



Industria y Comercio

SUPERINTENDENCIA

Delegatura de propiedad Industrial

División de Nuevas Creaciones

PCT
SOLICITUD

PATENTE DE INVENCION

21. EXPEDIENTE No.

06-107276

54. TÍTULO

Método de elaboración de materiales de empaque con bajo olor.

51. CLASIFICACIÓN INTERNACIONAL

B22B 27/16, 31/00 B41M 4/00, C09D 11/10 4/00 B65D 65/00

71. SOLICITANTE

Sun chemical Corporation

DOMICILIO

New jersey, USA.

74. APODERADO

Dilia Maria Rodriguez D'Alencar

22. BOGOTÁ, D. C.,

Oct. 23/06

Creación
En 31-10-2006

FORMULARIO ÚNICO DE SOLICITUD DE
PCT
ENTRADA EN FASE NACIONAL

1) SOLICITUD DE:			
☒ Patente de invención		☐ Patente de Modelo de Utilidad	
☒ Capítulo I		☐ Capítulo II.	
2) SOLICITANTE (71)	Nombre: Sun Chemical Corporation Dirección: 35 Waterview Boulevard Parsippany, NJ 07054, USA Nacionalidad o domicilio: New Jersey, Estados Unidos Lugar de constitución: New Jersey Estados Unidos		IDENTIFICACIÓN C.C. ☐ NIT ☒ C.E. ☐ OTRO ☐ Cual _____ NÚMERO _____
	Teléfono: _____ Fax: _____ E. Mail: _____		
3) REPRESENTANTE O APODERADO	Nombre: DILIA MARÍA RODRÍGUEZ D'ALEMAN Dirección: Carrera 11 N° 86-53 Piso 6 Bogotá D.C. Teléfono: 6181088 Fax: 6350824 E. Mail: info@clarkemodet.com.co		IDENTIFICACIÓN C.C. ☒ NIT: ☐ C.E. ☐ OTRO ☐ NÚMERO: 41.654.882 TP: 20824 CSJ
4) INVENTOR (ES) (72)	Nombre: 1. ROONEY, John, M.; 2. BIRO, David, Anthony Dirección: 1. 32 Berkeley Circle, Basking Ridge, NJ 07920 USA; 2. 42 Cayuga Ave., Rockaway, NJ 07866 USA Nacionalidad o Domicilio: 1. Estadounidense; 2. Canadiense		
5) PCT (86) Solicitud Internacional No. PCT/US2005/010649 Fecha: Marzo 31, 2005 Publicación Internacional No. WO2005/097495 A 1 Fecha: Octubre 20, 2005			
6) Título (54) MÉTODO DE ELABORACIÓN DE MATERIALES DE EMPAQUE CON BAJO OLOR			
7) Clasificación Internacional: B32B 27/16, 31/00, B41M 7/00, C09D 11/10, 4/00, B65D 65/00			
8) PRIORIDAD	33) País de Origen	(32) Fecha	(31) Número de Solicitud
SI ☒ NO ☐	Estados Unidos	Marzo 31, 2004	60/558,076
9) Comprobante de pago N°. 06-75,810 de Octubre 2, 2006			
Instrucciones para el diligenciamiento del presente formulario Ver reverso de esta pagina			

10)

ANEXOS

- ☒ Comprobante de pago de la tasa de presentación de la solicitud
- ☐ Comprobante de pago por reivindicación de prioridad
- ☒ Documento que acredita la existencia y representación legal cuando el solicitante sea persona Jurídica
- ☒ Poderes, si fuera el caso
- ☐ Documento de cesión del inventor al solicitante o a su causante
- ☐ Declaraciones
- ☒ Copia de la solicitud Internacional (Resumen, descripción, reivindicación, Dibujos)
- ☒ Traducción de la solicitud internacional al castellano (Resumen, descripción, reivindicación, Dibujos)
- ☐ Copia del examen preliminar efectuado por la IPEA
- ☐ De ser el caso, copia del contrato de acceso
- ☐ De ser el caso, documento que acredite la licencia o autorización de uso de conocimientos tradicionales de las comunidades indígenas
- ☐ De ser el caso, certificado de depósito del material biológico
- ☐ Arte final 12 x 12 y 6 x 6 cm
- ☐ De ser el caso, información sobre otras solicitudes de patente o títulos obtenidos en el extranjero por el mismo titular o su causante, relacionados parcial o totalmente con la invención de esta solicitud
- ☒ Otros
 - 1 Reporte de Búsqueda
 - 2 Opinión escrita
 - 3 Solicitud PCT

11) FIGURA CARACTERÍSTICA:

12) Solicitud concesión de la patente,

NOMBRE: DILIA RODRÍGUEZ D'ALEMAN

FIRMA:

C.C. 41.654 882 de Bogota TP 20824 CSJ

Instrucciones para el diligenciamiento del presente formulario. Ver reverso de esta pagina

8849

7

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 800176089-2

RECIBO OFICIAL DE CAJA : 06 - 75.810
FECHA : OCTUBRE 2 DE 2006

***** CONSIGNACION *****

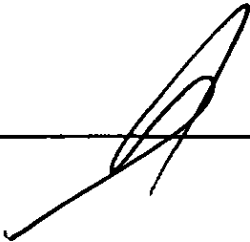
DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PGO	Vr. PAGO
CLARKE MODET Y CO. COLOMB	CONSIGNACION	BANCO POPULAR	050-00110-6	53370513	02/10/2006	11,649,000.00

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

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-01	SOLICITUDES	1 TRAMITES DE SOL. DE PATENTE DE IN 463,000.00
		TOTAL :	\$ 463,000.00

SON: CUATROCIENTOS SESENTA Y TRES MIL PESOS

RESPONSABLE : _____



DO DE CAJA APLICADO AL EXPEDIENTE No. _____

①
P. 258 P. 652.

13

TRADUCCIÓN OFICIAL No. 01/074 de un documento escrito en inglés, el cual para su identificación se sella con el sello del traductor al tiempo con la presente. Esta traducción ha sido preparada por Juan Pablo Piedrahita Aguilera, Traductor e Intérprete Oficial debidamente reconocido de conformidad con el Certificado de Idoneidad Profesional No 0045 expedido por la Universidad Nacional de Colombia.

(Se traduce un Certificado de Notarial, Legalización y Apostilla escritos en inglés, adjuntos a un poder otorgado por la compañía SUN CHEMICAL CORPORATION, escrito en inglés y español, con fecha Febrero 13, 2001.)

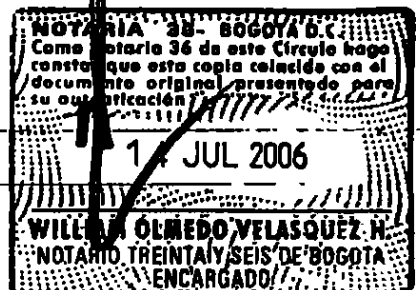
CERTIFICADO NOTARIAL (Cuando el Solicitante es una Sociedad)

(Poderes otorgados en El Salvador, México, Estados Unidos de América y Venezuela)

Expedido hoy 13 de Febrero, 2001 el suscrito Notario CERTIFICA que:

- 1) Melvin M. Cox (nombre de la persona que firma el poder), mayor de edad y domiciliada en Fort Lee, New Jersey, suscribió el anterior documento.
- 2) El otorgante le es conocido personalmente y tiene facultad legal para firmar el documento.
- 3) El otorgante ha suscrito el anterior documento en su calidad de Vicepresidente de la persona jurídica Sun Chemical Corporation.

TRADUCCION OFICIAL No. 01/074
JUAN PABLO PIEDRAHITA AGUILERA
TRADUCTOR E INTERPRETE OFICIAL
C. IDONEIDAD 045
UNIVERSIDAD NACIONAL DE COLOMBIA



4) La mencionada persona jurídica con domicilio comercial en 222 Bridge Plaza South, Fort Lee, New Jersey, está debidamente constituida, tiene actualmente existencia legal y el fin para el cual se otorga este poder se encuentra dentro de su objeto social

5) El otorgante tiene en efecto la idoneidad referida y su representación es legal y está autorizado para otorgar este poder.

6) Fundamento las certificaciones 3), 4) y 5) en los documentos auténticos que para tal fin me fueron exhibidos.

(Firmado) Elizabeth C. Reyes

Notario Público

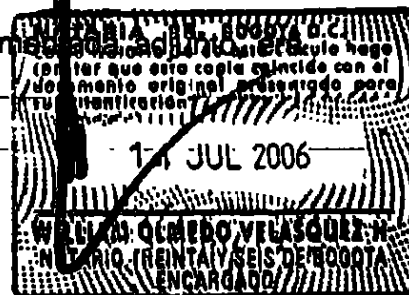
(Sello Notarial a Tinta. S. Elizabeth C. Reyes, Notario Público para New Jersey, Mi Comisión Expira Febrero 13, 2002)

(Sello Notarial Redondo en Relieve)

Nota: El Consulado de Colombia debe autenticar la firma del notario público

ESTADO DE NEW JERSEY,
CONDADO DE BERGEN} ss.

Yo, Kathleen A, Donovan, Escribano del Condado de Bergen, (el mismo siendo una Corte de Registro de dicho Condado, que tiene por ley un sello), POR EL PRESENTE CERTIFICO QUE Elizabeth C. Reyes, cuyo nombre está suscrito en el certificado de reconocimiento, prueba o declaración juramentada, es una persona que hego



en el momento de recibir tal reconocimiento, prueba o declaración juramentada un NOTARIO PUBLICO debidamente comisionado, juramentado y residente en dicho Estado y como tal NOTARIO PÚBLICO, es un funcionario de dicho Estado debidamente autorizado por sus leyes para tomarlos y certificarlos, asó como para tomar y certificar las pruebas y reconocimientos de escrituras para traspasos de tierra, tenencias o herencias, y otros instrumentos por escrito, para registro en dicho Estado; y que dicho reconocimiento está debidamente firmado y tomado conforme a las leyes de dicho Estado y que estoy bien familiarizado con su caligrafía y verdaderamente creo que la firma en el certificado adjunto es su firma auténtica.

Además certifico que no se requiere por las leyes de este Estado que la impresión del sello de dicho NOTARIO PÚBLICO esté en los archivos de mi oficina.

EN TESTIMONIO DE LO CUAL firmo y estampo mi sello oficial hoy 13 de Febrero de 2001 A.D.

(Firmado) Kathleen A. Donovan, Escribano
(Sello en Relieve del Condado de Bergen, NJ)

APOSTILLA

(Convención de la Haya de Octubre 5 de 1961)

- 1. País: Estados Unidos de América
Este documento público
- 2. Ha sido firmado por Kathleen A. Donovan

TRADUCCION OFICIAL No 01079
JUAN PABLO PIEDRAHITA AGUIJERA
TRADUCTOR E INTERPRETE OFICIAL
C/IDONEIDAD 045
UNIVERSIDAD NACIONAL DE COLOMBIA



3. Actuando en calidad de Escribano del Condado
4. Lleva el sello/estampilla de Condado de Bergen

CERTIFICADO

5. En Trenton, New Jersey 6. Hoy 21 de Febrero, 2001
7. Por Peter R Lawrence, Tesorero de New Jersey
8. Certificado Número A128014
9. (SELLO)

(Sello Redondo de Oblea en Relieve)

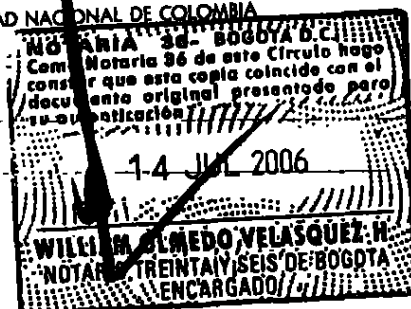
10. Firma: (Firmado) Peter R Lawrence

Certificado de Apostilla No. A128014 por el Tesorero de New Jersey, de fecha
Febrero 21, 2001.

ES TRADUCCIÓN FIEL Y COMPLETA de la cual se deja copia en los archivos de
esta oficina para su confrontación y a la cual me remito.

Bogotá, Marzo 8 de 2001.

Juan Pablo Piedrahita Aguilera
TRADUCCION OFICIAL No 01/C79
JUAN PABLO PIEDRAHITA AGUILERA
TRADUCTOR E INTERPRETE OFICIAL
C IDONEIDAD 045
UNIVERSIDAD NACIONAL DE COLOMBIA



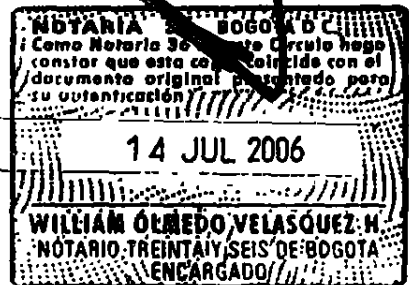
MINISTERIO DE
RELACIONES EXTERIORES

NO SE ASUME
RESPONSABILIDAD DEL TEXTO

245262
Juan P. Osorio
CUIA FIRMA APARECE EN EL
DOCUMENTO DESEMPENA
LAS FUNCIONES INDICADAS

2004 JUL 28 A 11:54

ues
JEFE DE LEGALIZACIONES
SECRETAD.C.



P.400

APOSTILLE

(CONVENTION DE LA HAYE DU 5 OCTOBRE 1961)

1. COUNTRY: UNITED STATES OF AMERICA
2. THIS PUBLIC DOCUMENT HAS BEEN SIGNED BY:
KATHLEEN A DONOVAN
3. ACTING IN THE CAPACITY OF:
COUNTY CLERK
4. BEARS THE SEAL/STAMP OF:
COUNTY OF BERGEN

CERTIFIED

5. AT TRENTON, NEW JERSEY
6. THE 21ST DAY OF FEBRUARY 2001
7. BY: Peter R Lawrance, NEW JERSEY TREASURER
8. NO. A128014
9. SEAL/STAMP:
10. SIGNATURE



Peter R Lawrance

NOTARIA 38- BOGOTAN
Como Notaria 38 de este Circulo
constar que esta copia coincide
documento original prototipo
su autentificación

14 JUL 2006

TRADUCCION OFICIAL No. 41/674
ABDO PIEDRAHITA AGUILERA
DOCTOR E INTERPRETE OFICIAL
IDONEIDAD 045
NACIONAL DE COLOMBIA

Clarke, Modet & Co. Colombia Ltda.

PROPIEDAD INDUSTRIAL y DERECHOS DE AUTOR

Apartado Aéreo 92397

Santafé de Bogotá, Colombia

PODER

Yo (nosotros), abajo firmante(s)

Melvin M Cox

en mi (nuestro) carácter de representante(s) legales de

Sun Chemical Corporation

una sociedad organizada y existente de acuerdo con las leyes de

Delaware

y en actual cumplimiento de su objeto social, con domicilio en

222 Bridge Plaza South
Fort Lee NJ 07024 USA

por el presente instrumento confiero (conferimos) poder especial a favor de DILIA MARIA RODRIGUEZ D'ALEMAN, con Cédula de Ciudadanía No. 41.654.882 de Bogotá, y tp. 20824 y CLAUDIA LUCIA CARO RAMIREZ, con Cédula de Ciudadanía No. 40.017.374 de Tunja, y tp. 36448, con domicilio en Santa Fé de Bogotá, Colombia, para que actuando en su orden en nombre del (de la) otorgante le (la) representen ante cualquier entidad, autoridad y/o persona, especialmente ante las del orden Administrativo, Contencioso Administrativo, Judicial, Tribunales de Arbitramento y/o cualquier otro en lo referente a los siguientes asuntos:

- 1) Solicitar, tramitar, obtener y/o registrar cualquiera de las modalidades de Propiedad Industrial, tales como: patentes de invención, modelos de utilidad; diseños industriales, variedades vegetales; marcas, lemas, nombres y enseñanzas comerciales y denominaciones de origen; así como sus renovaciones, prórogas, transferencias, cambios de nombre y/o domicilio, contratos y licencias.
- 2) Solicitar, tramitar, obtener y/o registrar derechos de autor, en cualquiera de sus presentaciones así como la protección de secretos industriales y know-how.
- 3) Solicitar, tramitar, obtener y/o registrar registros sanitarios, permisos y/o licencias de funcionamiento; así como sus renovaciones o prórogas, transferencias, cambios de nombre y/o domicilio, contratos y licencias.
- 4) Ejercer acciones de oposición, observación, reclamos, reconsideración, reposición, apelación, cancelación administrativa o judicial, nulidad, protección al consumidor, concesión de licencias, protección de secretos industriales y demás acciones y recursos relacionados con derechos derivados de los asuntos arriba indicados y en contra de la competencia desleal, acciones derivadas de la obtención o explotación de licencias, acciones de indemnización de perjuicios. También podrá(n) intervenir en juicios civiles, comerciales, penales, contencioso-administrativos, tutelas y de policía; en acciones o juicios promovidos por el (la) mandante o en contra el (ella).
- 5) Registrar nombres de dominio ante la entidad competente.
- 6) En el ejercicio de este mandato los mandatarios arriba mencionados quedan facultados para conciliar, cancelar, transigir, comprometer en árbitros, desistir, recibir y tomar posesión de la cosa objeto de litigio y renunciar o desistir a derechos concedidos o en curso de concesión, admitir los hechos del proceso.
- 7) Ratificar o no la agencia oficiosa.
- 8) Así mismo faculto (facultamos) a los mencionados apoderados para recibir notificaciones y designar apoderados judiciales o extrajudiciales, sustituir el presente poder y revocar las sustituciones que hicieren.

Dado y firmado en Fort Lee NJ USA

a los 13 días de Feb de 2001

Firma / Signature

By: Melvin M. Cox, Vice President, Sun Chemical

POWER OF ATTORNEY

I (we), the undersigned

Melvin M. Cox

legal representative(s) of

Sun Chemical Corporation
an organization existing under the laws of

Delaware

and in present execution of its business activity, domiciled at

222 Bridge Plaza South
Fort Lee, NJ 07024 USA

do hereby grant POWER OF ATTORNEY to DILIA MARIA RODRIGUEZ D'ALEMAN, identification card No. 41.654.882 of Bogotá, and tp. 20824 and CLAUDIA LUCIA CARO RAMIREZ, tp. 36448, identification card No. 40.017.374 of Tunja, residing in Santa Fé de Bogotá, Colombia, to act in the order of their appointment in behalf of grantor before any entity, authority and/or natural or juridical person, specially before those Administrative, Administrative-Contentious, Judicial, arbitration courts, and/or any other, in all matters concerning the following:

- 1) To apply, process, obtain and/or register any of the modalities of Industrial Property, such as: Patents of Invention, Utility Models, Designs, vegetal varieties; Marks, Slogans, Trade Names and emblems and appellations of Origin; as well as their renewal, extensions, assignments, changes of name and/or domicile, agreements and licenses.
- 2) To apply, process, obtain and/or register copyrights of any kind as well as protection of industrial secrets or know-how.
- 3) To apply, process, obtain and/or register sanitary registrations, operating authorizations and/or licenses; as well as their renewal or extensions, assignments, changes of name and/or domicile, agreements and licenses.
- 4) To bring actions of opposition, observations, claims, reconsideration, appeal or legal remedies, cancellations, nullity, protection to the consumer, granting of licenses, protection of trade secrets and other actions related with rights derived from the above-mentioned matters and against the unfair competition, actions resulting from the obtaining or exploitation of licenses, recovering damages actions. They can also intervene or participate in Civil, Commercial, Criminal or Contentious-Administrative Trials; the actions for writ mandamus, police actions; in actions, lawsuits or litigations instituted by the grantor or against him.
- 5) To register domain names before the competent entity.
- 6) To the effect of this mandate the above-named attorneys are empowered to conciliate, cancel, settle, submit to arbitration, withdraw and to receive awards, to desist, to receive and to waive or renounce the rights granted as in process of granting, and to take any other action.
- 7) To ratify or not the officious agency.
- 8) I (we) hereby appoint the afore-mentioned attorneys with powers to receive notifications and to designate judicial and extrajudicial attorneys, substitute the Power of Attorney and to revoke such substitution.

Granted and signed at Fort Lee, NJ, USA

on this 13th day of February of 2001

WILLIAM OLMEDEO VELASQUEZ H.
NOTARIO TREINTAY SEIS DE BOGOTA
ENCARGADO

CERTIFICADO NOTARIAL (Cuando el solicitante es SOCIEDAD)

(Poderes otorgados en El Salvador, Estados Unidos, Mexico y Venezuela)

A los _____ días del mes de _____
de _____, el Notario que suscribe DA FE de
que

1. _____
(nombre de la persona que firma el poder)

mayor de edad y domiciliado _____
_____ firmó de su puño
y letra el documento que antecede.

2. Conoce al (a la) otorgante y que este (a) está
legalmente capacitado para el otorgamiento.

3. El otorgante ha firmado el referido documento en
su carácter e _____
de la persona jurídica _____

4. La citada persona jurídica con sede en _____
_____ está
legalmente constituida, que tiene actualmente
existencia legal y que el acto para el cual se ha
otorgado este poder está comprendido entre los que
constituyen su objeto social.

5. El otorgante tiene efectivamente la representación
que ostenta, que esta es legítima y que está
facultado para otorgar este poder.

6. Las anteriores certificaciones de los puntos 3, 4 y 5, me
constan porque he tenido a la vista los
documentos auténticos.

Notario Público

NOTA: A continuación de lo anterior, el Consul de
Colombia debe autenticar la firma del Notario Público.

CERTIFICADO NOTARIAL (Cuando el solicitante es INDIVIDUO)

A los _____ días del mes de _____
de _____, el Notario que suscribe DA FE de
que.

1. _____
(nombre de la persona que firma el poder)

mayor de edad y domiciliado en _____
_____ firmó en su presencia
el documento que antecede, conoce al otorgante
y que este está legalmente capacitado para el
otorgamiento.

Notario Público

NOTA: A continuación de lo anterior, el Consul de
Colombia debe autenticar la firma del Notario Público.

Para todos los demás países el Señor Consul de
Colombia o ante quien se otorgue, debe expedir una
certificación dejando constancia 1) de la existencia
legal de la sociedad, 2) de que esta ejerce actualmente
su objeto social, y 3) de que la persona o personas que
otorgan el poder están facultadas para hacerlo, dejando
constancia así mismo de que tuvo a la vista las pruebas
que acrediten tales circunstancias.

NOTARIAL CERTIFICATE (When the applicant is a CORPORATION)

(Powers of attorney granted in El Salvador, Mexico, U.S.A. and Venezuela)

This 13th day of February 2001,
the undersigned Notary CERTIFIES that:

1. Melvin M. Cox
(name of the person who signs the power of attorney)

of legal age and domiciled
in Fort Lee, NJ
set his hand on the foregoing document.

