by weight with a
 35 cellulosic filler in the form of ground almond shell

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1 having a particle size range of 150 to 400 microns. The
mixture was then fed to a hopper through which it was
dispensed at a uniform rate onto a lightweight non-woven
polyester fabric having weight of 0.18 kg/m² supported by
5 the lower belt of a double-band press by which the fabric
was advanced beneath the hopper at a uniform rate.
"Downstream" of the hopper was arranged an infrared
heater by which an initial fusion of the mixture took
place, whereafter the thus initially fused composition
10 was covered with a second, similar, non-woven polyester
fabric and the laminate was then passed between the upper
and lower belts of the double-band press, in which heat
was first applied by platens arranged at opposite sides
of the belts and heated to a surface temperature of
15 150°C, whereafter, for a short period, the bands were
moved over cooling platens, also arranged at opposite
sides of the press, maintained at a temperature of 5°C.
Moreover, the gap between the belts progressively tapered
towards the outlet end in order thus to consolidate the
20 material to some extent. For consolidating the material
further, to a pre-determined gauge, moreover, the
material was then passed between two consolidating
rollers having also a surface temperature maintained at
or about 5°C. The material could thereafter either be
25 stored in roll form (the material still being
sufficiently mouldable for this purpose) or be cut into
sheets and stacked.

The material thus made had the following
characteristics:

30	Thickness	1.09mm
	Weight	1.020 kg/m ²
	Density	940 kg/m ³
35	Modulus (at ambient temperature)	373 MPa.

1 This material was capable of being used either
in strip form, e.g. as a bandage, or in sheet form.
Because of its relatively low gauge, it is unlikely that
such material in sheet form would be used other than for
5 splinting or perhaps for casting in the case of
relatively small body parts.

EXAMPLE II

10 The same polyhexamethylene adipate and filler
as used in Example I was also used in this Example in the
same ratio, but in this case the characteristics of the
finished material were as follows:

	Thickness	2.50mm
15	Weight	2.855 kg/m ²
	Density	1.14 kg/m ³
	Modulus	536 MPa

20 In this case it is unlikely, because of the
thickness of the material, that it would be used other
than in sheet form, and the material has been found to be
useful especially as a casting material. The advantages
of this material, as opposed to e.g. plaster of Paris,
are essentially ease of application and light weight.

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EXAMPLE III

In this Example the ground almond shell filler
was replaced by ground olive stone filler of the same
particle size range, all the other parameters for the
mixture remaining the same. It was found in practice
30 that this material did not significantly differ in
physical characteristics from the material of Example I.
From this it is concluded that the olive stone filler
acts in by and large the same manner with the same effect
35 as the almond shell filler over the whole range of

1 thicknesses of the material.

EXAMPLE IV

5 In this case the material was made in a laboratory using a conventional platen press with shims between the platens to determine the thickness to which the material was consolidated. The material in this case, moreover, was a powder mixture in the following ratio by weight:

10	Polycaprolactone (CAPA 656)	60
	Ground almond Shell having a particle size of 300-600 microns	20
15	Wood Flour have a particle size of 0-400 microns	20

The above mixture was dispersed on release paper and, after dispersion, a further release paper was placed over the mixture and the "sandwich" was placed in the platen press and consolidated at a temperature of 120°C. The finished product had the following physical features:

25	Thickness	1.43mm
	Weight	1.6 kg/m ²
	Density	1120 kg/m ³
	Modulus	860 MPa.

30 It will thus be appreciated that in this case a much stiffer material was achieved, which nevertheless could be handled in generally the same manner as the other Examples when softened to a temperature between 55 and 70°C.

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1 EXAMPLE V

5 In this case a two-ply material is produced. Each ply comprises a layer of a polyhexamethylene adipate in powder form having a molecular weight, viscosity and particle size in a similar range to that of the polyhexamethylene adipate of Example I, but in this case being identified by the designation Bostik HM5512AE. In the case of each layer, furthermore, the polyester was mixed with a cellulosic filler in the form of ground almond shell having a particle size range of 150 to 400 microns. The first ply of said material was produced by depositing a metered polyester:filler layer on a layer of non-woven polyester fabric and thereafter a further layer of the same fabric was placed thereover. The second ply was produced by depositing a metered layer of the polyester:filler mixture on a layer of polyester non-woven fabric. The two plies were then superposed with the fabric surface of the second ply exposed; that is to say with one of the fabric layers of the first ply intermediate the two polyester layers. The "sandwich" was then passed through a double-band press and the process was completed generally in the same manner as described in Example I.

25 The finished material had the following characteristics:

	Thickness (average)	2.64mm
	Weight	3125 kg/m ²
30	Density	1180 kg/m ³
	Modulus (at ambient temperature)	706 MPa (width) 770 MPa (length).

The moisture vapour permeability was 385mg/m²/hr.

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1 The material exhibited good handling qualities and
has been found suitable for use as a casting material.

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1 Claims:

1. The use, as an orthopaedic splinting or casting material, of a material in sheet or strip form comprising not less than 50% by weight of a polyester having a molecular weight of not less than 10,000 and a viscosity measured at 100°C of at least 30 Pa.s, and up to 50% by weight of a cellulosic filler, said material being:
- 10 - mouldable at a temperature in the range 55 to 70°C and being self-adherent at such moulding temperature,
 - having a weight in the range 0.75 to 4.0 kg/m²,
 - having a density in the range 900 to 1200 kg/m³, and
 - 15 - having a modulus, at ambient temperature, of not less than 350 mPa.

2. The use of a material as set out in Claim 1 wherein the polyester is an aliphatic polyester.

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3. The use of a material as set out in Claim 1 wherein the polyester is a polymer formed of a cyclic ester.

25 4. The use of a material as set out in Claim 1 wherein the polyester is a poly-epsilon-caprolactone.

5. The use of a material as set out in Claim 1 wherein the polyester is a polyhexamethylene adipate.

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6. The use of a material as set out in Claim 1 wherein the polyester has a molecular weight of at least 30,000 and a viscosity measured at 100°C of at least 600 Pa.s.

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1 7. The use of a material as set out in Claim 1 wherein the polyester:filler ratio is in the order of 60:40.

5 8. The use of a material as set out in Claim 1 incorporating a fabric layer at or adjacent at least one surface.

10 9. The use of a material as set out in Claim 8 wherein the fabric of said at least one layer is a non-woven fabric of synthetic material having a melt temperature higher than that of the polyester.

15 10. The use of a material as set out in Claim 1 wherein the filler is selected from one or a combination of the following:

- ground almond shell having a grain size distribution of 150 to 400 microns,
- ground olive stones having a grain size distribution of 150 to 400 microns, and
- wood flour having a grain size distribution of up to a maximum of 600 microns.

25 11. An orthopaedic splinting or casting material in sheet or strip form comprising not less than 50% by weight of a polyester having a molecular weight of not less than 10,000 and a viscosity measured at 100°C of at least 30 Pa.s, and

30 up to 50% by weight of a cellulosic filler, said material being mouldable at a temperature in the range 55 to 70°C, being self-adherent at such moulding temperature and having

- a weight in the range 0.75 to 4.0 kg/m², preferably 1.25 to 3.75 kg/m², more preferably 2.0 to 3.5 kg/m²,

- 1 - a density in the range 900 to 1200 kg/m³, and
- a modulus, at ambient temperature, of not less than 350 MPa.

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