

Q.P



Industria y Comercio
SUPERINTENDENCIA

PCT
SOLICITUD
PATENTE DE INVENCION
PCT

EXPEDIENTE N° **06-126987**

TITULO COMPUESTO DE BETÚN PARA CUERO
O CUERO SINTÉTICO

CLASIFICACION INTERNACIONAL _____

SOLICITANTE RECKITT BENCKISER (UK) LIMITED

DOMICILIO REINO UNIDO

APODERADO DARIO CARDENAS NAVAS

BOGOTÁ, D C _____

PETITORIO



SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
Red 08-126987-00000-0000
Fec 2005 12-19 16:46 15 Dep 2020 NUECREACIONES
Tq 11 PATENTE/II
Eva 379 FASENACIONALI
Act 411 PRESENTACION Folios 147

FORMULARIO UNICO DE SOLICITUD DE PATENTE PCT ENTRADA EN FASE NACIONAL

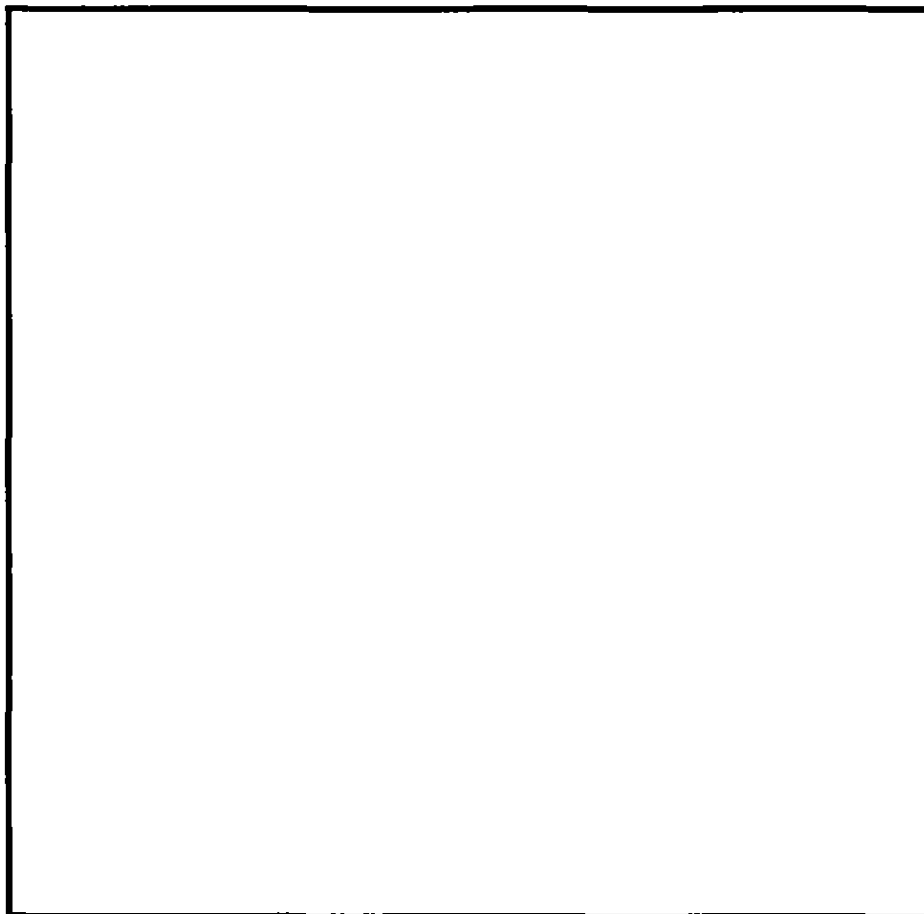
① SOLICITUD DE			
☒ Patente de Invención		☐ Patente de Modelo de Utilidad	
☐ Capítulo I		☒ Capítulo II	
② SOLICITANTE (71)	Nombre Reckitt Benckiser (UK) Limited Dirección 103-105 Bath Road Slough Berkshire SL1 3UH, Reino Unido Nacionalidad o Domicilio REINO UNIDO Lugar de Constitución REINO UNIDO Teléfono 3123800 Fax 3122410 E-mail general@cardenasycardenas.com	IDENTIFICACION C C ☐ NIT ☐ C E ☐ Otro ☒ Cual _____ Número _____	
③ REPRESENTANTE O APODERADO	Nombre DARIO CARDENAS NAVAS Dirección Carrera 7 No 71-52 Torre B Piso 9 Teléfono 3123800 Fax 3122410 E-Mail general@cardenasycardenas.com	IDENTIFICACION C C ☒ NIT ☐ C E ☐ Otro ☐ Número 17088829 Cual TP 1 250	
④ INVENTOR(ES) (72)	Nombre 1 Jason Radley 2 Chris Wigley Dirección 1 Dansom Lane, Hull HU8 7DS, Reino Unido 2 Dansom Lane, Hull HU8 7DS Reino Unido Nacionalidad o Domicilio 1 Reino Unido 2 Reino Unido		
⑤ PCT (86)			
Solicitud Internacional No		PCT/GB2005/002383	
Publicación Internacional No		WO 2005/123869 A1	
Fecha		Junio 17, 2005	
Fecha		Diciembre 29 2005	
⑥ Título(54)			
COMPUESTO DE BETUN PARA CUERO O CUERO SINTÉTICO			
⑦ Clasificación Internacional (51)			
⑧ Prioridad SI ☒ NO ☐	(33) País de Origen	(32) Fecha	(31) N° de Solicitud
	REINO UNIDO	Junio 21 2004	0413831 9
	_____	_____	_____
	_____	_____	_____
⑨ Comprobante de Pago No			
05-93.688		Fecha Diciembre 6, 2006	

ANEXOS

2

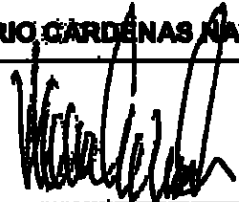
- ☒ Comprobante de pago de la tasa de presentación de la solicitud
- ☐ Documento que acredite la existencia y representación legal cuando el solicitante sea persona jurídica
- ☐ Poderes si fuere el caso
- ☐ Documento de cesión del inventor al solicitante o a su causante
- ☐ Declaraciones
- ☒ Copia de la solicitud Internacional (Resumen descripción reivindicaciones dibujos)
- ☒ Traducción de la solicitud Internacional al castellano (Resumen descripción reivindicaciones dibujos)
- ☐ Copia del examen preliminar internacional efectuado por la Autoridad Internacional de Examen Preliminar (IPEA)
- ☐ Traducción del examen preliminar internacional 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 12x12
- ☐ De ser el caso información sobre otras solicitudes de patente o títulos obtenidos en el extranjero por el mismo titular o su causante relacionadas parcial o totalmente con la invención de esta solicitud
- ☐ De ser el caso modificaciones efectuadas a la solicitud Internacional
- ☐ Otros

11 FIGURA CARACTERISTICA



12 Solicito la Concesión de la patente,

NOMBRE DARIO GARDENAS NAVAS

FIRMA. 

25 CC 12.000.029 BTA TP. 1.250 C s.

(21) N° de solicitud				(51) Int Cl	
22) Fecha de solicitud				(71) Solicitante(s) Reckitt Benckiser (UK) Limited	
(30) Prioridad	(31) No. Prioridad	(32) Fecha	(33) País		
X	0413831 9	21/06/04	REINO UNIDO	(72) Inventor(es)	
				1 Jason Radley	
				2 Chris Wigley	
				(74) Apoderado DARIO CARDENAS NAVAS	
(85) Fecha límite inicio fase nacional				(87) Publicación internacional	
(86) Datos relativos a la presentación de la solicitud PCT				Fecha. Fecha 29/12/05	
Fecha de presentación de la solicitud Fecha 17/06/05				N° publicación WO 2005/123989 A1	
No de solicitud PCT/GB2005/002383					
(54) Título COMPUESTO DE BETÚN PARA CUERO O CUERO SINTÉTICO					

Resumen

Un compuesto de betún para el tratamiento de betún para el tratamiento de artículos de cuero y/o cuero sintético, dicho compuesto incluye agua, por lo menos una cera, por lo menos un polímero que forma una película, y un silicato con capas que incluye un péptico inorgánico

4

RECIBO DE DEPÓSITO
Rm 06-126887-00000-0000
06:2006-12 19 16.45 16 Dep 2020 NUECREACIONES
Ita. 11 PATENTEIYN
3ra. 379 FASENACIONALI
46111 PRESENTACION Fondo 147

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT B00176089-2

RECIBO OFICIAL DE CAJA 06 93,688
FECHA DICIEMBRE 6 DE 2006

***** CONSIGNACION *****

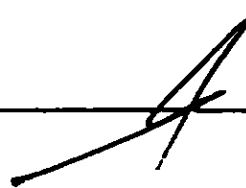
DEPOSITANTE	TIPO PASO	BANCO	CUENTA	Nº PASO	FECHA PASO	Vr PASO
CARDENAS Y CARDENAS P I	CONSIGNACION	BANCO POPULAR	050 00110-6	59171559	06/12/2006	3,124,600 00

***** 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



CARDENAS Y CARDENAS P I

RECIBIDOS

RECIBO DE CAJA APLICADO AL EXPEDIENTE No COMPUESTO DE BETUN PARA CUERO
O CUERO SINTETICO

4

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) 11449P1 WO/JMH

Box No. I TITLE OF INVENTION	
Improvements in or relating to a Composition	
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. 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.) Reckitt Benckiser (UK) Limited 103-105 Bath Road Slough Berkshire SL1 3UH UNITED KINGDOM	
Telephone No + 44 1753 217800 Facsimile No + 44 1753 217899 Teleprinter No Applicant's registration No. with the Office	
State (that is, country) of nationality GB	State (that is, country) of residence GB
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. 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.) RADLEY Jason Reckitt Benckiser (UK) Limited Dansom Lane Hull HU8 7DS UNITED KINGDOM	
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 GB	State (that is, country) of residence GB
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. The address must include postal code and name of country.) BOWERS, Craig Legal Department - Patents Group Reckitt Benckiser plc Dansom Lane Hull HU8 7DS UNITED KINGDOM	
Telephone No + 44 1482 583730 Facsimile No + 44 1482 216876 Teleprinter No Agent's registration No. with the Office	
☐ 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> WIGLEY Chris Reckitt Benckiser (UK) Limited Dansom Lane Hull HU8 7DS UNITED KINGDOM	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 (that is, country) of nationality GB	State (that is, country) of residence GB
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 (that is, country) of nationality	State (that is, country) 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 (that is, country) of nationality	State (that is, country) 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 (that is, country) of nationality	State (that is, country) 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 No. 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 State 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)(iv) 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)).

Additional Agents

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+44 (0) 1482 216876

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+44 (0) 1482 216876

Box No VIII (i) DECLARATION IDENTITY OF THE INVENTOR

The declaration must conform to the standardized wording provided for in Section 211 see Notes to Boxes Nos. VIII VIII (i) to (v) (in general) and the specific Notes to Box No. VIII (i) If this Box is not used this sheet should not be included in the request

Declaration as to the identity of the inventor (Rules 4 17(i) and 51 b4 1(a)(i))



This declaration is continued on the following sheet, "Continuation of Box No VIII (i)"

Box No VIII (ii) DECLARATION ENTITLEMENT TO APPLY FOR AND BE GRANTED A PATENT

The declaration must conform to the standardized wording provided for in Section 212 see Notes to Boxes Nos VIII VIII (i) to (v) (in general) and the specific Notes to Box No. VIII (ii) If this Box is not used, this sheet should not be included in the request

Declaration as to the applicant's entitlement, as at the international filing date, to apply for and be granted a patent (Rules 4 17(ii) and 51bis 1(a)(ii)), in a case where the declaration under Rule 4 17(iv) is not appropriate

☐ This declaration is continued on the following sheet, "Continuation of Box No VIII (ii)"

Box No. VIII (ii) DECLARATION ENTITLEMENT TO CLAIM PRIORITY

The declaration must conform to the standardized wording provided for in Section 213 see Notes to Boxes Nos. VIII VIII (i) to (v) (in general) and the specific Notes to Box No. VIII (ii) If this Box is not used, this sheet should not be included in the request

Declaration as to the applicant's entitlement, as at the international filing date, to claim the priority of the earlier application specified below where the applicant is not the applicant who filed the earlier application or where the applicant's name has changed since the filing of the earlier application (Rules 4.17(iii) and 51bis 1(a)(iii))

☐ This declaration is continued on the following sheet, "Continuation of Box No. VIII (iii)"

Box No. VIII (iv) DECLARATION INVENTORSHIP (only for the purposes of the designation of the United States of America)
The declaration must conform to the following standardized wording provided for in Section 21-1 see Notes to Boxes Nos VIII VIII (i) to (v) (in general) and the specific Notes to Box No. VIII (iv) If this Box is not used, this sheet should not be included in the request

**Declaration of inventorship (Rules 4 17(iv) and 51b1(a)(iv))
for the purposes of the designation of the United States of America**

I hereby declare that I believe I am the original first and sole (if only one inventor is listed below) or joint (if more than one inventor is listed below) inventor of the subject matter which is claimed and for which a patent is sought

This declaration is directed to the international application of which it forms a part (if filing declaration with application).

This declaration is directed to international application No PCT/ (if furnishing declaration pursuant to Rule 26ter)

I hereby declare that my residence mailing address and citizenship are as stated next to my name

I hereby state that I have reviewed and understand the contents of the above-identified international application including the claims of said application I have identified in the request of said application in compliance with PCT Rule 4 10 any claim to foreign priority and I have identified below under the heading "Prior Applications," by application number country or Member of the World Trade Organization day month and year of filing, any application for a patent or inventor's certificate filed in a country other than the United States of America, including any PCT international application designating at least one country other than the United States of America, having a filing date before that of the application on which foreign priority is claimed

Prior Applications

I hereby acknowledge the duty to disclose information that is known by me to be material to patentability as defined by 37 C F R § 1.56, including for continuation in-part applications, material information which became available between the filing date of the prior application and the PCT international filing date of the continuation in-part application

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Name

Residence
(city and either US state if applicable or country)

Mailing Address

Citizenship

Inventor's Signature
(if not contained in the request, or if declaration is corrected or added under Rule 26ter after the filing of the international application The signature must be that of the inventor not that of the agent)

Date
(of signature which is not contained in the request, or of the declaration that is corrected or added under Rule 26ter after the filing of the international application)

Name

Residence
(city and either US state if applicable or country)

Mailing Address

Citizenship

Inventor's Signature
(if not contained in the request or if declaration is corrected or added under Rule 26ter after the filing of the international application The signature must be that of the inventor not that of the agent)

Date
(of signature which is not contained in the request, or of the declaration that is corrected or added under Rule 26ter after the filing of the international application)

☐ This declaration is continued on the following sheet, "Continuation of Box No VIII (iv)"

Box No VIII (v) DECLARATION NON PREJUDICIAL DISCLOSURES OR EXCEPTIONS TO LACK OF NOVELTY
The declaration must conform to the standardized wording provided for in Section 215 see Notes to Boxes Nos. VIII VIII (i) to (v) (in general) and the specific Notes to Box No. VIII (v) If this Box is not used this sheet should not be included in the request

Declaration as to non-prejudicial disclosures or exceptions to lack of novelty (Rule 4 17(v) and 51bis 1(a)(v))

☐ This declaration is continued on the following sheet "Continuation of Box No VIII (v)"

Continuation of Box No VIII (i) to (v) DECLARATION

If the space is insufficient in any of Boxes Nos. VIII (i) to (v) to furnish all the information, including in the case where more than two inventors are to be named in Box No. VIII (iv) in such case write "Continuation of Box No. VIII" (Indicate the item number of the Box) and furnish the information in the same manner as required for the purposes of the Box in which the space was insufficient. If additional space is needed in respect of two or more declarations, a separate continuation box must be used for each such declaration. If this Box is not used, this sheet should not be included in the request.

Box No. IX CHECK FIRST LANGUAGE OF FILING		
This international application contains (a) In paper form the following number of sheets request (including declaration sheets) 5 description (excluding sequence listing and/or tables related thereto) 14 claims 3 abstract 1 drawings Sub-total number of sheets 23 sequence listing 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 23 (b) ☐ only in computer readable form (Section 801(a)(i)) (i) ☐ sequence listing (ii) ☐ tables related thereto (c) ☐ also in computer readable form (Section 801(a)(ii)) (i) ☐ sequence listing (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 microorganism 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 listing 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) Patents Form 23/77 1	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> <u>Craig Bowers</u> Agent for the Applicants		
For receiving Office use only		
1 Date of actual receipt of the purported international application	2 Drawings.	
3 Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application	☐ received	
4 Date of timely receipt of the required corrections under PCT Article 11(2)	☐ not received	
5 International Searching Authority (if two or more are competent) ISA /	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		

These Notes are intended to facilitate the filling in of the request form. For more detailed information, see the *PCT Applicant's Guide* a WIPO publication which is available together with other PCT related documents at WIPO's Website www.wipo.int/pc/en/index.html. The Notes are based on the requirements of the Patent Cooperation Treaty (PCT), the Regulations and the Administrative Instructions under the PCT. In case of any discrepancy between these Notes and those requirements, the latter are applicable.

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

Please use a typewriter; check boxes may be marked by hand with black ink (Rule 11.9(a) and (b)).

The request form and these Notes may be downloaded from WIPO's Website at the address given above.

WHERE TO FILE THE INTERNATIONAL APPLICATION

The international application (request, description, claims, abstract and drawings, if any) must be filed with a competent receiving Office (Article 11(1)(i))—that is, subject to any applicable prescriptions concerning national security at the choice of the applicant, either:

(i) the receiving Office of or acting for a PCT Contracting State of which the applicant or, if there are two or more applicants, at least one of them, is a resident or national (Rule 19.1(a)(i) or (ii) or (b)) or

(ii) the International Bureau of WIPO in Geneva, Switzerland, if the applicant or, if there are two or more applicants, at least one of the applicants is a resident or national of any PCT Contracting State (Rule 19.1(a)(iii)).

APPLICANT'S OR AGENT'S FILE REFERENCE

A file reference may be indicated, if desired. It should not exceed 12 characters. Characters in excess of 12 may be disregarded by the receiving Office or any International Authority (Rule 11.6(f) and Section 109).

BOX No. I

Title of Invention (Rules 4.3 and 5.1(a)). The title must be short (preferably two to seven words when in English or translated into English) and precise. It must be identical with the title heading the description.

BOXES Nos. II AND III

General. At least one of the applicants named must be a resident or national of a PCT Contracting State for which the receiving Office acts (Articles 9 and 11(1)(i) and Rules 18 and 19). If the international application is filed with the International Bureau under Rule 19.1(a)(iii), at least one of the applicants must be a resident or national of any PCT Contracting State.

Indication Whether a Person is Applicant and/or Inventor (Rules 4.5(a) and 4.6(a) and (b)).

All of the inventors must be named also as applicants for the purposes of the designation of the United States of America (see "Different Applicants for Different Designated States" below).

Check box: This person is also inventor (Box No. II). Mark this check box if the applicant named is also the inventor or one of the inventors; do not mark this check box if the applicant is a legal entity.

Check box: applicant and inventor (Box No. III). Mark this check box if the person named is both applicant and inventor; do not mark this check box if the person is a legal entity.

Check-box: applicant only (Box No. III). Mark this check box if the person named is a legal entity or if the person named is not also inventor.

Check-box: inventor only (Box No. III). Mark this check box if the person named is inventor but not also applicant. This would be the case in particular where the inventor is deceased or the particular inventor is not an inventor for the purposes of the designation of the United States of America. Do not mark this check box if the person is a legal entity.

In Box No. III, one of the three check boxes must always be marked for each person named.

A person must not be named more than once in Boxes Nos. II and III, even where that person is both applicant and inventor.

Different Applicants for Different Designated States (Rules 4.5(d), 18.3 and 19.2). It is possible to indicate different applicants for the purposes of different designated States. At least one of all the applicants named must be a national or resident of a PCT Contracting State for which the receiving Office acts, irrespective of the designated State(s) for the purposes of which that applicant is named. *All of the inventors must be named also as applicants for the United States of America (except as indicated above) and the check-boxes "This person is also inventor" (in Box No. II) and/or "applicant and inventor" (in Box No. III) must be marked.*

For the indication of the designated States for which a person is applicant, mark the applicable check box (only one for each person). The check box "the States indicated in the Supplemental Box" must be marked where none of the other three check-boxes fits the circumstances; in such a case, the name of the person must be repeated in the Supplemental Box with an indication of the States for which that person is applicant (see item 1(ii) in that Box).