2. The grantor is to him personally known and that
he/she has legal capacity to execute the document.

3. The grantor has executed the foregoing document
in his capacity of Vice President
of the juridical person Sun-Chemical Corporation

4. The mentioned juridical person, with place of
business in 222 Bridge Plaza South, Fort Lee
is duly organized, has actual legal existence and that
the purposes for which the power of attorney is granted
are within the scope of its corporate purposes.

5. The grantor has in fact the referred quality and
that his/her representation is legal and that he/she
is empowered to grant this power of attorney.

6. I have based the above certifications 3, 4 and 5, on
the authentic documents which for such purpose were
exhibited to me.

ELIZABETH C. REYES

A Notary Public of New Jersey
My Commission Expires February 13 2002

Notary Public

NOTA: Then the Colombian Consul must legalize the
signature of the Notary Public.

NOTARIAL CERTIFICATE (When the applicant is an INDIVIDUALS)

On this _____ day of _____
the undersigned Notary CERTIFIES that:

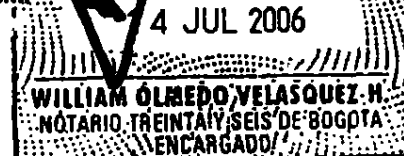
1. _____
(name of the person who signs the Power of Attorney)

of legal age and domiciled at _____
_____ signed in his presence
the foregoing document, the grantor is to him
personally known and that he/she has legal capacity to
execute the document.

Notary Public

NOTA: Then the Colombian Consul must legalize the
signature of the Notary Public

For all other countries the Colombian Consul or before
who it is granted must issue a certification stating 1) the
legal existence of the corporation, 2) that the corporate
purposes are actually being accomplished, 3) that the
person or persons who grant this power of attorney are
empowered to do so. The Consul or before whom the
documents are granted must have the documents
evidencing those circumstances were
exhibited to him.



STATE OF NEW JERSEY,
COUNTY OF BERGEN) SS.:

I, Kathleen A. Donovan, Clerk of the County of Bergen
(the same being an office of Record of the aforesaid County,
having by law a seal)

DO HEREBY CERTIFY, That

Elizabeth C. Reyes

whose name is subscribed to the attached certificate of acknowledgement, proof or affidavit, was at the time of taking said acknowledgement, proof or affidavit, a NOTARY PUBLIC, duly commissioned and sworn and residing in said State, and was, as such NOTARY PUBLIC, an officer of said State duly authorized by the laws thereof to take and certify the same, as well as to take and certify the proof and acknowledgement of deeds for the conveyance of land, tenements or hereditaments, and other instruments in writing to be recorded in said State, and that the said acknowledgement is duly executed and taken according to the laws of said State, and that I am well acquainted with his/her handwriting and verily believe the signature to the attached certificate is his/her genuine signature

And I do further certify that the impression of the seal of such NOTARY PUBLIC is not required by the laws of this State to be filed in my office

IN WITNESS WHEREOF, I have hereunto set my hand and affixed my official seal this

13

day of

February

A.D. 20 01

Kathleen A. Donovan

Clerk

Deputy

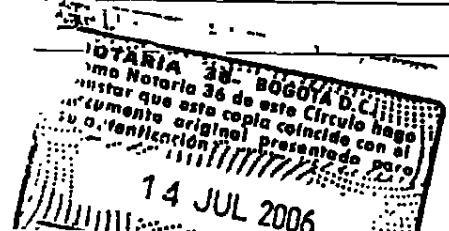
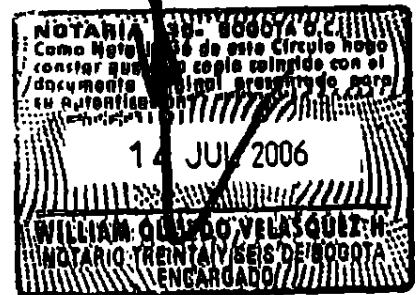
TRADUCCION OFICIAL No 01/024

JUAN PABLO PIEDRAHITA AGUILERA

TRADUCTOR E INTERPRETE OFICIAL

C. IDONEIDAD 045

UNIVERSIDAD NACIONAL DE COLOMBIA



1. **INTRODUCTION** 2. **STATEMENT OF WORK** 3. **SCOPE OF WORK** 4. **DELIVERABLES** 5. **ASSUMPTIONS** 6. **DEPENDENCIES** 7. **RISKS** 8. **CONCLUSION** 9. **APPENDICES** 10. **REFERENCES**

(10) International Publication Number
WO 2005/097495 A1

- (51) **International Patent Classification⁷:** B32B 27/16, 31/00, B41M 7/00, C09D 11/10, 4/00, B65D 65/00
- (21) **International Application Number:** PCT/US2005/010649
- (22) **International Filing Date:** 31 March 2005 (31 03 2005)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:** 60/558,076 31 March 2004 (31 03 2004) US
- (71) **Applicant (for all designated States except US):** SUN CHEMICAL CORPORATION [US/US]; 35 Waterview Boulevard, Parsippany, NJ 07054-1285 (US)
- (72) **Inventors; and**
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(54) Title: METHOD OF MANUFACTURING LOW-ODOR PACKAGING MATERIALS

(57) Abstract: The present invention provides a method for producing a low-odor, printed packaging material and the printed packaging material produced thereby. The printed packaging material of the present invention is especially suitable for packaging of substances, such as food, drugs and tobacco, which require low odor from printing inks. In this process, the printed ink is activated by exposure to actinic radiation such as UV light, before an actinic-radiation curable coating is applied thereto. The exposure of the printed ink to UV light reduces residual solvent content and odor of the packaging material and improves the friction resistance and gloss of the printed images. Furthermore, the exposure of the printed packaging material to UV light provides an additional benefit of reducing microbial count, thereby extending a shelf-life of the packaged substance such as food and drugs.

WO 2005/097495 A1

METHOD OF MANUFACTURING LOW-ODOR PACKAGING MATERIALS

1. FIELD OF THE INVENTION

5 This invention relates to a process of producing low-odor packaging materials utilizing actinic radiation-activatable solvent- or water-based liquid inks and an actinic radiation-curable coating, which provides ink protection and gloss enhancement of packaging.

10 2. BACKGROUND OF THE INVENTION

Organic solvent- and/or water-based liquid flexo or gravure inks ("solvent-based printing inks") have been widely used in various types of printing, such as packaging, using inkjet printer. The printed images should have good solvent and abrasion resistance. At the same time, it is necessary for solvent-based printing inks to have good re-solubility to avoid ink drying and clogging on the plate, anilox and gravure cylinders of the printers. Typically, low molecular weight (MW) resins and plasticizers offer good re-solubility, yet, in order to improve resistance properties of the printed images, higher MW resins are required. This represents a major contradiction and problem for the formulators of the solvent-based packaging liquid inks.

20 To solve these problems, various types of photocurable printing inks having specific combinations of photocurable resins and photoinitiators, have been developed (*see*, for example, U.S. Patent 4,066,582; U.S. Patent 4,221,686; U.S. Patent 4,303,924; U.S. Patent 5,057,398; and WO 01/57145 A1). However, incomplete polymerization of these inks often results in diffusion of uncured resins and causes smears or abrasion of the printed images.

As pointed out in U.S. Patent 6,528,127, the printing of thermoplastic packaging films has remained a bit of a black art despite advances in general

printing techniques. Packagers have recently been requiring film manufacturers to provide packaging films bearing photograph quality printed images, which is difficult in and of itself, sometimes for uses which add to the difficulty. Heat shrinkable films and thermoforming films are particularly challenging because of the need for the printing ink(s) to resist cracking or flaking off once the film has undergone heat shrinking, a process during which the film is subjected to heat, friction, and/or film-to-metal contact. Films intended for cook-in applications can undergo all of these strenuous conditions and provide film manufacturers and converters with some of their greatest printing challenges.

To prevent cracking and/or flaking of printed images, film manufacturers tried several strategies. Most often, these involve the use of new ink formulations to avoid using standard inks containing pigments carried in a resin which is soluble in a solvent such as an alcohol which must be evaporated, leaving behind the resin-pigment combination. The newer formulations have involved two-part polyurethane resin systems as well as solvent-free systems in which the resin(s) can be cured by means of ultraviolet (UV) light, which also have drawbacks, including concerns regarding operator exposure to components and the need to assure sufficient cross-linking to comply with applicable governmental food safety regulations.

To solve these problems, U.S Patent 6,528,127 teaches a manufacturing process for food packaging materials comprising printing the plastic film with solvent-based inks which are dried without electron beam or ultraviolet radiation, followed by applying a radiation-curable, pigment-free protective coating and radiation curing the coating. In this process that represents an advance, it has been found that an excessive amount of residual solvent is trapped in the ink under the protective coating and causes excessive odor from the packaging material. In addition, since drying rate of solvent varies significantly over multiple heating units

as well as the number and amount of ink traps, the cure and friction characteristics of the finished packaging material can be non-uniform throughout the printed images. This, in turn, can cause problems with processing the packaging material in the filling lines, particularly in relation to coefficient of friction (COF, which represents frictional resistance between two surfaces and can be expressed as static COF, where the surfaces are static, and kinetic COF, where the surfaces are in motion) and/or slipping issues. For example, a job printed at a customer with three solvent based inks on the polyethylene (PE) film and over-printed with electron-beam (EB) curable coating, has the following coating-crosslinking cure patterns: (i) coating over PE film - 30 MEK (methyl ethyl ketone) rubs (*see* the definition below); (ii) coating over white ink - 8-10 MEK rubs; (iii) coating over yellow and white inks - 3-4 MEK rubs; and (iv) coating over black, yellow and white inks - only 1 MEK rub. Thus, the EB coating cures differently over different color inks primarily because the solvent-based inks release their solvent differently. The thicker the underlying ink layer, the slower the cure of the overlaying energy-curable coating. Variations in degree of cure result in variations in COF value. Thus, there is a need for a printing method for, in particular, food packaging, that addresses these problems while providing an imaged film with the desired characteristics.

3. SUMMARY OF THE INVENTION

The present invention is based, partly, on the discovery by the present inventors that by activating a printed actinic-radiation activatable solvent- or water-based inks on packaging materials with actinic radiation before applying the protective coating reduces the residual solvent content and odor as well as improves the friction resistance and gloss of the printed images. The term "actinic-radiation activatable ink" used herein means that the ink is substantially free of curable functionality (*i.e.*, functional groups that can be cross-linked or polymerizable).

Accordingly, the present invention provides a method of producing a coated packaging material comprising printing on a packaging material with an actinic radiation activatable liquid ink, actinic-radiation activating the ink, applying a protective coating over the activated ink, and curing the coating by exposure to ionizing radiation.

The term "actinic radiation" used herein refers to its broadest sense as any radiation that can produce photochemical reactions.

In a preferred embodiment, the actinic radiation for activating the liquid ink is UV light. In another preferred embodiment, the actinic radiation for curing the protective coating is an electron beam (EB).

In a specific embodiment, the packaging material is plastic film or a plastic film laminate structure. In another specific embodiment, the packaging material is a foil-laminated plastic structure, or a paper plastic laminate. In yet another specific embodiment, the ink is solvent based. In another specific embodiment, the ink is water based. The present invention further provides a low odor packaging material produced by the method of the present invention. In a preferred embodiment, the packaging material of the present invention contains residual solvent or water after UV exposure of less than about 700 ppm total, more preferably less than about 600 ppm total, and most preferably less than about 400 ppm. In another preferred embodiment, the packaging material of the present invention has a degree of cure, as measured by solvent rubs, of at least 5 MEK (methyl ethyl ketone) rubs, more preferably at least 10 MEK rubs, and most preferably at least 20 MEK rubs.

The MEK test is a solvent rub technique using a methyl ethyl ketone for assessing the solvent resistance of an organic coating that chemically changes during the curing process (for details, see ASTM D5402-93; "Assessing the Solvent Resistance of Organic Coatings Using Solvent Rubs" in Annual Book of ASTM, 1999, by West Conshohocken, PA). The MEK resistance is expressed as a number of MEK

41

rubs, using a MEK saturated cotton ball or cotton-tipped swab, to which the coating can stand without any loss of the coating and it generally correlates with a degree of cure of the coating. The MEK resistance is also influenced by temperature, film thickness, air movement and relative humidity.

.5 The printed packaging material prepared according to the present invention has a broad range of applications, including, but not limited to, food packaging, drug packaging, tobacco packaging, and any other packaging which requires printing thereon.

10 4. **DETAILED DESCRIPTION OF THE INVENTION**

 The present invention provides a method of manufacturing low odor packaging materials comprising printing on a packaging material with a solvent- or water-based, actinic-radiation activatable printing ink, exposing the ink to first actinic radiation, applying energy-curable coating over the ink, and curing the
15 coating by exposure to second actinic radiation, preferably an electron beam. In a preferred embodiment, the first actinic radiation to activate the solvent-based printing ink is UV light emitted by a UV lamp. In this method, the heat and activity induced by the UV lamp help to remove residual solvent, which would be otherwise trapped under the EB coating and cause odor and migration of the printed ink.
20 Furthermore, UV light is anti-microbial and reduces microbial counts in the packaging material, extending shelf life of packaged food. Thus, the present invention further provides a low-odor packaging material produced by the method of the present invention. The printed images of the packaging material of the present invention can stand strenuous conditions, such as heat and friction, during
25 subsequent filling steps of the packaging with a substance to be packaged.

4.1 Packaging Materials

Packaging materials to be used in the present invention should be capable of achieving good preservation of their contents (*e.g.*, food, drugs, tobacco, etc.) and safety, and include, but are not limited to, various thermoplastic flexible packaging films (single layer as well as multilayer plastic films), foil-laminated plastic structure, a paper plastic laminate and a plastic/foil/paper laminates, all of which are well known to those skilled in the art. Appropriate thermoplastic flexible packaging films to be used in the present invention include, but not by way of limitation, polyester, polypropylene, nylon, polyolefin, various homopolymers, copolymers, and or interpolymers, of polystyrene, polyisoprene, 1,2- or 1,4-polybutadinene, poly(meth)acrylic acid, polymethyl methacrylate, polyethylene oxide, polybutylene oxide, poly 2-vinylpyridine, polydiethylamino ethylmethacrylate, poly dimethylamino ethylmethacrylate, and so forth. The film may incorporate a gas barrier component, such as ethylene vinyl alcohol, polyvinylidene chloride, nylon, polyacrylonitrile, polysilicate, melamine, polyhydroxy ethers (*e.g.*, Blox® by Dow), and so forth. Various packaging materials are described in U.S. patents 6,815,057, 6,846,530, 6,846,532, 6,866,907 and 6,861,478, each of which is incorporated by reference in its entirety. Paper plastic laminates are described in U.S. patent 6,843,371 and U.S. patent application publication no. 2005/0031887 and examples of foil-laminated plastic structure can be found in U.S. patents 4,402,172, 5,098,751, 6,716,499 and 5,800,724, all of which are incorporated by reference in their entireties.

4.2 Organic Solvent- and/or Water-based Ink

The organic solvent- and/or water-based inks used in the present invention are any polymers or resins well known to one of ordinary skill in the art. The term "resin" used herein in relation to organic solvent- and/or water-based inks refers to both homopolymers and copolymers known as hard solid polymers.

Preferably, such resins have relatively low weight average molecular weight (Mw). The preferred Mw is greater than about 500 but less than about 500,000 daltons, more preferably greater than about 1,000 but less than about 50,000 daltons, and most preferably greater than about 1,000 but less than about 10,000 daltons. The resins preferably have melting points at temperatures between about 0° and about 200°C, more preferably between about 10°C and about 180°C, and most preferably between about 20°C and 150°C. Examples of useful organic solvent- and/or water-soluble polymer resin includes, but not limited to, natural polymers, such as rosin based resins, cellulosic resins, such as nitrocellulose, carboxymethyl cellulose and ethyl hydroxyethyl cellulose; and synthetic polymers, such as polyamides, polyvinyl esters, polyvinyl acetals, polyvinyl ethers, epoxide resins, polyacrylic acid esters, polymethacrylic acid esters, polyesters, alkyd resins, polyacrylamide, polyvinyl alcohol, polyethylene oxide, polydimethyl acrylamide, polyvinyl pyrrolidone, polyvinylmethyl formamide, polyvinyl methyl acetamide, polyether polyurethane, aliphatic and aromatic polyurethane, polystyrene resin, styrene-maleic anhydride copolymer (SMA), styrene-(meth)acrylate ester copolymer resin or styrene-conjugated diene copolymer resin, butyral resin, xylene resin, coumarone-indene resin, phenolic resin, as well as a mixture of or copolymer of those listed above.

In a preferred embodiment, an organic solvent- and/or water-soluble polymer is in a range between about 0.1% and about 40% by weight of the total ingredients of the ink, more preferably between about 1% and about 30% by weight of the total ink, and most preferably between about 10% and about 20 % by weight of the total ink.

The printed images are then irradiated by actinic radiation which activates the printed inks. In a preferred embodiment, actinic radiation is UV light from a UV lamp. An appropriate UV light may be obtained from, for example, a medium pressure mercury lamp, a metal halide lamp, a xenon lamp, a carbon arc light source,

a chemical lamp, low-pressure or high-pressure mercury lamp, a UV-light emitting diode (LED) lamp and so forth. The appropriate UV light intensity is in the range of about 20 to about 10,000 mJ/cm², preferably about 40 to about 1,000 mJ/cm², and most preferably about 50 to about 700 mJ/cm². It should be noted that the organic solvent-
5 and/or water-based inks used in the present invention do not contain any photoinitiator even when the first actinic radiation to activate the liquid ink is UV light.

In another preferred embodiment, actinic radiation is an electron beam between about 0.5 to about 8 Mrads, more preferably about 1 to about 6 Mrads, and
10 most preferably about 1.3 to about 4 Mrads. An electron beam acceleration voltage ranges preferably about 30-200 kV, more preferably 60-165 kV, and most preferably about 70-140 kV. During the irradiation of the printed ink, an inert environment is preferably provided by, for instance, nitrogen gas, resulting in preferably less than about 600 parts per million (ppm), more preferably less than about 400 ppm, and
15 most preferably less than about 200 ppm, of O₂ present in the environment.

4.3 Ink Vehicle

Any vehicle which has previously been used in printing inks may be used for the present invention. Typical are solvents that are low in viscosity and compatible
20 with any other components of the ink. Thus, a choice of solvents depends on the types of the resin components selected for the printing ink of the present invention. Usable solvents for the present printing ink include, but not by way of limitation, water; alcohols, such as ethanol, methanol, isopropanol and n-butanol; esters, such as ethyl acetate, isopropyl acetate, butyl acetate (BuAc) and 2-ethoxyethyl acetate;
25 glycol-ethers, such as 2-methoxyethanol, 2-ethoxyethanol, 2-butoxyethanol, 2-methoxyethoxethanol, 2-ethoxyethoxethanol and 2-butoxyethoxethanol; aliphatics, such as VM&P Naptha and mineral spirits; aromatics, such as toluol and xylol;

ketones, such as acetone, methyl ethyl ketone (MEK) and methyl isobutyl ketone (MIBK) and other solvents, such as methylene chloride, 1,1,1-trichloroethane, N-methyl-2-pyrrolidone, dimethylsulfoxide, mesityl oxide, dimethyl formamide, thiophene, and so forth.

5 In a preferred embodiment, water and/or low molecular weight aliphatic alcohol, such as methanol, ethanol and isopropyl alcohol, or ester, such as ethyl acetate, may be used. In a preferred embodiment, the vehicle is in a range between about 1% and about 90%, more preferably about 30% and 85%, and most preferably about 45% and about 75%, by weight of the total weight of the printing ink.

4.4 Energy-Curable Resin

1 The energy curable resin or photocurable or photopolymerizable resin to be used as protective coating in the present invention may be selected from the broad range of ethylenically unsaturated monofunctional or polyfunctional
15 monomers and oligomers derived therefrom, capable of undergoing photopolymerization (see U.S. Patent 4,066,582; JP H1-115974; WO 01/57145; WO 03/093378; and U.S. Patent 6,706,777). The term "oligomer" as used herein refers to a low molecular weight polymer with degree of polymerization (DP) of less than about 10. Examples of suitable monomers are (poly)ester(meth)acrylates having at
20 least one ester bond in the main chain; urethane(meth)acrylates having at least one urethane bond in the main chain; epoxyacrylates obtained by a reaction between (meth)acrylic acid and epoxide with one and more than one functional groups; (poly)ether (meth)acrylates having at least one ether bond in the main chain; alkyl(meth)acrylates or alkylene(meth)acrylates comprising the main chain formed
25 by a linear alkyl, a branched alkyl, a linear alkylene or a branched alkylene, and side chains or terminal ends having halogen atoms and/or hydroxyl groups; (meth)acrylates having an aromatic ring at the main chain or the side chain;

(meth)acrylates having an alicyclic group having, in the main chain or the side chain, alicyclic groups which may include oxygen atoms or nitrogen atoms as the structural unit; and the like. It will be understood that "(meth)acrylate" is being used in its conventional sense to reference both acrylate and methacrylate.

5 Examples of (poly)ester(meth)acrylates include, but are not limited to, monofunctional (poly)ester(meth)acrylates such as alicyclic-modified neopentylglycol(meth)acrylate, caprolactone-modified 2-hydroxyethyl(meth)acrylate, ethyleneoxide- and/or propyleneoxide-modified phthalate(meth)acrylate, ethyleneoxide-modified succinate(meth)acrylate, caprolactone-modified

10 tetrahydrofurfuryl(meth)acrylate; pivalate-esterneopentylglycoldi(meth)acrylate, caprolactone-modified hydroxypivalateesterneopentylglucoldi(meth)acrylate, epichlorohydrin-modified phthalatedi(meth)acrylate; mono-, di- or tri-(meth)acrylates of triol obtained by addition of more than 1 mole of cyclic lactones such as epsilon-caprolactone, gamma-butyrolactone, delta-valerolactone or

15 methylvalerolactone to 1 mole of trimethylolpropane or glycerin; mono-, di-, tri, or tetra-(meth)acrylates of triol obtained by addition of more than 1 mole of cyclic lactones such as epsilon-caprolactone, gamma-butyrolactone, delta-valerolactone or methylvalerolactone to 1 mole of pentaerythritol or ditrimethylolpropane; mono- or poly-(meth)acrylates of polyhydric alcohols such as triol, tetraol, pentaol, or hexaol,

20 obtained by addition of more than 1 mole of cyclic lactones such as epsilon-caprolactone, gamma-butyrolactone, delta-valerolactone or methylvalerolactone to 1 mole of dipentaerythritol; (meth)acrylates of polyester polyols composed of diol components, such as (poly)ethylene glycol, (poly)propylene glycol, (poly)tetramethylene glycol, (poly)butylene glycol, (poly)pentanediol, (poly)methyl-

25 pentanediol, and (poly)hexanediol, and polybasic acids such as maleic acid, fumaric acid, succinic acid, adipic acid, phthalic acid, hexahydrophthalic acid, tetrahydrophthalic acid, itaconic acid, citraconic acid, hetic acid, chlorendic acid, dimeric acid, alkenylsuccinic acid, sebacic acid, azelaic acid, 2,2,4-trimethyladipic

acid, 1,4-cyclo-hexanedicarboxylic acid, terephthalic acid, 2-sodium-sulfoterephthalic acid, 2-potassium sulfoterephthalic acid, isophthalic acid, 5-sodium sulfoisophthalic acid, 5-potassium sulfoisophthalic acid, orthophthalic acid, 4-sulfophthalic acid, 1,10-decamethylenedicarboxylic acid, muconic acid, oxalic acid, malonic acid, glutaric acid, trimellitic acid, pyromellitic acid; and polyfunctional (poly)ester (meth)acrylates composed of the above diol components, polybasic acids, and cyclic lactone-modified polyesterdiols such as epsilon-caprolactone, gamma-butyrolactone, delta-valerolactone or methylvalerolactone.

Urethane(meth)acrylates represent (meth)acrylates obtained by a reaction between hydroxy compounds having at least one acryloyloxy group and isocyanate compounds. Urethane(meth)acrylate may also be selected from water dilutable aliphatic acrylate or aromatic urethanes. Examples of hydroxy compounds having at least one acryloyloxy group include, for example, 2-hydroxyethyl(meth)acrylate, 2-hydroxypropyl(meth)acrylate, 2-hydroxybutyl(meth)acrylate, 3-hydroxybutyl(meth)acrylate, 4-hydroxybutyl(meth)acrylate, cyclohexanedimethanolmono(meth)acrylate, polyethylene glycol(meth)acrylate, polypropylene glycol(meth)acrylate, trimethylolpropanedi(meth)acrylate, trimethyloethanedi(meth)acrylate, pentaerythritoltri(meth)acrylate or an adduct of (meth)acrylate with glycidyl(meth)acrylate, (meth)acrylate compounds having hydroxyl groups such as 2-hydroxy-3-phenolpropyl(meth)acrylate, and ring-opening reaction products of the above acrylate compounds having hydroxyl groups with epsilon-caprolactone.

Examples of isocyanate compounds include, for example, aromatic diisocyanates such as p-phenylenediisocyanate, m-phenylenediisocyanate, p-xylenediisocyanate, m-xylenediisocyanate, 2,4-tolylenediisocyanate, 2,6-tolylenediisocyanate, 4,4'-diphenylmethanediisocyanate, 3,3'-dimethyldiphenyl-4,4'-diisocyanate, 3,3'-diethyldiphenyl-4,4'-diisocyanate, and naphthalenediisocyanate;

aliphatic or alicyclic diisocyanates, such as isophoronediiisocyanate, hexamethylenediiisocyanate, 4,4'-dicyclohexylmethanediiisocyanate, hydrogenated xylenediiisocyanate, norbornenediiisocyanate, and lysinediiisocyanate; polyisocyanates, such as buret products of more than one type of isocyanates and isocyanate-trimers of the above isocyanates; and polyisocyanates obtained by the esterification reaction of the above isocyanate with various polyols. Examples of polyols used to produce polyisocyanates include, but are not limited to, (poly)alkylene glycols such as (poly)ethylene glycol, (poly)propylene glycol, (poly)butylene glycol, and (poly)tetramethylene glycol; alkylene glycols modified by ethyleneoxide, propyleneoxide, butyleneoxide, tetrahydrofuran, epsilon-caprolactone, gamma-butyrolactone, delta-valerolactone or methylvalerolactone, such as ethylene glycol, propanediol, propylene glycol, tetramethylene glycol, pentamethylolpropane, hexanediol neopentyl glycol, glycerin, trimethylolpropane, pentaerythritol, diglycerin, ditrimethylolpropane, and dipentaerythritol; aliphatic polyols such as copolymers of ethyleneoxide and propyleneoxide, copolymers of propylene glycol and tetrahydrofuran, copolymers of ethylene glycol and tetrahydrofuran, polyisoprene glycol, hydrogenated polyisoprene glycol, polybutadiene glycol, and hydrogenated polybutadiene glycol; aliphatic polyester polyols obtained by esterification reactions between aliphatic dicarboxylic acids such as adipic acid and dimeric acid with polyols such as neopentyl glycols and methpentanediol; aromatic polyester polyols obtained by esterification reaction between aromatic dicarboxylic acids, such as terephthalic acid with polyols, such as neopentyl glycol; polycarbonate polyols; acryl polyols; polyhydric alcohols, such as polytetramethylenhexaglyceryl ether (hexaglycerin modified by tetrahydrofuran); mono- or polyhydric compounds having an ether group at a terminal; polyhydric compound obtained by esterification of the compound having polyhydroxyl groups with dicarboxylic acids, such as fumaric acid, phthalic acid, isophthalic acid, itaconic acid, adipic acid, sebacic acid, and maleic acid; compound containing polyhydroxyl

groups such as monoglyceride obtained by transesterification reaction of compound having polyhydroxyl groups such as glycerin with ester of fatty acid of animals or plants.

Epoxy(meth)acrylates are obtained by a reaction of epoxides having more than one functional group and (meth)acrylic acid. Epoxides as the raw material for epoxy(meth)acrylates includes, but are not limited to, epichlorohydrin-modified-hydrogenated bisphenol-type epoxy resin, synthesized by (methyl)epichlorohydrin and compounds such as hydrogenated bisphenol A, hydrogenated bisphenol S, hydrogenated bisphenol F, and their modified compounds with ethylene oxide or propylene oxide; alicyclic epoxy resins such as 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate, bis-(3,4-epoxycyclohexyl)adipate; alicyclic epoxides such as epoxy resin containing heterocycles such as triglycidylisocyanurate; epichlorohydrin-modified bisphenol-type epoxy resins synthesized by a reaction of (methyl)epichlorohydrin and a compound such as bisphenol A, bisphenol S, bisphenol F, and their modified compounds with ethylene oxide or propyleneoxide; phenol Novolak type epoxy resins; cresol Novolak type epoxy resins; epoxy resins of dicyclopentadiene-modified phenol resin obtained by the reaction of dicyclopentadiene and various types of phenol resins; an aromatic epoxidized compounds of 2,2',6,6'-tetramethylbis-phenol; aromatic epoxides such as phenylglycidyl ether; (poly)glycidyl ethers of glycol compounds such as (poly)ethylene glycol, (poly)propylene glycol, (poly)butylene glycol, (poly)tetramethylene glycol, neopentyl glycol; (poly)glycidyl ether of glycols modified with alkylene oxide; (poly)glycidyl ethers of aliphatic polyhydric alcohols, such as trimethylolpropane, trimethylolethane, glycerin, diglycerin, erythritol, pentaerythritol, sorbitol, 1,4-butanediol, 1,6-hexanediol; alkylene type epoxides of (poly)glycidyl ether modified of aliphatic polyhydric alcohols by alkylene; glycidylesters of carboxylic acids, such as adipic acid, sebacic acid, maleic acid, and itaconic acid; glycidyl ethers of polyesterpolyols of polyhydric alcohols with

polycarboxylic acids; a copolymer of glycidyl(meth)acrylate or methylglycidyl(meth)acrylate; glycidylester of higher fatty acids; aliphatic epoxy resins, such as an epoxidized linseed oil, an epoxidized castor oil, and an epoxidized polybutadiene.

5 (Poly)ether(meth)acrylates include, but are not limited to, aliphatic epoxy acrylates, monofunctional (poly)ether(meth)acrylates, such as butoxyethyl(meth)acrylate, butoxytriethylene glycol(meth)acrylate, epichlorohydrin-modified butyl(meth)acrylate, dicyclopentenylloxylethyl(meth)acrylate, 2-ethoxyethyl(meth)acrylate, ethylcarbitol(meth)acrylate, 2-methoxy(poly)ethylene glycol(meth)acrylate, methoxy(poly)propylene glycol(meth)acrylate, 10 nonylphenoxypolyethylene glycol(meth)acrylate, nonylphenoxypolypropylene glycol(meth)acrylate, phenoxyhydroxypropyl(meth)acrylate, phenoxy(poly)ethylene glycol(meth)acrylate, polyethylene glycol mono(meth)acrylate, polypropylene glycol mono(meth)acrylate, and polyethylene glycol, polypropylene glycol 15 mono(meth)acrylate; alkylene glycol di(meth)acrylates such as polyethylene glycol di(meth)acrylate, polypropylene glycol di(meth)acrylate, polybutylene glycol di(meth)acrylate, polytetramethylene glycol di(meth)acrylate; polyfunctional (meth)acrylates induced by (meth)acrylic acid with aliphatic polyols, such as a copolymer of ethylene oxide and propylene oxide, a copolymer of propylene glycol 20 and tetrahydrofuran, a copolymer of ethylene glycol and tetrahydrofuran, polyisoprene glycol, hydrogenated polyisoprene glycol, polybutadieneglycol, hydrogenated polybutadiene glycol; polyfunctional (meth)acrylates induced by acrylic acid with polyhydric alcohols such as polytetramethylenehexaglyceryl ether (tetrahydrofuran-modified hexaglycerin); di(meth)acrylates of diol obtained by 25 addition of equimolar or more than 1 mole of cyclic ethers, such as ethylene oxide, propylene oxide, butylene oxide and/or tetrahydrofuran to 1 mole of neopentyl oxide; di(meth)acrylates of alkylene oxides-modified bisphenols, such as bisphenol A, bisphenol F and bisphenol S; di(meth)acrylate of alkylene oxide-modified

51

hydrogenated bisphenols, such as hydrogenated bisphenol A, hydrogenated bisphenol F, hydrogenated bisphenol S; di(meth)acrylates of alkylene oxide-modified trisphenols; di(meth)acrylates of alkylene oxide-modified hydrogenated trisphenols; di(meth)acrylates of alkylene oxide-modified p,p'-bisphenols;

5 di(meth)acrylates of alkylene oxide-modified hydrogenated bisphenols; di(meth)acrylates of alkylene oxide-modified p,p'-dihydroxybenzophenones; mono-, di-, and tri-(meth)acrylates of triols obtained by addition of equimolar or more than 1 mole of ethylene oxide, propylene oxide, butylene oxide, and/or cyclic ethers such as tetrahydrofuran to 1 mole of trimethylolpropane or glycerin; mono-, di-, tri- or

10 tetra-(meth)acrylates obtained by addition of equimolar or more than 1 mole of ethylene oxide, propylene oxide, butylene oxide, and/or cyclic ethers, such as tetrahydrofuran to 1 mole of pentaerythritol, ditrimethylolpropane or highly alkoxyated trimethylolpropane triacrylate; monofunctional (poly)ether(meth)acrylates or polyfunctional (poly)ether(meth)acrylates of

15 polyhydric alcohols such as triol, tetraol, pentaol, or hexaol of mono- or poly-(meth)acrylates obtained by addition of equimolar or more than 1 mole of ethylene oxide, propylene oxide, butylene oxide, and/or cyclic ethers, such as tetrahydrofuran to 1 mole of dipentaerythritol.

Alkyl(meth)acrylates or alkylene(meth)acrylates include, but are not

20 limited to, monofunctional (meth)acrylates, such as methyl(meth)acrylate, ethyl(meth)acrylate, propyl(meth)acrylate, isopropyl(meth)acrylate, butyl(meth)acrylate, isobutyl(meth)acrylate, pentyl(meth)acrylate, isopentyl(meth)acrylate, neopentyl(meth)acrylate, hexyl(meth)acrylate, heptyl(meth)acrylate, 2-ethylhexyl(meth)acrylate, octyl(meth)acrylate, isooctyl(meth)acrylate,

25 nonyl(meth)acrylate, decyl(meth)acrylate, dodecyl(meth)acrylate, tridecyl(meth)acrylate, pentadecyl(meth)acrylate, miristyl(meth)acrylate, palmityl(meth)acrylate, stearyl(meth)acrylate, neryl(meth)acrylate, geranyl(meth)acrylate, farnecyl(meth)acrylate, hexadecyl(meth)acrylate,

octadecyl(meth)acrylate, dodecyl(meth)acrylate, and trans-2-hexene(meth)acrylate; di(meth)acrylates of aliphatic diols such as ethylene glycol di(meth)acrylate, propylene glycol di(meth)acrylate, 1,2-butylene glycol di(meth)acrylate, 1,3-butylene glycol di(meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, neopentyl glycol di(meth)acrylate, 2-methyl-1,8-octanediol di(meth)acrylate, 1,9-nonanediol di(meth)acrylate, and 1,10-decanediol di(meth)acrylate; mono(meth)acrylates or poly(meth)acrylates of polyhydric alcohols such as trimethylolpropane, (hereinafter, the term "poly" is used as the general term of the poly-functional including di, tri, tetra, and poly compounds such as

mono(meth)acrylate, di(meth)acrylate, and tri(meth)acrylate of trimethylolpropane), and mono(meth)acrylates or poly(meth)acrylates of polyhydric alcohols, such as triol, tetraol, and hexaol, for example, glycerin, pentaerythritol, ditrimethylolpropane, and dipentaerythritol; (meth)acrylates having hydroxyl groups such as 2-hydroxyethyl(meth)acrylate, 2-hydroxypropyl(meth)acrylate, 4-hydroxybutyl(meth)acrylate, 3-chloro-2-hydroxyethyl(meth)acrylate; (meth)acrylates having bromine atoms such as 2,3-dibromopropyl(meth)acrylate, tribromophenyl(meth)acrylate, ethylene oxide-modified tribromophenyl(meth)acrylate, ethylene oxide-modified tetrabromobisphenol A di(meth)acrylate; (meth)acrylates having fluorine atoms such as

trifluoroethyl(meth)acrylate, pentafluoropropyl(meth)acrylate, tetrafluoropropyl(meth)acrylate, octafluoropentyl(meth)acrylate, dodecafluoroheptyl(meth)acrylate, hexadecafluorononyl(meth)acrylate, hexafluorobutyl(meth)acrylate, 3-perfluorobutyl-2-hydroxypropyl(meth)acrylate, 3-perfluorohexyl-2-hydroxypropyl(meth)acrylate, 3-perfluorooctyl-2-hydroxypropyl(meth)acrylate, 3-(perfluoro-5-methylhexyl)-2-hydroxypropyl(meth)acrylate, 3-(perfluoro-7-methyloctyl)-2-hydroxypropyl(meth)acrylate, and 3-(perfluoro-8-methyldecyl)-2-hydroxypropyl(meth)acrylate.

(Meth)acrylates having aromatic groups include, for example, but are not limited to, monofunctional (meth)acrylates, such as phenyl(meth)acrylate, benzylacrylate; and di(meth)acrylates, such as bisphenol A diacrylate, bisphenol F diacrylate, bisphenol S diacrylate.

- 5 (Meth)acrylates having alicyclic groups include, but not by way of limitation, monofunctional (meth)acrylates having alicyclic structures, such as cyclohexyl(meth)acrylate, cyclopentyl(meth)acrylate, cycloheptyl(meth)acrylate, bicycloheptyl(meth)acrylate, isobornyl(meth)acrylate, bicyclopentylidi(meth)acrylate, tricyclodecyl(meth)acrylate, bicyclopentenyl(meth)acrylate, norbornyl(meth)acrylate, bicyclooctyl(meth)acrylate, tricycloheptyl(meth)acrylate, and cholesterol skeleton-substituted(meth)acrylate; di(meth)acrylates of hydrogenated bisphenols, such as hydrogenated bisphenol A, hydrogenated bisphenol F, hydrogenated bisphenol S, di(meth)acrylates of hydrogenated trisphenols, such as hydrogenated trisphenols, and di(meth)acrylates of hydrogenated p,p'-bisphenols; polyfunctional
- 10 (meth)acrylates having cyclic structures such as dicyclopentane type di(meth)acrylate, such as "Kayarad R684" (available from Nihon Kayaku Co., Japan), tricyclodecane dimethyloldi(meth)acrylate, bisphenolfluorene dihydroxy(meth)acrylate; and alicyclic acrylates having oxygen atoms and/or nitrogen atoms, such as tetrahydrofurfuryl(meth)acrylate, and
- 15 morpholinoethyl(meth)acrylate.

- Compounds having acryloyl groups or methacryloyl groups which are suitable for the present invention, beside the above recited compounds, include poly(meth)acryl(meth)acrylates, such as a reaction product of (meth)acrylic acid polymer and glycidyl(meth)acrylate, and a reaction product of
- 20 glycidyl(meth)acrylate polymer and (meth)acrylic acid; (meth)acrylate having amino groups such as dimethylaminoethyl(meth)acrylate; isocyanul(meth)acrylates, such as tris(meth)acryloxyethyl isocyanurate; phosphagene(meth)acrylates, such as

hexakis(meth)acryloyloxyethyl cyclotriphosphagen; (meth)acrylate having a skeleton of polysiloxane; polybutadiene(meth)acrylate; and melamine(meth)acrylate. Among these compounds having acryloyl or methacryloyl group, it is preferable to use the compound having 1 to 6 acryloyl or methacryloyl groups.

5 (Meth)acrylamide derivatives which can be used in the present invention include, for example, monofunctional (meth)acrylamides, such as N-isopropyl(meth)acrylamide; and polyfunctional (meth)acrylamides, such as methylenebis(meth)acrylamide.

Compounds having vinyl ether groups suitable for the present invention
10 include, but are not limited to, those containing: an alkyl vinyl ether having a terminal group substituted with at least one selected from the group consisting of a hydrogen atom, a halogen atom, a hydroxyl group, and an amino group; a cycloalkyl vinyl ether having a terminal group substituted with at least one selected from the group consisting of a hydrogen atom, a halogen atom, a hydroxyl group, and an
15 amino group; at least one vinyl ether selected from the group consisting of a monovinyl ether, a divinyl ether, and a polyvinyl ether in which a vinyl ether group is connected with alkylene group; and a vinyl ether group connected with at least one group with and without substituent selected from the group consisting of alkyl group, cycloalkyl group, and aromatic group, via at least one linkage selected from
20 the group consisting of an ether linkage, an urethane linkage, and an ester linkage.

Alkylvinyl ethers include, but are not limited to, methyl vinyl ether, hydroxymethyl vinyl ether, chloromethyl vinyl ether, ethyl vinyl ether, 2-hydroxyethylvinylether, 2-chloroethylvinylether, diethyl aminoethyl vinyl ether, propyl vinyl ether, 3-hydroxypropyl vinyl ether, 2-hydroxypropyl vinyl ether, 3-
25 chloropropyl vinyl ether, 3-aminopropyl vinyl ether, isopropyl vinyl ether, butyl vinyl ether, 4-hydroxybutyl vinyl ether, isobutyl vinyl ether, 4-aminobutyl vinyl ether, pentyl vinyl ether, isopentyl vinyl ether, hexyl vinyl ether, 1,6-hexanediol

monovinyl ether, heptyl vinyl ether, 2-ethylhexyl vinyl ether, octyl vinyl ether, isooctyl vinyl ether, nonyl vinyl ether, isononyl vinyl ether, decyl vinyl ether, isodecyl vinyl ether, dodecyl vinyl ether, isododecyl vinyl ether, tridecyl vinyl ether, isotridecyl vinyl ether, pentadecyl vinyl ether, isopentadecyl vinyl ether, hexadecyl vinyl ether, octadecyl vinyl ether, methylene glycol divinyl ether, ethylene glycol divinyl ether, propylene glycol divinyl ether, 1,4-butanediol divinyl ether, 1,6-hexanediol divinyl ether, cyclohexanediol divinyl ether, trimethylolpropane trivinyl ether, pentaerythritol tetravinyl ether and hexanedioic acid, bis(4-ethenyloxy)butyl ester.

Cycloalkyl vinyl ethers suitable for the present invention include, but not

by way of limitation, cyclopropyl vinyl ether, 2-hydroxycyclopropyl vinyl ether, 2-chloro-cyclopropyl vinyl ether, cyclopropylmethyl vinyl ether, cyclobutyl vinyl ether, 3-hydroxycyclobutyl vinyl ether, 3-chlorocyclobutyl vinyl ether, cyclobutylmethyl vinyl ether, cyclopentyl vinyl ether, 3-hydroxycyclopentyl vinyl ether, 3-

chlorocyclopentyl vinyl ether, cyclopentylmethyl vinyl ether, cyclohexyl vinyl ether, 4-hydroxycyclohexyl vinyl ether, cyclohexylmethyl vinyl ether, 4-aminocyclohexyl vinyl ether, cyclohexanediol monovinyl ether, cyclohexanedimethanol monovinyl ether, and cyclohexanedimethanol divinyl ether. Compounds containing monovinyl ethers, divinyl ethers, and/or polyvinyl ethers, include those in which the vinyl ether

linkage connects with an alkylene group, and at least one group selected from a group consisting of a C₂-C₂₄ alkyl group, a C₂-C₂₄ alicyclic group and a C₂-C₂₄ aromatic group which may have a substituents connecting with a linkage selected from the group consisting of an ether linkage, an urethane linkage, and an ester linkage. Examples of the compounds containing an ether linkage include, but are not limited to, ethylene glycol methyl vinyl ether, diethylene glycol monovinyl ether, diethylene glycol methylvinyl ether, diethylene glycol divinyl ether, triethylene glycol monovinyl ether, triethylene glycol methylvinyl ether, triethylene glycol divinyl ether, polyethylene glycol monovinyl ether, polyethylene glycol methylvinyl

ether, polyethylene glycol divinyl ether, propylene glycol methylvinyl ether, dipropylene glycol monovinyl ether, dipropylene glycol methylvinyl ether, dipropylene glycol divinyl ether, tripropylene glycol monovinyl ether, tripropylene glycol methylvinyl ether, tripropylene glycol divinyl ether, polypropylene glycol monovinyl ether, polypropylene glycol methylvinyl ether, polypropylene glycol divinyl ether, tetramethylene glycol methylvinyl ether, di(tetramethylene glycol)monovinyl ether, di(tetramethylene glycol)methyl vinyl ether, di(tetramethylene glycol)divinylether, tri(tetramethylene glycol)monovinyl ether, tri(tetramethylene glycol)methylvinyl ether, tri(tetramethylene glycol)divinyl ether, poly(tetramethylene glycol)monovinyl ether, poly(tetramethylene glycol)methylvinyl ether, poly(tetramethylene glycol)divinyl ether, 1,6-hexanediolmethyl vinyl ether, di(hexamethylene glycol)monovinyl ether, di(hexamethylene glycol)methylvinyl ether, di(hexamethylene glycol)divinyl ether, tri(hexamethylene glycol)monovinyl ether, tri(hexamethylene glycol)methylvinyl ether, tri(hexamethylene glycol)divinyl ether, poly(hexamethylene glycol)monovinyl ether, poly(hexamethylene glycol)methylvinyl ether, poly(hexamethylene glycol)divinyl ether.