Naming of Inventor (Rule 4.1(a)(v) and (c)(i)). The inventor's name and address must be indicated since the national law of the United States of America requires that the name of the inventor be furnished at the time of filing. It is strongly recommended to always name the inventor. For details, see the *PCT Applicant's Guide*, Volume I/A, Annexes B1 and B2.

Different Inventors for Different Designated States (Rule 4.6(c)). Different persons may be indicated as inventors for different designated States (for example, where, in this respect, the requirements of the national laws of the designated States are not the same). In such a case, the Supplemental Box must be used (see item 1(iii) in that Box). In the absence of any indication, it will be assumed that the inventor(s) named is (are) inventor(s) for all designated States.

Names and Addresses (Rule 4.4). The family name (preferably in capital letters) must be indicated before the given name(s). Titles and academic degrees must be omitted. Names of legal entities must be indicated by their full official designations.

The address must be indicated in such a way that it allows prompt postal delivery, it must consist of all the relevant administrative units (up to and including the indication of the house number if any) the postal code (if any) and the name of the country

Only one address may be indicated per person. For the indication of a special address for correspondence see the notes to Box No. IV

Telephone, Facsimile and/or Teleprinter Numbers should be indicated for the person named in Box No. II in order to allow rapid communication with the applicant. Any such number should include the applicable country and area codes

Applicant's Registration Number with the Office (Rule 4.5(e)). Where the applicant is registered with the national or regional Office acting as receiving Office, the request may indicate the number or other indication under which the applicant is so registered

Nationality (Rules 4.5(a) and (b) and 18.1). For each applicant, the nationality must be indicated by the name or two-letter code of the State (that is, country) of which the person is a national. A legal entity constituted according to the national law of a State is considered a national of that State. The indication of the nationality is not required where a person is inventor only

Residence (Rules 4.5(a) and (c) and 18.1). For each applicant, the residence must be indicated by the name or two-letter code of the State (that is, country) of which the person is a resident. If the State of residence is not indicated, it will be assumed to be the same as the State indicated in the address. Possession of a real and effective industrial or commercial establishment in a State is considered residence in that State. The indication of the residence is not required where a person is inventor only

Names of States (Section 115). For the indication of names of States, the two-letter codes appearing in WIPO Standard ST 3 and in the *PCT Applicant's Guide* Volume I/B, Annex K, may be used

BOX No. IV

Who Can Act as Agent (Article 49 and Rule 83.1(b)). For each of the receiving Offices, information as to who can act as agent is given in the *PCT Applicant's Guide* Volume I/B, Annex C

Agent or Common Representative (Rules 4.7, 4.8, 90.1 and 90.2 and Section 108). Mark the applicable check box in order to indicate whether the person named is (or has been) appointed as agent or common representative (the "common representative" must be one of the applicants). For the manner in which name(s) and address(es) (including names of States) must be indicated, see the notes to Boxes Nos. II and III. Where several agents are listed, the agent to whom correspondence should be addressed is to be listed first. If there are two or more applicants but no common agent is appointed to represent all of them, one of the applicants who is a national or resident of a PCT Contracting State may be appointed by the other applicants as their common representative. If this is not done, the applicant first named in the request who is entitled to file an international application with the receiving Office concerned will be considered to be the common representative

Manner of Appointment of Agent or Common Representative (Rules 90.4 and 90.5 and Section 106). The appointment of an agent or a common representative may be effected by designating the agent or common representative in Box No. IV and by the applicant signing the request or a separate power of attorney. Where there are two or more applicants, the appointment of a common agent or common representative must be effected by each applicant signing, at his choice, the request or a separate power of attorney. If the

separate power of attorney is not signed, or if the required separate power of attorney is missing, or if the indication of the name or address of the appointed person does not comply with Rule 4.4, the power of attorney will be considered non-existent unless the defect is corrected. However, the receiving Office may waive the requirement that a separate power of attorney be submitted to it (for details about each receiving Office, see the *PCT Applicant's Guide* Volume I/B, Annex C)

Where a general power of attorney has been filed and is referred to in the request, a copy thereof must be attached to the request. Any applicant who did not sign the general power of attorney must sign either the request or a separate power of attorney, unless the receiving Office has waived the requirement that a separate power of attorney be submitted to it (for details, see the *PCT Applicant's Guide* Volume I/B, Annex C)

Agent's Registration Number with the Office (Rule 4.7(b)). Where the agent is registered with the national or regional Office that is acting as receiving Office, the request may indicate the number or other indication under which the agent is so registered

Address for Correspondence (Rule 4.4(d) and Section 108). Where an agent is appointed, any correspondence intended for the applicant will be sent to the address indicated for that agent (or for the first-mentioned agent, if more than one is appointed). Where one of two or more applicants is appointed as common representative, the address indicated for that applicant in Box No. IV will be used

Where no agent or common representative is appointed, any correspondence will be sent to the address indicated in Box No. II or III of the applicant (if only one person is named as applicant) or of the applicant who is considered to be common representative (if there are two or more persons named as applicants). However, if the applicant wishes correspondence to be sent to a different address in such a case, that address must be indicated in Box No. IV instead of the designation of an agent or common representative. In this case and only in this case, the last check box of Box No. IV must be marked (that is, the last check box must not be marked if either of the check-boxes "agent" or "common representative" has been marked)

BOX No. V

Designations (Regional and national patents) (Rule 4.9). Upon filing of the request, the applicant will obtain an automatic and all-inclusive coverage of all designations available under the PCT on the international filing date, in respect of every kind of protection available and where applicable in respect of both regional and national patents. If the applicant wishes the international application to be treated in a certain designated or elected State, as an application not for a patent but for another kind of protection available under the national law of the designated or elected State concerned, the applicant will have to indicate his choice directly to the designated or elected Office when performing the acts, referred to in Articles 22 or 39(1), for entry into the national phase. For details about various kinds of protection available in designated or elected States, see the *PCT Applicant's Guide* Volume I/A, Annexes B1 and B2

However, for the reasons explained below, it is possible to indicate, by marking the applicable check box(es), that DE Germany, KR Republic of Korea and/or RU Russian Federation are not designated for any kind of national protection. Each of those States has notified the International Bureau that Rule 4.9(b) applies to it since its national law provides that the filing of an international application which contains the designation of that State and claims the priority of an earlier national application (for DE, for the same kind of protection) having effect in that State shall have the result that the earlier national application ceases, where applicable, after the expiration of certain time limits, to have effect with the same consequences as the withdrawal of the earlier national application. The designation of DE Germany for the purposes of a EP European patent and of

RU Russian Federation for the purposes of a EA Eurasian patent are not affected by what is said above. For details see the *PCT Applicant's Guide* Volume I/A in the relevant Annex B1

Even though no other State has notified the International Bureau that Rule 4 9(b) applies to it, note that the consequences described above with respect to the earlier national application whose priority is claimed may also apply to other States for example JP Japan. For details, see the *PCT Applicant's Guide* Volume I/A, in the relevant Annex B1. Therefore the applicant may wish to consider submitting separately from the request, a separate notice of withdrawal of the designation concerned. Important: Should a notice of withdrawal be filed that notice will have to be signed by the applicant or, if there are two or more applicants, by all of them (Rule 90bis.5(a)), or by an agent or a common representative whose appointment has been effected by each applicant signing, at his choice the request, the demand or a separate power of attorney (Rule 90.4(a)).

BOX No VI

Priority Claims(s) (Rule 4 10) If the priority of an earlier application is claimed, the declaration containing the priority claim must be made in the request.

The request must indicate the *date* on which the earlier application from which priority is claimed was filed and the *number* it was assigned. Note that that date must fall within the period of 12 months preceding the international filing date.

Where the earlier application is a national application the *country* party to the Paris Convention for the Protection of Industrial Property or the *Member* of the World Trade Organization that is not a party to that Convention, in which that earlier application was filed must be indicated. Where the earlier application is a regional application the *regional Office* concerned must be indicated. Where the earlier application is an international application, the *receiving Office* with which that earlier application was filed must be indicated.

Where the earlier application is a regional application (other than an ARIPO application), or an international application, the priority claim may also, if the applicant so wishes, indicate one or more countries party to the Paris Convention for which that earlier application was filed (Rule 4 10(b)(i)). Such an indication is not, however, mandatory. Where the earlier application is an ARIPO application at least one country party to the Paris Convention or one Member of the World Trade Organization for which that earlier application was filed must be indicated (Rule 4 10(b)(ii)).

As to the possibility of correcting or adding a priority claim see Rule 26bis and the *PCT Applicant's Guide* Volume I/A General Part.

Certified Copy of Earlier Application (Rule 17 1) A certified copy of each earlier application the priority of which is claimed (priority document) must be submitted by the applicant irrespective of whether that earlier application is a national, regional or international application. The priority document must be submitted to the receiving Office or to the International Bureau before the expiration of 16 months from the (earliest) priority date or, where an early start of the national phase is requested, not later than at the time such request is made. Any priority document received by the International Bureau after the expiration of the 16-month time limit but before the date of international publication shall be considered to have been received on the last day of that time limit (Rule 17 1(a)).

Where the priority document is issued by the receiving Office, the applicant may instead of submitting the priority document, request the receiving Office (not later than 16 months after the priority date) to prepare and transmit the priority document to the International Bureau (Rule 4 1(c)(ii)). Such request may be made by marking the applicable check boxes which identify the respective documents. *Attention:* where

such a request is made, the applicant must, where applicable pay to the receiving Office the *fee for priority document* otherwise the request will be considered not to have been made (see Rule 17 1(b)).

Dates (Section 110) Dates must be indicated by the Arabic number of the day, the name of the month and the Arabic number of the year—in that order, after, below or above such indication, the date should be repeated in parentheses using two-digit Arabic numerals each for the number of the day and for the number of the month followed by the number of the year in four digits, in that order and separated by periods, slants or hyphens for example “20 March 2004 (20 03 2004)” “20 March 2004 (20/03/2004)” or “20 March 2004 (20-03 2004)”

BOX No. VII

Choice of International Searching Authority (ISA) (Rules 4 1(b)(iv) and 4 14bis) If two or more International Searching Authorities are competent for carrying out the international search in relation to the international application—depending on the language in which that application is filed and the receiving Office with which it is filed—the name of the competent Authority chosen by the applicant must be indicated in the space provided either by its full name or two letter code.

Request to Use Results of Earlier Search, Reference to that Search (Rules 4 11(a)(i) and (ii) and 4 11) The earlier search, if any, must be identified in such a manner that the ISA can retrieve the results easily. Where those results can be used the ISA may refund the international search fee or a portion thereof.

BOX No. VIII

Declarations Containing Standardized Wording (Rules 4 1(c)(iii) and 4 17) At the option of the applicant, the request may, for the purposes of the national law applicable in one or more designated States, contain one or more of the following declarations.

- (i) declaration as to the identity of the inventor
- (ii) declaration as to the applicant's entitlement, as at the international filing date, to apply for and be granted a patent
- (iii) declaration as to the applicant's entitlement, as at the international filing date, to claim the priority of the earlier application
- (iv) declaration of inventorship (only for the purposes of the designation of the United States of America),
- (v) declaration as to non prejudicial disclosures or exceptions to lack of novelty

which must conform to the standardized wording provided for in Sections 211 to 215 respectively, and which must be set forth in Boxes Nos VIII (i) to (v), as detailed below. Where any such declarations are included, the appropriate check boxes in Box No VIII should be marked and the number of each type of declaration should be indicated in the right hand column. As to the possibility of correcting or adding a declaration see Rule 26ter, Section 216 and the *PCT Applicant's Guide* Volume I/A General Part.

If the circumstances of a particular case are such that the standardized wordings are not applicable, the applicant should not attempt to make use of the declarations provided for in Rule 4 17 but rather will have to comply with the national requirements concerned upon entry into the national phase.

The fact that a declaration is made under Rule 4 17 does not of itself establish the matters declared; the effect of those matters in the designated States concerned will be determined by the designated Offices in accordance with the applicable national law.

Even if the wording of a declaration does not conform to the standardized wording provided for in the Administrative Instructions pursuant to Rule 4 17 any designated Office may accept that declaration for the purposes of the applicable national law but is not required to do so

Details as to National Law Requirements For information on the declarations required by each designated Office see the *PCT Applicant's Guide* Volume II in the relevant National Chapter

Effect in Designated Offices (Rule 51bis 2) Where the applicant submits any of the declarations provided for in Rule 4 17(i) to (iv) containing the required standardized wording (either with the international application or to the International Bureau within the relevant time limit under Rule 26ter or directly to the designated Office during the national phase) the designated Office may not in the national phase, require further documents or evidence on the matter to which the declaration relates unless that designated Office may reasonably doubt the veracity of the declaration concerned.

Incompatibility of Certain Items of Rule 51bis 2(a) with National Laws (Rule 51bis 2(e)) Certain designated Offices listed below have informed the International Bureau that the applicable national law is not compatible in respect of certain declarations provided in Rule 4 17(i) (ii) and (iii) Those designated Offices are therefore entitled to require further documents or evidence on the matters to which those declarations relate For regularly updated information on such Offices, see the WIPO Website http://www.wipo.int/pct/en/texts/reservations/rea_incomp.pdf

BOXES Nos. VIII (i) to (v) (IN GENERAL)

Different Declaration Boxes There are six different declaration boxes in the pre-printed request form—one box for each of the five different types of declarations provided for in Rule 4 17 (Box No VIII (i) to Box No VIII (v)) and a continuation sheet (Continuation of Box No VIII (i) to (v)) to be used in case any single declaration does not fit in the corresponding box The title of each type of declaration which is found in the standardized wording provided for in the Administrative Instructions is pre printed on the appropriate sheet of the request

Separate Sheet for Each Declaration Each declaration must start on a separate sheet of the request form in the appropriate Declaration Box

Titles Items Item Numbers, Dotted Lines, Words in Parentheses and Words in Brackets The prescribed standardized wording of the declarations includes titles, various items, item numbers, dotted lines, words in parentheses and words in brackets Except for Box No. VIII (iv) which contains the pre-printed standardized wording, only those items which are applicable should be included in a declaration where necessary to support the statements in that declaration (that is, omit those items which do not apply) and item numbers need not be included Dotted lines indicate where information is required to be inserted Words in parentheses are instructions to applicants as to the information which may be included in the declaration depending upon the factual circumstances. Words in brackets are optional and should appear in the declaration without the brackets if they apply if they do not apply they should be omitted together with the corresponding brackets

Naming of Several Persons More than one person may be named in a single declaration In the alternative with one exception a separate declaration may be made for each person With respect to the declaration of inventorship set forth in Box No VIII (iv) which is applicable only for the purposes of the

designation of the United States of America, all inventors must be indicated in a single declaration (see Notes to Box No VIII (iv), below) The wording of declarations to be set forth in Boxes Nos VIII (i), (ii), (iii) and (v) may be adapted from the singular to the plural as necessary

Designated States to Which the Declarations Apply Each declaration must indicate the designated States to which it applies In this regard, the standardized wording of the declaration of inventorship (Box No VIII (iv)) see also Rule 4 17(iv) and Section 214) indicates in the title that it is for the purposes of the designation of the United States of America. The other declarations include prescribed wording to indicate whether the declaration is made for all designations or specific designations, one of these choices should always be included in the declaration Where the declaration is for more than one person, the declaration may include separate statements indicating whether the declaration is made for all designations or specific designations with respect to each separate applicant For example this may be expected to occur where the request indicates different applicants for different States in accordance with Rule 4 5(d) However in such a case it is advisable to include a separate declaration for each person.

BOX No VIII (i)

Declaration as to the Identity of the Inventor (Rule 4 17(i) and Section 211) The declaration must be worded as follows

Declaration as to the identity of the inventor (Rules 4 17(i) and 51bis 1(a)(i))

in relation to [this] international application [No PCT/]

- (i) (name) of (address) is the inventor of the subject matter for which protection is sought by way of [the] [this] international application
- (ii) this declaration is made for the purposes of (include as applicable)
 - (a) all designations [except the designation of the United States of America]
 - (b) the following designations for national and/or regional patents

Such a declaration is not necessary in respect of any inventor who is indicated as such (either as inventor only or applicant and inventor) in Box No II or No III in accordance with Rule 4 5 or 4 6 However where the inventor is indicated as applicant in Box No. II or No III in accordance with Rule 4 5 a declaration as to the applicant's entitlement to apply for and be granted a patent (Rule 4 17(ii)) may be appropriate for the purposes of all designated States except the United States of America. Where indications regarding the inventor in accordance with Rule 4 5 or 4 6 are not included in Box No II or No III this declaration may be combined with the prescribed wording of the declaration as to the applicant's entitlement to apply for and be granted a patent (Rule 4 17(ii)) For details on such a combined declaration, see Notes to Box No VIII (ii) below For details as to the declaration of inventorship for the purposes of the designation of the United States of America, see Notes to Box No VIII (iv), below

BOX No VIII (ii)

Declaration as to the Applicant's Entitlement to Apply for and Be Granted a Patent (Rule 4 17(ii) and Section 212) The declaration must be worded as follows, with such inclusion omission repetition and re-ordering of the matters listed as items (i) to (viii) as is necessary to explain the applicant's entitlement

"Declaration as to the applicant's entitlement, as at the international filing date, to apply for and be granted a patent (Rules 4 17(ii) and 51bis 1(a)(ii)) in a case where the declaration under Rule 4 17(iv) is not appropriate

in relation to [this] international application [No PCT/]

(name) is entitled to apply for and be granted a patent by virtue of the following

- (i) (name) of (address) is the inventor of the subject matter for which protection is sought by way of [the] [this] international application
- (ii) (name) [is] [was] entitled as employer of the inventor (inventor's name)
- (iii) an agreement between (name) and (name), dated
- (iv) an assignment from (name) to (name) dated
- (v) consent from (name) in favor of (name) dated
- (vi) a court order issued by (name of court) effecting a transfer from (name) to (name) dated
- (vii) transfer of entitlement from (name) to (name) by way of (specify kind of transfer) dated
- (viii) the applicant's name changed from (name) to (name) on (date)
- (ix) this declaration is made for the purposes of (include as applicable)
 - (a) all designations [except the designation of the United States of America]
 - (b) the following designations for national and/or regional patents

Either (a) or (b) of item (ix) should always be included in the declaration. The remainder of the items may be incorporated as is necessary to explain the applicant's entitlement. *This declaration is only applicable to those events which have occurred prior to the international filing date.* The possible kinds of transfer of entitlement in item (vii) include merger, acquisition, inheritance, donation, etc. Where there has been a succession of transfers from the inventor, the order in which transfers are listed should follow the actual succession of transfers, and items may be included more than once as necessary to explain the applicant's entitlement. Where the inventor is not indicated in Box No II or No III, this declaration may be presented as a combined declaration explaining the applicant's entitlement to apply for and be granted a patent and identifying the inventor. In such a case, the introductory phrase of the declaration must be as follows:

"Combined declaration as to the applicant's entitlement as at the international filing date to apply for and be granted a patent (Rules 4 17(ii) and 51bis 1(a)(ii)) and as to the identity of the inventor (Rules 4 17(i) and 51bis 1(a)(i)), in a case where the declaration under Rule 4 17(iv) is not appropriate."

The remainder of the combined declaration must be worded as indicated in the preceding paragraphs.

For details as to the declaration as to the identity of the inventor, see the Notes to Box No VIII (i), above.