In a preferred embodiment, the energy curable monomer and/or oligomers are in a range between about 1% and about 100%, more preferably between about 5% and about 95%, and most preferably between about 10% and about 90% by weight of the total ingredients of the protective coating.

In another preferred embodiment, the energy curable protective coating is clear or free of pigment. In yet another preferred embodiment, the energy curable protective coating is dyed or contains organic or inorganic pigments.

The types of actinic radiation to polymerize the protective coating for the printed packaging materials of the present invention may be an electron beam, or a UV light, and the like. In a preferred embodiment, the energy source for photo-

polymerization is an electron beam. Preferably, an electron beam dose necessary for curing of the ink ranges between about 0.5 to about 8 Mrads, more preferably about 1 to about 6 Mrads, and most preferably about 1.3 to about 4 Mrads. An electron beam acceleration voltage ranges preferably about 30-200 kV, more preferably 60-165 kV, and most preferably about 70-140 kV. During the electron-beam curing of the ink, an inert environment is provided by nitrogen gas, resulting in preferably less than about 600 parts per million (ppm), more preferably less than about 400 ppm, and most preferably less than about 200 ppm, of O₂ present in the environment. In another preferred embodiment, the energy source for photo-polymerization of the protective coating is UV light. The appropriate UV light intensity is in the range of about 20 to about 10,000 mJ/cm², preferably about 40 to about 1,000 mJ/cm², and most preferably about 50 to about 700 mJ/cm².

4.5 Photoinitiator

Unless the second actinic radiation source is an electron beam, the energy curable resin for protective coating in the present invention will typically contain a photoinitiator that generates free radicals upon exposure to actinic radiation, such as UV light. Such a photoinitiator may have one or more compounds that directly produce free radicals when activated by actinic radiation. The photoinitiator may also contain a sensitizer or activator which either extends the spectral response into the near ultraviolet, visible or near infrared spectral regions, or affects the rate of reaction. In free radical initiated curing systems, irradiation of a photoinitiator produces free radicals that initiate polymerization and/or crosslinking of photocurable resins. Various types of photoinitiators are well known to one of ordinary skill in the art (*see, for example, "Photoinitiators for free-radical-initiated photoimaging systems" by Monroe, B.M. et al., 1994, Chem. Rev. 93:435-448*). Examples of photoinitiators suitable for the present invention include, but not

limited to, organic halogen compound as disclosed in U.S. Patent 5,057,398 and those disclosed in U.S. Patent 4,066,582, such as benzophenone, acetophenone, fluorenone, xanthone, thioxanthone, carbazole, benzoin, the allyl benzoin ethers, 2- or 3- or 4-bromoacetophenone, 3- or 4- allylacetophenone, m- or p-diacetylbenzene, 2- or 3- or 4-methoxybenzophenone, 3,3'- or 3,4'- or 4,4'-dimethoxybenzophenone, 4-chloro-4'-benzylbenzophenone, 2- or 3-chloroxanthone, 3,9-dichloroxanthone, 2- or 3-chlorothioxanthone, 3-chloro-8-nonylxanthone, 3-methoxyanthone, 3-iodixanthone, 2-acetyl-4-methylphenyl acetate, alkyl and aryl ethers of benzoin, phenylglyoxal alkyl acetals, 2,2'-dimethoxy-2-phenyl-acetophenone, 2,2-diethoxyacetophenone, 2,2-diiso-propoxyacetophenone, 1,3-diphenyl acetone, naphthalene sulfonyl chloride, and mixtures thereof.

Suitable sensitizers or activators that can be used in combination with the aforementioned photoinitiators include, but not by way of limitation, methylamine, tributylamine, methyldiethanolamine, 2-aminoethylethanolamine, allylamine, cyclohexylamine, cyclopentadienylamine, diphenylamine, ditolylamine, trixylylamine, tribenzylamine, N-cyclohexylethylenimine, piperidine, 2-methylpiperidine, N-ethylpiperidine, 1,2,3,4-tetrahydropyridine, 2- or 3- or 4-picoline, morpholine, N-methylmorpholine, piperazine, N-methylpiperazine, 2,2-dimethyl-1,3-bis-(3-N-morpholinyl) propionyloxy)) diethyl ether, isopropylthioxanthone (ITX), dibutoxyanthracene, dipropoxyanthracene, and mixtures thereof.

In a preferred embodiment, the photoinitiator is in a range between about 0.1% and about 20%, more preferably between about 0.2% to 12%, and most preferably about 0.5% to 8%, by weight of the total weight of the coating.

5. EXAMPLES

The following examples illustrate the energy curable solvent-based liquid printing ink provided by the present invention. These examples should not be construed as limiting.

5.1 Example 1

A 75- μ thick opaque polyethylene film was coated with a solvent-based red ink (nitocellulose/polyurethane based) and dried using a hot-air gun. Thereafter, a thin protective layer of EB curable coating was applied over the red-coated film with a #3 Meyer bar. This was EB-cured at 3 Mrads, 100 kV acceleration voltage and less than 200 ppm oxygen. The resultant glossy film has a 60-degree reflective gloss of 71-73% and had a solvent resistance of 17-20 MEK double rubs. The face-to-face coefficient of friction (COF) was 0.39-0.40 static/0.31-0.42 kinetic as measured on a TMI (model 32-06; Testing Machine Instruments, Amityville, NY) slip friction tester. The residual solvent as measured by GC-headspace was 593 mg/ream (1 ream = 3000 square feet of the film).

5.2 Example 2

A 75- μ thick opaque polyethylene film was coated with a solvent-based red ink (nitrocellulose/polyurethane based) and dried using a hot air gun. Immediately thereafter, the coated film was subjected to 250 mJ/cm² of UV. A thin protective layer of EB-curable coating was applied over the red-coated film with a #3 Meyer bar. This was EB-cured at 3 Mrads, 100 kV acceleration voltage and less than 200 ppm oxygen. The resultant glossy film has a 60-degree reflective gloss of 71-73% and had a solvent resistance of 24-32 MEK double rubs. The face-to-face COF was 0.39-0.40 static/0.31-0.32 kinetic as measured on a TMI slip friction tester. The residual solvent as measured by GC-headspace was 402 mg/ream.

The results of the above two (2) examples are summarized in Table 1 below.

Table 1

	MEK rubs	Residual Solvent	COF	60° Gloss
Example 1 (no UV activation)	17-20	593 mg/ream	0.39-0.40/0.31-0.32	71-73
Example 2 (UV activation)	24-32	402 mg/ream	0.39-0.40/0.30-0.31	71-73

5.3 Example 3

A 50- μ m thick polypropylene film is coated with a solvent-based blue ink (polyurethane based) and dried using a hot-air gun. Immediately thereafter, the coated film is subjected to 100 mJ/cm² of UV. A thin protective layer of polyester acrylate containing 5% benzophenone (photoinitiator) is applied over the blue-coated film with a #3 Meyer bar. The protective coating is then cured by UV light at 500 mJ/cm².

5.4 Example 4

A 50- μ m thick polyolefin foil laminated paper film is coated with a solvent-based red ink (polyurethane based) and dried using a hot-air gun. Immediately thereafter, the coated film is subjected to 330 mJ/cm² of UV. A thin protective layer of EB-curable coating, containing a red pigment, is applied over the red-coated film with a #3 Meyer bar. This is EB-cured at 2 Mrads, 100-kV, acceleration voltage and less than 200 ppm oxygen.

12

5.5 Example 5

A 80- μm thick paper plastic film laminate structure is coated with a water-based orange ink (acrylic based) and dried using a hot-air gun. Immediately thereafter, the coated film is subjected to 305 mJ/cm² of UV. A thin protective layer of EB-curable coating is applied over the orange-coated film with a #3 Meyer bar. This is EB-cured at 1.5 Mrads, 100 kV acceleration voltage and less than 200 ppm oxygen.

5.6 Example 6

A 50- μm thick polyolefin foil laminated paper film is coated with a photoinitiator-free solvent-based red ink (polyurethane based) and dried using a hot-air gun. Immediately thereafter, the coated film is subjected to an EB at 2 Mrads, 100 kV acceleration voltage and less than 200 ppm oxygen. A thin protective layer of UV-curable coating, containing a photoinitiator, is applied over the red-coated film with a #3 Meyer bar. This is UV-cured at 330 mJ/cm².

6. EQUIVALENTS

Those skilled in the art will recognize, or be able to ascertain many equivalents to the specific embodiments of the invention described herein using no more than routine experimentation. Such equivalents are intended to be encompassed by the following claims.

All publications and patents mentioned in this specification are herein incorporated by reference into the specification.

CLAIMS

What is claimed is:

1. A method of producing a printed packaging material comprising:
applying an actinic radiation activatable liquid ink to a packaging material;
5 exposing the ink to first actinic radiation;
applying an energy-curable coating over the ink; and
curing the coating with second actinic radiation.
2. The method of claim 1, wherein the packaging material is a thermoplastic flexible film, and wherein a to-be-packaged substance is enclosed within the plastic film
10 subsequent to the actinic radiation curing thereof.
3. The method of claim 1, wherein the packaging material is a foil laminate paper or paper plastic laminate, and wherein a to-be-packaged substance is enclosed within the plastic film subsequent to the actinic radiation curing thereof.
4. The method of claim 1, wherein the first actinic radiation is UV light.
- 15 5. The method of claim 1, wherein the second actinic radiation is an electron beam.
6. The method of claim 1, wherein the second actinic radiation is UV light.
7. The method of claim 1, wherein the energy-curable coating is free of pigment.
8. The method of claim 1, wherein the liquid ink is applied more than once.
9. The method of claim 1, wherein the liquid ink is solvent-based.
- 20 10. The method of claim 1, wherein the liquid ink is water-based.
11. A packaging material produced according to the method of claim 1.
12. The packaging material of claim 11, wherein the packaging material contains less
than 700 ppm total of residual solvent or water.

13. The packaging material of claim 12, wherein the packaging material contains less than 600 ppm total of residual solvent or water.
14. The packaging material of claim 13, wherein the packaging material contains less than 500 ppm total of residual solvent or water.
15. The packaging material of claim 11, wherein the packaging material has a degree of cure of at least 5 MEK rubs.
16. The packaging material of claim 15, wherein the packaging material has a degree of cure of at least 10 MEK rubs.
17. The packaging material of claim 16, wherein the packaging material has a degree of cure of at least 20 MEK rubs.

INTERNATIONAL SEARCH REPORT

Inte I Application No
PC1/US2005/010649

A CLASSIFICATION OF SUBJECT MATTER

IPC 7 B32B27/16 B32B31/00 B41M7/00 C09D11/10 C09D4/00
B65D65/00

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

B FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B32B B41M C09D B65D

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

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

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
X	US 3 552 986 A (ROBERT W. BASSEMIR ET AL) 5 January 1971 (1971-01-05)	1-17
Y	the whole document	2-10, 12-17
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X	WO 02/051915 A (CRYOVAC, INC; SPEER, DREW, V, KENNEDY, THOMAS, D) 4 July 2002 (2002-07-04)	1-17
Y	page 12, column 4 - page 21, column 30	2-10, 12-17
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☒ Further documents are listed in the continuation of box C

☒ Patent family members are listed in annex

* Special categories of cited documents:

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

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

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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

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

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"S" document member of the same patent family

Date of the actual completion of the international search

15 July 2005

Date of mailing of the international search report

29/07/2005

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Authorized officer

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INTERNATIONAL SEARCH REPORT

Inter Application No
PCT/US2005/010649

C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
X	US 5 407 708 A (LOVIN ET AL) 18 April 1995 (1995-04-18)	1-17
Y	abstract column 3, line 22 - line 57 column 5, line 23 - line 29 claims 1-13	2-10, 12-17
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Information on patent family members

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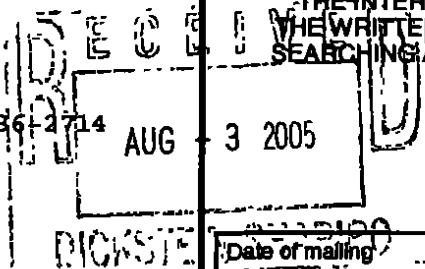
From the INTERNATIONAL SEARCHING AUTHORITY

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To

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 UNITED STATES OF AMERICA

NOTIFICATION OF TRANSMITTAL OF
 THE INTERNATIONAL SEARCH REPORT AND
 THE WRITTEN OPINION OF THE INTERNATIONAL
 SEARCHING AUTHORITY, OR THE DECLARATION



(PCT Rule 44.1)

Date of mailing (day/month/year) 29/07/2005	
Applicant's or agent's file reference S9025.0025	FOR FURTHER ACTION See paragraphs 1 and 4 below
International application No PCT/US2005/010649	International filing date (day/month/year) 31/03/2005
Applicant SUN CHEMICAL CORPORATION	

- 1 ☒ The applicant is hereby notified that the international search report and the written opinion of the International Searching Authority have been established and are transmitted herewith

Filing of amendments and statement under Article 19

The applicant is entitled, if he so wishes, to amend the claims of the International Application (see Rule 46):

When? The time limit for filing such amendments is normally 2 months from the date of transmittal of the International Search Report; however, for more details, see the notes on the accompanying sheet.

Where? Directly to the International Bureau of WIPO, 34 chemin des Colombettes
 1211 Geneva 20, Switzerland, Facsimile No. (41-22) 740 14.35

For more detailed instructions, see the notes on the accompanying sheet

- 2 ☐ The applicant is hereby notified that no international search report will be established and that the declaration under Article 17(2)(a) to that effect and the written opinion of the International Searching Authority are transmitted herewith

- 3 ☐ With regard to the protest against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that

☐ the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices

☐ no decision has been made yet on the protest, the applicant will be notified as soon as a decision is made

4 Reminders

Shortly after the expiration of 18 months from the priority date, the international application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau as provided in Rules 90bis.1 and 90bis.3, respectively, before the completion of the technical preparations for international publication.

The applicant may submit comments on an informal basis on the written opinion of the International Searching Authority to the International Bureau. The International Bureau will send a copy of such comments to all designated Offices unless an international preliminary examination report has been or is to be established. These comments would also be made available to the public but not before the expiration of 30 months from the priority date.

Within 19 months from the priority date, but only in respect of some designated Offices, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase until 30 months from the priority date (in some Offices even later); otherwise, the applicant must, within 20 months from the priority date, perform the prescribed acts for entry into the national phase before those designated Offices.

In respect of other designated Offices, the time limit of 30 months (or later) will apply even if no demand is filed within 19 months.

See the Annex to Form PCT/IB/301 and, for details about the applicable time limits, Office by Office, see the *PCT Applicant's Guide*, Volume II, National Chapters and the WIPO Internet site.

Name and mailing address of the International Searching Authority  European Patent Office, P B 5818 Patentlaan 2 NL-2280 HV Rijswijk Tel (+31-70) 340-2040, Tx 31 651 epo nl, Fax (+31-70) 340-3016	Authorized official Laure Acquayiva C/L: _____ ENTERED BY: <u>JAN</u> (See notes on accompanying sheet) ATTY: <u>AM/14</u>
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Form PCT/ISA/220 (January 2004)

These Notes are intended to give the basic instructions concerning the filing of amendments under article 19. The Notes are based on the requirements of the Patent Cooperation Treaty, the Regulations and the Administrative Instructions under that Treaty. In case of discrepancy between these Notes and those requirements, the latter are applicable. For more detailed information, see also the PCT Applicant's Guide, a publication of WIPO.

In these Notes, "Article", "Rule", and "Section" refer to the provisions of the PCT, the PCT Regulations and the PCT Administrative Instructions respectively.

INSTRUCTIONS CONCERNING AMENDMENTS UNDER ARTICLE 19

The applicant has, after having received the international search report, one opportunity to amend the claims of the international application. It should however be emphasized that, since all parts of the international application (claims, description and drawings) may be amended during the international preliminary examination procedure, there is usually no need to file amendments of the claims under Article 19 except where, e.g. the applicant wants the latter to be published for the purposes of provisional protection or has another reason for amending the claims before international publication. Furthermore, it should be emphasized that provisional protection is available in some States only.

What parts of the international application may be amended?

Under Article 19, only the claims may be amended.

During the international phase, the claims may also be amended (or further amended) under Article 34 before the International Preliminary Examining Authority. The description and drawings may only be amended under Article 34 before the International Examining Authority.

Upon entry into the national phase, all parts of the international application may be amended under Article 28 or, where applicable, Article 41.

When?

Within 2 months from the date of transmittal of the international search report or 16 months from the priority date, whichever time limit expires later. It should be noted, however, that the amendments will be considered as having been received on time if they are received by the International Bureau after the expiration of the applicable time limit but before the completion of the technical preparations for international publication (Rule 46.1).

Where not to file the amendments?

The amendments may only be filed with the International Bureau and not with the receiving Office or the International Searching Authority (Rule 46.2).

Where a demand for international preliminary examination has been/is filed, see below.

How?

Either by cancelling one or more entire claims, by adding one or more new claims or by amending the text of one or more of the claims as filed.

A replacement sheet must be submitted for each sheet of the claims which, on account of an amendment or amendments, differs from the sheet originally filed.

All the claims appearing on a replacement sheet must be numbered in Arabic numerals. Where a claim is cancelled, no renumbering of the other claims is required. In all cases where claims are renumbered, they must be renumbered consecutively (Administrative Instructions, Section 205(b)).

The amendments must be made in the language in which the international application is to be published.

What documents must/may accompany the amendments?

Letter (Section 205(b)):

The amendments must be submitted with a letter.

The letter will not be published with the international application and the amended claims. It should not be confused with the "Statement under Article 19(1)" (see below, under "Statement under Article 19(1)").

The letter must be in English or French, at the choice of the applicant. However, if the language of the international application is English, the letter must be in English; if the language of the international application is French, the letter must be in French.

NOTES TO FORM PCT/ISA/220 (continued)

The letter must indicate the differences between the claims as filed and the claims as amended. It must, in particular, indicate, in connection with each claim appearing in the international application (it being understood that identical indications concerning several claims may be grouped), whether

- (i) the claim is unchanged,
- (ii) the claim is cancelled,
- (iii) the claim is new,
- (iv) the claim replaces one or more claims as filed,
- (v) the claim is the result of the division of a claim as filed

The following examples illustrate the manner in which amendments must be explained in the accompanying letter:

- 1 [Where originally there were 48 claims and after amendment of some claims there are 51]
"Claims 1 to 29, 31, 32, 34, 35, 37 to 48 replaced by amended claims bearing the same numbers;
claims 30, 33 and 36 unchanged, new claims 49 to 51 added"
- 2 [Where originally there were 15 claims and after amendment of all claims there are 11]
"Claims 1 to 15 replaced by amended claims 1 to 11"
- 3 [Where originally there were 14 claims and the amendments consist in cancelling some claims and in adding new claims]
"Claims 1 to 6 and 14 unchanged, claims 7 to 13 cancelled, new claims 15, 16 and 17 added" or
"Claims 7 to 13 cancelled, new claims 15, 16 and 17 added, all other claims unchanged"
- 4 [Where various kinds of amendments are made]
"Claims 1-10 unchanged, claims 11 to 13, 18 and 19 cancelled, claims 14, 15 and 16 replaced by amended claim 14, claim 17 subdivided into amended claims 15, 16 and 17, new claims 20 and 21 added"

"Statement under article 19(1)" (Rule 48.4)

The amendments may be accompanied by a statement explaining the amendments and indicating any impact that such amendments might have on the description and the drawings (which cannot be amended under Article 19(1)).

The statement will be published with the international application and the amended claims.

It must be in the language in which the international application is to be published.

It must be brief, not exceeding 500 words if in English or if translated into English.

It should not be confused with and does not replace the letter indicating the differences between the claims as filed and as amended. It must be filed on a separate sheet and must be identified as such by a heading, preferably by using the words "Statement under Article 19(1)".

It may not contain any disparaging comments on the international search report or the relevance of citations contained in that report. Reference to citations, relevant to a given claim, contained in the international search report may be made only in connection with an amendment of that claim.

Consequence if a demand for international preliminary examination has already been filed

If, at the time of filing any amendments under Article 19, a demand for international preliminary examination has already been submitted, the applicant must preferably, at the same time of filing the amendments with the International Bureau, also file a copy of such amendments with the International Preliminary Examining Authority (see Rule 62.2(a), first sentence).

Consequence with regard to translation of the international application for entry into the national phase

The applicant's attention is drawn to the fact that, where upon entry into the national phase, a translation of the claims as amended under Article 19 may have to be furnished to the designated/elected Office, instead of, or in addition to, the translation of the claims as filed.

For further details on the requirements of each designated/elected Office, see Volume II of the PCT Applicant's Guide.

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference S9025.0025	FOR FURTHER ACTION see Form PCT/ISA/220 as well as, where applicable, item 5 below.	
International application No PCT/US2005/010649	International filing date (day/month/year) 31/03/2005	(Earliest) Priority Date (day/month/year) 31/03/2004
Applicant SUN CHEMICAL CORPORATION		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 4 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

- a With regard to the language, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ The International search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b ☐ With regard to any nucleotide and/or amino acid sequence disclosed in the international application, see Box No. I.

- 2 ☐ Certain claims were found unsearchable (See Box II)

- 3 ☐ Unity of invention is lacking (see Box III)

4 With regard to the title,

☐ the text is approved as submitted by the applicant

☒ the text has been established by this Authority to read as follows.

METHOD OF MANUFACTURING LOW-ODOR PACKAGING MATERIALS

5. With regard to the abstract,

☒ the text is approved as submitted by the applicant

☐ the text has been established, according to Rule 38 2(b), by this Authority as it appears in Box No. IV. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. With regard to the drawings,

- a the figure of the drawings to be published with the abstract is Figure No. _____

☐ as suggested by the applicant.

☐ as selected by this Authority, because the applicant failed to suggest a figure.

☐ as selected by this Authority, because this figure better characterizes the invention.