BOX No VIII (iii)

Declaration as to the Applicant's Entitlement to Claim Priority of the Earlier Application (Rule 4 17(iii) and Section 213). The declaration must be worded as follows, with such inclusion, omission, repetition and re-ordering of the matters listed as items (i) to (viii) as is necessary to explain the applicant's entitlement:

"Declaration as to the applicant's entitlement, as at the international filing date, to claim the priority of the earlier application specified below, where the applicant is not the applicant who filed the earlier application or where the applicant's name has changed since the filing of the earlier application (Rules 4 17(iii) and 51bis 1(a)(iii))."

in relation to [this] international application [No PCT/],

(name) is entitled to claim priority of earlier application No. by virtue of the following:

- (i) the applicant is the inventor of the subject matter for which protection was sought by way of the earlier application
- (ii) (name) [is] [was] entitled as employer of the inventor (inventor's name)
- (iii) an agreement between (name) and (name), dated
- (iv) an assignment from (name) to (name) dated
- (v) consent from (name) in favor of (name), dated
- (vi) a court order issued by (name of court) effecting a transfer from (name) to (name) dated
- (vii) transfer of entitlement from (name) to (name) by way of (specify kind of transfer) dated
- (viii) the applicant's name changed from (name) to (name) on (date)
- (ix) this declaration is made for the purposes of (include as applicable)
 - (a) all designations
 - (b) the following designations for national and/or regional patents

Either (a) or (b) of item (ix) should always be included in the declaration. The remainder of the items may be incorporated as is necessary to explain the applicant's entitlement. *This declaration is only applicable to those events which have occurred prior to the international filing date.* In addition, this declaration is only applicable where the person or name of the applicant is different from that of the applicant who filed the earlier application from which priority is claimed. For example, this declaration may be applicable where only one applicant out of five is different from the applicants indicated in respect of an earlier application. The possible kinds of transfer of entitlement in item (vii) include merger, acquisition, inheritance, donation, etc. Where there has been a succession of transfers from the applicant in respect of the earlier application, the order in which transfers are listed should follow the actual succession of transfers, and items may be included more than once, as necessary to explain the applicant's entitlement.

BOX No. VIII (iv)

Declaration of Inventorship (Rule 4 17(iv) and Section 214). The standardized wording for the declaration is pre-printed in Box No. VIII (iv).

All inventors must be named in the declaration, even if they do not all sign the same (copy of) the declaration (Section 214(b)). Bibliographic data, such as address of residence and citizenship, must be included for each inventor. Where the declaration is included in the request, the inventor(s) need not sign and date the declaration if they have signed in Box No. X of the request. If there are more than two inventors, those other inventors must be indicated on the "continuation sheet for declaration." In such a case, write "Continuation of Box No. VIII (iv)" and indicate only the bibliographical data in respect of each inventor. The text of the declaration itself should not be repeated on that continuation sheet. The inventor(s) identified on the continuation sheet must sign and date such sheet unless the declaration, including the continuation sheet, is included with the request and the inventor(s) has (have) signed in Box No. X of the request.

BOX No. VIII (v)

Declaration as to Non-prejudicial Disclosures or Exceptions to Lack of Novelty (Rule 4 17(v) and Section 215)
The declaration must be worded as follows, with such inclusion, omission repetition and re-ordering of the matters listed as items (i) to (iv) as is necessary

Declaration as to non-prejudicial disclosures or exceptions to lack of novelty (Rules 4 17(v) and 51bis 1(a)(v))

in relation to [this] international application [No PCT/]

(name) declares that the subject matter claimed in [the] [this] international application was disclosed as follows

- (i) kind of disclosure (include as applicable)
 - (a) international exhibition
 - (b) publication
 - (c) abuse
 - (d) other (specify)
- (ii) date of disclosure
- (iii) title of disclosure (if applicable)
- (iv) place of disclosure (if applicable)
- (v) this declaration is made for the purposes of (include as applicable)
 - (a) all designations
 - (b) the following designations for national and/or regional patents

Either (a), (b), (c) or (d) of item (i) should always be included in the declaration. Item (ii) should also always be included in the declaration. Either (a) or (b) of item (v) should always be included in the declaration. Items (iii) and (iv) may be incorporated depending upon the circumstances

BOX No IX

Items Constituting the International Application The number of sheets of the various parts of the international application must be given in the check list in Arabic numerals. Sheets containing any of Boxes Nos VIII (i) to (v) must be counted as part of the request

Where the application contains disclosure of one or more *nucleotide and/or amino acid sequences* the applicant has the following three options.

First, the applicant may choose to file the sequence listing and/or tables related thereto *in paper form only* ("option (a)"), in which case the number of sheets of the listing and/or tables, respectively must be indicated under item (a) in the left column of Box No IX (and therefore included in the total number of sheets) noting that a copy of the sequence listing and/or a copy of the tables in computer readable form, may accompany the international application but only for the purposes of international search under Rule 13ter and/or Section 802(b-quater) in such a case check boxes Nos 9 9(i) and/or 10(i) and, where applicable 9(iii) and/or 10(iii) must be marked in the right column of Box No IX

Second, the applicant may choose to file the sequence listing and/or tables related thereto *in computer readable form only* under Section 801(a)(i) ("option (b)"), in which case check boxes b(i) and/or b(ii) must be marked but the spaces for the number of sheets of the sequence listing and/or tables respectively under item (a) must be left blank the type and number of carriers must also be indicated on the dotted lines at the bottom of the left column in addition check boxes Nos 9 9(ii) and/or 10(ii) and where applicable 9(iii) and/or 10(iii) must be marked if additional copies of the sequence listing and/or tables in computer readable form are furnished.

Third the applicant may choose to file the sequence listing and/or tables related thereto *both in computer readable form*

and *in paper form* under Section 801(a)(ii) ("option (c)"), in which case the number of sheets (in paper form) of the sequence listing and/or tables, respectively must be indicated under item (a) in the left column of Box No IX (although those numbers of sheets will not be taken into account for calculation of the international filing fee) and check boxes c(i) and/or c(ii) respectively must be marked, the type and number of carriers must also be indicated on the dotted lines at the bottom of the left column in addition, check boxes Nos 9 9(ii) and/or 10(ii) and, where applicable 9(iii) and/or 10(iii) must be marked if additional copies of the sequence listing and/or tables in computer readable form are furnished

Under all three options described above the sequence listing must be presented as a separate part of the description ("sequence listing part of description") in accordance with the standard contained in Annex C of the Administrative Instructions. Also tables related to sequence listing must be presented in accordance with the standard contained in Annex C-bis of the Administrative Instructions

Items Accompanying the International Application
Where the international application is accompanied by certain items the applicable check boxes must be marked any applicable indication must be made on the dotted line after the applicable item, and the number of such items should be indicated at the end of the relevant line, detailed explanations are provided below only in respect of those items which so require

Check-box No 4 Mark this checkbox where a copy of a general power of attorney is filed with the international application where the general power of attorney has been deposited with the receiving Office, and that Office has accorded to it a reference number that number may be indicated

Check-box No 5 Mark this checkbox where a statement explaining the lack of signature of an inventor/applicant for the purposes of the United States of America is furnished together with the international application (see also Notes to Box No X)

Check-box No 7 Mark this checkbox where a translation of the international application for the purposes of international search (Rule 12.3) is filed together with the international application and indicate the language of that translation

Check-box No 8 Mark this checkbox where a filled-in Form PCT/RO/134 or any separate sheet containing indications concerning deposited microorganisms and/or other biological material is filed with the international application. If Form PCT/RO/134 or any sheet containing the said indications is included as one of the sheets of the description (as required by certain designated States (see the *PCT Applicant's Guide* Volume I/B Annex L)) do not mark this checkbox (for further information, see Rule 13bis and Section 209)

Check-box No 9 Where the international application contains a sequence listing and a copy thereof in computer readable form is required by the ISA under Rule 13ter the applicant may furnish the listing in computer readable form (together with the required statement) to the receiving Office with the international application in which case check boxes Nos 9 9(i) and, where applicable, 9(iii) must be marked. Where the applicant has chosen option (b) or option (c) mentioned above and an additional copy or copies of the sequence listing in computer readable form are required under Section 804 the applicant may furnish such additional copies together with the international application in which case check boxes Nos 9 9(ii) and, where applicable 9(iii) must be marked. In all cases mentioned above, the applicant should indicate at the end of each applicable entry the type and number of diskettes CD-ROMs, CD Rs, or other data carriers furnished

Check box No 10 Where the international application contains tables related to a sequence listing and a copy thereof in computer readable form is required by the ISA under Section 802(b-quater), the applicant may furnish the tables in

computer readable form (together with the required statement) to the receiving Office with the international application in which case check boxes Nos 10 10(i) and where applicable 10(iii) must be marked. Where the applicant has chosen option (b) or option (c) mentioned above and an additional copy or copies of the tables in computer readable form are required under Section 804 the applicant may furnish such additional copies together with the international application in which case check boxes Nos 10 10(ii) and where applicable 10(iii) must be marked. In all cases mentioned above the applicant should indicate at the end of each applicable entry the type and number of diskettes, CD-ROMs, CD-Rs or other data carriers furnished.

Language of Filing of the International Application (Rules 12 1(a) and 20 4(c) and (d)). With regard to the language in which the international application is filed, for the purposes of according an international filing date it is subject to the following sentence, sufficient that the description and the claims are in the language or one of the languages accepted by the receiving Office for the filing of international applications that language should be indicated in that check box (as regards the language of the abstract and any text matter in the drawings, see Rule 26 3ter(a) and (b) as regards the language of the request, see Rules 12 1(c) and 26 3ter(c) and (d)). Note that where the international application is filed with the United States Patent and Trademark Office as receiving Office, all elements of the international application (request, description, claims abstract text matter or drawings) must for the purposes of according an international filing date, be in English except that the free text in any sequence listing part of the description, complying with the standard set out in Annex C of the Administrative Instructions, may be in a language other than English.

BOX No X

Signature (Rules 4 1(d), 4 15 26 2bis(a) 51bis 1(a)(vi) 90 and 90bis 5). The signature must be that of the applicant if there are several applicants all must sign. However if the signature of one or more of the applicants is missing, the receiving Office will not invite the applicant to furnish the missing signature(s) provided that at least one of the applicants signed the request.

Important Should a notice of withdrawal be filed at any time during the international phase that notice will have to be signed by the applicant or, if there are two or more applicant's by all of them (Rule 90bis 5(a)), or by an agent or a common representative whose appointment has been effected by each applicant signing, at his choice, the request, the demand or a separate power of attorney (Rule 90 4(a)).

Furthermore for the purposes of the national phase processing, each designated Office will be entitled to require the applicant to furnish the confirmation of the international application by the signature of any applicant for the designated State concerned who has not signed the request.

Where the signature on the request is not that of the applicant but that of the agent, or the common representative a separate power of attorney appointing the agent or the common representative respectively or a copy of a general power of attorney already in the possession of the receiving Office must be furnished. If the power is not filed with the request the receiving Office will invite the applicant to furnish it, unless it has waived the requirement for a separate power of attorney (for details about each receiving Office see the *PCT Applicant's Guide* Volume I/B Annex C).

If an inventor/applicant for the designation of the United States of America refused to sign the request or could not be found or reached after diligent effort, a statement explaining the

lack of signature may be furnished. It should be noted that this applies only where there are two or more applicants and the international application has been signed by at least one other applicant. The statement must satisfy the receiving Office. If such a statement is furnished with the international application check box No 5 in Box No IX should be marked.

SUPPLEMENTAL BOX

The cases in which the Supplemental Box may be used and the manner of making indications in it are explained in the left column of that Box.

Items 2 and 3. Even if an indication is made in respect of items 2 and 3 under Rule 49bis 1(a), (b) or (d) the applicant will be required to make an indication to this effect upon entry into the national phase before the designated offices concerned.

If the applicant wishes to specify that the international application be treated in any designated State as an application for a utility model see Notes to Box No V.

GENERAL REMARKS

Language of Correspondence (Rule 92 2 and Section 104). Any letter from the applicant to the receiving Office must be in the language of filing of the international application provided that, where the international application is to be published in the language of a translation required under Rule 12 3 such letter should be in the language of that translation however the receiving Office may authorize the use of another language.

Any letter from the applicant to the International Bureau must be in the same language as the international application if that language is English or French otherwise, it must be in English or French, at the choice of the applicant.

Any letter from the applicant to the ISA must be in the same language as the international application, provided that, where a translation of the international application for the purposes of international search has been transmitted under Rule 23 1(b) such letter is in the language of that translation. However the ISA may authorize the use of another language.

Arrangement of Elements and Numbering of Sheets of the International Application (Rule 11 7 and Section 207). The elements of the international application must be placed in the following order: the request, the description (excluding the sequence listing part, if any), the claim(s), the abstract, the drawings (if any), the sequence listing part of the description (if any).

All sheets of the description (excluding the sequence listing part) claims and abstract must be numbered in consecutive Arabic numerals, which must be placed at the top or bottom of the sheet, in the middle but not in the margin which must remain blank. The number of each sheet of the drawings must consist of two Arabic numerals separated by an oblique stroke, the first being the sheet number and the second being the total number of sheets of drawings (for example, 1/3 2/3 3/3). For numbering of the sheets of the sequence listing part of the description, see Section 207.

Indication of the Applicant's or Agent's File Reference on the sheets of the description (excluding the sequence listing part, if any) claim(s), abstract, drawings and sequence listing part of the description (Rule 11 6(f)). The file reference indicated on the request may also be indicated in the left hand corner of the top margin within 1.5 cm from the top of any 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

11449P1 WO/JMH

Applicant

Reckitt Benckiser (UK) Limited et al

CALCULATION OF PRESCRIBED FEES

1 TRANSMITTAL FEE

55 00 T

2 SEARCH FEE

1078 00 S

International search to be carried out by

(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 items (b) and/or (c) of Box No IX apply enter Sub-total number of sheets

23

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

11 first 30 sheets

628 00 11

12

number of sheets
in excess of 30

x

fee per sheet

12

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

fee per sheet

13

Add amounts entered at 11 12 and 13 and enter total at 1

628 00 T

(Applicants from certain States are entitled to a reduction of 75% of the international filing fee. Where the applicant is (or all applicants are) so entitled, the total to be entered at 1 is 25% of the international filing fee.)

4 FEE FOR PRIORITY DOCUMENT (if applicable)

22 00 P

5 TOTAL FEES PAYABLE

1783 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

☐ coupons

☐ cheque

☐ bank draft

☐ revenue stamps

☐ other (specify)

AUTHORIZATION TO CHARGE (OR CREDIT) DEPOSIT ACCOUNT

(This mode of payment may not be available at all receiving Offices)

☒ Authorization to charge the total fees indicated above

☒ (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

☒ Authorization to charge the fee for priority document

Receiving Office RO/ United Kingdom

Deposit Account No D02903

Date 16 June 2005

Name Craig Bowers

Signature

The purpose of the fee calculation sheet is to help the applicant to identify the prescribed fees and to calculate the amounts to be paid. It is strongly recommended that the applicant complete the sheet by entering the appropriate amounts in the boxes provided and submit the fee calculation sheet at the time of filing the international application. This will help the receiving Office to verify the calculations and to identify any error in them.

Information about the applicable fees payable can be obtained from the receiving Office. The amounts of the international filing and search fees may change due to currency fluctuations. Applicants are advised to check what are the latest applicable amounts. All fees must be paid within one month from the date of receipt of the international application.

CALCULATION OF PRESCRIBED FEES

Box T Transmittal Fee for the benefit of the receiving Office (Rule 14.1). The amount of the transmittal fee, if any, is fixed by the receiving Office. It must be paid within one month from the date of receipt of the international application by the receiving Office. Information about this fee is contained in the *PCT Applicant's Guide*, Volume I/B, Annex C.

Box S Search Fee for the benefit of the International Searching Authority (ISA) (Rule 16.1). The amount of the search fee is fixed by the ISA. It must be paid within one month from the date of receipt of the international application by the receiving Office. Information about this fee is contained in the *PCT Applicant's Guide*, Volume I/B, Annex D.

Where two or more ISAs are competent, the applicant must indicate his choice in the space provided for this purpose and pay the amount of the international search fee fixed by the ISA chosen. Information on the competent ISA and whether the applicant has a choice between two or more ISAs is contained in the *PCT Applicant's Guide*, Volume I/B, Annex C.

Box I International Filing Fee for the benefit of the International Bureau (Rule 15). The amount of the international filing fee is as set out in Swiss francs in the Schedule of Fees and the applicable amount of this fee in other currencies is as published in the *PCT Gazette* (Rule 15.2). Information about this fee is also contained in the *PCT Applicant's Guide*, Volume I/B, Annex C.

Reduction of the International Filing Fee Where PCT-EASY Software Is Used. A fee reduction of 100 Swiss francs (or the equivalent in the currency in which the international filing fee is paid to the receiving Office) is available in certain cases where the PCT EASY software is used to prepare the request, provided that the necessary conditions are met. For further details, see the *PCT Applicant's Guide*, Volume I/A, General Part, and Volume I/B, Annex C, as well as information published in the *PCT Gazette* and the *PCT Newsletter*. Since applicants using the PCT EASY software will file the Request Form and Fee Calculation Sheet in the form of a printout prepared using that software, no provision is made for this fee reduction in the Fee Calculation Sheet annexed to Form PCT/RO/101.

Reduction of the International Filing Fee Where the International Application Is Filed in Electronic Form. The international filing fee is reduced by 200 Swiss francs (or the equivalent in the currency in which the international filing fee is paid to the receiving Office) if the international application is, in accordance with and to the extent provided for in Part 7 and Annex F of the Administrative Instructions, filed in electronic form where the text of the description, claims and abstract is not in character coded format, or by 300 Swiss francs (or the equivalent in the currency in which the international filing fee is paid to the receiving Office) where the international application is filed in electronic form where the text of the description, claims and abstract is in character coded format. For further details, see the *PCT Applicant's*

Guide, Volume I/A, General Part, and Volume I/B, Annex C, as well as information published in the *PCT Gazette* and the *PCT Newsletter*. Since international applications filed in electronic form will contain the Request Form and Fee Calculation Sheet in such electronic form, no provision is made for this fee reduction in the Fee Calculation Sheet annexed to Form PCT/RO/101.

Reduction of the International Filing Fee for Applicants from Certain States. An applicant who is a natural person and who is a national of and resides in a State whose per capita national income is below 3 000 US dollars (according to the average per capita national income figures used by the United Nations for determining its scale of assessments for the contributions payable for the years 1995, 1996 and 1997) or an applicant, whether a natural person or not, who is a national of and resides in a State that is classed as a least developed country by the United Nations, is entitled, to a reduction of 75% of certain PCT fees including the international filing fee. If there are several applicants, each must satisfy the above mentioned criteria. The reduction of the international filing fee is automatically available to any applicant (or applicants) who is (or are) so entitled on the basis of the indications of name, nationality and residence given in Boxes Nos. II and III of the request.

The fee reduction is available even if one or more of the applicants are not from PCT Contracting States, provided that each of them is a national and resident of a State that meets the above-mentioned requirements and that at least one of the applicants is a national or resident of a PCT Contracting State and thus is entitled to file an international application.

Information about PCT Contracting States whose nationals and residents are entitled to a reduction of 75% of certain PCT fees, including the international filing fee, is contained in the *PCT Applicant's Guide*, Volume I/B, Annex C and on the WIPO Website (see <http://www.wipo.int/pct/en/index.html>) and is also published and regularly updated in the *PCT Gazette* and the *PCT Newsletter*.

Calculation of the International Filing Fee in Case of Fee Reduction. Where the applicant is (or all applicants are) entitled to a reduction of the international filing fee, the total to be entered in box I is 25% of the international filing fee (see below).

Box I International Filing Fee. The amount of the international filing fee depends on the number of sheets of the international application indicated under item (a) of Box No. IX of the request as explained below.

That number is the Total number of sheets where items (b) and (c) of Box No. IX of the request do not apply (that is, where the international application either does not contain a sequence listing and/or tables related thereto or where it contains such listing and/or tables but not filed in computer readable form under Section 801(a)(i) or (ii)) in such a case item "3" must not be filled in.

Otherwise where items (b) and/or (c) of Box No IX of the request apply (that is, where the international application contains a sequence listing and/or tables related thereto which are filed in computer readable form only under Section 801(a)(i) or both in that form and in paper form under Section 801(a)(ii)), the number of sheets to be used for the purpose of calculating the amount of the international filing fee is the Sub-total number of sheets. In such a case item "13" must be filled in on the basis that the sequence listing and/or tables related thereto in computer readable form are considered to be equal to 400 sheets (see Section 803).

The international filing fee must be paid within one month from the date of receipt of the international application by the receiving Office.

Box P Fee for Priority Document (Rule 17.1(b)). Where the applicant has requested, by marking the applicable check box in Box No VI of the request, that the receiving Office prepare and transmit to the International Bureau a certified copy of the earlier application the priority of which is claimed, the amount of the fee prescribed by the receiving Office for such service may be entered (for information see the *PCT Applicant's Guide* Volume I/B Annex C).

If that fee is not paid at the latest before the expiration of 16 months from the priority date, the receiving Office may consider the request under Rule 17.1(b) as not having been made.

Total Box. The total of the amounts entered in boxes T, S, I and P should be entered in this box. If the applicant so wishes, the currency in which the fees are paid may be indicated next to or in the total box.

MODE OF PAYMENT

In order to help the receiving Office identify the mode of payment of the prescribed fees, it is recommended that the applicable check-box(es) be marked.

AUTHORIZATION TO CHARGE (OR CREDIT) DEPOSIT ACCOUNT

The receiving Office will not charge (or credit) fees to deposit accounts unless the deposit account authorization is signed and indicates the deposit account number.

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Published.

— with international search report

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

WO 2005/123969 A1

(54) Title: POLISH COMPOSITION FOR LEATHER OR SYNTHETIC LEATHER

(57) Abstract: A polish composition for treating a leather and/or synthetic leather article, said composition comprising water at least one way at least one film forming polymer and a layered silicate incorporating an inorganic peptizer.

Polish Composition for Leather or Synthetic Leather

This invention relates to a polish composition suitable for treating leather and/or synthetic leather articles. In particular, although not exclusively, this invention relates to self-shining polish compositions.

Polish compositions are often used to impart a shine to leather and synthetic leather articles, such as items of footwear. Conventional polish compositions are typically formed of wax and organic solvents. Such polishes dry to form a dull finish on the treated article. Subsequent buffing is required to provide the article with a shiny finish.

Self-shining polishes in liquid form have been developed to allow a shine to be achieved without any buffing.

More recently, gel or cream self-shining compositions have also been developed. Such compositions are generally based on aqueous emulsions of wax and acrylic polymers. When applied to an article, the compositions dry to form a glossy finish. Buffing is not generally required to provide the treated article with the desired shine.

We have found that known self-shine polish compositions tend to suffer from storage problems. For example, when stored for prolonged periods, liquid may separate from the known compositions. The separation of liquid from the bulk of the composition is known as syneresis.

28

According to the present invention, there is provided a polish composition for treating leather and/or synthetic leather articles, said composition comprising

- water,
- 5 at least one wax,
- at least one film-forming polymer, and
- a layered silicate incorporating an inorganic peptiser

By including a layered silicate in the polish
10 composition, the storage problems of the polish composition can advantageously be reduced. In particular, the use of the layered silicate may reduce the likelihood of liquid separating from the polish composition even after prolonged periods of storage. The layered silicate, therefore, may be
15 used in the polish composition to reduce or prevent syneresis. The layered silicate may also help to ensure that the rheological properties of the polish composition are maintained, for example, to ensure ease of application

20 Preferably, the composition of the present invention is storage stable for at least 4 weeks, more preferably, at least 8 weeks, and most preferably, at least 12 weeks

Preferably, the layered silicate is a synthetic layered
25 silicate. The layered silicate may be a metal silicate, such as silicate of an alkali metal and/or alkali earth metal. Suitable alkali metal silicates include silicates of lithium, sodium and potassium. Suitable alkali earth metal silicates include silicates of magnesium and calcium.

30 Preferably, the metal silicate is a silicate of at least one alkali metal and at least one alkali earth metal. In one embodiment, sodium lithium magnesium silicate is employed

28

Preferably, the layered silicate comprises less than 2 weight %, more preferably, less than 1 weight %, even more preferably, less than 0.5 weight %, and most preferably, less than 0.1 weight % of crystalline silica. In one embodiment, the layered silicate is substantially free of crystalline silica.

The layered silicate may also have a low transition metal content. For example, the layered silicate may have a transition metal content of less than 2 weight %, more preferably less than 1 weight %, yet more preferably less than 0.5 weight %, for example, less than 0.1 weight %. In one embodiment, the layered silicate is substantially free of transition metal.

The layered silicate incorporates an inorganic peptiser. Preferably, the inorganic peptiser is a phosphate. Any suitable phosphate peptiser may be employed. However, metal phosphates, such as alkali metal and/or alkali earth metal phosphates are preferred. Suitable alkali metal phosphates include phosphates of lithium, sodium and potassium. Suitable alkali earth metal phosphates include phosphates of magnesium and calcium.

Preferably, the phosphate is a polyphosphate, such as a pyrophosphate. In a preferred embodiment, sodium tetrakis pyrophosphate is employed.

An example of a suitable layered silicate is Laptonite.
© RDS

The layered silicate is preferably provided in finely divided form

The layered silicate may be present in an amount of 0.01 to 5 weight % of the overall polish composition. Preferably, the layered silicate is present in an amount of 0.05 to 4 weight %, more preferably, 0.1 to 3 weight %, for example, 0.2 to 2 weight %. In a preferred embodiment, 0.4 to 1 weight %, for example, 0.5 to 0.7 weight % of layered silicate is employed.

The polish composition comprises at least one wax. Mixtures of one or more waxes may also be employed. Suitable waxes include insect waxes, such as beeswax, vegetable waxes, such as carnauba wax and candelilla wax, mineral ester waxes and acid waxes. Preferably, mineral ester waxes are employed. Suitable mineral ester waxes include montanic wax (e.g. montanic wax ester). Synthetic waxes, such as polyethylene wax (e.g. oxidised) and polyol ether/ester wax may also be employed. In a preferred embodiment, the polish composition comprises montanic wax ester and a synthetic wax, such as oxidised polyethylene wax. Where a montanic wax ester is employed, it may be a refined montanic wax ester.

The wax or wax mixture employed in the polish composition of the present invention preferably has an acid value of 5 to 50, preferably, 10 to 30.

The wax or wax mixture employed in the polish composition preferably has an average molecular weight of

500 to 5000, preferably, 1000 to 4000, for example, 2000 to 3000

5 The amount of wax in the polish composition may be 1 to 20 weight %, preferably, 2 to 15 weight %, more preferably, 5 to 10 weight % In a preferred embodiment, the polish composition comprises 1 to 6 (e g 2 to 4) weight % oxidised polyethylene wax and 2 to 10 (e g 3 to 8) weight % montanic wax ester

10

The polish composition includes a film-forming polymer One or more film-forming polymers may be included in the polish composition Suitable film-forming polymers include, acrylic polymers (e g modified acrylic polymers),
15 polyurethane and silicones

Suitable acrylic polymers include polymers of monomers selected from at least one of acrylic acid, methacrylic acid and esters thereof Homopolymers and copolymers may be
20 employed Suitable copolymers include styrene/acrylic copolymers, such as copolymers of methacrylic acid ester and styrene acrylic copolymer In one embodiment, a mixture of methacrylic acid ester copolymer and styrene acrylic copolymer is employed

25

The film-forming polymer may be present in the polish composition in an amount of 1 to 20 weight %, preferably, 8 to 18 weight %, for example, 4 to 12 weight % of the total composition In one embodiment, the polish composition
30 comprises 2 to 4 weight % of a styrene acrylic copolymer and 2 to 4 weight % of a methacrylic acid ester copolymer

The polish composition of the present invention is preferably in the form of a gel or cream. Thus, the polish composition of the present invention preferably has a viscosity of 50 to 100,000 centipoise

5

The polish composition preferably includes an alkali soluble resin. Preferably, maleinic acid resin is employed as the alkali soluble resin. A suitable maleinic resin is sold under the trademark ALRESAT®. The alkali soluble resin may improve shine and may help to gel the composition

The alkali soluble resin may be present in an amount of 0.01 to 10 weight %, preferably, 0.5 to 8 weight %, for example, 1 to 5 weight %

15

The polish composition of the present invention is preferably in the form of an emulsion, for example, an oil-in-water emulsion

Water may be present in the polish composition in an amount of 5 to 90 weight %, preferably, 10 to 75 weight %, more preferably, 20 to 60 weight %, for example, 40 to 55 weight %

The polish composition preferably comprises at least one alcohol, such as a C₁ to C₁₀ alcohol. The alcohol may help to gel the polish composition. Examples of suitable alcohols include methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol, octanol, nonanol and decanol. Preferably, a C₂ to C₆ alcohol, such as ethanol, propanol, butanol, pentanol and/or hexanol, is employed. In a preferred embodiment, a C₃ or C₄ alcohol, such as propanol

or butanol is employed Isopropyl alcohol is preferred Alcohols may be employed in an amount of 1 to 30 weight %, preferably, 5 to 20 weight %, more preferably, 8 to 15 weight % In a preferred embodiment, the polish composition
5 contains 8 to 15 weight % isopropyl alcohol

Other organic solvents may also be present in the polish composition For example, the polish composition may include one or more hydrocarbon solvents Without wishing
10 to be bound by any theory, the hydrocarbon solvent may help to stabilise the composition, particularly, when the composition is in the form of a gel When hydrocarbon solvents are employed, the hydrocarbon solvent is preferably treated to remove any aromatic components A suitable
15 hydrocarbon solvent is sold under the trademark EXXSOL ® D40 When a hydrocarbon solvent is used, it is preferably used in an amount of 1 to 5 weight %

The polish composition of the present invention may
20 optionally include a surfactant or emulsifier Nonionic surfactants, such as fatty alcohol ethoxylates, are preferred Fatty alcohol ethoxylates derived from the reaction between a C₁₂ to C₁₅ alcohol and ethylene oxide are particularly preferred Preferably, each mole of alcohol
25 reacts with 8 to 15 moles of ethylene oxide Examples of suitable surfactants and emulsifiers are sold under the trademarks Emulsifier 4106 (Clariant) and Genopol X060 (ex Clariant)

30 Emulsifiers or surfactants may be employed in an amount of 0.1 to 10 weight %, preferably, 1 to 10 weight %, for example, 2 to 5 weight % of the total composition

34

The polish composition may optionally include dyes
Suitable dyes include Acid black 2 In one embodiment,
carbon black dispersion is included in the polish
5 composition

Dye(s) may be present in an amount of 0.01 to 10 weight
%, for example, 0.1 to 5 weight %

10 Other optional components such as perfumes and
preservatives may also be included in the polish
composition

The composition may also include a stabilising additive
15 such as 2-amino 2-methyl propan-1-ol Such additives are
believed to promote emulsion stability

In one embodiment, the polish composition of the
present invention is an aqueous emulsion comprising
20 water (e.g. in an amount of 20 to 60 weight %),
wax (e.g. in an amount of 5 to 10 weight %),
film-forming polymer (e.g. in an amount of 8 to 20
weight %),
alkali soluble resin (e.g. in an amount of 0.5 to 8
25 weight %),
alcohol (e.g. in an amount of 5 to 20 weight %),
layered silicate incorporating an inorganic
polyphosphate (e.g. in an amount of 0.01 to 5 weight %),
and, optionally,
30 hydrocarbon solvent and/or surfactant

34

In the embodiment above, the wax is preferably a mixture of montanic ester wax and oxidised polyethylene wax, the film-forming polymer preferably comprises at least one acrylic polymer, the alkali soluble resin is preferably
5 maleinic acid resin, and the alcohol is preferably isopropyl alcohol. More preferably, the film-forming polymer comprises a copolymer of methacrylic acid esters and a styrene acrylic copolymer.

10 The polish composition of the present invention is suitable for treating leather and synthetic leather articles. Suitable articles include items of footwear, such as shoes, boots and sandals, as well as bags, belts, gloves, saddles and furniture.

15 Preferably, the polish composition of the present invention provides a shiny or glossy finish to the article under treatment. The polish composition may also help to increase the leather's (or synthetic leather's) resistance
20 to weathering, scuffing and scratching.

25 The polish composition of the present invention may be applied to a leather or synthetic leather article and left to dry. Once dry, the composition leaves a shiny film on the surface of the article. The treated article may be buffed to increase the shine but, in a preferred embodiment, buffing is not necessary to provide the treated article with a shine. Thus, in this preferred embodiment, the polish composition is self-shining. The layered silicate is
30 believed to be especially useful in a self-shining polish composition, as the silicate is believed to provide the composition with a shear-thinning rheology that assists in

the formation of a shiny film on the article upon application

5 The polish composition of the present invention may be dispensed using a sponge applicator The polish composition may be contained in a tube or, preferably, a jar

10 The polish composition of the present invention may be prepared by mixing the individual components of the composition together, for example, to form an emulsion

15 In one embodiment, the film-forming polymer and layered silicate are added to an aqueous emulsion of the wax(es), preferably, with vigorous stirring Preferably, the layered silicate (e g sodium lithium magnesium silicate modified with tetrakis sodium pyrophosphate) is added to the wax emulsion in the form of a pre-formed aqueous solution

20 In addition to the film-forming polymer and layered silicate, components such as resins, dye(s), surfactants, emulsifiers and solvents may also be added to the wax emulsion, preferably, with continuous stirring When employed, the surfactant (e g fatty acid polyglycol ether) and solvent (e g hydrocarbon solvent) may be added as a pre-formed mixture In a preferred embodiment, an alcohol solvent, such as iso-propyl alcohol is added to the resulting mixture in a steady stream, so as to aid gel formation

30 The wax emulsion may be formed in a preliminary step, for example, by melting the wax(es) at an elevated temperature of, for example, 80 to 150°C, preferably, 100 to

130°C, more preferably, 120 to 125°C In a separate container, water may be heated to a temperature of, for example, 80 to 100°C, preferably, 90 to 95°C The molten wax may then be added to the water and the resulting mixture stirred to form an emulsion (e.g. oil-in-water emulsion) 5 Optionally, an emulsifier (e.g. fatty acid polyglycol ethers) and/or a stabilizing additive (e.g. 2-amino-2-methyl propan-1-ol) may be added to the molten wax, for example, before the molten wax is mixed with water Once the molten 10 wax has been mixed with water, the resulting mixture may be cooled, for example, by crash cooling to a temperature of, for example, 10 to 50°C, for example, 30 to 40°C

Example

15

The self-shining composition of Table 1 was prepared by first heating waxes (ii and iii) with component (iv) at a temperature of 120 to 125°C to form a molten wax mixture Component (v) was added to the mixture The molten wax 20 mixture was then slowly added to hot water (90 to 95°C) with vigorous stirring The resulting mixture was then crash cooled to 40°C to form a wax emulsion Approximately 75% of the 46.58 w/w% water in the composition is employed to form the wax emulsion The remaining water is mixed with 25 component (xi) to form a dispersion (see below)

Components (xiv), (xiii), (x), (ix) and (viii) were then added to the wax emulsion with vigorous stirring Thereafter, a mixture of component (xi) and water was added 30 and the resulting mixture stirred for a further 15 minutes

A premix of components (v1) and (v11) was then added
The resulting mixture was stirred for a further 20 minutes
before component (x11) was added in a steady stream

- 5 Creamy gel formation took place within 1 hour of the
addition of component (x11)

Comparative Example

- 10 The procedure described with reference to the Example
above was repeated to prepare the self-shining composition
of Table 2 Component (x1), however, was omitted from the
composition of the Comparative Example Thus, all of the
49 16 w/w% water in this Comparative Example is used to form
15 the wax emulsion

- The compositions of the Example and the Comparative
Example were stored in sealed glass jars for one month The
composition according to the Example was storage stable
20 In contrast, composition of the Comparative Example
exhibited syneresis

Table 1

Component	w/w%
(i) Water (soft)	46 58
(ii) Refined montanic wax ester (Licowax KSL, Clariant)	5 85
(iii) Oxidised polyethylene wax (Polyethylene wax PED 522, Clariant)	3 60
(iv) Blend of fatty acid polyglycol ethers (Emulsifier 4106, Clariant)	1 80
(v) 2-amino-2-methyl propan-1-ol (AMP 90, Angus Chemie)	0 90
(vi) Fatty acid polyglycol ether (Genopol X060, Clariant)	3 00
(vii) Hydrocarbon solvent with low aromatic content (Exxsol D40, Exxon)	6 00
(viii) Styrene acrylic copolymer (Vinacryl 7190, Vinacryl - 50% actives)	6 00
(ix) Copolymer of methacrylic acid esters (Mowilith DM 772, Clariant - 46% actives)	8 00
(x) Aqueous solution of modified maleinic acid resin (NaOH Alresat Resin Solution 30%, Dick Peters)	6 00
(xi) Hydrous sodium lithium magnesium silicate modified with tetra sodium pyrophosphate (Laponite RDS, Rockwood)	0 50
(xii) isopropyl alcohol	10 00
(xiii) Acid black 2 dye colour index 504201 (Water soluble Nigrosine WLF)	1 27
(xiv) Aqueous carbon black dispersion (Colanyl Black PR 130)	0 50

Table 2

Component	w/wt
(i) Water (soft)	49 16
(ii) Refined montanic wax ester (Licowax KSL, Clariant)	5 46
(iii) Oxidised polyethylene wax (polyethylene wax PED 522, Clariant)	3 36
(iv) Blend of fatty acid polyglycol ethers (Emulsifier 4106, Clariant)	1 68
(v) 2-amino-2-methyl propan-1-ol (AMP 90, Angus Chemie)	0 84
(vi) Fatty acid polyglycol ether (Genopol X060, Clariant)	3 00
(vii) Hydrocarbon solvent with low aromatic content (Exxsol D40, Exxon)	6 00
(viii) Styrene acrylic copolymer (Vinacryl 7190, Vinacryl - 50% actives)	6 00
(ix) Copolymer of methacrylic acid esters (Mowilith DM 772, Clariant - 46% actives)	8 00
(x) Aqueous solution of modified maleinic resin (NaOH Alresat Resin Solution 30%, Dick Peters)	6 00
(xi) isopropyl alcohol	10 00
(xiv) Aqueous carbon black dispersion (Colanyl Black PR 130)	0 500

CLAIMS

1 A polish composition for treating a leather and/or
synthetic leather article, said composition comprising
5 water,
at least one wax,
at least one film-forming polymer, and
a layered silicate incorporating an inorganic peptiser

10 2 A composition as claimed in claim 1, wherein the
inorganic peptiser is an inorganic polyphosphate

3 A composition as claimed in claim 1 or 2, wherein the
wax comprises montanic wax ester and oxidised polyethylene
15 wax

4 A composition as claimed in any one of the preceding
claims, wherein the film-forming polymer is selected from at
least one of silicone, polyurethane and acrylic polymer
20

5 A composition as claimed in claim 4, wherein the film-
forming polymer comprises a mixture of styrene acrylic
copolymer and a copolymer of methacrylic acid ester

25 6 A composition as claimed in any one of the preceding
claims, which further comprises an alkali soluble resin

7 A composition as claimed in claim 6, wherein the alkali
soluble resin is a maleinic acid resin
30

8 A composition as claimed in any one of the preceding
claims, which is in the form of an oil-in-water emulsion

9 A composition as claimed in any one of the preceding claims, which comprises

1 to 20 weight % of said wax,

5 1 to 20 weight % of said at least one film-forming polymer,

0 01 to 5 weight % of said layered silicate

10 A composition as claimed in any one of the preceding claims, which further comprises an alcohol

11 A composition as claimed in claim 10, wherein the alcohol is isopropyl alcohol

15 12 A composition as claimed in any one of the preceding claims, which is a self-shining polish composition

13 A method of preparing a composition as claimed in any one of claims 1 to 12, said method comprising

20 forming an aqueous emulsion of said wax, said film-forming polymer, and said synthetic layered silicate

14 A method as claimed in claim 15, which further comprises the addition of an alcohol

25

15 A method of treating a leather and/or synthetic leather article, which comprises applying a composition as claimed in any one of claims 1 to 12 to a leather and/or synthetic leather article

30

16 A method as claimed in claim 15, wherein said composition is allowed to dry to form a shiny finish without buffing

5 17 Use of a synthetic layered silicate incorporating an inorganic peptiser in a polish composition to reduce or prevent syneresis of the polish composition

10 18 Use as claimed in claim 17, wherein said polish composition comprises water, at least one wax and at least one film-forming polymer

15 19 Use as claimed in claim 18, wherein said polish composition is a self-shining polish composition

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AbstractPolish Composition for Leather or Synthetic Leather

- 5 A polish composition for treating a leather and/or synthetic leather article, said composition comprising water, at least one wax, at least one film-forming polymer, and a layered silicate incorporating an inorganic peptiser

PATENT COOPERATION TREATY

33

PCT

From the INTERNATIONAL BUREAU

NOTIFICATION OF THE RECORDING
OF A CHANGE(PCT Rule 92bis 1 and
Administrative Instructions, Section 422)

To

BOWERS Craig
Legal Department Patents Group
Reckitt Benckiser plc
Dansom Lane
Hull HU8 7DS
United Kingdom

Date of mailing (day/month/year)

15 September 2005 (15 09 2005)

Applicant's or agent's file reference

11449P1 WO/JMH

IMPORTANT NOTIFICATION

International application No.