- b ☐ none of the figures is to be published with the abstract

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2005/010649

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B32B27/16 B32B31/00 B41M7/00 C09D11/10 C09D4/00
B65D65/00

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B32B B41M C09D B65D

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

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

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
X	US 3 552 986 A (ROBERT W. BASSEMIR ET AL) 5 January 1971 (1971-01-05)	1-17
Y	the whole document	2-10, 12-17
	claims 9-15	
X	WO 02/051915 A (CRYOVAC, INC; SPEER, DREW, V; KENNEDY, THOMAS, D) 4 July 2002 (2002-07-04)	1-17
Y	page 12, column 4 - page 21, column 30	2-10, 12-17
	----- -/--	

☒ Further documents are cited in the continuation of box C

☒ Patent family members are listed in annex

* Special categories of cited documents

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

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

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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

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

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

A document member of the same patent family

Date of the actual completion of the international search

15 July 2005

Date of mailing of the international search report

29/07/2005

Name and mailing address of the ISA

European Patent Office, P B 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel (+31-70) 340-2040, Tx 31 651 epo nl,
Fax (+31-70) 340-3016

Authorized officer

Vogel, T

34

C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
X	US 5 407 708 A (LOVIN ET AL) 18 April 1995 (1995-04-18)	1-17
Y	abstract column 3, line 22 - line 57 column 5, line 23 - line 29 claims 1-13	2-10, 12-17
X	WO 97/19763 A (RANGWALLA, IMTIAZ; CLOUGH, HARVEY; MCINTYRE, FREDERIC, S) 5 June 1997 (1997-06-05)	1-17
Y	the whole document	2-10, 12-17
Y	WO 02/081576 A (SUN CHEMICAL CORPORATION) 17 October 2002 (2002-10-17) the whole document	2-10, 12-17
A	US 2003/180507 A1 (OHMAN PETER ET AL) 25 September 2003 (2003-09-25) paragraph '0016! - paragraph '0019! paragraph '0031! - paragraph '0035!	1-17
A	US 4 113 895 A (WATT ET AL) 12 September 1978 (1978-09-12) abstract column 1, line 55 - column 2, line 6	1-17

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US2005/010649

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 3552986	A	05-01-1971	GB 1241823 A GB 1241824 A JP 54001758 B	04-08-1971 04-08-1971 29-01-1979
WO 02051915	A	04-07-2002	US 2002119295 A1 CA 2432086 A1 EP 1345768 A2 JP 2004525786 T MX PA03005537 A NZ 526379 A WO 02051915 A2	29-08-2002 04-07-2002 24-09-2003 26-08-2004 24-10-2003 28-01-2005 04-07-2002
US 5407708	A	18-04-1995	AT 172675 T AU 678695 B2 AU 1731695 A BR 9506660 A CA 2127416 A1 DE 69505640 D1 DE 69505640 T2 EP 0741644 A1 ES 2124530 T3 WO 9520492 A1	15-11-1998 05-06-1997 15-08-1995 18-11-1997 28-07-1995 03-12-1998 08-04-1999 13-11-1996 01-02-1999 03-08-1995
WO 9719763	A	05-06-1997	AU 1160897 A WO 9719763 A1	19-06-1997 05-06-1997
WO 02081576	A	17-10-2002	WO 02081576 A1 EP 1373414 A1	17-10-2002 02-01-2004
US 2003180507	A1	25-09-2003	AU 8635901 A EP 1324929 A1 JP 2004509025 T SE 0003245 A WO 0222462 A1	26-03-2002 09-07-2003 25-03-2004 14-03-2002 21-03-2002
US 4113895	A	12-09-1978	AU 507630 B2 AU 3037377 A CA 1074253 A1 DE 2751612 A1 FR 2371241 A1 GB 1554519 A JP 1318895 C JP 53067517 A JP 60040997 B	21-02-1980 17-05-1979 25-03-1980 24-05-1978 16-06-1978 24-10-1979 29-05-1986 16-06-1978 13-09-1985

PCT REQUEST The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty	For receiving Office use only International Application No International Filing Date Name of receiving Office and "PCT International Application" Applicant's or agent's file reference (if desired) (12 characters maximum) S9025.0025
Box No. I TITLE OF INVENTION METHOD OF MANUFACTURING LOW-ODOR PACKAGING MATERIALS	
Box No. II APPLICANT ☐ This person is also inventor	
Name and address. (Family name followed by given name, for a legal entity, full official designation) <i>The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.</i> SUN CHEMICAL CORPORATION 35 Waterview Blvd. Parsippany, New Jersey 07054-1285 United States of America	Telephone No. Facsimile No. Teleprinter No. Applicant's registration No. with the Office
State (that is, country) of nationality US	State (that is, country) of residence US
This person is applicant for the purposes of: ☐ all designated States ☒ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box	
Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)	
Name and address. (Family name followed by given name, for a legal entity, full official designation) <i>The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.</i> ROONEY, John M. 32 Berkeley Circle, Basking Ridge, New Jersey 07920 United States of America	This person is: ☐ applicant only ☒ applicant and inventor ☐ inventor only (If this check-box is marked, do not fill in below) Applicant's registration No. with the Office
State (that is, country) of nationality US	State (that is, country) of residence. US
This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box	
☒ Further applicants and/or (further) inventors are indicated on a continuation sheet	
Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE	
The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as. ☒ agent ☐ common representative	
Name and address. (Family name followed by given name, for a legal entity, full official designation) <i>The address must include postal code and name of country.</i> MEILMAN, Edward A. Dickstein Shapiro Morin & Oshinsky LLP 1177 Avenue of the Americas 41st Floor New York, New York 10036-2714 United States of America	Telephone No. (212) 896-5471 Facsimile No. (212) 997-9880 Teleprinter No. Agent's registration No. with the Office 24,735
☐ Address for correspondence: Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent	

Continuation of Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)	
<i>If none of the following sub-boxes is used, this sheet should not be included in the request.</i>	
Name and address: <i>(Family name followed by given name, for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)</i> BIRO, David Anthony 42 Cayuga Ave. Rockaway, New Jersey 07866 United States of America	This person is: ☐ applicant only ☒ applicant and inventor ☐ inventor only <i>(If this check-box is marked, do not fill in below.)</i> Applicant's registration No. with the Office
State <i>(that is, country)</i> of nationality: CA	State <i>(that is, country)</i> of residence: US
This person is applicant for the purposes of ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box	
Name and address: <i>(Family name followed by given name, for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)</i>	This person is: ☐ applicant only ☐ applicant and inventor ☐ inventor only <i>(If this check-box is marked, do not fill in below.)</i> Applicant's registration No. with the Office
State <i>(that is, country)</i> of nationality	State <i>(that is, country)</i> of residence
This person is applicant for the purposes of ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box	
Name and address: <i>(Family name followed by given name, for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)</i>	This person is: ☐ applicant only ☐ applicant and inventor ☐ inventor only <i>(If this check-box is marked, do not fill in below.)</i> Applicant's registration No. with the Office
State <i>(that is, country)</i> of nationality.	State <i>(that is, country)</i> of residence.
This person is applicant for the purposes of ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box	
Name and address: <i>(Family name followed by given name, for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)</i>	This person is: ☐ applicant only ☐ applicant and inventor ☐ inventor only <i>(If this check-box is marked, do not fill in below.)</i> Applicant's registration No. with the Office
State <i>(that is, country)</i> of nationality:	State <i>(that is, country)</i> of residence:
This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box	
☐ Further applicants and/or (further) inventors are indicated on another continuation sheet	

Supplemental Box *If the Supplemental Box is not used, this sheet should not be included in the request.*

1. *If, in any of the Boxes except Boxes Nos. VIII(i) to (v) for which a special continuation box is provided, the space is insufficient to furnish all the information in such case, write "Continuation of box No. " (Indicate the number of the Box) and furnish the information in the same manner as required according to the captions of the Box in which the space was insufficient, in particular*

(i) *If more than two persons are to be indicated as applicants and/or inventors and no "continuation sheet" is available in such case, write "Continuation of Box No. III" and indicate for each additional person the same type of information as required in Box No. III. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below,*

(ii) *If, in Box No. II or in any of the sub-boxes of Box No. III, the indication "the States indicated in the Supplemental Box" is checked, in such case, write "Continuation of Box No. II" or "Continuation of Box No. III" or "Continuation of Boxes No. II and No. III" (as the case may be), indicate the name of the applicant(s) involved and, next to (each) such name, the State(s) (and/or, where applicable, ARIPO, Eurasian, European or OAPI patent) for the purposes of which the named person is applicant,*

(iii) *If, in Box No. II or in any of the sub-boxes of Box No. III, the inventor or the inventor/applicant is not inventor for the purposes of all designated States or for the purposes of the United States of America in such case, write "Continuation of Box No. II" or "Continuation of Box No. III" or "Continuation of Boxes No. II and No. III" (as the case may be), indicate the name of the inventor(s) and, next to (each) such name, the State(s) (and/or, where applicable, ARIPO, Eurasian, European or OAPI patent) for the purposes of which the named person is inventor,*

(iv) *If, in addition to the agent(s) indicated in Box No. IV, there are further agents in such case, write "Continuation of Box No. IV" and indicate for each further agent the same type of information as required in Box IV,*

(v) *If, in Box No. VI, there are more than three earlier applications whose priority is claimed in such case, write "Continuation of Box No. VI" and indicate for each additional earlier application the same type of information as required in Box No. VI*

2 *If, the applicant intends to make an indication of the wish that the international application be treated, in certain designated States, as an application for a patent of addition, certificate of addition, inventor's certificate of addition or utility certificate of addition, in such a case, write the name or two-letter code of each designated States concerned and the indication "patent of addition," "certificate of addition," "inventor's certificate of addition" or "utility certificate of addition," the number of the parent application or parent patent or other parent grant and the date of grant of the parent patent or other patent grant or the date of filing of the parent application (Rules 4.11(a)(iii) and 49bis.1(a) or (b)).*

3 *If the applicant intends to make an indication of the wish that the international application be treated, in the United States of America, as a continuation or continuation-in-part of an earlier application in such a case, write "United States of America" or "US" and the indication "continuation" or "continuation-in-part" and the number and the filing date of the parent application (Rules 4.11(a)(iv) and 49bis.1(d))*

Continuation of Box No. IV:

Practitioners associated with customer number 32172

Box No. V DESIGNATIONS

The filing of this request constitutes under Rule 4.9(a), the designation of all Contracting States bound by the PCT on the international filing date, for the grant of every kind of protection available and, where applicable, for the grant of both regional and national patents

However,

- ☐ DE Germany is not designated for any kind of national protection
- ☐ KR Republic of Korea is not designated for any kind of national protection
- ☐ RU Russian Federation is not designated for any kind of national protection

(The check-boxes above may be used to exclude (irrevocably) the designations concerned in order to avoid the ceasing of the effect, under the national law, of an earlier national application from which priority is claimed. See the Notes to Box No. V as to the consequences of such national law provisions in these and certain other States.)

Box No. VI PRIORITY CLAIM

The priority of the following earlier application(s) is hereby claimed:

Filing date of earlier application (day/month/year)	Number of earlier application	Where earlier application is.		
		national application country or Member of WTO	regional application * regional Office	international application receiving Office
item (1) 31 March 2004 (31.03.2004)	60/558,076	US		
item (2)				
item (3)				

☐ Further priority claims are indicated in the Supplemental Box

The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) (only if the earlier application was filed with the Office which for the purposes of this international application is the receiving Office) identified above as:

☒ all items ☐ item (1) ☐ item (2) ☐ item (3) ☐ other, see Supplemental Box

* Where the earlier application is an ARIPO application, indicate at least one country party to the Paris Convention for the Protection of Industrial Property or one Member of the World Trade Organization for which that earlier application was filed (Rule 4.10(b)(ii)).

Box No. VII INTERNATIONAL SEARCHING AUTHORITY

Choice of International Searching Authority (ISA) (if two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen, the two-letter code maybe used)

ISA/EP

Request to use results of earlier search; reference to that search (if an earlier search has been carried out by or requested from the International Searching Authority)

Date (day/month/year)

Number

Country (or regional Office)

Box No. VIII DECLARATIONS

The following declarations are contained in Boxes Nos. VIII (i) to (v) (mark the applicable check-boxes below and indicate in the right column the number of each type of declaration)

Number of declarations

- ☐ Box No. VIII (i) Declaration as to the identity of the inventor :
- ☐ Box No. VIII (ii) Declaration as to the applicant's entitlement, as at the international filing date, to apply for and be granted a patent .
- ☐ Box No. VIII (iii) Declaration as to the applicant's entitlement, as at the international filing date, to claim the priority of the earlier application .
- ☐ Box No. VIII (iv) Declaration of inventorship (only for the purposes of the designation of the United States of America) :
- ☐ Box No. VIII (v) Declaration as to non-prejudicial disclosures or exceptions to lack of novelty .

Box No. IX CHECK LIST; LANGUAGE OF FILING		
This international application contains: (a) In paper form, the following number of sheets: request (including declaration sheets) : 5 description (excluding sequence listings and/or tables related thereto) : 25 claims : 2 abstract : 1 drawings : 0 Sub-total number of sheets : 33 sequence listings : tables related thereto : <i>(for both, actual number of sheets if filed in paper form, whether or not also filed in computer readable form, see (c) below)</i> Total number of sheets : 33 (b) ☐ only in computer readable form (Section 801(a)(i)) (i) ☐ sequence listings (ii) ☐ tables related thereto (c) ☐ also in computer readable form (Section 801(a)(ii)) (i) ☐ sequence listings (ii) ☐ tables related thereto Type and number of carriers (diskette, CD-ROM, CD-R or other) on which are contained the ☐ sequence listing. ☐ tables related thereto <i>(additional copies to be indicated under items 9(ii) and/or 10(ii), in right column)</i>	This international application is accompanied by the following item(s) (mark the applicable check-boxes below and indicate in right column the number of each item) 1. ☒ fee calculation sheet 1 2. ☐ original separate power of attorney 3. ☐ original general power of attorney 4. ☐ copy of general power of attorney, reference number, if any: 5. ☐ statement explaining lack of signature 6. ☐ priority document(s) identified in Box No. VI as item(s): 7. ☐ translation of international application into (language): 8. ☐ separate indications concerning deposited microorganisms or other biological material 9. ☐ sequence listing in computer readable form (indicate type and number of carriers) (i) ☐ copy submitted for the purposes of international search under Rule 13ter only (and not as part of the international application) (ii) ☐ (only where check-box (b)(i) or (c)(i) is marked in left column) additional copies including, where applicable, the copy for the purposes of international search under Rule 13ter (iii) ☐ together with relevant statement as to the identity of the copy or copies with the sequence listings part mentioned in left column 10. tables in computer readable form related to sequence listing (indicate type and number of carriers) (i) ☐ copy submitted for the purposes of international search under Section 802 (b-quater) only (and not as part of the international application) (ii) ☐ (only where check-box (b)(ii) or (c)(ii) is marked in left column) additional copies including, where applicable, the copy for the purposes of international search under Section 802 (b-quater) (iii) ☐ together with relevant statement as to the identity of the copy or copies with the tables mentioned in left column 11. other (specify)	Number of items
Figure of the drawings which should accompany the abstract	Language of filing of the international application: English	
Box No. X SIGNATURE OF APPLICANT, AGENT OR COMMON REPRESENTATIVE <i>Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).</i>		
Edward A. Meilman, Agent for Applicant(s) DICKSTEIN SHAPIRO MORIN & OSHINSKY LLP		
For receiving Office use only		
1. Date of actual receipt of the purported international application: 3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application 4. Date of timely receipt of the required corrections under PCT Article 11(2): 5. International Searching Authority (if two or more are competent): ISA /	2. Drawings: ☐ received: ☐ not received: 6. ☐ Transmittal of search copy delayed until search fee is paid	
For International Bureau use only		
Date of receipt of the record copy by the International Bureau:		

This sheet is not part of and does not count as a sheet of the international application.

PCT

FEE CALCULATION SHEET Annex to the Request

For receiving Office use only

International Application No.

Date stamp of the receiving Office

Applicant's or agent's
file reference

S9025.0025

Applicant

Sun Chemical Corporation, et al.

CALCULATION OF PRESCRIBED FEES

1. TRANSMITTAL FEE 300.00 T

2. SEARCH FEE 2,075.00 S

International search to be carried out by EP
(If two or more International Searching Authorities are competent to carry out the international search, indicate the name of the Authority which is chosen to carry out the international search.)

3. INTERNATIONAL FILING FEE

Where item (b) and/or (c) of Box No. IX apply, enter Sub-total number of sheets

Where item (b) and (c) of Box No. IX do not apply, enter Total number of sheets

} 33

☐ 11 first 30 sheets 1,211.00 ☐ 11

☐ 12 3 x 13.00 = 39.00 ☐ 12
number of sheets in fee per sheet
excess of 30

☐ 13 additional component (only if sequence listing and /or tables related thereto are filed in computer readable form under Section 801(a)(i), or both in that form and on paper, under Section 801(a)(ii)).

400 x = ☐ 13
fee per sheet

Add amounts entered at 11, 12 and 13 and enter total at I 1,250.00 I

(Applicants from certain States are entitled to a reduction of 75% of the international fee. Where the applicant is (or all applicants are) so entitled, the total to be entered at I is 25% of the international filing fee.)

4. FEE FOR PRIORITY DOCUMENT (if applicable) 20.00 P

5. TOTAL FEES PAYABLE \$ 3,645.00

Add amounts entered at T, S, I and P, and enter total in the TOTAL box

TOTAL

MODE OF PAYMENT

☐ authorization to charge
deposit account (see below)

☐ postal money order

☐ cash

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☐ cheque

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AUTHORIZATION TO CHARGE (OR CREDIT) DEPOSIT ACCOUNT

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☒ This check-box may be marked only if the conditions for deposit accounts of the receiving office so permit) Authorization to charge any deficiency or credit any overpayment in the total fees indicated above

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Receiving Office RO/

US

Deposit Account No:

50-2215

Date:

31 March 2005

Name:

Edward A. Meilman

Signature:

Edward A. Meilman

From the INTERNATIONAL BUREAU

PCT

SECOND AND SUPPLEMENTARY NOTICE
INFORMING THE APPLICANT OF THE
COMMUNICATION OF THE INTERNATIONAL
APPLICATION (TO DESIGNATED OFFICES
WHICH APPLY THE 30 MONTH TIME
LIMIT UNDER ARTICLE 22(1))

(PCT Rule 47.1(c))

To

MEILMAN, Edward, A
Dickstein Shapiro Morin & Oshinsky LLP
1177 Avenue of the Americas 41st Floor
New York, NY 10036-2714
ETATS-UNIS D'AMERIQUE

AUG 10 2006

DICKSTEIN SHAPIRO

Date of mailing (day/month/year)

03 August 2006 (03 08 2006)

Applicant's or agent's file reference

S9025.0025

IMPORTANT NOTICE

International application No

PCT/US2005/010649

International filing date (day/month/year)

31 March 2005 (31 03 2005)

Priority date (day/month/year)

31 March 2004 (31 03 2004)

Applicant

SUN CHEMICAL CORPORATION et al

1 **ATTENTION** For any designated Office(s), for which the time limit under Article 22(1), as in force from 1 April 2002 (30 months from the priority date), **does not apply**, please see Form PCT/IB/308(First Notice) issued previously

2 Notice is hereby given that the following designated Office(s), for which the time limit under Article 22(1), as in force from 1 April 2002, **does apply**, has/have requested that the communication of the international application, as provided for in Article 20, be effected under Rule 93bis 1. The International Bureau has effected that communication on the date indicated below
20 October 2005 (20 10 2005)

AU, AZ, BY, CN, CO, DZ, EP, HU, KG, KP, KR, MD, MK, MZ, NA, PG, RU, SY, TM, US

In accordance with Rule 47 1(c-bis)(i), those Offices will accept the present notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s)

3 The following designated Offices, for which the time limit under Article 22(1), as in force from 1 April 2002, **does apply**, have not requested, as at the time of mailing of the present notice, that the communication of the international application be effected under Rule 93bis 1

AE, AG, AL, AM, AP, AT, BA, BB, BG, BR, BW, BZ, CA, CR, CU, CZ, DE, DK, DM, EA, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, ID, IL, IN, IS, JP, KE, KZ, LC, LK, LR, LS, LT, LV, MA, MG, MN, MW, MX, NI, NO, NZ, OA, OM, PH, PL, PT, RO, SC, SD, SG, SK, SL, SM, TJ, TN, TR, TT, UA, UZ, VC, VN, YU, ZA, ZW

In accordance with Rule 47 1(c-bis)(ii), those Offices accept the present notice as conclusive evidence that the Contracting State for which that Office acts as a designated Office does not require the furnishing, under Article 22, by the applicant of a copy of the international application

4. TIME LIMITS for entry into the national phase

For the designated or elected Office(s) listed above, the applicable time limit for entering the national phase will, **subject to what is said in the following paragraph**, be **30 MONTHS** from the priority date

In practice, time limits other than the 30-month time limit will continue to apply, for various periods of time, in respect of certain of the designated or elected Office(s) listed above. For regular updates on the applicable time limits (30 or 31 months, or other time limit), Office by Office, refer to the *PCT Gazette*, the *PCT Newsletter* and the *PCT Applicant's Guide*, Volume II, National Chapters, all available from WIPO's Internet site, at <http://www.wipo.int/pct/en/index.html>

It is the applicant's sole responsibility to monitor all these time limits

SEARCH FILE NO. 59025.0025
FILED
CLASS.
EXAMINED BY HA
ATTY EM

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Authorized officer

Philippe Becamel

Facsimile No +41 22 338 82 70

e-mail pt12@wipo.int

PCT

NOTIFICATION CONCERNING
SUBMISSION OR TRANSMITTAL
OF PRIORITY DOCUMENT

From the INTERNATIONAL BUREAU

RECEIVED
JUL - 1 2005

To

MBILMAN, Edward, A
Dickstein Shapiro Morin & Oshinsky LLP
1177 Avenue of the Americas 41st Floor
New York, NY 10036-2714
ETATS-UNIS D'AMERIQUE

(PCT Administrative Instructions, Section 411)

Date of mailing (day/month/year) 23 June 2005 (23 06.2005)	
Applicant's or agent's file reference S9025.0025	IMPORTANT NOTIFICATION
International application No PCT/US2005/010649	International filing date (day/month/year) 31 March 2005 (31.03.2005)
International publication date (day/month/year)	Priority date (day/month/year) 31 March 2004 (31 03 2004)
Applicant SUN CHEMICAL CORPORATION et al	

- 1 By means of this Form, which replaces any previously issued notification concerning submission or transmittal of priority documents, the applicant is hereby notified of the date of receipt by the International Bureau of the priority document(s) relating to all earlier application(s) whose priority is claimed. Unless otherwise indicated by the letters "NR", in the right-hand column or by an asterisk appearing next to a date of receipt, the priority document concerned was submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b)
- 2 (If applicable) The letters "NR" appearing in the right-hand column denote a priority document which, on the date of mailing of this Form, had not yet been received by the International Bureau under Rule 17.1(a) or (b). Where, under Rule 17.1(a), the priority document must be submitted by the applicant to the receiving Office or the International Bureau, but the applicant fails to submit the priority document within the applicable time limit under that Rule, the attention of the applicant is directed to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances
- 3 (If applicable) An asterisk (*) appearing next to a date of receipt, in the right-hand column, denotes a priority document submitted or transmitted to the International Bureau but not in compliance with Rule 17.1(a) or (b) (the priority document was received after the time limit prescribed in Rule 17.1(a) or the request to prepare and transmit the priority document was submitted to the receiving Office after the applicable time limit under Rule 17.1(b)). Even though the priority document was not furnished in compliance with Rule 17.1(a) or (b), the International Bureau will nevertheless transmit a copy of the document to the designated Offices, for their consideration. In case such a copy is not accepted by the designated Office as the priority document, Rule 17.1(c) provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances

Priority date	Priority application No.	Country or regional Office or PCT receiving Office	Date of receipt of priority document
31 March 2004 (31 03 2004)	80/558,076	US	12 May 2005 (12 05 2005)

DSMO FILE NO. S9025.0025

DUE: _____

C/L: _____

ENTERED BY: SIM

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Authorized officer

ATTY: Olivia TEFY (fax 338-7090)

Facsimile No +41 22 338 82 70

Facsimile No (41-22) 338 70 90

Telephone No. +41 22 338 8516

Form PCT/IB/304 (January 2004)

CHOM4KXB

PATENT COOPERATION TREATY

RECEIVED
JUL - 1 2005
NOTIFICATION OF RECEIPT OF
RECORD COPY
DICKSTEIN SHAPIRO

(PCT Rule 24.2(a))

From the INTERNATIONAL BUREAU

To:

MEILMAN, Edward, A.
Dickstein Shapiro Morin & Oshinsky
LLP
1177 Avenue of the Americas-41st
Floor
New York, NY 10036-2714
United States of America

Date of mailing (day/month/year) 20 June 2005 (20.06.2005)	IMPORTANT NOTIFICATION
Applicant's or agent's file reference S9025.0025	International application No. PCT/US2005/010649

The applicant is hereby notified that the International Bureau has received the record copy of the international application as detailed below

Name(s) of the applicant(s) and State(s) for which they are applicants.