PCT/GB2005/002383

International filing date (day/month/year)

17 June 2005 (17 06 2005)

1 The following indications appeared on record concerning

☒ the applicant☒ the inventor☐ the agent☐ the common representative

Name and Address

BROWN Oily

EPO-DG 1

07.09.2005

TEAM 14

State of Nationality

State of Residence

Telephone No.

Facsimile No.

Teleprinter No.

2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning

☒ the person☐ the name☐ the address☐ the nationality☐ the residence

Name and Address

RADLEY, Jason
Reckitt Benckiser (UK) Limited
Dansom Lane
Hull HU8 7DS
United Kingdom

State of Nationality

GB

State of Residence

GB

Telephone No.

Facsimile No.

Teleprinter No.

3. Further observations, if necessary

The person in Box 2 is now recorded as applicant for the United States of America only and inventor for all designated states. The person in Box 1 has been deleted from the records.

4. A copy of this notification has been sent to

☒ the receiving Office☒ the International Searching Authority☐ the International Preliminary Examining Authority☐ the designated Offices concerned☐ the elected Offices concerned☐ otherThe International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No. (41-22) 338.88 85

Authorized officer

Juan CRUZ

Telephone No. (41-22) 338 8238

PATENT COOPERATION TREATY

46

From the
INTERNATIONAL SEARCHING AUTHORITY

PCT

To

see form PCT/ISA220

WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY
(PCT Rule 43bis 1)

Date of mailing
(day/month/year) see form PCT/ISA210 (second sheet)

Applicant's or agent's file reference
see form PCT/ISA220

FOR FURTHER ACTION
See paragraph 2 below

International application No.
PCT/GB2005/002383

International filing date (day/month/year)
17 08 2005

Priority date (day/month/year)
21 08 2004

International Patent Classification (IPC) or both national classification and IPC
C14C11/00 C09G1/10

Applicant
RECKITT BENCKISER (UK) LIMITED

1 This opinion contains indications relating to the following items

- ☒ Box No I Basis of the opinion
- ☐ Box No II Priority
- ☐ Box No III Non-establishment of opinion with regard to novelty inventive step and industrial applicability
- ☐ Box No IV Lack of unity of invention
- ☒ Box No V Reasoned statement under Rule 43bis.1(a)(i) with regard to novelty inventive step or industrial applicability citations and explanations supporting such statement
- ☐ Box No VI Certain documents cited
- ☒ Box No VII Certain defects in the international application
- ☐ Box No VIII Certain observations on the international application

2 FURTHER ACTION

If a demand for international preliminary examination is made this opinion will usually be considered to be a written opinion of the International Preliminary Examining Authority ("IPEA") However this does not apply where the applicant chooses an Authority other than this one to be the IPEA and the chosen IPEA has notified the International Bureau under Rule 66 1bis(b) that written opinions of this International Searching Authority will not be so considered.

If this opinion is as provided above considered to be a written opinion of the IPEA, the applicant is invited to submit to the IPEA a written reply together where appropriate with amendments before the expiration of three months from the date of mailing of Form PCT/ISA220 or before the expiration of 22 months from the priority date, whichever expires later

For further options see Form PCT/ISA220

3 For further details see notes to Form PCT/ISA220

Name and mailing address of the ISA.



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Box No 1 Basis of the opinion

- 1 With regard to the language this opinion has been established on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item
 - ☐ This opinion has been established on the basis of a translation from the original language into the following language which is the language of a translation furnished for the purposes of international search (under Rules 12.3 and 23.1(b))
2. With regard to any nucleotide and/or amino acid sequence disclosed in the international application and necessary to the claimed invention this opinion has been established on the basis of
 - a type of material
 - ☐ a sequence listing
 - ☐ table(s) related to the sequence listing
 - b format of material
 - ☐ in written format
 - ☐ in computer readable form
 - c time of filing/furnishing
 - ☐ contained in the international application as filed.
 - ☐ filed together with the international application in computer readable form
 - ☐ furnished subsequently to this Authority for the purposes of search
- 3 ☐ In addition, in the case that more than one version or copy of a sequence listing and/or table relating thereto has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that in the application as filed or does not go beyond the application as filed as appropriate, were furnished
- 4 Additional comments

43

48

Box No. V Reasoned statement under Rule 43bis.1(a)(i) with regard to novelty, inventive step or industrial applicability, citations and explanations supporting such statement

1 Statement

Novelty (N)	Yes	Claims	1 19
	No	Claims	
Inventive step (IS)	Yes	Claims	1 19
	No	Claims	
Industrial applicability (IA)	Yes	Claims	1 19
	No	Claims	

2 Citations and explanations

see separate sheet

Box No. VII Certain defects in the international application

The following defects in the form or contents of the international application have been noted

see separate sheet

49

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability, citations and explanations supporting such statement

Reference is made to the following documents

D1 US-A-4 497 919

D2 US-A-5 837 763

1. Novelty (Art. 33(2) PCT)/ Inventive step (Art. 33(3) PCT)

The subject-matter of claims 1-19 is regarded as novel over the prior art documents cited in the International Search Report and the application (Art. 33 (2) PCT) since none of the documents discloses a polish composition which is suitable for treating a (synthetic) leather article and which comprises water, wax(es), film-forming polymer(s) and a layered silicate incorporating an inorganic peptiser, a method of preparing said composition, a method of treating a leather article with said composition and the use of a synthetic layered silicate incorporating an inorganic peptiser in a polish composition to reduce/prevent syneresis of the polish composition

The subject-matter of present claims 1-19 is based upon an inventive step, since there is no hint in document D1, which is considered to represent the closest prior art, alone or in combination with any other document cited in the International Search Report for the claimed compositions, methods and use for the following reasons

Document D1 discloses an aqueous polish composition suitable for the treatment of leather which is self-polishing and comprises besides water, wax, a film-forming polymer (modified alkyd resins, silicon resins) and organic emulsifiers. The present claims differ from the subject-matter of D1 in the use of a layered silicate incorporating an inorganic peptiser

The provision of a self-shining polish composition which does not suffer from the separation of the liquid from the bulk (= syneresis) is regarded to be the technical problem of the present application, which is solved by the polish composition as described above. A composition sample based on water, waxes, (meth)acrylic polymer and sodium lithium magnesium silicate modified with a pyrophosphate salt shows improved storage stability compared with a composition prepared without said layered silicate (see example and

comparative example)

Although the use of layered silicates with polymers intercalation in combination with waxes in a nonaqueous leather sizing composition is known from D2, there was found no indication for the use of said layered silicates in aqueous wax compositions in the cited prior art alone or in combination. Thus, inventive step is acknowledged.

2. Industrial Applicability (Art. 33(4) PCT)

The application deals with a self-shining polish composition for (synthetic) leather and is thus useful in industry.

Re item VII

1. A document reflecting the prior art described on page 1 is not identified in the description (Rule 5.1(a)(ii) PCT).

Contrary to the requirements of Rule 5.1(a)(ii) PCT, the relevant background art disclosed in the documents D1 and D2 is not mentioned in the description, nor are these documents identified therein.

2. The wording "sodium tetrakis pyrophosphate" (see at least page 3, lines 27-28) appears to be erroneous, probably tetrasodium pyrophosphate is meant instead.

51

Improvements in or relating to a Composition

5 This invention relates to a polish composition suitable for treating leather and/or synthetic leather articles. In particular, although not exclusively, this invention relates to self-shining polish compositions.

10 Polish compositions are often used to impart a shine to leather and synthetic leather articles, such as items of footwear. Conventional polish compositions are typically formed of wax and organic solvents. Such polishes dry to form a dull finish on the treated article. Subsequent buffing is required to provide the article with a shiny finish.

15

Self-shining polishes in liquid form have been developed to allow a shine to be achieved without any buffing.

20 More recently, gel or cream self-shining compositions have also been developed. Such compositions are generally based on aqueous emulsions of wax and acrylic polymers. When applied to an article, the compositions dry to form a glossy finish. Buffing is not generally required to provide the treated article with the desired shine.

30 We have found that known self-shine polish compositions tend to suffer from storage problems. For example, when stored for prolonged periods, liquid may separate from the known compositions. The separation of liquid from the bulk of the composition is known as syneresis.

- - - - -

51

According to the present invention, there is provided a polish composition for treating leather and/or synthetic leather articles, said composition comprising

- water,
- 5 at least one wax,
- at least one film-forming polymer, and
- a layered silicate incorporating an inorganic peptiser

By including a layered silicate in the polish
10 composition, the storage problems of the polish composition can advantageously be reduced. In particular, the use of the layered silicate may reduce the likelihood of liquid separating from the polish composition even after prolonged periods of storage. The layered silicate, therefore, may be
15 used in the polish composition to reduce or prevent syneresis. The layered silicate may also help to ensure that the rheological properties of the polish composition are maintained, for example, to ensure ease of application

20 Preferably, the composition of the present invention is storage stable for at least 4 weeks, more preferably, at least 8 weeks, and most preferably, at least 12 weeks

Preferably, the layered silicate is a synthetic layered
25 silicate. The layered silicate may be a metal silicate, such as silicate of an alkali metal and/or alkali earth metal. Suitable alkali metal silicates include silicates of lithium, sodium and potassium. Suitable alkali earth metal silicates include silicates of magnesium and calcium.
30 Preferably, the metal silicate is a silicate of at least one alkali metal and at least one alkali earth metal. In one embodiment, sodium lithium magnesium silicate is employed

Preferably, the layered silicate comprises less than 2 weight %, more preferably, less than 1 weight %, even more preferably, less than 0.5 weight %, and most preferably, less than 0.1 weight % of crystalline silica. In one embodiment, the layered silicate is substantially free of crystalline silica.

The layered silicate may also have a low transition metal content. For example, the layered silicate may have a transition metal content of less than 2 weight %, more preferably less than 1 weight %, yet more preferably less than 0.5 weight %, for example, less than 0.1 weight %. In one embodiment, the layered silicate is substantially free of transition metal.

The layered silicate incorporates an inorganic peptiser. Preferably, the inorganic peptiser is a phosphate. Any suitable phosphate peptiser may be employed. However, metal phosphates, such as alkali metal and/or alkali earth metal phosphates are preferred. Suitable alkali metal phosphates include phosphates of lithium, sodium and potassium. Suitable alkali earth metal phosphates include phosphates of magnesium and calcium.

Preferably, the phosphate is a polyphosphate, such as a pyrophosphate. In a preferred embodiment, sodium tetrakis pyrophosphate is employed.

An example of a suitable layered silicate is Laptonite.
© RDS

The layered silicate is preferably provided in finely divided form

The layered silicate may be present in an amount of 0.01 to 5 weight % of the overall polish composition. Preferably, the layered silicate is present in an amount of 0.05 to 4 weight %, more preferably, 0.1 to 3 weight %, for example, 0.2 to 2 weight %. In a preferred embodiment, 0.4 to 1 weight %, for example, 0.5 to 0.7 weight % of layered silicate is employed.

The polish composition comprises at least one wax. Mixtures of one or more waxes may also be employed. Suitable waxes include insect waxes, such as beeswax, vegetable waxes, such as carnauba wax and candelilla wax, mineral ester waxes and acid waxes. Preferably, mineral ester waxes are employed. Suitable mineral ester waxes include montanic wax (e.g. montanic wax ester). Synthetic waxes, such as polyethylene wax (e.g. oxidised) and polyol ether/ester wax may also be employed. In a preferred embodiment, the polish composition comprises montanic wax ester and a synthetic wax, such as oxidised polyethylene wax. Where a montanic wax ester is employed, it may be a refined montanic wax ester.

The wax or wax mixture employed in the polish composition of the present invention preferably has an acid value of 5 to 50, preferably, 10 to 30.

The wax or wax mixture employed in the polish composition preferably has an average molecular weight of

500 to 5000, preferably, 1000 to 4000, for example, 2000 to 3000

The amount of wax in the polish composition may be 1 to 20 weight %, preferably, 2 to 15 weight %, more preferably, 5 to 10 weight %. In a preferred embodiment, the polish composition comprises 1 to 6 (e g 2 to 4) weight % oxidised polyethylene wax and 2 to 10 (e g 3 to 8) weight % montanic wax ester

10

The polish composition includes a film-forming polymer. One or more film-forming polymers may be included in the polish composition. Suitable film-forming polymers include, acrylic polymers (e g modified acrylic polymers), polyurethane and silicones

Suitable acrylic polymers include polymers of monomers selected from at least one of acrylic acid, methacrylic acid and esters thereof. Homopolymers and copolymers may be employed. Suitable copolymers include styrene/acrylic copolymers, such as copolymers of methacrylic acid ester and styrene acrylic copolymer. In one embodiment, a mixture of methacrylic acid ester copolymer and styrene acrylic copolymer is employed

25

The film-forming polymer may be present in the polish composition in an amount of 1 to 20 weight %, preferably, 8 to 18 weight %, for example, 4 to 12 weight % of the total composition. In one embodiment, the polish composition comprises 2 to 4 weight % of a styrene acrylic copolymer and 2 to 4 weight % of a methacrylic acid ester copolymer

30

Sp

The polish composition of the present invention is preferably in the form of a gel or cream. Thus, the polish composition of the present invention preferably has a viscosity of 50 to 100,000 centipoise

5

The polish composition preferably includes an alkali soluble resin. Preferably, maleinic acid resin is employed as the alkali soluble resin. A suitable maleinic resin is sold under the trademark ALRESAT®. The alkali soluble resin may improve shine and may help to gel the composition

The alkali soluble resin may be present in an amount of 0.01 to 10 weight %, preferably, 0.5 to 8 weight %, for example, 1 to 5 weight %

15

The polish composition of the present invention is preferably in the form of an emulsion, for example, an oil-in-water emulsion

Water may be present in the polish composition in an amount of 5 to 90 weight %, preferably, 10 to 75 weight %, more preferably, 20 to 60 weight %, for example, 40 to 55 weight %

The polish composition preferably comprises at least one alcohol, such as a C₁ to C₁₀ alcohol. The alcohol may help to gel the polish composition. Examples of suitable alcohols include methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol, octanol, nonanol and decanol. Preferably, a C₂ to C₆ alcohol, such as ethanol, propanol, butanol, pentanol and/or hexanol, is employed. In a preferred embodiment, a C₃ or C₄ alcohol, such as propanol

5b

5 or butanol is employed Isopropyl alcohol is preferred Alcohols may be employed in an amount of 1 to 30 weight %, preferably, 5 to 20 weight %, more preferably, 8 to 15 weight % In a preferred embodiment, the polish composition contains 8 to 15 weight % isopropyl alcohol

10 Other organic solvents may also be present in the polish composition For example, the polish composition may include one or more hydrocarbon solvents Without wishing to be bound by any theory, the hydrocarbon solvent may help to stabilise the composition, particularly, when the composition is in the form of a gel When hydrocarbon solvents are employed, the hydrocarbon solvent is preferably treated to remove any aromatic components A suitable hydrocarbon solvent is sold under the trademark EXXSOL D40 15 When a hydrocarbon solvent is used, it is preferably used in an amount of 1 to 5 weight %

20 The polish composition of the present invention may optionally include a surfactant or emulsifier Nonionic surfactants, such as fatty alcohol ethoxylates, are preferred Fatty alcohol ethoxylates derived from the reaction between a C₁₂ to C₁₅ alcohol and ethylene oxide are particularly preferred Preferably, each mole of alcohol reacts with 8 to 15 moles of ethylene oxide 25 Examples of suitable surfactants and emulsifiers are sold under the trademarks Emulsifier 4106 (Clariant) and Genopol X060 (ex Clariant)

30 Emulsifiers or surfactants may be employed in an amount of 0.1 to 10 weight %, preferably, 1 to 10 weight %, for example, 2 to 5 weight % of the total composition

5 The polish composition may optionally include dyes
Suitable dyes include Acid black 2 In one embodiment,
carbon black dispersion is included in the polish
composition

Dye(s) may be present in an amount of 0.01 to 10 weight
%, for example, 0.1 to 5 weight %

10 Other optional components such as perfumes and
preservatives may also be included in the polish
composition

15 The composition may also include a stabilising additive
such as 2-amino 2-methyl propan-1-ol Such additives are
believed to promote emulsion stability

In one embodiment, the polish composition of the
present invention is an aqueous emulsion comprising
20 water (e.g. in an amount of 20 to 60 weight %),
wax (e.g. in an amount of 5 to 10 weight %),
film-forming polymer (e.g. in an amount of 8 to 20
weight %),
alkali soluble resin (e.g. in an amount of 0.5 to 8
25 weight %),
alcohol (e.g. in an amount of 5 to 20 weight %),
layered silicate incorporating an inorganic
polyphosphate (e.g. in an amount of 0.01 to 5 weight %),
and, optionally,
30 hydrocarbon solvent and/or surfactant

In the embodiment above, the wax is preferably a mixture of montanic ester wax and oxidised polyethylene wax, the film-forming polymer preferably comprises at least one acrylic polymer, the alkali soluble resin is preferably maleinic acid resin, and the alcohol is preferably isopropyl alcohol. More preferably, the film-forming polymer comprises a copolymer of methacrylic acid esters and a styrene acrylic copolymer.

10 The polish composition of the present invention is suitable for treating leather and synthetic leather articles. Suitable articles include items of footwear, such as shoes, boots and sandals, as well as bags, belts, gloves, saddles and furniture.

15 Preferably, the polish composition of the present invention provides a shiny or glossy finish to the article under treatment. The polish composition may also help to increase the leather's (or synthetic leather's) resistance to weathering, scuffing and scratching.

20 The polish composition of the present invention may be applied to a leather or synthetic leather article and left to dry. Once dry, the composition leaves a shiny film on the surface of the article. The treated article may be buffed to increase the shine but, in a preferred embodiment, buffing is not necessary to provide the treated article with a shine. Thus, in this preferred embodiment, the polish composition is self-shining. The layered silicate is believed to be especially useful in a self-shining polish composition, as the silicate is believed to provide the composition with a shear-thinning rheology that assists in

the formation of a shiny film on the article upon application

5 The polish composition of the present invention may be dispensed using a sponge applicator The polish composition may be contained in a tube or, preferably, a jar

10 The polish composition of the present invention may be prepared by mixing the individual components of the composition together, for example, to form an emulsion

In one embodiment, the film-forming polymer and layered silicate are added to an aqueous emulsion of the wax(es), preferably, with vigorous stirring Preferably, the layered silicate (e g sodium lithium magnesium silicate modified with tetrakis sodium pyrophosphate) is added to the wax emulsion in the form of a pre-formed aqueous solution

20 In addition to the film-forming polymer and layered silicate, components such as resins, dye(s), surfactants, emulsifiers and solvents may also be added to the wax emulsion, preferably, with continuous stirring When employed, the surfactant (e g fatty acid polyglycol ether) and solvent (e g hydrocarbon solvent) may be added as a pre-formed mixture In a preferred embodiment, an alcohol solvent, such as iso-propyl alcohol is added to the resulting mixture in a steady stream, so as to aid gel formation

30 The wax emulsion may be formed in a preliminary step, for example, by melting the wax(es) at an elevated temperature of, for example, 80 to 150°C, preferably, 100 to

130°C, more preferably, 120 to 125°C In a separate container, water may be heated to a temperature of, for example, 80 to 100°C, preferably, 90 to 95°C The molten wax may then be added to the water and the resulting mixture stirred to form an emulsion (e g oil-in-water emulsion) 5 Optionally, an emulsifier (e g fatty acid polyglycol ethers) and/or a stabilizing additive (e g 2-amino-2-methyl propan-1-ol) may be added to the molten wax, for example, before the molten wax is mixed with water Once the molten 10 wax has been mixed with water, the resulting mixture may be cooled, for example, by crash cooling to a temperature of, for example, 10 to 50°C, for example, 30 to 40°C

Example

15

The self-shining composition of Table 1 was prepared by first heating waxes (ii and iii) with component (iv) at a temperature of 120 to 125°C to form a molten wax mixture Component (v) was added to the mixture The molten wax 20 mixture was then slowly added to hot water (90 to 95°C) with vigorous stirring The resulting mixture was then crash cooled to 40°C to form a wax emulsion Approximately 75% of the 46.58 w/w% water in the composition is employed to form the wax emulsion The remaining water is mixed with 25 component (xi) to form a dispersion (see below)

Components (xiv), (xiii), (x), (ix) and (viii) were then added to the wax emulsion with vigorous stirring Thereafter, a mixture of component (xi) and water was added 30 and the resulting mixture stirred for a further 15 minutes

A premix of components (v1) and (v11) was then added
The resulting mixture was stirred for a further 20 minutes
before component (x11) was added in a steady stream

- 5 Creamy gel formation took place within 1 hour of the
addition of component (x11)

Comparative Example

- 10 The procedure described with reference to the Example
above was repeated to prepare the self-shining composition
of Table 2 Component (x1), however, was omitted from the
composition of the Comparative Example Thus, all of the
49 16 w/w% water in this Comparative Example is used to form
15 the wax emulsion

- The compositions of the Example and the Comparative
Example were stored in sealed glass jars for one month The
composition according to the Example was storage stable
20 In contrast, composition of the Comparative Example
exhibited syneresis

Table 1

Component	w/w%
(i) Water (soft)	46 58
(ii) Refined montanic wax ester (Licowax KSL, Clariant)	5 85
(iii) Oxidised polyethylene wax (Polyethylene wax PED 522, Clariant)	3 60
(iv) Blend of fatty acid polyglycol ethers (Emulsifier 4106, Clariant)	1 80
(v) 2-amino-2-methyl propan-1-ol (AMP 90, Angus Chemie)	0 90
(vi) Fatty acid polyglycol ether (Genopol X060, Clariant)	3 00
(vii) Hydrocarbon solvent with low aromatic content (Exxsol D40, Exxon)	6 00
(viii) Styrene acrylic copolymer (Vinacryl 7190, Vinacryl - 50% actives)	6 00
(ix) Copolymer of methacrylic acid esters (Mowilith DM 772, Clariant - 46% actives)	8 00
(x) Aqueous solution of modified maleinic acid resin (NaOH Alresat Resin Solution 30%, Dick Peters)	6 00
(xi) Hydrous sodium lithium magnesium silicate modified with tetra sodium pyrophosphate (Laponite RDS, Rockwood)	0 50
(xii) isopropyl alcohol	10 00
(xiii) Acid black 2 dye colour index 504201 (Water soluble Nigrosine WLF)	1 27
(xiv) Aqueous carbon black dispersion (Colanyl Black PR 130)	0 50

Table 2

Component	w/w%
(i) Water (soft)	49 16
(ii) Refined montanic wax ester (Licowax KSL, Clariant)	5 46
(iii) Oxidised polyethylene wax (polyethylene wax PED 522, Clariant)	3 36
(iv) Blend of fatty acid polyglycol ethers (Emulsifier 4106, Clariant)	1 68
(v) 2-amino-2-methyl propan-1-ol (AMP 90, Angus Chemie)	0 84
(vi) Fatty acid polyglycol ether (Genopol X060, Clariant)	3 00
(vii) Hydrocarbon solvent with low aromatic content (Exxsol D40, Exxon)	6 00
(viii) Styrene acrylic copolymer (Vinacryl 7190, Vinacryl - 50% actives)	6 00
(ix) Copolymer of methacrylic acid esters (Mowilith DM 772, Clariant - 46% actives)	8 00
(x) Aqueous solution of modified maleinic resin (NaOH Alresat Resin Solution 30%, Dick Peters)	6 00
(xi) isopropyl alcohol	10 00
(xiv) Aqueous carbon black dispersion (Colanyl Black PR 130)	0 500

CLAIMS

- 1 A polish composition for treating a leather and/or
synthetic leather article, said composition comprising
5 water,
at least one wax,
at least one film-forming polymer, and
a layered silicate incorporating an inorganic peptiser
- 10 2 A composition as claimed in claim 1, wherein the
inorganic peptiser is an inorganic polyphosphate
- 3 A composition as claimed in claim 1 or 2, wherein the
wax comprises montanic wax ester and oxidised polyethylene
15 wax
- 4 A composition as claimed in any one of the preceding
claims, wherein the film-forming polymer is selected from at
least one of silicone, polyurethane and acrylic polymer
20
- 5 A composition as claimed in claim 4, wherein the film-
forming polymer comprises a mixture of styrene acrylic
copolymer and a copolymer of methacrylic acid ester
- 25 6 A composition as claimed in any one of the preceding
claims, which further comprises an alkali soluble resin
- 7 A composition as claimed in claim 6, wherein the alkali
soluble resin is a maleinic acid resin
30
- 8 A composition as claimed in any one of the preceding
claims, which is in the form of an oil-in-water emulsion

9 A composition as claimed in any one of the preceding claims, which comprises

1 to 20 weight % of said wax,

5 1 to 20 weight % of said at least one film-forming polymer,

0 01 to 5 weight % of said layered silicate

10 A composition as claimed in any one of the preceding

10 claims, which further comprises an alcohol

11 A composition as claimed in claim 10, wherein the alcohol is isopropyl alcohol

15 12 A composition as claimed in any one of the preceding claims, which is a self-shining polish composition

13 A method of preparing a composition as claimed in any one of claims 1 to 12, said method comprising

20 forming an aqueous emulsion of said wax, said film-forming polymer, and said synthetic layered silicate

14 A method as claimed in claim 15, which further comprises the addition of an alcohol

25

15 A method of treating a leather and/or synthetic leather article, which comprises applying a composition as claimed in any one of claims 1 to 12 to a leather and/or synthetic leather article

30

16 A method as claimed in claim 15, wherein said composition is allowed to dry to form a shiny finish without buffing

5 17 Use of a synthetic layered silicate incorporating an inorganic peptiser in a polish composition to reduce or prevent syneresis of the polish composition

10 18 Use as claimed in claim 17, wherein said polish composition comprises water, at least one wax and at least one film-forming polymer

19 Use as claimed in claim 18, wherein said polish composition is a self-shining polish composition

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AbstractImprovements in or relating to a Composition

- 5 A polish composition for treating a leather and/or synthetic leather article, said composition comprising water, at least one wax, at least one film-forming polymer, and a layered silicate incorporating an inorganic peptiser

TRATADO DE COOPERACION DE PATENTES

De
LA AUTORIDAD DE BUSQUEDA INTERNACIONAL

Para		PCT OPINIÓN ESCRITA DE LA AUTORIDAD DE BUSQUEDA INTERNACIONAL (Norma 43 bis 1)	
Ver formato PCT/ISA/220			
Archivo de referencia del solicitante o agente Ver formato PCT/ISA/220		Fecha de envío (día/mes/año) Ver formato PCT/ISA/210 (2ª hoja) PARA ACCIONES ADICIONALES Ver párrafo 2 abajo	
Solicitud internacional No	Fecha de presentación internacional (día/mes/año)	Fecha de prioridad (día/mes/año)	
PCT/GB2005/002383	17 06 2005	21 06 2004	
Clasificación Internacional de Patentes (IPC) o ambas clasificación nacional e IPC C14C11/40, C09C11/0			
Solicitante RECKITT BENCKISER (UK) LIMITED			

- 1 Esta opinión contiene indicaciones relacionadas con los siguientes ítems
- | | |
|---|---|
| ☒ Casilla No. I | Bases de la opinión |
| ☐ Casilla No. II | Proridad |
| ☐ Casilla No. III | No se establece opinión respecto a la novedad, pasos inventivos y aplicabilidad industrial |
| ☐ Casilla No. IV | La falta de novedad al invento |
| ☒ Casilla No. V | Declaración motivada bajo la norma 43bis.1(a)(i) sobre la novedad, la actividad inventiva y la posibilidad de aplicación industrial, citas y explicaciones en apoyo de esta declaración |
| ☐ Casilla No. VI | Ciertos documentos citados |
| ☒ Casilla No. VII | Ciertos defectos en la solicitud internacional |
| ☐ Casilla No. VIII | Ciertas observaciones sobre la solicitud internacional |
2. ACCIONES ADICIONALES
- Si se realiza una solicitud de examen preliminar internacional, esta opinión será considerada como una opinión escrita de la Autoridad Internacional de Examen Preliminar ("IPEA"). Sin embargo, esto no aplica cuando el solicitante escoge una Autoridad diferente del IPEA y el IPEA escogido a notificado a la Agencia Internacional Bureau bajo la norma 66.1bis(b) que las opiniones escritas de esta Autoridad de Búsqueda Internacional no serán consideradas.
- Si esta opinión, como se estableció anteriormente, es considerada como la opinión escrita del IPEA, se invita al solicitante a que presente ante el IPEA un respuesta escrita y cuando sea apropiado junto con las modificaciones antes del vencimiento de tres meses a partir de la fecha de envío por correo del Formato PCT/ISA/220 o antes de la fecha de vencimiento de 22 meses a partir de la fecha de prioridad, la que se venza más tarde.
- Para opciones adicionales, ver el Formato PCT/ISA/220
- 3 Para información adicional, ver las notas del Formato PCT/ISA/220

Nombre y dirección del ISA Oficina Europea de Patentes D-80298 Munich Tel : +49 89 23399 0 Tx 523565 epxm d Fax : +49 89 23399 4445	FUNCIONARIO AUTORIZADO Daniel J Colilla Teléfono No 571-272 2800
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Formato (PCT/ISA/237) (hoja de portada) (Enero 2004)

**OPINIÓN ESCRITA DE LA AUTORIDAD DE
BUSQUEDA INTERNACIONAL**

Solicitud Internacional No

PCT/GB2005/002383

Casilla No 1 Base de la Opinion

1 Por lo que respecta al idioma esta opinion está basada en la solicitud internacional en el idioma de presentacion de la solicitud internacional, salvo que en este ítem se indique otra cosa

☐ La solicitud internacional en el lenguaje en el que fue presentado

☐ Esta opinion esta basada en la traduccion del idioma original al siguiente idioma _____, el cual es el idioma de una traduccion suministrada para los propositos de busqueda internacional (bajo las Normas 12.3 y 23.1 (b))

2 Con respecto a alguna secuencia de nucleótidos y/o aminoácidos presentada en la solicitud internacional y necesaria para el invento reivindicado, esta opinion ha sido establecida con base en

a Tipo de material

☐ Listado de secuencias

☐ Tablas relacionadas con el listado de secuencias

b Formato del material

☐ Formato escrito

☐ En formato electronico

c Fecha de radicación/ presentacion

☐ Contenido en la solicitud internacional tal como fue radicado

☐ Radicado junto con la solicitud internacional en formato electronico

☐ Suministrado posteriormente a esta autoridad con el proposito de búsqueda

3 ☐ Además, en el caso en que más de una version o copia del listado de secuencia y/o tabla(s), que está incluida en la que ha sido radicada o suministrada, las declaraciones requeridas de que la informacion en las copias subsecuentes o adicionales es identica a aquella de la solicitud tal como fue radicada, o no va más allá de la solicitud tal como fue radicada y fueron suministradas de manera adecuada

4 Comentarios adicionales

Formulario (PCT/ISA/237) (Enero 2004)

Casilla No V Base de la Opinion Declaración motivada bajo la regla 43bis 1 (a) (i) en relación con la novedad, altura inventiva o aplicabilidad industrial, citasiones y explicaciones soportando tal declaración

1 Declaracion

Novedad (N)	Reivindicaciones 1-19	SI
	Reivindicaciones	NO
Altura Inventiva	Reivindicaciones 1-19	SI
	Reivindicaciones	NO
Aplicabilidad Industrial	Reivindicaciones 1-19	SI
	Reivindicaciones	NO

2 Citaciones y explicaciones

Ver hoja separada

Casilla No VII Ciertos defectos en la solicitud Internacional

Los siguientes defectos en la forma o contenidos de la solicitud internacional han sido notados

Ver hoja separada

Ref Item V

Declaración razonada con relación a novedad, paso inventivo o aplicabilidad industrial, citaciones y explicaciones que respaldan dicha declaración

Se hace referencia a los siguientes documentos

D1 US-A-4 497 919

D2 US-A-5 837 763

1 Novedad (Art. 33(2) PCT)/ Paso Inventivo (Art. 33(3) PCT)

El asunto del objeto de las reivindicaciones 1-19 se considera novedad sobre los documentos anteriores citados sobre el arte en el internacional Search Report (Informe Internacional de Busqueda) y la solicitud (Art. 33 (2) PCT) ya que ninguno de los documentos revela un compuesto de lustrador (betun) que sea apto para el tratamiento de un artículo (sintético) de cuero y que comprende agua, cera(s), polímero(s) que forman película y un silicato en capas que incorpora un péptido inorgánico, un método para preparar dicho compuesto, un método para tratar un artículo de cuero con dicho compuesto y el uso de un silicato en capas sintético que incorpora un péptido inorgánico en un compuesto de betun para reducir/prevenir sinéresis del compuesto del betun.

El asunto del objeto de las reivindicaciones 1-19 se basa en un paso inventivo ya que no hay trazas en el documento D1, que se considera que representa el arte anterior más próximo solo o en combinación con cualquier otro documento citado en el Informe Internacional de Busqueda para los compuestos reivindicados, métodos y uso por las siguientes razones:

El documento D1 revela un compuesto acuoso de betun apto para el tratamiento de cuero, el cual es auto-brillante y comprende, fuera de agua, cera un polimero que forma película (resinas álcalis modificadas, resinas de silicona) y emulsionadores organicos. La presente reivindicacion difiere del asunto de D1 en el uso de un silicato en capas incorporando un peptido inorgánico.

El aprovisionamiento de un compuesto auto-brillante que no sufre por la separación del liquido del volumen total (= sineresis) se considera que es el problema técnico de la presente solicitud la cual se soluciona por el compuesto del betun como se ha descrito más arriba. Una muestra del compuesto basado en agua, ceras (polimero (met)acrílico y silicato de magnesio de litio de sodio modificado con una sal de pirofosfato muestra mejoria en la estabilidad de almacenamiento comparado con un compuesto sin el citado silicato en capas (ver ejemplo y

Formato PCT/ISA/237 (Página Separada) (1ª Página) (EPO-enero de 2004)

ejemplo comparativo)

Aunque el uso de silicatos en capas con intercalacion de polimeros en combinacion con ceras en un compuesto encolado de cuero no acuoso se conoce desde el D2, no se encontro indicacion alguna para el uso de dichos silicatos en compuestos de cera acuosos en el citado arte previo, ni solo ni en combinacion. Asi, queda reconocido el paso inventivo.

2 Aplicabilidad Industrial (Art. 33(4) PCT)

La solicitud trata de un compuesto auto-brillante para lustrar cuero (sintético) y por ende es útil en las industrias.

Ref. Item VII

1 Un documento que refleja el arte anterior descrito en la pagina 1 no está identificado en la descripción (Norma 5.1(a)(ii) PCT).

Contrario a los requerimientos de la Norma 5.1(a)(ii) PCT, el antecedente pertinente del arte revelado en los documentos D1 y D2 no se mencionan en la descripción, ni estos documentos quedan identificados en este.

2 Las palabras "pirofosfato tera de sodio" (ver por lo menos la pagina 3, l. 27-28) parece estar errado, probablemente en su lugar significaba "pirofosfato de tetrasodio".

SOLICITUD

PCT

Los datos suministrados solicitan que la presente solicitud internacional sea
procesada de acuerdo con el Tratado de Washington de Patentes

PARA EL USO EXCLUSIVO DE LA OFICINA RECEPTORA Solicitud Internacional No. Fecha de Presentación Internacional Nombre de la Oficina Receptora y "Solicitud Internacional PCT"
Archivo de Referencia del Agente o Solicitante (si se desea) (12 caracteres máximo) 11449P1 WO/JMH

25

Casilla No.1	Título del invento	MEJORAS EN UN COMPUESTO O RELACIONADAS CON ESTE			
Casilla No.2	Solicitante	☐ Esta persona también es inventor			
Nombre y dirección (apellido seguido por nombre para una persona jurídica o nombre legal completo. La dirección debe incluir código postal y nombre del país. El país de la dirección indicada en esta casilla es el Estado del solicitante (que es el país de residencia si no se indica adelante Estado de residencia)) Rockitt Benckiser (I.A.) Limited 103-105 Bath Road Wough Berkshire SL1 3YH REINO UNIDO		Teléfono no +44 1753 217800		Facsimil no. +44 1753 217800	
		Teléfono no			
		No. de registro del solicitante con la oficina			
Estado (que es el país) de nacionalidad		Estado (que es el país) de residencia			
GB		GB			
Esta persona es solicitante para los propósitos de		☐ Todos los estados designados		☒ Todos los estados designados excepto los E.U. de América	
		☐ Solo los Estados Unidos de América		☐ Los estados indicados en la casilla complementaria	
Casilla No.3	SOLICITANTE(S) Y/O INVENTOR(ES) ADICIONAL(ES)				
Nombre y dirección (apellido seguido por nombre para una persona jurídica o nombre legal completo. La dirección debe incluir código postal y nombre del país. El país de la dirección indicada en esta casilla es el Estado del solicitante (que es el país de residencia si no se indica adelante Estado de residencia)) RADLEY Jason Rockitt Benckiser (I.A.) Limited Damon Lane Hull HU11 7DS REINO UNIDO		Esta persona es ☐ Solicitante ☒ Solicitante e inventor ☐ Solo inventor (si esta casilla de verificación es marcada, rellene adelante)			
		No. de Registro del solicitante con la oficina			
Estado (que es el país) de nacionalidad		Estado (que es el país) de residencia			
GB		GB			
Esta persona es solicitante para los propósitos de		☐ Todos los estados designados		☒ Solo los Estados Unidos de América	
		☐ Todos los estados designados excepto los E.U. de América		☐ Los estados indicados en la casilla complementaria	
☐ Solicitantes adicionales y/o inventores (adicionales) se indican en una hoja de continuación.					
Casilla No.4	AGENTE O REPRESENTANTE COMÚN O DIRECCIÓN DE CORRESPONDENCIA				
Por medio de la presente la persona identificada adelante ha sido señalada para actuar en nombre del (los) solicitante (s) ante las Autoridades Internacionales competentes como ☒ Agente ☐ Representante común					
Nombre y dirección (apellido seguido por nombre para una persona jurídica nombre legal completo. La dirección debe incluir código postal y nombre del país. El país de la dirección indicada en esta casilla es el Estado del solicitante (que es el país) de residencia si no se indica adelante Estado de residencia) BOYERS, Craig Legal Department - Patents Group Rockitt Benckiser plc Damon Lane Hull HU11 7DS REINO UNIDO		Teléfono +44 1482 583730		Facsimil: +44 1482 216876	
		Registro del Solicitante con la Oficina No.			
☐ Dirección para correspondencia. marque esta casilla de verificación cuando ningún agente o representante común se haya sido señalado y el espacio anterior se utiliza en cambio para indicar una dirección especial a la cual la correspondencia se deba enviar					