SUN CHEMICAL CORPORATION (for all designated States except US)
ROONEY, John, M. et al (for US)

International filing date : 31 March 2005 (31.03.2005)
Priority date(s) claimed : 31 March 2004 (31.03.2004)
Date of receipt of the record copy by the International Bureau : 09 May 2005 (09.05.2005)

List of designated Offices

AP : BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW
EA : AM, AZ, BY, KG, KZ, MD, RU, TJ, TM
EP : AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR
OA : BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG
National : AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW

DSMO FILE NO. S9025.0025
DUE: _____
C/L: _____
ENTERED BY: SA
ATTY: EMLEY

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No (41-22) 338 70 90	Authorized officer Laurence NICOLO Telephone No (41-22) 338 9949
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Continuation of Form PCT/IB/301

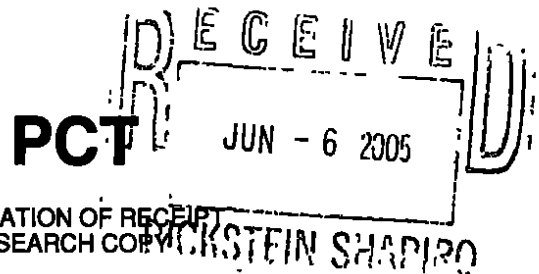
NOTIFICATION OF RECEIPT OF RECORD COPY

Date of mailing (day/month/year) 20 June 2005 (20.06.2005)	IMPORTANT NOTIFICATION
Applicant's or agent's file reference S9025.0025	International application No. PCT/US2005/010649
ATTENTION The applicant should carefully check the data appearing in this Notification. In case of any discrepancy between these data and the indications in the international application, the applicant should immediately inform the International Bureau. In addition, the applicant's attention is drawn to the information contained in the Annex, relating to: - time limits for entry into the national phase - see updated important information (as of April 2002) - requirements regarding priority documents (if applicable) A copy of this Notification is being sent to the receiving Office and to the International Searching Authority.	

PATENT COOPERATION TREATY

From the INTERNATIONAL SEARCHING AUTHORITY

To
DICKSTEIN SHAPIRO MORIN &
OSHINSKY LLP
Attn. Meilman, Edward A.
1177 Avenue of the Americas
41st Floor, New York NY 10036-2714
UNITED STATES OF AMERICA



(PCT Rule 25.1)

Date of mailing
(day/month/year) 24/05/2005

Applicant's or agent's file reference
S9025.0025

IMPORTANT NOTIFICATION

International application No
PCT/US2005/010649

International filing date(day/month/year)
31/03/2005

Priority date (day/month/year)
31/03/2004

Applicant

SUN CHEMICAL CORPORATION

1 Where the International Searching Authority and the receiving Office are not the same office:

The applicant is hereby notified that the search copy of the international application was received by this International Searching Authority on the date indicated below

Where the International Searching Authority and the receiving Office are the same office

The applicant is hereby notified that the search copy of the international application was received on the date indicated below

09/05/2005 (date of receipt)

2 ☐ The search copy was accompanied by a nucleotide and/or amino acid sequence listing or tables related thereto in computer readable form

3 Time limit for establishment of international search report and written opinion of the International Searching Authority

The applicant is informed that the time limit for establishing the international search report and the written opinion of the International Searching Authority is three months from the date of receipt indicated above or nine months from the priority date, whichever time limit expires later (Rules 42.1 and 43bis 1(a))

DSMO FILE NO. S9025.0025

DUE: _____

C/L: _____

4 A copy of this notification has been sent to the International Bureau and, where the first sentence of paragraph 1 applies, to the receiving Office

ENTERED BY: JIM

ATTY: EAM/24

Name and mailing address of the International Searching Authority
 European Patent Office, P B 5818 Patentlaan 2
NL-2280 HV Rijswijk
Tel (+31-70) 340-2040, Tx 31 651 apo nl,
Fax (+31-70) 340-3016

Authorized officer

ISA/EP

**MÉTODO DE ELABORACIÓN DE MATERIALES DE EMPAQUE CON BAJO
OLOR**

1. CAMPO DE LA INVENCION.

Esta invención se relaciona con un proceso para producir materiales de empaque de bajo olor que utiliza tintas líquidas con solvente activable con radiación actínica o basada en agua y un recubrimiento curable con radiación actínica, que suministra protección a la tinta y mejora el brillo del empaque.

2. ANTECEDENTES DE LA INVENCION.

Las tintas para flexo o bajo relieve líquidas con solvente orgánico y/o basadas en agua ("tintas de impresión basadas en solventes") han sido ampliamente utilizadas en varios tipos de impresión, tales como empaques, que utilizan impresora de chorro. Las imágenes impresas deben tener buena resistencia a los solventes y a la abrasión. Al mismo tiempo, es necesario que las tintas de impresión basadas en solvente tengan buena resolubilidad para evitar el secado y el taponamiento de la tinta sobre la placa, anilox y cilindros de hueco gravado de las impresoras.

Típicamente, las resinas de bajo peso molecular (PM) y los plastificadores ofrecen buena resolubilidad, aún, con el fin de mejorar las propiedades de resistencia de las imágenes impresas, que las resinas con PM superior requieren. Esto representa una mayor contradicción y problema para los formuladotes de tintas líquidas para empaques basados en solvente.

Para resolver estos problemas, se han desarrollado varios tipos de tinta de impresión fotocurables que tienen combinaciones específicas de resinas fotocurables y fotoiniciadores (ver, por ejemplo, Patente U.S. 4,066,582; Patente U.S. 4,221,686; Patente U.S. 4,303,924; Patente U.S. 5,057,398, y WO 01/57145 A1). Sin embargo, la polimerización incompleta de estas tintas resulta a menudo en la difusión de resinas no curadas y origina manchas o abrasión de las imágenes impresas.

Como se puntualiza en la Patente U.S. 6,528,127, la impresión de las películas de empaque termoplástico ha permanecido un poco como arte negro a pesar de los avances de las técnicas de impresión en general. Los empacadores le han requerido recientemente a los fabricantes de películas suministrar películas de empaque que lleven imágenes

83

impresas con calidad fotográfica, que son difícil en si mismas, algunas veces para usos que le agregan dificultad. Las películas termoencogibles y las películas termoformantes son particularmente complicadas por la necesidad de él o las tintas de impresión a resistir el cuarteamiento o descamamiento una vez que la película ha sufrido de termoencogido, un proceso durante el cual la película es sometida a calor, fricción y/o contacto de película a metal. Las películas destinadas a aplicaciones para cocina pueden sufrir todas estas condiciones fuertes y suministrarles a los fabricantes de película y convertidores algunos de sus retos de impresión más grandes.

Para evitar el cuarteamiento y/o el escamamiento de las imágenes impresas, los fabricantes de película ensayaron varias estrategias. Más a menudo, éstas involucran el uso de nuevas formulaciones de tinta para evitar utilizar pigmentos que contengan tintas estándar llevadas en una resina que es soluble en un solvente tal como alcohol que se debe evaporar, dejando de tal la combinación de resina-pigmento. Las formulaciones más nuevas han involucrado sistemas de resina de poliuretano de dos partes así como también sistemas libres de solvente en

607

las cuales él o las resinas se pueden curar por medio de luz ultravioleta (UV), que también tienen inconvenientes, incluyendo preocupaciones con relación a la exposición del operador y a los componentes y a la necesidad de asegurar suficiente reticulación para cumplir con las regulaciones de seguridad de alimentos gubernamentales aplicables.

Para resolver estos problemas, la Patente U.S. 6,528,127 enseña un proceso de manufactura para materiales de empaque de alimentos que comprenden la impresión de la película plástica con las tintas basadas en solvente que son ensayadas sin haz de electrones o radiación ultravioleta, seguida por la aplicación de un recubrimiento protector curable con radiación, libre de pigmento y radiación que cubre el recubrimiento. En este proceso que representa un avance, se ha encontrado que una cantidad excesiva del solvente residual se atrapa en la tinta bajo el recubrimiento protector y origina un olor excesivo proveniente del material de empaque. Además, en razón a que la velocidad de secado del solvente varía significativamente sobre las unidades de calentamiento múltiples así como también el número y cantidad de trampas de tinta, las características de curado y fricción de el material de empaque terminado pueden no ser completamente

25

uniformes en todas las imágenes impresas. Esto, a su vez, puede originar problemas con el procesamiento del material de empaque en las líneas de llenado, particularmente en relación con el coeficiente de fricción (COF, que representa la resistencia a la fricción entre dos superficies y se puede expresar como el COF estático, donde la superficies son estáticas, y el COF cinético, donde las superficies están en movimiento) y/o los temas de deslizamiento. Por ejemplo, un trabajo impreso para un cliente con tintas basadas en tres solventes sobre la película de polietileno (PE) y sobre impresa con un recubrimiento curable con haz de electrones (EB), tiene los siguientes patrones de curado de recubrimiento-reticulación: (i) recubrimiento sobre la película PE-30 MEK (metil etil cetona) fricciones 30 MEK (metil etil cetona) (ver definición adelante); (ii) recubrimiento sobre tinta blanca-fricciones 8-10 MEK; (iii) recubrimiento sobre tintas amarilla y blanca - fricciones 3-4 MEK; y (iv) recubrimiento sobre tintas negra, amarilla y blanca-solamente 1 fricción MEK. Así, los recubrimientos EB curan diferente sobre distintos colores de tintas principalmente por las tintas basadas en solvente que liberan sus solventes de manera diferente. Entre más gruesa la capa de tinta subyacente, más lento el curado del

45

recubrimiento sobreadyacente curable con energía. Las variaciones en el grado de curación dan como resultado variaciones en el valor COF. Así, subsiste la necesidad de un método de impresión para, en particular, empaques de alimento, que maneje estos problemas aunque suministrando una película con imágenes con las características deseadas.

3. RESUMEN DE LA INVENCION

La presente invención está basada, parcialmente, en el descubrimiento de los presentes inventores que al activar o imprimir con tintas basadas en solvente o agua activables con radiación actínica sobre materiales de empaque con radiación actínica antes de aplicar el recubrimiento protector se reduce el contenido del solvente residual y el olor así como también se mejora la resistencia a la fricción y el brillo de las imágenes impresas. El término "tinta activable con radiación actínica" utilizado aquí significa que la tinta está sustancialmente libre de funcionalidad curable (es decir grupos funcionales que se pueden reticular o son polimerizables).

De acuerdo con esto, la presente invención suministra un método para producir un material de empaque recubierto

que comprende la impresión sobre un material de empaque con una tinta líquida activable con radiación actínica, la radiación actínica que activa la tinta, aplicando un recubrimiento protector sobre la tinta activada, y curando el recubrimiento al exponer la radiación ionizante.

El término "radiación actínica" utilizado aquí se refiere en su más amplio sentido a cualquier radiación que pueda producir reacciones fotoquímicas.

En una modalidad preferida, la radiación actínica para activar la tinta líquida es luz UV. En otra modalidad preferida, la radiación actínica para curar el recubrimiento protector es un haz de electrones (EB).

En una modalidad específica, el material de empaque es una película plástica o una estructura de laminado de película plástica. En otra modalidad específica, el material de empaque es una estructura plástica laminada con hojuelas, o una lámina plástica de papel. En aún otra modalidad específica, la tinta está basada en solvente. En otra modalidad preferida, la tinta está basada en agua. La presente invención suministra además un material de empaque de bajo olor producido mediante el método de la presente

15

invención. En una modalidad preferida, el material de empaque de la presente invención contiene solvente residual o agua después de la exposición a UV de menos de aproximadamente 700 ppm en total, más preferiblemente menos de aproximadamente 600 ppm en total, más preferiblemente menos de aproximadamente 400 ppm. En otra modalidad preferida, el material de empaque de la presente invención tiene un grado de cura, como se midió por los restregantes de solvente, de al menos 5 restregantes MEK (metil etil cetona), más preferiblemente al menos 10 restregantes MEK, y más preferiblemente al menos 20 restregantes MEK.

La prueba MEK es una técnica de restregado de solvente que utiliza metil etil cetona para evaluar la resistencia del solvente de un recubrimiento orgánico que cambia químicamente durante el proceso de curado (para detalles, ver ASTM D5402-93; "Assessing the solvent Resistance of Organic Coatings Using Solvent Rubs" en el Annual Book de la ASTM, 1999, BY West Conshohocken, PA). La resistencia MEK se expresa como el número de restregantes MEK, que utilizan una bola de algodón saturada con MEK o un estropajo con terminaciones en algodón, en el cual el recubrimiento puede permanecer sin ninguna pérdida de recubrimiento y este generalmente se correlaciona con el

15

grado de curado del recubrimiento. La resistencia MEK también está influenciada por la temperatura, el movimiento del aire y la humedad relativa.

El material de empaque impreso preparado de acuerdo con la presente invención tiene un amplio rango de aplicaciones, que incluye, pero no está limitado a, empaque de alimento, empaque de droga, empaque de tabaco, y cualquier otro empaque que requiera impresión sobre este.

4. DESCRIPCIÓN DETALLADA DE LA INVENCION.

La presente invención suministra un método para elaborar materiales de empaque de bajo olor que comprenda la impresión sobre un material de empaque con una tinta de impresión activable con relación actínica basada en solvente o agua, que expone la tinta a una primer radiación actínica, aplicando un recubrimiento curable con energía sobre la tinta, y curando el recubrimiento mediante la exposición a una segunda radiación actínica, preferiblemente un haz de electrones. En una modalidad preferida, la primer radiación actínica para activar las tintas de impresión basadas en solvente es la luz UV emitida por una lámpara UV. En este método, el calor y la

55

actividad inducidas por la lámpara UV ayudan a remover el solvente residual, lo que quedaría atrapado de otra manera bajo el recubrimiento EB y originaría olor y migración de la tinta impresa. Adicionalmente, la luz UV es antimicrobiana y reduce los conteos microbianos en el material de empaque, extendiendo la vida de almacenamiento del alimento empaquetado. Así, la presente invención suministra además un material de empaque de bajo olor producido por el método de la presente invención. Las imágenes impresas del material de empaque de la presente invención pueden soportar condiciones fuertes, tales como calor y fricción durante las subsecuentes etapas de llenado del empaque con una sustancia a ser empaquetada.

4.1 Materiales de Empaque.

Los materiales de empaque para ser utilizados en la presente invención deben ser capaces de lograr buena preservación de sus contenidos (por ejemplo, alimentos, drogas, tabaco, etc.) y seguridad e incluyen, pero no están limitados a, varias películas de empaque flexible termoplásticas (capa simple) así como también películas plásticas multicapa), estructuras plásticas laminadas con hojuela, o láminas plásticas de papel y unos laminados de

plástico/hojuelas/papel, todas las cuales son bien conocidas por aquellos expertos en la técnica. Las películas de empaque flexible termoplástica apropiadas a ser utilizadas en la presente invención incluyen, pero no por vía de limitación poliéster, nylon, poliolefina, varios homopolímeros, copolímeros, e interpolímeros de polistireno, poliisopreno, 1,2- o 1,4-polibutadieno, ácido poli(met) acrílico, poli metil metacrilato, óxido de polietileno, óxido de polibutileno, poli 2-vinilpiridina, polidietilamino etilmetacrilato, poli dimetilamino etilmetacrilato, y así sucesivamente. La película puede incorporar un componente de barrera al gas, tal como etileno vinil alcohol, cloruro de polivinilideno, nylon, poliacrilonitrilo, polisilicato, melamina, ésteres de poliidroxí (por ejemplo Blox® By Dow), y así sucesivamente. Se describen varios materiales de empaque en las Patentes U.S. 6,815,057, 6,846,530, 6,846,532, 6,866,907 y 6,861,478, cada una de las cuales se incorpora como referencia en su totalidad. Los laminados plásticos de papel se describen en la Patente U.S. 6,843,371 y la Publicación de la Solicitud de Patente No. 2005/0031887 y ejemplos de estructuras plásticas laminadas con hojuela se pueden encontrar a las Patentes U.S. 4,402,172, 5,098,151,

6,716,499 y 5,800,724, todas las cuales se incorporan como referencia en su totalidad.

4.2 Solvente Orgánico y/o Tintas Basadas en Agua.

El solvente orgánico y/o las tintas basadas en agua utilizadas en la presente invención son cualquier polímero o resina bien conocidos por un experto en la técnica. El término "resina" utilizado aquí en relación con las tintas basadas en solvente orgánico y/o agua se refieren tanto a homopolímeros y copolímeros conocidos como polímeros sólidos duros. Preferiblemente tales resinas tienen un peso molecular promedio de peso relativamente bajo (Pm). El Pm preferido es mayor de aproximadamente 500 pero menor de aproximadamente 500,000 daltons, más preferiblemente mayor de aproximadamente 1,000 pero menor de aproximadamente 50,000 daltons, y más preferiblemente mayor de aproximadamente 1,000 pero menor de aproximadamente 10,000 daltons. Las resinas tienen preferiblemente puntos de fusión a temperaturas entre aproximadamente 0° C y aproximadamente 200° C, más preferiblemente entre aproximadamente 10° C y aproximadamente 180° C, y más preferiblemente entre aproximadamente 20° C y 150° C. Ejemplos de resinas de polímero útiles solubles en solvente

orgánico y/o agua incluyen, pero no están limitadas a, polímeros naturales, tales como resinas basadas en colofonia, resinas celulósicas, tales como nitrocelulosa, carboximetil celulosa y etil hidroxietil celulosa, y polímeros sintéticos tales como poliamidas, polivinil ésteres, polivinil acetatos, polivinil éteres, resinas de epóxido, ésteres de ácido poliacrílico, ésteres de ácido polimetacrílico, poliésteres, resinas alquídicas, poliacrilamida, polivinil alcohol, óxido de polietileno, poli dimetil acrilamida, polivinil pirrolidona, polivinilmetil formamida, polivinil metil acetamida, poliéter poliuretano, poliuretano alifático y aromático, resina de poliestireno, copolímero de estireno-anhídrido maléico (SMA), resina de copolímero de éster de estireno-(met)acrilato o resina de copolímero de dieno conjugada con estireno, resina de butiral, resina de xileno, resina de cumarona-indeno, resina fenólica, así como también una mezcla de de copolímeros de aquellos listados anteriormente.

En una modalidad preferida, un polímero soluble en solvente orgánico y/o agua está en un rango entre aproximadamente 0.1% a aproximadamente 40% en peso de los ingredientes totales de la tinta, más preferiblemente entre

5

aproximadamente 1% y aproximadamente 30% en peso de la tinta total, y más preferiblemente entre aproximadamente 10% y aproximadamente 20% del peso de la tinta total.

Las imágenes impresas son luego irradiadas mediante radiación actínica que activa las tintas impresas. En una modalidad preferida, la radiación actínica es luz UV proveniente de una lámpara UV. Una luz UV apropiada se puede obtener de, por ejemplo, una lámpara de mercurio con presión media, una lámpara de haluro metálico, una lámpara de xenón, una fuente de luz con arco de carbono, una lámpara química, una lámpara de mercurio de baja presión o alta presión, una lámpara con diodo que emite luz UV (LED) y así sucesivamente. La intensidad de luz UV apropiada está en el rango de aproximadamente 20 a aproximadamente 10,000 mJ/cm², preferiblemente aproximadamente 40 a aproximadamente 1,000 mJ/cm², y más preferiblemente aproximadamente 50 a aproximadamente 700 mJ/cm². Se debe notar que el solvente orgánico y/o las tintas basadas en agua utilizadas en la presente invención no contienen ningún fotoiniciador a un cuando la primer radiación actínica para activar la tinta líquida es luz UV.

En otra modalidad preferida la radiación actínica es un haz de electrones entre aproximadamente 0.5 a aproximadamente 8 Mrads, más preferiblemente aproximadamente 1 a aproximadamente 6 Mrads, y más preferiblemente aproximadamente 1.3 a aproximadamente 4 Mrads. Un voltaje de aceleración de haz de electrones varía preferiblemente aproximadamente 30-200 kV, más preferiblemente 60-165 kV y más preferiblemente aproximadamente 70-140 kV. Durante la radiación de la tinta impresa, un ambiente inerte se suministra preferiblemente mediante, por ejemplo, gas nitrógeno, resultando en preferiblemente menos de aproximadamente 600 partes por millón (ppm), más preferiblemente menos de aproximadamente 400 ppm, y más preferiblemente menos de aproximadamente 200 ppm, de O₂ presentes en el ambiente.

4.3 Vehículo de Tinta

Cualquier vehículo que haya sido previamente utilizado en tintas de impresión se puede utilizar para la presente invención. Típicos son los solventes que tienen baja viscosidad y son compatibles con cualquier otros componentes de la tinta. Así, una elección de solventes depende de los tipos de los componentes de resina

seleccionados para la tinta de impresión de la presente de la presente invención. Los solventes utilizables para las tintas d impresión presentes incluyen, pero no por vía de limitación, agua; alcoholes, tales como etanol, metanol, isopropanol, y N-butanol; ésteres, tal como etil acetato, isopropil acetato, butil acetato, (BuAc) y 2-etoxietil acetato, glicol-éteres, tales como 2-metoxietanol, 2-etoxietanol, 2-butoxietanol, 2-metoxietoxietanol, 2-etoxietoxetanol y 2-butoxietoxetanol; alifáticos, tales como VM&P Nafta y Spirits minerales; aromáticos, tales como toluol y xilol; cetonas, tales acetona, metil etil cetona (MEK) y metil isobutil cetona (MIBK) y otros solventes, tales como cloruro de metileno, 1,1,1-tricloroetano, N-metil-2-pirrolidona, dimetilsulfóxido, mesitil óxido, dimetil formamida, tiofeno, y así sucesivamente.

En una modalidad preferida, agua y/o alcohol alifático de peso molecular bajo, tal como metanol, etanol, e isopropil alcohol, o éster, tal como etilacetato, se pueden utilizar. En una modalidad preferida, el vehículo está en el rango entre aproximadamente 1% a aproximadamente 90%, más preferiblemente aproximadamente 30% y 85%, y más preferiblemente aproximadamente 45% y aproximadamente 75%, en peso del peso total de la tinta impresa.

4.4 Resina Curable con Energía.

La resina curable con energía o fotocurable o resina fotopolimerizable a ser utilizada como recubrimiento protector en la presente invención se puede seleccionar del amplio rango de monómeros y oligómeros monofuncional o polifuncionales etilénicamente insaturados derivados de estos, capaces de sufrir fotopolimerización (Ver, U.S. Patente 4,066,582; JP H1-115974; WO 01/57145; WO 03/093378; y U.S. Patente 6,706,777). El término "oligómero" como se utiliza aquí se refiere a un polímero de bajo peso molecular con grado de polimerización de (DP) de menos de aproximadamente 10. Ejemplos de monómeros adecuados son (poli)éster(met)acrilatos que tienen al menos un enlace éster en la cadena principal; uretano(met)acrilatos que tienen al menos un enlace uretano en la cadena principal; epoxiacrilatos obtenidos mediante una reacción entre ácido (MET)acrílico y epóxido con uno o más de unos grupos funcionales; (poli)éster (met)acrilatos que tienen al menos un enlace éter en la cadena principal; alquil(met)acrilatos o alquilenos(met)acrilatos que comprenden la cadena principal formada por un alquilo lineal, un alquilo ramificado, un alquilenos lineal o un

alquileno ramificado, y cadenas laterales o extremos terminales que tienen átomos de halógenos y/o grupos hidrófilo; (met)acrilatos que tienen un anillo aromático en la cadena principal o la cadena lateral, (met)acrilatos que tienen un grupo alicíclico, que tiene , en la cadena principal o la cadena lateral, grupos alicíclicos que pueden incluir átomos de oxígeno o átomos de nitrógeno como la unidad estructural; y similares. Se entenderá que "(met)acrilatos" este siendo utilizado en su sentido convencional como referencia tanto a acrilato como metacrilato.

Ejemplos de (poli)éster(met)acrilatos incluyen, pero no están limitados a, (poli)éster(met)acrilatos monofuncionales tales como neopentilglicol (met)acrilato modificado alicíclico, 2-hidroxietil(met)acrilato, ftalato (met)acrilato modificado con etilenóxido y/o propilenóxido, succinato(met)acrilato modificado con etilenóxido, tetrahidrofurfuril(met)acrilato modificado con caprolactona; pivalato-esterneopentilglicoldi(met)acrilato, hidroxipivalatoésterneopentilglucoldi(met)acrilato modificado con caprolactona, ftalatodi(met)acrilato modificado con epiclorohidrina; mono-, di- o tri-(met)acrilatos de triol obtenidos mediante la adición de

más de 1 mol de lactonas cíclicas tales como epsilon-caprolactona, gamma-butilolactona, delta-valerolactona o metilvarelolactona a una mol de trimetilolpropano o glicerina; mono-, di-, tri, o tetra-((met)acrilatos de triol obtenidos mediante la adición de más de 1 mol de lactonas cíclicas tales como epsilon-caprolactona, gamma-butilolactona, delta-valerolactona o metilvarelolactona a una mol de pentaeritritol o ditrimetilolpropano; mono-o poli-((met)acrilatos de alcoholes polihídricos tales como triol, tetraol, pentaol, o hexaol, obtenidos mediante la adición de más de 1 mol de lactona cíclicas tales como epsilon-caprolactona, gamma-butilolactona, delta-valerolactona o metilvarelolactona a 1 mol de dipentaeritritol; (met)acrilatos de polioles de poliéster compuestos de componente diol tales como (poli)etilenglicol, (poli)propilenglicol, (poli)tetrametilenglicol, (poli)butilenglicol, (poli)pentanodiol, (poli)metil pentanodiol, y (poli)hexanodiol, y ácidos polibásicos tales como ácido maleico, ácido fumárico, ácido succínico, ácido adípico, ácido ftálico, ácido hexahidroftálico, ácido tetrahidroftálico, ácido itacónico, ácido citracónico, ácido hetico, ácido cloréndico, ácido dimérico, ácido alquenilsuccínico, ácido sebásico, ácido azelaico, ácido

2,2,4-trimetiladípico, ácido 1,4-ciclo-hexanodicarboxílico, ácido tereftálico, ácido 2-sodio-sulfotereftálico, ácido 2-potasio sulfa tereftálico, ácido isoftálico, ácido 5-sulfoisoftálico, ácido 5-potasio sulfoisoftálico, ácido ortoftálico, ácido 4-sulfoftálico, ácido 1, 10-decametilenodicarboxílico, ácido mucónico, ácido oxálico, ácido malónico, ácido glutárico, ácido trimelítico, ácido piromelítico, y (poli)éster(met)acrilatos polifuncionales compuestos de los componentes diol, ácidos polibásicos, y poliésterdioles modificados con lactona cíclica tal como epsilon-caprolactona, gamma-butilolactona, delta-valerolactona o metil valerolactona.

Los uretano(met)acrilatos representan (met)acrilatos obtenidos mediante una reacción entre los compuestos hidroxí que tienen al menos un grupo acrilóiloxi y compuestos isocianato. El uretano(met)acrilato también se puede seleccionar de acrilato alifático diluible en agua o uretanos aromáticos. Ejemplos de compuestos hidroxí que tienen al menos un grupo acrilóiloxi incluyen, por ejemplo, 2-hidroxietil(met)acrilatos, 2-hidroxipropil(met)acrilato, 2-hidroxibutil(met)acrilato, 3-hidroxibutil(met)acrilato, 4-hidroxibutil(met)acrilato, ciclohexanodimetanolmono(met)acrilato,

polietilenglicol(met)acrilato,
polipropilenglicol(met)acrilato,
trimetilonpropanodi(met)acrilato,
trimetiloletanodi(met)acrilato,
pentaeritritoltri(met)acrilato, y un aducto de
(met)acrilato con glicidil(met)acrilato, compuestos de
(met)acrilato que tienen grupos hidroxilo tales como 2-
hidroxilo-3-fenolpropil(met)acrilato, y productos de
reacción de anillo abierto de los compuestos acrilato
anteriores que tienen grupos hidroxilo con épsilon-
caprolactona.

Ejemplos de compuestos isocianato incluyen, por
ejemplo, diisocianatos aromáticos tales como p-
fenilenodiisocianato, m-fenilenodiisocianato, p-
xilenodiisocianato, m-xilenodiisocianato, 2,4-
tolilenodiisocianato, 2,6-tolilenodiisocianato, 4,4'-
difenilmetanodiisocianato, 3,3'-dimetildifenil-4,4'-
diisocianato, 3,3'-dietildifenil-4,4'-diisocianato, y
naftalenodiisocianato; Diisocianatos alifáticos o
alicíclicos, tales como isoforonodiisocianato,
hexametilenodiisocianato, 4,4'-
diciclohexilmetanodiisocianato, xilenodiisocianato
hidrogenado, norbornenodiisocianato, y lisinodiisocianato,

poliisocianatos, tales como productos de más de un tipo de isocianato e isocianato-trimeros de los isocianatos anteriores; y poliisocianatos obtenidos mediante la reacción de esterificación de isocianato anterior con varios polioles. Ejemplos de polioles utilizados para producir poliisocianatos incluyen, pero no están limitados a, (poli)alquilenglicoles tales como (poli)etilenglicol, (poli)propilenglicol, (poli)butilenglicol, y (poli)tetrametilenglicol; alquilenglicoles modificados por etilenodioxido, propilenodioxido, butilenodioxido, tetrahidrofurano, epsilon-caprolactona, gamma-butilo lactona, delta-valerolactona y metil valerolactona, tales como etilenglicol, propanodiol, propilenglicol tetrametilenglicol, pentametilol propano hexanodiol, neopentil glicol, glicerina, trimetilolpropano, pentaeritritol, diglicerina, ditrimetilolpropano, y dipentaeritritol; polioles alifáticos tales como copolímeros de etilenoóxido y propilenoóxido, copolímeros de propilenglicol y tetrahidrofuran, copolímeros de etilenglicol y tetrahidrofurano, poliisopreno glicol, polisopreno glicol hidrogenado, polibutanodieno glicol, y polibutadieno glicol hidrogenado; polioles de poliéster alifático obtenido mediante las reacciones de esterificación entre los ácidos dicarboxílicos alifáticos

tal como ácido atípico y ácido dimérico con polioles tales como neopentil glicoles y metpentanodiol; polioles de poliéster aromático obtenidos mediante la reacción de esterificación entre ácidos dicarboxílicos aromáticos, tales como ácido tereftálico, con polioles tales como neopentil glicol; polycarbonatopolioles; acril polioles; alcohol polihídrico, tal como politetramettilenohexagliceril éter (hexaglicerina modificado por tetrahidrofurano); compuestos mono o polihídricos que tienen un grupo éter en un terminal; compuesto por polihídrico obtenido mediante esterificación del compuesto que tiene grupos polihidroxilo con ácidos dicarboxílicos, tales como ácido fumárico, ácido ftálico, ácido isoftálico, ácido itacónico, ácido adípico, ácido sebásico, y ácido maleico; compuestos que tienen grupos polihidroxilo tales como monoglicerido obtenido mediante reacción de transesterificación del compuesto que tiene grupos polihidroxilo tal como glicerina con éster de ácido graso de animales o plantas.

Los epoxi (met)acrilatos son obtenidos mediante una reacción de epóxidos que tienen más de un grupo funcional y ácido(met)acrílico. Los epóxidos como la materia prima para los epoxi(met)acrilatos incluyen, pero no están limitados

a, resina epoxi tipo bisfenol hidrogenada modificada con epiclorhidrina, sintetizada mediante (netil)epiclorhidrina y compuestos tales como bisfenol hidrogenado A, bisfenol hidrogenado S, bisfenol hidrogenado F, y sus compuestos modificados con óxido de etileno u óxido de propileno; resinas epoxi alicíclicas tales como 3,4-epoxiciclohexilmetil-3,4-epoxiciclohexano carboxi-lato, bis-(3,4-epoxiciclohexil)adipato; epóxidos alicíclicos tales como resina epoxi que contiene heterociclos tales como triglicidilisocianurato; resinas epoxi tipo bisfenol modificadas con epiclorohidrina sintetizadas mediante una reacción de (metil)epiclorohidrina y un compuesto tal como bisfenol A, bisfenol S, bisfenol F, y sus compuestos modificados con óxido de etileno y propilenoóxido; resinas epoxi tipo fenol Novolak; resinas epoxi tipo cresol Novolak; resinas epoxi de resina de fenol modificada con dicitropentadieno obtenida mediante la reacción de dicitropentadieno y varios tipos de resinas de fenol; unos compuestos epoxidizados aromáticos de 2,2',6,6'-tetrametilbis-fenol; epóxidos aromáticos tales como fenilglicidiléter; (poli)glicidil éteres de compuestos de glicol tales como (poli)etilenglicol, (poli)propilenglicol, (poli)butilenglicol, (poli)tetrametilenglicol, neopentil glicol; (poli)glicidil éter de glicoles modificados con

2

óxido de alquileo; (poli)glicidil éteres de alcoholes polihídricos alifáticos, tales como trimetilolpropano, trimetiloletano, glicerina, diglicerina, eritritol, pentaeritritol, sorbitol, 1,4-butanodiol, 1,6-hexanodiol; epóxidos tipo alquileo de (poli)glicidiléter modificado de alcoholes polihídricos alifáticos mediante alquileo; glicidilésteres de ácido carboxílicos, tales como ácido adípico, ácido sebácico, ácido maleico, y ácido itacónico; ésteres glicidilo de poliésterpolioles de alcoholes polihídricos con ácidos policarboxílicos; un copolímero de glicidil(met)acrilato o metilglicidil(met)acrilato; glicidiléter de ácidos grasos altos; resinas epoxi alifáticas, tales como aceite de linaza, un aceite de castor epoxidizado, y un polibutadierno epoxidizado.

Compuestos de (poli) éter (met)acrilatos incluyen, pero no se limitan a, epoxi acrilatos alifáticos, (poli)éter(met)acrilatos monofuncionales, tales como butoxietil(met)acrilato, butoxitrietilenglicol(met)acrilato, butil(met)acrilato modificado con epíclorohidrin, diciclopenteniloxietil(met)acrilato, 2-etoxietil(met)acrilato, etilcarbitol(met)acrilato, 2-metoxi(poli)etilenglicol(met)acrilato,

metoxi (poli)propilenglicol (met)acrilato,
nonilfenoxipolietilenglicol (met)acrilato,
nonilfenoxipolipropilenglicol (met)acrilato,
fenoxihidroxipropil (met)acrilato,
fenoxi (poli)etilenglicol (met)acrilato, polietilenglicol
mono (met)acrilato, polipropilenglicol mono (met)acrilato, y
polietilenglicol, polipropilenglicol mono (met)acrilato;
alquilenglicol di (met)acrilatos tales como polietilenglicol
di (met)acrilato, polipropilenglicol di (met)acrilato,
polibutilenglicol di (met)acrilato, politetrametilenglicol
di (met)acrilato; (met)acrilatos polifuncionales inducidos
por ácido (met)acrílico con polioles alifáticos, tales como
un copolímero de óxido de etileno y óxido de propileno, un
copolímero de propilenglicol y tetrahidrofurano, un
copolímero de etilenglicol y tetrahidrofurano, poliisopren
glicol, poliisopren glicol hidrogenado, polibutadienglicol,
polibutadien glicol hidrogenado; (met)acrilatos
polifuncionales inducidos por ácido acrílico con alcoholes
polihídricos tales como politetrametilenehexagliceril éter
(tetrahidrofurano modificado con hexaglicerina);
di (met)acrilatos de diol obtenidos por adición de éteres
cíclicos equimolares o más de 1 mol de éteres cíclicos,
tales como óxido de etileno, óxido de propileno, óxido de
butileno y/o tetrahidrofurano a 1 mol de óxido de

27

neopentilo; di(met)acrilatos de bisfenoles modificados con óxidos de alquilenos, tales como bisfenol A, bisfenol F y bisfenol S; bisfenoles hidrogenados modificados con di(met)acrilato de óxido de alquilenos, tales como bisfenol A hidrogenado, bisfenol F hidrogenado, bisfenol S hidrogenado; trifenoles modificados con di(met)acrilatos de óxido de alquilenos; trifenoles hidrogenados modificados con di(met)acrilatos de óxido de alquilenos; p,p'-bisfenoles modificados con di(met)acrilatos de óxido de alquilenos; bisfenoles hidrogenados modificados con di(met)acrilatos de óxido de alquilenos; p,p'.dihidrobisfenonas modificadas con di(met)acrilatos de óxido de alquilenos; mono-, di-, y tri-(met)acrilatos de trioles obtenidos por adición de óxido de etileno equimolar o más de 1 mol de óxido de etileno, óxido de propileno, óxido de butileno, y/o ésteres cíclicos tales como tetrahidrofurano a 1 mol de trimetilolpropano o glicerina; mono-, di-, tri- o tetra-(met)acrilatos obtenidos por adición de óxido de etileno equimolar o más de 1 mol, óxido de propileno, óxido de butileno, y/o éteres cíclicos, tales como tetrahidrofurano a 1 mol de pentaertritol, ditrimetilolpropano o triacrilato de trimetilpropano altamente alcoxilado; compuesto de (poli)éter(met)acrilatos monofuncionales o (poli)éter(met)acrilatos polifuncionales de alcoholes

polihídricos tales como triol, tetraol, pentaol, o hexaol de mono- o poli-(met)acrilatos obtenidos por adición de óxido de etileno equimolar o más de de 1 mol de óxido de etileno, óxido de propileno, óxido de butileno, y/o éteres cíclicos, tales como tetrahidrofurano a 1 mol de dipentaeritritol.

Compuestos de alquil(met)acrilatos o alquilen(met)acrilatos incluyen, pero no se limitan a, compuestos de (met)acrilatos monofuncionales, tales como metil(met)acrilato, etil(met)acrilato, propil(met)acrilato, isopropil(met)acrilato, butil(met)acrilato, isobutil(met)acrilato, pentil(met)acrilato, isopentil(met)acrilato, neopentil(met)acrilato, hexil(met)acrilato, heptil(met)acrilato, 2-etilhexil(met)acrilato, optil(met)acrilato, isooptil(met)acrilato, nonil(met)acrilato, decil(met)acrilato, dodecil(met)acrilato, tridecil(met)acrilato, pentadecil(met)acrilato, miristil(met)acrilato, palmitil(met)acrilato, estearil(met)acrilato, neril(met)acrilato, geranil(met)acrilato, farnecil(met)acrilato, hexadecil(met)acrilato, octadecil(met)acrilato, dodecil(met)acrilato, y trans-2-hexeno(met)acrilato;

di(met)acrilatos de dioles alifáticos tales como etilenglicol di(met)acrilato, propilenglicol di(met)acrilato, 1,2-butilenglicol di(met)acrilato, 1,3-butilenglicol di(met)acrilato, 1,4-butanediol di(met)acrilato, 1,6-hexanediol di(met)acrilato, neopentil glicol di(met)acrilato, 2-metil-1,8-octanediol di(met)acrilato, 1,9-nonanediol di(met)acrilato, y 1,10-decanediol di(met)acrilato; mono(met)acrilatos o poli(met)acrilatos de alcoholes polihídricos tales como trimetilolpropano, (de aquí en adelante, el término "poli" se usa como el término general del compuesto poli-funcional incluyendo di, tri, tetra, y poli compuestos tales como mono(met)acrilato, di(met)acrilato, y tri(met)acrilato de trimetilolpropano), y mono(met)acrilatos o poli(met)acrilatos de alcoholes polihídricos, tales como triol, tetraol, y hexaol, por ejemplo, glicerina, pentaeritritol, ditri-metilolpropano, y dipentaeritritol; los compuestos (Met)acrilatos tienen grupos hidroxilo tales como 2-hidroxietil(met)acrilato, 2-hidroxipropil(met)acrilato, 4-hidroxibutil(met)acrilato, 3-cloro-2-hidroxietil(met)acrilato; los compuestos (Met)acrilatos tienen átomos de bromo tales como 2,3-dibromopropil(met)acrilato, tribromofenil(met)acrilato, tribromofenil(met)acrilato modificado con óxido de etileno,

tetrabroinobisfenol A di(met)acrilato de óxido de etileno;
los compuestos (Met)acrilatos tienen átomos de flúor tales
como trifluoroetil(met)acrilato,
pentafluoropropil(met)acrilato,
tetrafluoropropil(met)acrilato,
octafluoropentil(met)acrilato,
dodecafluoroheptil(met)acrilato,
hexadecafluorononil(met)acrilato,
hexafluorobutil(met)acrilato, 3-perfluorobutil-2-
hidroxipropil(met)acrilato, 3-perfluorohexil-2-
hidroxipropil(met)acrilato, 3-perfluorooptil-2-
hidroxipropil(met)acrilato, 3-(perfluoro-5-metilhexil)-2-
hidroxipropil(met)acrilato, 3-(perfluoro-7-metiloetil)-2-
hidroxipropil(met)acrilato, y 3-(perfluoro-8-metildecil)-2-
hidroxipropil(met)acrilato.

Los compuestos (Met)acrilatos tienen grupos aromáticos
que incluyen, por ejemplo, pero no se limitan a, compuestos
(met)acrilatos monofuncionales, tales como
fenil(met)acrilato, bencilacrilato; y di(met)acrilatos,
tales como bisfenol A diacrilato, bisfenol F diacrilato,
bisfenol S diacrilato.

2

Los compuestos (Met)acrilatos tienen grupos alicíclicos que incluyen, pero no por vía de limitación, los compuestos (met)acrilatos monofuncionales tienen estructuras alicíclicas, tales como ciclohexil(met)acrilato, ciclopentil(met)acrilato, cicloheptil(met)acrilato, bicicloheptil(met)acrilato, isobornil(met)acrilato, biciclopentildi(met)acrilato, triciclodecil(met)acrilato, biciclopentenil(met)acrilato, norbornil(met)acrilato, biciclooptil(met)acrilato, tricicloheptil(met)acrilato, y (met)acrilato sustituido con esqueleto colesteroide; di(met)acrilatos de bifenoles hidrogenados, tales como bisfenol A hidrogenado, bisfenol F hidrogenado, bisfenol S hidrogenado, di(met)acrilatos de trifenoles hidrogenados, tales como trifenoles hidrogenados, y di(met)acrilatos de p,p'-bisfenoles hidrogenados; compuestos (met)acrilatos polifuncionales que tienen estructuras cíclicas tales como diciclopentano tipo di(met)acrilato, tales como "Kayarad R684" (disponible de Nihon Kayaku Co., Japan), triciclodecano dimetiloldi(met)acrilato, bisfenolfluoreno dihidroxi(met)acrilato; y acrilatos alicíclicos tienen átomos de oxígeno y/o átomos de nitrógeno, tales como tetrahidrofurfuril(met)acrilato, y morfolinoetil(met)acrilato.



Los compuestos que tienen grupos acrililoilo o grupos metacrililoilo que son adecuados para la presente invención, comparados con los anteriores compuestos citados incluyen poli(met)acril(met)acrilatos, tales como un producto de reacción de polímero de ácido (met)acrílico y glicidil(met)acrilato, y un producto de reacción de polímero de glicidil(met)acrilato y ácido (met)acrílico; los compuestos (met)acrilato tienen grupos amino tales como dimetilaminoetil(met)acrilato; isocianul(met)acrilatos, tales como tris(met)acriloxietil isocianurato; fosfagen(met)acrilatos, tales como hexakis(met)acrililoiloxietil ciclotrifosfagen; el (met)acrilato tiene un esqueleto de polisiloxano; polibutadien(met)acrilato; y melamina(met)acrilato. Entre estos compuestos que tienen grupo acrililoilo o metacrililoilo, se prefiere para uso los compuestos que tienen 1 a 6 grupos acrililoilo o metacrililoilo.