25

CONTINUACIÓN DE CASHIA NO 03 SOLICITANTES Y/O INVENTORES ADICIONALES				
<i>Si ninguna de las siguientes subcasillas es usada, esta hoja puede no ser incluida en la solicitud</i>				
Nombre y dirección (apellido seguido por nombre para una persona jurídica nombre legal completo. La dirección debe incluir código postal y nombre del país. El país de la dirección indicada en esta casilla es el Estado del solicitante (que es el país) de residencia si no se indica adelante Estado de residencia)			Esta persona es ☐ Solo solicitante ☒ Solicitante e inventor ☐ Solo inventor (si esta casilla de verificación es marcada, no tiene adelante)	
WICIFY Chris Reckitt Benckiser (I K) Limited Damen Lane Hull HU10 7HS UNITED KINGDOM			No de Registro del solicitante con la oficina	
Estado (que es el país) de nacionalidad GB		Estado (que es el país) de residencia GB		
Esta persona es solicitante para los propósitos de	☐ Todos los estados designados	☐ Todos los estados designados excepto los E U de América	☒ Solamente los Estados Unidos de América	☐ Los estados indicados en la casilla complementaria
Nombre y dirección (apellido seguido por nombre para una persona jurídica nombre legal completo. La dirección debe incluir código postal y nombre del país. El país de la dirección indicado en esta casilla es el Estado del solicitante (que es el país) de residencia si no se indica adelante Estado de residencia)			Esta persona es ☐ Solo solicitante ☐ Solicitante e inventor ☐ Solo inventor (si esta casilla de verificación es marcada, no tiene adelante)	
			No de Registro del solicitante con la oficina	
Estado (que es el país) de nacionalidad		Estado (que es el país) de residencia		
Esta persona es solicitante para los propósitos de	☐ Todos los estados designados	☐ Todos los estados designados excepto los E U de América	☐ Solamente los Estados Unidos de América	☐ Los estados indicados en la casilla complementaria
Nombre y dirección (apellido seguido por nombre para una persona jurídica nombre legal completo. La dirección debe incluir código postal y nombre del país. El país de la dirección indicado en esta casilla es el Estado del solicitante (que es el país) de residencia si no se indica adelante Estado de residencia)			Esta persona es ☐ Solo solicitante ☐ Solicitante e inventor ☐ Solo inventor (si esta casilla de verificación es marcada, no tiene adelante)	
			No de Registro del solicitante con la oficina	
Estado (que es el país) de nacionalidad		Estado (que es el país) de residencia		
Esta persona es solicitante para los propósitos de	☐ Todos los estados designados	☐ Todos los estados designados excepto los E U de América	☐ Solamente los Estados Unidos de América	☐ Los estados indicados en la casilla complementaria
Nombre y dirección (apellido seguido por nombre para una persona jurídica nombre legal completo. La dirección debe incluir código postal y nombre del país. El país de la dirección indicado en esta casilla es el Estado del solicitante (que es el país) de residencia si no se indica adelante Estado de residencia)			Esta persona es ☐ Solo solicitante ☐ Solicitante e inventor ☐ Solo inventor (si esta casilla de verificación es marcada, no tiene adelante)	
			No de Registro del solicitante con la oficina	
Estado (que es el país) de nacionalidad		Estado (que es el país) de residencia		
Esta persona es solicitante para los propósitos de	☐ Todos los estados designados	☐ Todos los estados designados excepto los E U de América	☐ Solamente los Estados Unidos de América	☐ Los estados indicados en la casilla complementaria

27

Casilla Suplementaria Si la casilla suplementaria no es utilizada esta hoja no debe ser incluida en la solicitud

- 1 Si cualquiera de las casillas excepto las casillas no. VII(i) a (v) para la cual existe una casilla especial el espacio es insuficiente para proporcionar toda la información en tal caso escriba "Continuación de la casilla no (anote el no de la casilla) y escriba la información de la misma manera como requiere el subtitulo de la casilla en donde el espacio fue insuficiente en particular

Si mas de dos personas se indican como solicitantes y/o inventores y no hay hoja de continuación en tal caso escriba "Continuación de la casilla no. III" he indique para cada persona adicional la misma información que se requiere en la casilla III El país de la dirección puesta en esta casilla es el Estado (es decir país) de residencia si no se anota ningún Estado de residencia

Si en la casilla no. II o cualquiera de sub-casillas de la casilla no. III la indicación El estado que se anota en la casilla adicional se chequea en tal caso escriba "Continuación de la casilla no. II" o "Continuación de la casilla no. III" o "Continuación de las casillas no. II y no. III" (como sea el caso) anote el nombre del solicitante(s) involucrado y junto a cada uno de estos nombres el Estado(s) (y/o, donde aplica patente ARIPO Euroasiática Europea o OAPI) pa. a cuyo propósito dicha persona es el solicitante

Si en la casilla no. II o cualquiera de las sub-casillas de la casilla no. III el inventor o el inventor-solicitante no es el inventor para todos los Estados designados o para los Estados Unidos de America en tal caso escriba "Continuación de la casilla no. II" o "Continuación de la casilla no. III" o "Continuación de las casillas no. II y no. III" (como sea el caso) anote el nombre del inventor(s), y junto a cada uno de estos nombres el Estado(s) (y/o donde aplica patente ARIPO Euroasiática Europea o OAPI) para cuya propósito dicha persona es el inventor

Si adicionalmente al agente(s) indicado en la casilla no. IV hay mas agentes en tal caso escriba "Continuación de la casilla no. IV" he indique para cada agente adicional el mismo tipo de información que se requiere en la casilla no. IV

Si en la casilla VI hay mas de tres solicitudes tempranas cuya reivindicación de prioridad en tal caso escriba "Continuación de la casilla no. IV" he indique para cada aplicación temprana el mismo tipo de información que se requiere en la casilla no. VI
- 2 Si el solicitante desea que la solicitud internacional se trate en un Estado específico, como patente de adición "certificado de adición" "certificado de adición de inventor" "certificado utilitario de adición", en tal caso escriba el nombre y el código de dos letras del estado concerniente y la indicación "patente de adición" "certificado de adición" "certificado del inventor de adición" o "certificado utilitario de adición" el numero de la solicitud maestra o patente maestra u otra concesión maestra y el día de la concesión de la patente maestra o de otra concesión o el día en que se archiva la aplicación maestra (Regla 4.11 (a)(ii) y 49bis 1(a) o (b))
- 3 Si el solicitante desea que la solicitud internacional se trate en los Estados Unidos de América como una continuación o continuación en parte de una solicitud anterior en tal caso, escriba "Estados Unidos de America" o "US" e indicar "continuación" o "continuación en parte" y el numero y fecha en que se archiva la solicitud maestra (Regla 4.11(a)(iv) y 49bis 1(d))

Continuación de la casilla No. IV

DICKSON Elizabeth Anne
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27

Casilla No. 5 DESIGNACIONES

El diligenciamiento de esta solicitud constituye bajo la regla 49 (a) la designación de todos los estados contratantes vinculados por el PCT en la fecha de diligenciamiento internacional, para garantizar toda clase de protección disponible y donde fuere aplicable, para garantizar patentes nacionales y regionales.

No obstante:

- ☐ DF Vietnam no está designado para cualquier clase de protección nacional
- ☐ KR República de Corea no está designado por cualquier clase de protección nacional
- ☐ RI Federación Rusa no está designado por cualquier clase de protección nacional

(Las casillas de choque arriba pueden ser usadas para excluir (irrevocablemente) designaciones convenientes en virtud de evitar el coste del efecto, bajo la ley nacional de una solicitud nacional previa desde la cual la prioridad es reivindicada. Ver las notas para casilla No. 5 con para las conexiones de prioridades de cada ley nacional en este y otros sheets estadivos)

Casilla No. VI REIVINDICACIONES DE PRIORIDAD

Por medio de la presente se reivindica la prioridad de la(s) siguiente(s) solicitud(es) temprana(s):

Fecha de presentación de la solicitud temprana (día, mes, año)	Número de la solicitud temprana	Países o miembros del WFO		
		Solicitud nacional País o miembro del WFO	Solicitud regional Oficina regional	Solicitud internacional Oficina receptora
item(1) 21 Junio 2004 (21.06.2004)	04138319	GB		
item(2)				
item(3)				

☐ Las reivindicaciones de prioridad se indican en la Casilla Complementaria.

Se solicita a la Oficina receptora preparar y transmitir a la Oficina Internacional una copia certificada de la(s) solicitud(es) temprana(s) (solo si la solicitud temprana fue presentada con la Oficina que para propósitos de esta solicitud internacional es la Oficina receptora) identificada en/los como:

☐ Todos los items ☒ item (1) ☐ item (2) ☐ item (3) ☐ item (4) ☐ item (5) ☐ otros, ver casilla complementaria

En donde la solicitud temprana es una solicitud ARIPO, indique el número de la Convención de París para la Protección de Propiedad Industrial y el número de la Organización Mundial de Comercio para el cual la solicitud temprana se presentó (Regla 4.1 (b) (1) (ii)).

Casilla No. VII AUTORIDAD DE BÚSQUEDA INTERNACIONAL

Elección de la Autoridad de Búsqueda Internacional (ISA) (o dos o más Autoridades de Búsqueda Internacionales son competentes para llevar a cabo la búsqueda internacional, indique la autoridad escogida - se puede utilizar el código de dos letras).

ISA/

Solicitud para utilizar los resultados de la búsqueda temprana: Investigación de tal búsqueda (si una búsqueda temprana se ha llevado a cabo por solicitud de la Autoridad de Búsqueda Internacional)

Fecha (día/mes/año) Número País (u Oficina Regional)

Casilla No. VIII DECLARACIONES

Las siguientes declaraciones están contenidas en las Casillas Nos. VIII (i) a (v) (marque las casillas de verificación aplicables adelante e indique en la columna de la derecha el número de cada tipo de declaración)

- ☐ Casilla No. VIII(i) Declaración de la identidad del inventor
- ☐ Casilla No. VIII(ii) Declaración del derecho del solicitante, como la fecha de presentación internacional, para solicitar y otorgarse una patente
- ☐ Casilla No. VIII(iii) Declaración del derecho del solicitante, como la fecha de presentación internacional, para reivindicar la prioridad de una solicitud temprana
- ☐ Casilla No. VIII(iv) Declaración de inventor (solo para los propósitos de designación de los Estados Unidos de América)
- ☐ Casilla No. VIII(v) Declaración de descripción no perjudicial o escuipenosa para falta de novedad

CASILLA VIII (i) DECLARACION IDENTIDAD DEL INVENTOR

La declaración debe ser conforme a la formulación estandarizada prevista para tal en la sección 211 ver notas a las casillas Nos. VIII (iii) a (vi) (en general) y las notas específicas a la casilla No. VIII (ii). Si esta casilla no es usada esta hoja no debe incluirse en la solicitud

La Declaración como la identidad del inventor (Reglas 4 17(i) y 51bis 1(a)(i)).

☐ Esta declaración continua en la siguiente hoja, continuación de casilla No. VIII (i)

Forma PCT/RO/101 (hoja de declaración (i)) (Enero 2004)

Casilla No. VIII (ii) DECLARACION DERECHO PARA SOLICITAR Y SER OTORGADA UNA PATENTE

La declaración debe ser conforme a la formulación estandarizada prevista para tal en la sección 212 ver notas para casillas Nos. VIII (ii) a (iv) (en general) y las notas a la casilla No. VIII (ii). Si esta casilla no es usada esta hoja no debe incluirse en la solicitud

Declaración como derecho del solicitante a partir de la fecha de presentación internacional, para aplicar y ser otorgada una patente (Reglas 4 17(ii) y 51bis 1(a)(ii)), en un caso donde la declaración bajo la regla 4 17(iv) no sea apropiada

☐ Esta declaración continua en la siguiente hoja, continuación de casilla No. VIII (ii)

Forma PCT/RO/101 (hoja de declaración (ii)) (Enero 2004)

Casilla No. VIII (iii) DECLARACION DERECHO A REIVINDICAR PRIORIDAD

La declaración debe ser conforme a la formulación estandarizada prevista para tal en la sección 213 ver notas para casillas Nos. VIII (iii) a (iv) (en general) y las notas a la casilla No. VIII (iii). Si esta casilla no es usada esta hoja no debe incluirse en la solicitud

Declaración como derecho del solicitante a partir de la fecha de presentación internacional, para reivindicar la prioridad de la solicitud temprana especificada abajo donde el solicitante no es el solicitante que presentó la solicitud temprana o donde el nombre del solicitante ha cambiado desde la presentación de la solicitud de la solicitud temprana (Reglas 4 17(iii) y 51bis 1(a)(iii)).

☐ Esta declaración continua en la siguiente hoja, continuación de casilla No. VIII (iii)

Forma PCT/RO/101 (hoja de declaración (iii)) (Enero 2004)

Casilla No. VIII (iv) DECLARACIÓN AUTORIA DEL INVENTO (solo para propósito de la designación de los Estados Unidos de América)

La declaración debe ser conforme a la formulación estandarizada prevista para tal en la sección 214 ver Notas para casillas Nos. VIII (III ii) u (v) (en general) y las Notas a la casilla No. I III (iii). Si esta casilla no es usada esta hoja no debe incluirse en la solicitud.

**Declaración de autoría del Invento (Reglas 4.17(h) y 51bis.1(a)(h))
for the purposes of the designation of the United States of America:**

Por medio de la presente declaro que creo que soy el (original, primero y único (si únicamente está listado un inventor a continuación) o colectivo (si más de un inventor es nombrado abajo) inventor del objeto materia de esta reivindicación y por la cual la patente es buscada.

Esta declaración está dirigida a la solicitud internacional de la cual esta forma parte (si se presentó declaración con la solicitud).

Esta declaración está dirigida a la solicitud internacional No. PCT/

(si suministro declaración según la regla 26ter)

Por la presente declaro que mi residencia, dirección de correspondencia y ciudadanía están declaradas junto a mi nombre. Por la presente declaro que he revisado y comprendido los contenidos de la solicitud internacional arriba identificada incluyendo las reivindicaciones de dicha solicitud. He identificado en la petición de dicha solicitud, de conformidad con la regla PCT 4.10, cualquier reivindicación para prioridad extranjera y he identificado a continuación bajo el título "solicitudes previas" por número de solicitud país o miembro de la Organización Mundial de Comercio día, mes y año de presentación, cualquier solicitud para una patente o certificado de inventor presentado en un país diferente a los Estados Unidos de América, teniendo una fecha de presentación anterior a la de la solicitud en la cual una prioridad extranjera es reivindicada.

Solicitudes Previas

Por la presente reconozco el deber de revelar información que es conocida por mí para ser material de patentabilidad delimitado por 37 C.F.R. § 1.56, incluyendo la continuación de parte de solicitudes, información material que sea disponible entre la fecha de presentación de la solicitud previa y de la fecha de presentación internacional PCT de la solicitud de continuación en parte.

Por la presente declaro que todas las declaraciones hechas aquí de mi propio conocimiento son verdaderas y todas esas declaraciones están hechas en información y creencia de que son verdaderas, y más allá de esas declaraciones fueron hechas con el conocimiento de que falsas declaraciones malintencionadas hechas son punibles por multa o prisión o ambas bajo la sección 1001 del título 18 del código de Los Estados Unidos y que esas declaraciones malintencionadas pueden hacer peligrar la validez de la solicitud o cualquier patente basada en ellas.

Nombre

Residencia

(ciudad y cualquier estado de USA si aplica, o país)

Dirección de correspondencia

Ciudadanía

Firma del inventor

Fecha

(si no está contenida en la solicitud o si la declaración es corregida o adicionada bajo la regla 26ter luego de la presentación de la solicitud internacional. La firma debe ser del inventor no del agente).

(Fecha de la firma que no está contenida en la solicitud, o de la declaración si esta corregida o adicionada bajo la regla 26ter luego de la presentación de la solicitud internacional)

☐ Esta declaración continúa en la siguiente hoja, "continuación de casilla No. VIII (iv)"

Forma PCT/RO/101 (hoja de declaración (iv)) (Enero 2004)

Casilla No. VIII (1) DECLARACION REVELACIONES NO PREJUDICIALES O EXCEPCIONES DE FALTA DE NOVEDAD

La Declaración debe ser conforme a la formulación estandarizada presentada para las secciones 213 y 214 para las secciones 171 y 172 (en general)

1. **Let's start at the cradle No. 1 III (III)** Si con canillo es es grande esta haca es dehe mchurra es la pñicard

Declaración como revelación no prejudicial o excepciones de falta de novedad (Reglas 1.17(v) y 51b.x 1(a)(v))

☐ Esta declaración continua en la siguiente hoja. Continuación de casilla No. VIII (v).

Forma PCT/RO/101 (Guia de depuneri) (v.1) (Iunie 2001)

Castilla No. VIII (D) u (I) DECLARACION

Si el espacio es insuficiente en cualquiera de las casillas Nos. III (i) a (v) para suministrar toda la información incluyendo el caso en que haya mas de dos inventores a ser nombrados en la casilla No. III (iv) en cuyo caso escriba "Comunicación de la casilla No. III" (indicando el número de item sobre la casilla) y suministre la información de la misma forma que se requiere para propósitos de la casilla en la cual el espacio es insuficiente. Si necesita espacio adicional respecto de dos o mas declaraciones, una casilla separada debe ser utilizada para cada una de las mismas. Si esta casilla no es utilizada, esta línea no debe incluirse en la solicitud.

☐ Esta declaración continúa en la siguiente hoja. Continuación de casilla No VII (v)

Forma PCT/RO/101 (hoja de continuación para declaración) (Enero 2004)

Cajilla No. 15 LISTA DE VERIFICACIÓN IDIOMA DE PRESENTACIÓN																																																																									
Esta solicitud internacional contiene: (a) en forma de papel, el siguiente número de hojas: <table><tr><td>Solicitud</td><td>3</td></tr><tr><td>incluidas Hojas de declaraciones</td><td></td></tr><tr><td>Descripción (esquema) listado de «secuencias» y/o tablas relacionadas con estas</td><td>14</td></tr><tr><td>Reivindicaciones</td><td>3</td></tr><tr><td>Resumen</td><td>1</td></tr><tr><td>Dibujos</td><td>0</td></tr><tr><td>Subtotal de hojas</td><td></td></tr><tr><td>Listas de secuencias</td><td></td></tr><tr><td>Tablas relacionadas</td><td>23</td></tr></table> Parte de la lista de secuencias de las descripciones (el número actual de hojas, si se archivarán en papel, así se hacen leyendo en computador ver (c) más abajo. Total número de hojas 27 (b) ☐ solo en forma legible por computador (Sección 801 (a)(i)) (i) ☐ listado de «secuencias» (ii) ☐ tablas relacionadas con estas (c) ☐ también en forma legible por computador (Sección 801 (a)(ii)) (i) ☐ listado de «secuencias» (ii) ☐ tablas relacionadas con estas Número y tipo de portadores (floppy, CD-ROM, CD-R o otro) en el cual está contenido el: ☐ listado de secuencias. ☐ las tablas relacionadas con esta (copias adicionales para ser indicadas de acuerdo con los ítems 9(n) y o 10(n), en la columna derecha)	Solicitud	3	incluidas Hojas de declaraciones		Descripción (esquema) listado de «secuencias» y/o tablas relacionadas con estas	14	Reivindicaciones	3	Resumen	1	Dibujos	0	Subtotal de hojas		Listas de secuencias		Tablas relacionadas	23	Esta solicitud internacional es acompañada por el(los) siguiente(s) item(s) (marque las casillas de verificación aplicables adelante o indique en la columna derecha el número de cada ítem) <table><thead><tr><th></th><th></th><th>Número de ítems</th></tr></thead><tbody><tr><td>1</td><td>☒ Hoja de cálculo de tasas</td><td>1</td></tr><tr><td>2</td><td>☐ Original del Poder de abogado por separado</td><td></td></tr><tr><td>3</td><td>☐ Original del Poder general de abogado</td><td></td></tr><tr><td>4</td><td>☐ copia del Poder general de Abogado, número de referencia si existe.</td><td></td></tr><tr><td>5</td><td>☐ Declaración que explica falta de firma</td><td></td></tr><tr><td>6</td><td>☐ Documento(s) de propiedad intelectual(es) en cajilla No. 11 como item(s)</td><td></td></tr><tr><td>7</td><td>☐ Traducción de la solicitud internacional en (idioma(s))</td><td></td></tr><tr><td>8</td><td>☐ Indicaciones separadas en relación con microorganismos u otro material biológico</td><td></td></tr><tr><td>9</td><td>☐ Lista de secuencias en forma legible por computador</td><td></td></tr><tr><td></td><td>(i) ☐ copia presentada para los propósitos de búsqueda internacional de acuerdo con la Regla 13ter solamente (y no como parte de la solicitud internacional);</td><td></td></tr><tr><td></td><td>(ii) ☐ (solo cuando la casilla de verificación (b)(i) o (c)(i) se marca en la columna de la izquierda) copias adicionales incluyen cuando aplica, la copia para los propósitos de búsqueda internacional de acuerdo con la Regla 13ter</td><td></td></tr><tr><td></td><td>(iii) ☐ junto con las declaraciones importantes para la identidad de la copia, u copias con los listados de secuencias mencionados en la columna izquierda</td><td></td></tr><tr><td>10</td><td>☐ Tablas en forma legible por computador relacionadas con la lista de secuencias (indique número y tipo de portadores)</td><td></td></tr><tr><td></td><td>(i) ☐ copia presentada para los propósitos de búsqueda internacional de acuerdo con la Sección 802(802b-cuarto) solamente (y no como parte de la solicitud internacional).</td><td></td></tr><tr><td></td><td>(ii) ☐ (solo cuando la casilla de verificación (b)(ii) o (c)(ii) se marca en la columna de la izquierda) copias adicionales incluyen cuando aplica, la copia para los propósitos de búsqueda internacional de acuerdo con la Sección 802(b-cuarto)</td><td></td></tr><tr><td></td><td>(iii) ☐ junto con las declaraciones importantes para la identidad de la copia, u copias con las tablas mencionadas en la columna izquierda</td><td></td></tr><tr><td>11</td><td>☒ Otra (especifique): FORMATOS PATENTES 21/77</td><td>1</td></tr></tbody></table>			Número de ítems	1	☒ Hoja de cálculo de tasas	1	2	☐ Original del Poder de abogado por separado		3	☐ Original del Poder general de abogado		4	☐ copia del Poder general de Abogado, número de referencia si existe.		5	☐ Declaración que explica falta de firma		6	☐ Documento(s) de propiedad intelectual(es) en cajilla No. 11 como item(s)		7	☐ Traducción de la solicitud internacional en (idioma(s))		8	☐ Indicaciones separadas en relación con microorganismos u otro material biológico		9	☐ Lista de secuencias en forma legible por computador			(i) ☐ copia presentada para los propósitos de búsqueda internacional de acuerdo con la Regla 13ter solamente (y no como parte de la solicitud internacional);			(ii) ☐ (solo cuando la casilla de verificación (b)(i) o (c)(i) se marca en la columna de la izquierda) copias adicionales incluyen cuando aplica, la copia para los propósitos de búsqueda internacional de acuerdo con la Regla 13ter			(iii) ☐ junto con las declaraciones importantes para la identidad de la copia, u copias con los listados de secuencias mencionados en la columna izquierda		10	☐ Tablas en forma legible por computador relacionadas con la lista de secuencias (indique número y tipo de portadores)			(i) ☐ copia presentada para los propósitos de búsqueda internacional de acuerdo con la Sección 802(802b-cuarto) solamente (y no como parte de la solicitud internacional).			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Figura de los dibujos que pueda acompañar al Resumen.	N/A	Idioma de Presentación de la Solicitud Internacional	Inglés																																																																						
Cajilla No. X FIRMA DEL SOLICITANTE O AGENTE																																																																									
Ante o cada firma, indique el nombre de la persona firmante y la capacidad en la cual la persona firma (si tal capacidad no es obvia de la lectura de la solicitud)																																																																									
CRAIG BOWERS																																																																									
Agente de los Solicitantes																																																																									