Los derivados de (Met)acrilamida que pueden ser utilizados en la presente invención incluyen, por ejemplo, (met)acrilamidas, tales como N-isopropil(met)acrilamida; y compuestos de (met)acrilamidas polifuncionales, tales como metilenobis(met)acrilamida .

23

Los compuestos que tienen grupos de éter de vinilo adecuado para la presente invención incluyen, pero no se limitan a, estos contienen: un alquil vinil éter que tiene un grupo terminal sustituido con al menos uno seleccionado del grupo que consiste de un átomo de hidrógeno, un átomo de halógeno, un grupo hidroxilo, y un grupo amino, un vinil éter cicloalquilo que tiene un grupo terminal sustituido con al menos uno seleccionado del grupo que consiste de un átomo de hidrógeno, un átomo de halógeno, un grupo hidroxilo, y un grupo amino; al menos un vinil éter seleccionado del grupo que consiste de un monovinil éter, un divinil éter, y un polivinil éter en el que un grupo vinil éter se conecta con un grupo alquilenos; y un grupo vinil éter conectado con al menos un grupo con y sin sustituyentes seleccionados del grupo que consiste de grupo alquilo, grupo cicloalquilo, y grupo aromático, por vía de al menos un enlace seleccionado del grupo que consiste de un enlace de éter, un enlace de uretano, y un enlace de éster.

Alquilvinil éteres incluyen, pero no se limitan a, metil vinil éter, hidroximetil vinil éter, clorometil vinil éter, etil vinil éter, 2-hidroxietilviniléter, 2-

cloroetilviniléter, dietil aminoetil vinil éter, propil vinil éter, 3-hidroxipropil vinil éter, 2-hidroxipropil vinil éter, 3-cloropropil vinil éter, 3-aminopropil vinil éter, isopropil vinil éter, butil vinil éter, 4-hidroxibutil vinil éter, isobutil vinil éter, 4-aminobutil vinil éter, pentil vinil éter, isopentil vinil éter, hexil vinil éter, 1,6-hexanodiol monovinil éter, heptil vinil éter, 2-etilhexil vinil éter, optil vinil éter, isooptil vinil éter, nonil vinil éter, isononil vinil éter, decil vinil éter, isodecil vinil éter, dodecil vinil éter, isododecil vinil éter, tridecil vinil éter, isotridecil vinil éter, pentadecil vinil éter, isopentadecil vinil éter, hexadecil vinil éter, octadecil vinil éter, metilenglicol divinil éter, etilenglicol divinil éter, propilenglicol divinil éter, 1,4-butanediol divinil éter, 1,6-hexanodiol divinil éter, ciclohexanodiol divinil éter, trimetilolpropano trivinil éter, pentaeritritol tetravinil éter y ácido hexanodiólico, bis(4-eteniloxi)butil] éster.

Cicloalquil vinil éteres adecuados para la presente invención incluyen, pero no por vía de limitación, ciclopropil vinil éter, 2-hidroxiciclopropil vinil éter, 2-cloro-ciclopropil vinil éter, ciclopropilmetil vinil éter, ciclobutil vinil éter, 3-hidroxiciclobutil vinil éter, 3-

clorociclobutil vinil éter, ciclobutilmetil vinil éter, ciclopentil vinil éter, 3-hidroxíciclopentil vinil éter, 3-clorociclopentil vinil éter, ciclopentilmetil vinil éter, ciclohexil vinil éter, 4-hidroxíciclohexil vinil éter, ciclohexilmetil vinil éter, 4-aminociclohexil vinil éter, ciclohexanodiol monovinil éter, ciclohexanodimetanol monovinil éter, y ciclohexanodimetanol divinil éter. Los compuestos que contienen monovinil éteres, divinil éteres, y/o polivinil éteres, incluyen estos en los que los enlaces de vinil éter se conectan con un grupo alquileo, y al menos un grupo seleccionado de un grupo que consiste de un grupo alquilo C_2-C_{24} , un grupo cicloalquilo C_2-C_{24} y un grupo aromático C_2-C_{24} que puede tener un sustituyente conectado a un enlace seleccionado del grupo que consiste de un enlace de éter, un enlace de uretano, y un enlace de éster. Ejemplos de los compuestos que contienen un enlace de éter incluyen, pero no se limitan a, etilenglicol metil vinil éter, dietilenglicol monovinil éter, dietilenglicol metilvinil éter, dietilenglicol divinil éter, trietilenglicol monovinil éter, trietilenglicol metilvinil éter, trietilenglicol divinil éter, polietilenglicol monovinil éter, polietilenglicol metilvinil éter, polietilenglicol divinil éter, propilenglicol metilvinil éter, dipropilenglicol monovinil éter, dipropilenglicol

18

metilvinil éter, dipropilenglicol divinil éter,
tripropilenglicol monovinil éter, tripropilenglicol
metilvinil éter, tripropilenglicol divinil éter,
polipropilenglicol monovinil éter, polipropilenglicol
metilvinil éter, polipropilenglicol divinil éter,
tetrametilenglicol metilvinil éter,
di(tetrametilenglicol)monovinil éter,
di(tetrametilenglicol)metil vinil éter,
di(tetrametilenglicol)diviniléter,
tri(tetrametilenglicol)monovinil éter,
tri(tetrametilenglicol)metilvinil éter,
tri(tetrametilenglicol) divinil éter,
poli(tetrametilenglicol)monovinil éter,
poli(tetrametilenglicol)metilvinil éter,
poli(tetrametilenglicol)divinil éter, 1,6-hexanodiolmetil
vinil éter, di(hexametilenglicol)monovinil éter,
di(hexametilenglicol)metilvinil éter, di(hexametilenglicol)
divinil éter, tri(hexametilenglicol)monovinil éter,
tri(hexametilenglicol)metilvinil éter,
tri(hexametilenglicol) divinil éter,
poli(hexametilenglicol)monovinil éter,
poli(hexametilenglicol)metilvinil éter,
poli(hexametilenglicol)divinil éter.

En una modalidad preferida, los monómeros curables con energía y/o oligómeros están en un rango entre aproximadamente 1% y aproximadamente 100%, más preferiblemente entre aproximadamente 5% y aproximadamente 95%, y más preferiblemente entre aproximadamente 10% y aproximadamente 90% por peso de los ingredientes totales del recubrimiento protector.

En otra modalidad preferida, el recubrimiento protector curable con energía es claro o libre de pigmento. En aún otra modalidad preferida, el recubrimiento protector curable con energía se tiñe o contiene pigmentos orgánicos o inorgánicos.

Los tipos de radiación actínica para polimerizar el recubrimiento protector para los materiales de empaque impresos de la presente invención pueden ser un haz de electrones, o luz UV, y similares. En una modalidad preferida, la fuente de energía para foto-polimerización es un haz de electrones. Preferiblemente, una dosis necesaria de haz de electrones para curado de la tinta varía entre aproximadamente 0.5 a aproximadamente 8 Mrads, más preferiblemente aproximadamente de 1 a aproximadamente 6 Mrads, y más preferiblemente de aproximadamente 1.3 a

aproximadamente 4 Mrads. Un voltaje de aceleración de haz de electrones varía preferiblemente aproximadamente 30-200 kV, más preferiblemente 60-165 kV, y más preferiblemente aproximadamente 70-140 kV. Durante el curado de tinta por haz de electrones, se suministra un ambiente inerte por gas nitrógeno, lo que resulta en preferiblemente menos de cerca de 600 partes por millón (ppm), más preferiblemente menos de cerca de 400 ppm, y más preferiblemente menos de cerca de 200 ppm, de O₂ presente en el ambiente. En otra modalidad preferida, la fuente de energía para fotopolimerización del recubrimiento protector son rayos UV. La intensidad de Luz UV apropiado está en el rango entre aproximadamente 20 a aproximadamente 10,000 mJ/cm², preferiblemente aproximadamente 40 a aproximadamente 1,000 mJ/cm², y más preferiblemente aproximadamente 50 a aproximadamente 700 mJ/cm².

4.5 Fotoiniciador

A menos que la segunda fuente de radiación actínica sea un haz de electrones, la resina curable con energía del revestimiento protector en la presente invención contendrá típicamente un fotoiniciador que genera radicales libres sobre exposición a radiación actínica, tales como alumbrado

18

UV. Tal un fotoiniciador puede tener uno o más compuestos que directamente producen radicales libres cuando se activan por radiación actínica. El fotoiniciador también puede contener un sensibilizador o un activador que extiende la respuesta espectral en las regiones espectrales cerca al infrarrojo o visibles, cerca al ultravioleta, o afecta el índice de reacción. En los sistemas de curado iniciados por radical libre, la irradiación de un fotoiniciador produce radicales libres que inician la polimerización y/o reticulación de resinas fotocurables. Varios tipos de fotoiniciadores son bien conocidos por un experto en la técnica (ver, por ejemplo, "Photoinitiators for free-radical-initiated photoimaging systems" by Monroe, B.M. et al, 1994, Chem. Rev. 93:435-448). Ejemplos de fotoiniciadores adecuados para la presente invención incluyen, pero no se limitan a, compuestos halógenos orgánicos como se describe en la Patente U.S. 5,057,398 y estos se describen en la Patente U.S. 4,066,582, tales como benzofenona, acetofenona, fluorenona, xantona, tioxantona, carbazol, benzoina, los éteres de benzoina alilo, 2- o 3- o 4-bromoacetofenona, 3- o 4-alilacetofenona, m- o p-diacetilbenceno, 2- o 3- o 4-metoxibenzofenona, 3,3'- o 3,4'- o 4,4'-dimetoxibenzofenona, 4-cloro-4'-bencilbenzofenona, 2- o 3-cloroxantona, 3,9-dicloroxantona,

50

2- o 3-clorotioxantona, 3-cloro-8-nonilxantona, 3-metoxiantona, 3-yodixantona, 2-acetil-4-metilfenil acetato, éteres de alquilo y arilo de benzoina, fenilglioal alquil acetales, 2,2'-dimetoxi-2-fenil-acetofenona, 2,2-dietoxiacetofenona, 2,2-diiso-propoxiacetofenona, 1,3-difenil acetona, cloruro de naftaleno sulfonilo, y mezclas de estos.

Sensibilizadores o activadores adecuados que pueden ser usados en combinaciones con los fotoiniciadores anteriormente mencionados incluyen, pero no por vía de limitación, metilamina, tributilamina, metildietanolamina, 2-aminoetiletanolamina, alilamina, ciclohexilamina, ciclopentadienilamina, difenilamina, ditolilamina, trixililamina, tribencilamina, N-ciclohexiletilenimina, piperidina, 2-metilpiperidina, N-etilpiperidina, 1,2,3,4-tetrahidropiridina, 2- o 3- o 4-picolina, morfolina, N-metilmorfolina, piperazina, N-metilpiperazina, 2,2-dimetil-1,3-bis-(3-N-morfolinil) propioniloxi)) dietil éter, isopropiltioxantona (ITX), dibutoxiantraceno, dipropoxiantraceno, y mezclas de estos.

En una modalidad preferida, el fotoiniciador está entre un rango entre aproximadamente 0.1% y aproximadamente

20%, más preferiblemente entre aproximadamente 0.2% a 12%, y más preferiblemente aproximadamente 0.5% a 8%, por peso del peso total del recubrimiento

5. EJEMPLOS

Los siguientes ejemplos ilustran la tinta de impresión líquida basada en solvente curable por energía suministrado por la presente invención. Estos ejemplos no se deben constituir como limitantes

5.1 Ejemplo 1

Una película de polietileno opaco con 75- μ de espesor se cubre con una tinta roja basada en solvente (basado en nitrocelulosa/poliuretano) y se seca utilizando una pistola de aire caliente. Después, un recubrimiento protector delgado de recubrimiento curable de EB se aplica sobre la película cubierta roja con una barra Meyer #3. Este se cura con EB a 3 Mrads, 100 kV de voltaje de aceleración y menos de 200 ppm de oxígeno. La película brillante resultante tiene un brillo reflectivo de 60 grados de 71-73% y tiene una resistencia de solvente de 17-20 estregaduras dobles MEK. El coeficiente de fricción cara-a-cara (COF) fue 0.39-

0.40 estático/0.31-0.42 cinético según se mide en un TMI (modelo 32-06; Testing Machine Instruments, Amityville, NY) probador de fricción deslizable. El solvente residual según se mide por cámara de aire GC fue 593 mg/resma (1 resma = 3000 pie cuadrado de la película).

5.2 Ejemplo 2

Una película de polietileno opaco con 75- μ de espesor se cubre con una tinta roja basada en solvente (basado en nitrocelulosa/poliuretano) y se seca utilizando una pistola de aire caliente. Inmediatamente después, la película recubierta se somete a 250 mJ/cm² de UV. Una capa de recubrimiento protectora delgada de recubrimiento curable EB se aplica sobre la película cubierta roja con una barra Meyer #3. Este se cura con EB a 3 Mrads, 100 kV de voltaje de aceleración y menos de 200 ppm de oxígeno. La película brillante resultante tiene un brillo reflectivo de 60 grados de 71-73% y tiene una resistencia de solvente de 24-32 estregadura dobles MEK. El COF de cara-a-cara fue 0.39-0.40 estático/0.31-0.32 cinético según se mide en un Probador de fricción deslizable TMI. El solvente residual según se mide por cámara de aire GC fue 402 mg/resma. Los



resultados de los anteriores dos (2) ejemplos se resumen en la Tabla 1 adelante.

	Estregadura MEK	Solvente Residual	COF	Brillo 60°
Ejemplo 1 (sin activación UV)	17-20	593 mg/resma	0.39- 0.40/0.31- 0.32	71-73
Ejemplo 2 (activación UV)	24-32	402 mg/resma	0.39- 0.40/0.30- 0.31	71-73

5.3 Ejemplo 3

Una película de polipropileno de 50- μ m de espesor se cubre con una tinta azul basada en solvente (basada en poliuretano) y se seca utilizando una pistola de aire caliente. Inmediatamente después, la película recubierta se somete a 100 mj/cm² de UV. Una capa de recubrimiento protectora delgada de poliéster acrilato que contiene 5% de benzofenona (fotoiniciador) se aplica sobre la película cubierta azul con una barra Meyer #3. El revestimiento protector luego se cura por Luz UV a 500 mj/cm².

5.4 Ejemplo 4

Una película de papel laminado de hoja de poliolefina de 50- μm se cubre con una tinta roja basada en solvente (basada en poliuretano) y se seca utilizando una pistola de aire caliente. Inmediatamente después, la película recubierta se somete a 330 mj/cm^2 de UV. Una capa de recubrimiento protectora delgada de recubrimiento curable EB, que contiene un pigmento rojo, se aplica sobre la película cubierta roja con una barra Meyer #3. Esta se cura con EB a 2 Mrads, 100 kV de voltaje de aceleración y menos de 200 ppm de oxígeno.

5.5 Ejemplo 5

Se recubre una estructura laminada de película plástica de papel de 80- μm de espesor con una tinta naranja basada en agua (basada en acrílico) y se seca utilizando una pistola de aire caliente. Inmediatamente después, la película recubierta se somete a 305 mj/cm^2 de UV. Una capa de recubrimiento protectora delgada de recubrimiento curable EB se aplica sobre la película cubierta naranja con una barra Meyer #3. Esta se cura con EB a 1.5 Mrads, 100 kV de voltaje de aceleración y menos de 200 ppm de oxígeno.

20

5.6 Ejemplo 6

Una película de hoja de papel laminado de 50- μm de espesor se cubre con un fotoiniciador-libre de tinta roja basada en solvente (basada en poliuretano) y se seca utilizando una pistola de aire caliente. Inmediatamente después, la película recubierta se somete a un EB a 2 Mrads, 100 kV de voltaje de aceleración y menos de 200 ppm de oxígeno. Una capa de recubrimiento protectora delgada curable con UV recubierta, que contiene un fotoiniciador, se aplica sobre la película cubierta roja con una barra Meyer #3. Este se cura con UV a 330 mj/cm^2 .

6. EQUIVALENTES

Estos expertos en la técnica reconocerán, o pueden comprobar muchos equivalentes de las modalidades específicas de la invención descritas aquí utilizando solo experimentación de rutina. Se entiende que tales equivalentes se abarcan por las siguientes reivindicaciones. Todas las publicaciones y patentes mencionadas en esta especificación se incorporan aquí como referencia en la especificación.

REIVINDICACIONES

Lo que se reivindica es:

1 Un método para producir un material de empaque impreso comprende:

aplicar una tinta líquida activable con radiación actínica a un material de empaque;

exponer la tinta a una primer radiación actínica;

aplicar un recubrimiento curable con energía sobre la tinta; y

cubrir el recubrimiento con una segunda radiación actínica.

2. El método de la reivindicación 1, en donde el material de empaque es una película flexible termoplástica, y en donde una sustancia a ser empacada se incluye dentro de la posterior película plástica al curado por radiación actínica de esta.

3. El método de la reivindicación 1, en donde el material de empaque es una hoja de papel laminado o papel plástico laminado, y en donde una sustancia a ser empacada se incluye dentro de la posterior película plástica al curado por radiación actínica de esta.
4. El método de la reivindicación 1, en donde la primera radiación actínica son rayos UV.
5. El método de la reivindicación 1, en donde la segunda radiación actínica es un haz de electrones.
6. El método de la reivindicación 1, en donde la segunda radiación actínica son rayos UV.
7. El método de la reivindicación 1, en donde la cubierta curable con energía está libre de pigmento.
8. El método de la reivindicación 1, en donde la tinta líquida se aplica más de una vez.

9. El método de la reivindicación 1, en donde la tinta líquida está basada en solvente.
10. El método de la reivindicación 1, en donde la tinta líquida se basa en agua.
11. Un material de empaque producido de acuerdo al método de la reivindicación 1.
12. El material de empaque de la reivindicación 11, en donde el material de empaque contiene al menos 700 ppm total de solvente residual o agua.
13. El material de empaque de la reivindicación 12, en donde el material de empaque contiene al menos 600 ppm total de solvente residual o agua.
14. El material de empaque de la reivindicación 13, en donde el material de empaque contiene al menos 500 ppm total de solvente residual o agua.
15. El material de empaque de la reivindicación 11, en donde el material de empaque tiene un grado de cura de al menos 5 MEK estregaduras.

7/5

16. El material de empaque de la reivindicación 15,
en donde el material de empaque tiene un grado de
cura de al menos 10 MEK estregaduras.

17. El material de empaque de la reivindicación 16,
en donde el material de empaque tiene un grado de
cura de al menos 20 MEK estregaduras.

MÉTODO DE ELABORACIÓN DE MATERIALES DE EMPAQUE CON BAJO**OLOR****RESUMEN**

La presente invención suministra un método para producir un material de empaque impreso con bajo olor y el material de empaque impreso producido de esta manera. El material de empaque impreso de la presente invención es especialmente adecuado para empacar sustancias, tales como alimento, Drogas y tabaco, que requieren bajo olor de las tintas de impresión. En este proceso, la tinta de impresión es activada por la exposición a la radiación actínica, tal como la luz UV, antes de que se aplique a ésta un recubrimiento curable con radiación actínica. La exposición de la tinta impresa a la luz UV reduce el contenido de solvente residual y el olor del material de empaque y mejora la resistencia a la fricción y el brillo de las imágenes impresas. Adicionalmente, la exposición del material de empaque impreso a la luz UV suministra o proporciona un beneficio adicional de reducir el conteo microbiano, excediendo de esta manera la vida de estante de la sustancia empacada, tal como alimento y drogas.

Industria y Comercio
SUPERINTENDENCIA

**REQUISITOS MINIMOS PARA ADMISION A TRAMITE
PCT**

PATENTE DE INVENCION



MODELO DE UTILIDAD []

- ◆ Indicación de que se solicita la concesión de una patente []
- ◆ Datos de identificación del solicitante o de la persona que presenta la solicitud []
- ◆ Descripción de la invención []
- ◆ Dibujos de ser estos pertinentes []
- ◆ Comprobante de pago de las tasas establecidas []

COMPLETA []

INCOMPLETA []

DISEÑO INDUSTRIAL []

- ◆ Indicación de que se solicita el registro de Diseño Industrial []
- ◆ Datos de identificación del solicitante o de la persona que presenta la solicitud []
- ◆ Representación gráfica y fotográfica del Diseño Industrial o muestra del material que incorpora el diseño []
- ◆ Comprobante de pago de las tasas establecidas []

COMPLETA []

INCOMPLETA []

ESQUEMA DE TRAZADO []

- ◆ Indicación de que se solicita el registro de un Esquema de Trazado []
- ◆ Datos de identificación del solicitante o de la persona que presenta la solicitud []
- ◆ Representación gráfica del esquema trazado []
- ◆ Comprobante de pago de las tasas establecidas []

COMPLETA []

INCOMPLETA []

Firma Responsable

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REPUBLICA DE COLOMBIA
SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

Bogotá,
2020

Doctor(a)
RODRIGUEZ DILIA MARIA
Apoderado(a) y/o Representante de
SUN CHEMICAL CORPORATION.

BWS

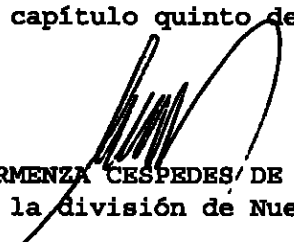
REFERENCIA	Radicación No.	6 107276
	Solicitud internacional	PCT/US2005/010649
	Fecha inicio fase nacional	31/10/2006
	Trámite	11
	Evento	378
	Actuación	430
	Oficio No.	13923

Como resultado del examen de forma, realizado con fundamento en el artículo 38 de la Decisión 486 de la Comisión de la Comunidad Andina, artículo 27 del Tratado de Cooperación en Materia de Patentes (PCT), regla 51 bis del Reglamento y Circular Única de la Superintendencia de Industria y Comercio, se le comunica que:

1. La solicitud no contiene la copia del documento en que consta la cesión del derecho a la patente del inventor al solicitante o a su causante. (Art. 26-k) Decisión 486.

En cumplimiento de lo dispuesto por el artículo 39 de la Decisión 486, se le requiere para que dentro del término de dos meses siguientes a la fecha de notificación del presente oficio, complete los requisitos anteriormente enunciados. En caso de no dar cumplimiento al presente requerimiento, la solicitud se considerará abandonada y perderá su prelación.

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


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

El anterior requerimiento fue notificado por fijación en lista de fecha 01 DIC. 2006
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