Para uso exclusivo de la Oficina Receptora

1 Fecha de recibo actual que da a entender la solicitud internacional	2 Dibujos ☐ Recibido ☐ No recibido
3 Dato corregido del actual recibo debido a papeles recibidos erróneamente pero en tiempo o dibujos completados la debida solicitud internacional	
4 Fecha del recibo en tiempo de las correcciones requeridas bajo el artículo PCT 11(2).	
5 Autoridad de Búsqueda Internacional (si dos o mas son competentes) ISA.	6 ☐ Transmisión de la copia de búsqueda retrasada hasta que la tasa de búsqueda es pagada

Fecha de recibo de la copia del record por la Oficina Internacional

83

Esta hoja no hace parte y no cuenta como hoja de la solicitud internacional

PCT

HOJA DE CÁLCULO DE TASAS (ANEXO A LA SOLICITUD)

Solicitud Internacional No.
Fecha de Presentación Internacional

Archivo de Referencia del Agente o Solicitante: 1144892 WO/2005

FECHA DE PRESENTACIÓN: 11/05/2005

Calculo de la tasa prescrita

1 Tasa de transmisión ... 55 00(T)

2 Tasa de búsqueda ... 1078 00(s)

La búsqueda internacional debe ser conducida por EU

(Si dos o mas autoridades internacionales de búsqueda son competentes para conducir la búsqueda internacional indique el nombre de la autoridad que ha de llevar a cabo la búsqueda internacional)

3 Tasa de archivo internacional

Donde las letras (b) y o (c) de la casilla No. 1X aplican, ponga el Sub-total de hojas

Donde las letras (b) y o (c) de la casilla No. 1X no aplican, ponga el Total de hojas ... 23

b1 Primeras 30 hojas ... 628 00(1)

(b2) numero de hojas que pasan de 30 ... Tasa por hoja ... (12)

(b3) componentes adicionales solo si la secuencia de títulos y o tablas resumidas allí se archivan en medios legibles por computador bajo la seccion 801(a)(1) o ambas en esta forma y papel bajo la seccion 801(a)(u)

400 ... tasa por hoja ... 12

Suma: renglones (1) (2) y (3) y anote el total en 1 ... 628 00B

4 Tasa por el documento prioritario 22.00(p)

5 Total a pagar

Suma las cantidades en 1, 5 (1) y 5 (P) y anote el total en la casilla Total

\$ 1783.00
TOTAL

Forma de Pago

☒ autorización para cargar a una cuenta corriente ☐ Giro postal ☐ Efectivo ☐ Cheque

☐ Cheque ☐ Retiro bancario ☐ Estampillas redimibles ☐ otras (especifique)

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Cuenta corriente no. D02903

Fecha Junio 16 2005

Nombre Craig Bowern

Firma.

83

TRATADO DE COOPERACION DE PATENTES

De La Oficina Internacional

PCT	
NOTIFICACIÓN DEL REGISTRO DE UN CAMBIO	Para
(PCT Regla 92bis.1 e Instrucciones Administrativas sección 422)	BOWERS, Craig Grupo de Patentes, Departamento Legal Reckitt Benckiser plc Dansom Lane Hull HU8 7DS Reino Unido
Fecha de envío (día/mes/año) 15 de septiembre de 2005 (15 09 2005)	
Archivo de referencia del solicitante o agente 11449P1 WO/JMH	NOTIFICACION IMPORTANTE
Solicitud internacional No PCT/GB2005/002383	Fecha de presentación internacional 17 de junio de 2005 (17 06 2005)

1 Las indicaciones siguientes aparecen en un registro concerniente a		
☒ El solicitante ☒ El inventor ☐ El agente ☐ El representante		
Nombre y Dirección	Estado de Nacionalidad GB	Estado de Residencia GB
	Telefono No.	
	Fax No.	
	Teleprinter No	
2 La Oficina por medio de la presente notifica al solicitante que el siguiente cambio ha sido registrado concerniente a		
☒ La persona ☐ El nombre ☐ La dirección ☐ La nacionalidad ☐ La residencia		
Nombre y Dirección	Estado de Nacionalidad GB	Estado de Residencia GB
	Telefono No.	
	Fax No.	
	Teleprinter No.	
RADLEY, Jason Reckitt Benckiser (UK) Limited Dansom Lane Hull HU8 7DS Reino Unido		
3 Observaciones adicionales si son necesarias La persona en la casilla 2 ahora está registrada como solicitante únicamente en los Estados Unidos de America e inventor en todos los países designados. La persona en la casilla 1 sea eliminada de los registros		
4 Una copia de esta notificación ha sido enviada a		
☒ La Oficina Receptora ☐ Las Oficinas designadas correspondientes ☒ La Autoridad de Busq Intl ☐ Las Oficinas elegidas correspondientes ☐ La autoridad examinadora Intl ☐ Otros		
La oficina Internacional de WIPO 34 chemin des Colombettes 1211 Geneva 20 Switzerland		Oficial autorizado Juan CRUZ Telefono No (41-22) 338 8239

Compuesto d Betún para Cuero Cu ro Sintétic

Este invento hace referencia a un compuesto de betun para el tratamiento de articulos de cuero y/o cuero sintetico En particular este invento
5 hace referencia, aunque no exclusivamente, a compuestos de betun auto-brillantes

Los compuestos de betun se utilizan frecuentemente para dar brillo a articulos de cuero y/o cuero sintetico, tales como calzado Los compuestos
10 tradicionales de betun incluyen típicamente cera y solventes orgánicos Estos betunes se secan y dan un terminado opaco al articulo tratado Se requiere pulir los articulos para darles un acabado brillante

Los betunes auto-brillantes en presentación liquida fueron creados para
15 lograr brillo sin necesidad de pulir

Recientemente fueron creados tambien otros compuestos auto-brillantes en gel o crema. Estos compuestos estan fabricados a base de emulsiones acuosas de cera y polimeros acrilicos Al aplicarlos a un artículo, los
20 compuestos se secan, dando un acabado brillante Por lo general no s requiera pulir el artículo tratado para lograr el brillo deseado

Hemos observado que los compuestos de betun auto-brillantes que existen tienden a sufrir problemas con el almacenamiento Cuando por
25 ejemplo se almacenan durante periodos prolongados, el liquido se pued separar de los compuestos conocidos La separacion del liquido del resto del compuesto se conoce como sinéresis

Segun este invento, se proporciona un compuesto de betun para el
30 tratamiento de articulos de cuero y/o cuero sintetico, y dicho compuesto incluye agua

por lo menos una cera,

por lo menos un polimero que forma una película, y

un silicato con capas que incluye un peptico inorganico

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Al incluir un silicato con capas en el compuesto, los problemas de almacenamiento del compuesto se ven sustancialmente reducidos. De manera particular, la utilización del silicato con capas puede reducir la probabilidad de que el líquido se separe del compuesto aun después de largos periodos de almacenamiento. Por lo tanto el silicato con capas puede ser utilizado en el compuesto de betún para reducir o prevenir la sinéresis. El silicato con capas también puede asegurar la preservación de las propiedades reológicas del compuesto, por ejemplo, para asegurar la facilidad en la aplicación.

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De preferencia el compuesto de este invento se puede mantener estable durante su almacenamiento por un mínimo de 4 semanas, aun mejor por 8 semanas y mas preferiblemente por un mínimo de 12 semanas.

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Idealmente, el silicato con capas es un silicato con capas sintético. El silicato con capas puede ser un silicato de metal, tal como el silicato de un metal alcalino y/o un metal alcalinotérreo. Algunos silicatos de metal alcalino adecuados incluyen silicatos de litio, sodio y potasio. Algunos silicatos alcalinotérreos incluyen silicatos de magnesio y calcio. Es preferible que el silicato de metal sea un silicato de por lo menos un metal alcalino y por lo menos uno alcalinotérreo. En una incorporación se utiliza el silicato de magnesio de litio sodico.

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De preferencia, el silicato con capas tiene menos de % de peso 2, y aun mejor si es menos del % peso 1, y todavia mas si es menos del % peso 0.5, y lo ideal seria menos del % de peso 0.1 de sílice cristalino. En una incorporación, el silicato con capas esta practicamente libre de sílice cristalino.

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El silicato con capas también puede tener un contenido de metal de baja transición. Por ejemplo, el silicato con capas puede incluir un contenido de metal de transición de menos del % de peso 2, de preferencia menos del % de peso 1, aun mejor si es menos del % de peso 0.5, por ejemplo, menos del % de peso 0.1. En una incorporación, el silicato con capas está prácticamente libre de metal de transición.

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El silicato con capas incluye un péptico inorgánico. Es preferible que el péptico inorgánico sea un fosfato. Se puede utilizar cualquier péptico de fosfato adecuado. Sin embargo, son preferibles los fosfatos de metal, tales como los metales alcalinos y/o fosfatos alcalinoterreos. Los fosfatos de metal alcalino considerados adecuados incluyen fosfatos de litio, sodio y potasio. Los fosfatos de metal alcalinoterreos adecuados incluyen fosfatos de magnesio y calcio.

- 10 Es preferible que el fosfato sea un poli-fosfato, como un pirofosfato. En una incorporación preferida, se utiliza el pirofosfato de sodio tera

Un ejemplo de un silicato con capas adecuado es Laptonite ® RDS

- 15 El silicato con capas se suministra preferiblemente de forma finamente dividida

- 20 El silicato con capas puede estar presente en una cantidad de entre el % de peso 0.01 y 5 de la totalidad del compuesto de betún. De preferencia, el silicato con capas se encuentra presente en una cantidad del % de peso entre 0.05 y 4, preferiblemente entre el % de peso 0.1 y 3, por ejemplo entre el % de peso 0.2 y 2. En una incorporación preferida, se utiliza entre el % de peso 0.4 y 1, por ejemplo entre % de peso 0.5 y 0.7 de silicato con capas

- 25 El compuesto de betún incluye por lo menos una cera. También se pueden utilizar mezclas de una o más ceras. Algunas ceras adecuadas incluyen ceras de insecto, como cera de abejas, ceras vegetales, como cera de camauba y candelilla, ceras de mineral ester y ceras ácidas. De preferencia se utilizan ceras de mineral ester. Algunas ceras de mineral ester adecuadas incluyen cera montana (ozoquenta) (ej. Ester de cera montana). También se pueden utilizar ceras sintéticas como cera de polietileno (ej. oxidada) y ester poliol/cera de ester. En una incorporación preferida, el compuesto de betún incluye un ester de cera montana y una cera sintética como una cera oxidada
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de polietileno. En el caso de utilizar un éster de cera montana, éste puede ser un éster refinado de cera montana.

La cera o mezcla de cera utilizada en el compuesto de betún de este invento preferiblemente tiene un número de acidez de entre 5 y 50, idealmente entre 10 y 30.

La cera o mezcla de cera utilizada en el compuesto de betún preferiblemente tiene un peso molecular de entre 500 y 5000, idealmente entre 1000 y 4000, por ejemplo, entre 2000 y 3000.

La cantidad de cera en el compuesto de betún puede estar entre el % de peso 1 y 20, preferiblemente, entre el % de peso 2 y 15, aun mejor, entre el % de peso 5 y 10. En una incorporación preferida, el compuesto de betún tiene entre % de peso 1 y 6 (ej. entre 2 y 4) de cera de polietileno oxidado y entre % de peso 2 y 10 (ej. entre 3 y 8) éster de cera montana.

El compuesto de betún incluye un polímero que forma una película. Se pueden incluir uno o más polímeros que forman una película en el compuesto de betún. Algunos polímeros adecuados que forman una película son polímeros acrílicos (ej. Polímeros de acrílico modificado), poliuretano y siliconas.

Algunos polímeros acrílicos adecuados incluyen polímeros de monómeros seleccionados de entre por lo menos uno de los siguientes, ácido acrílico, ácido metacrílico y los ésteres derivados. Se pueden utilizar homopolímeros y copolímeros. Algunos copolímeros adecuados incluyen copolímeros de estireno/acrílico, tales como copolímeros de éster ácido metacrílico y copolímero de estireno acrílico. En una incorporación se utiliza una mezcla de copolímero de éster ácido metacrílico y copolímero de estireno acrílico.

El polímero que forma una película puede estar presente en el compuesto de betún en una cantidad de % de peso entre 1 y 20,

preferiblemente % de peso entre 8 y 18, por ejemplo, % de peso entre 4 y 12 del compuesto total. En una incorporación, el compuesto de betún incluye % de peso entre 2 y 4 de copolímero de estireno acrílico y % de peso entre 2 y 4 de un copolímero de éster ácido metacrílico.

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El compuesto de betún de este invento se encuentra de preferencia en presentación de gel o crema. Por ende, el compuesto de betún de este invento tiene preferiblemente una viscosidad de entre 50 y 100,000 centipoise.

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El compuesto de betún incluye preferiblemente una resina alcalina soluble. Se utiliza preferiblemente una resina de ácido maleínico como resina alcalina soluble. Una resina maleínica adecuada se vende bajo la marca registrada ALRESAT®. La resina alcalina soluble puede aumentar el brillo y ayudar a dar la consistencia de gel al compuesto.

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La resina alcalina soluble puede estar presente en una cantidad de % de peso entre 0.01 y 10, preferiblemente % de peso entre 0.5 y 8, por ejemplo, % de peso entre 1 y 5.

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El compuesto de betún de este invento se encuentra preferiblemente en presentación como emulsión, por ejemplo, una emulsión de aceite en agua.

Puede haber agua en el compuesto de betún en una cantidad de % de peso entre 5 y 90, preferiblemente % de peso entre 10 y 75, aun mejor, % de peso entre 20 y 60, por ejemplo, % de peso entre 40 y 55.

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El compuesto de betún incluye preferiblemente por lo menos un alcohol, como el alcohol entre C_1 y C_{10} . El alcohol puede ayudar a dar la consistencia de gel al compuesto. Algunos ejemplos de alcoholes adecuados incluyen metanol, etanol, propanol, butanol, pentanol, hexanol, heptanol, octanol, nonanol y decanol. De preferencia se utiliza un alcohol entre C_2 y C_6 , como el etanol, propanol, butanol, pentanol y/o hexanol. En una incorporación preferida, se utiliza un alcohol C_3 o C_4 , como el propanol o el butanol. Se prefiere el alcohol isopropilo. Los alcoholes pueden ser utilizados en una cantidad % d

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peso entre 1 y 30, preferiblemente, % de peso entre 5 y 20, aun mejor, % de peso entre 8 y 15 En una incorporacion preferenda, el compuesto de betun contiene % de peso entre 8 y 15 de alcohol isopropilo

5 Pueden estar presentes también otros solventes orgánicos en el compuesto de betun Por ejemplo, el compuesto de betun puede incluir uno o más solventes de hidrocarburo Sin pretender estar ligado a una teoría, el solvente de hidrocarburo puede ayudar a estabilizar el compuesto, sobretodo si este se encuentra en forma de gel Al utilizar solventes de hidrocarburo, se
10 trata de preferencia al solvente de hidrocarburo para remover cualquier componente aromático Existe un solvente de hidrocarburo adecuado bajo la marca registrada EXXSOL ® D40 Al utilizar un solvente de hidrocarburo, se utiliza preferiblemente en una cantidad de % de peso entre 1 y 5

15 El compuesto de betun de este invento también puede incluir como opcion un surfactante o emulsificadores Se prefieren surfactantes no ionicos como etoxilatos de alcohol graso Se prefieren los etoxilatos de alcohol graso derivados de la reaccion entre un alcohol entre C₁₂ y C₁₅ y oxido de etileno De preferencia, cada molecula gramo de alcohol reacciona con entre 8 y 15
20 moleculas gramo de oxido de etileno Algunos ejemplos de surfactantes y emulsificadores adecuados se venden bajo las marcas registradas Emulsifier 4106 (Clariant) y Genopol X060 (ex Clariant)

Se pueden utilizar los emulsificadores o surfactantes en una cantidad de
25 % de peso entre 0.1 y 10, preferiblemente, % de peso entre 1 y 10, por ejemplo, % de peso entre 2 y 5 del compuesto total

El compuesto de betun puede incluir colorantes como opcion Algunos colorantes adecuados incluyen ácido negro 2 (Acid black 2) En una
30 incorporación, la dispersion de negro carbon se incluye en el compuesto de betun

El (Los) colorante(s) pueden estar presentes en una cantidad de % de peso entre 0.01 y 10, por ejemplo % de peso entre 0.1 y 5

Otros componentes opcionales como perfumes y preservativos tambien se pueden incluir en el compuesto de betun

- 5 El compuesto tambien puede incluir un aditivo estabilizador como 2-amino 2-metil propano-1-ol Se cree que estos aditivos estimulan la estabilidad de la emulsión

En una incorporacion, el compuesto de betun de este invento es una emulsión acuosa que incluye

- 10 agua (ej En una cantidad de % de peso entre 20 y 60),
 cera (ej En una cantidad de peso entre 5 y 10),
 un polímero que forma una película (e g ej en una cantidad de % de peso entre 8 y 20),
 15 una resina alcalina soluble (ej en una cantidad de % de peso entre 0.5 y 8),
 alcohol (ej en una cantidad de % de peso entre 5 y 20),
 silicato con capas que incluye un polifosfato inorgánico (ej en una cantidad de % de peso entre 0.01 y 5) y, opcionalmente,
 20 un solvente de hidrocarburo y/o surfactante

En la incorporacion previa, la cera es preferiblemente una mezcla de cera ester montana y cera de polietileno oxidada, el polimero que forma una película incluye preferiblemente por lo menos un polimero acrilico, la resina
 25 alcalina soluble es preferiblemente una resina de acido maleinico y el alcohol es preferiblemente un alcohol isopropilo. Aun mejor, el polimero que forma una película incluye un copolimero de esteres ácidos metacrílicos y un copolimero de estireno acrilico

- 30 El compuesto de betun de este invento es ideal para el tratamiento de articulos de cuero y cuero sintético. Estos articulos incluyen articulos de calzado, como zapatos, botas y sandalias, así como carteras, cinturones, guantes, sillas para montar a caballo y muebles

De preferencia el compuesto de betun de este invento proporciona un acabado brillante al articulo tratado El compuesto de betun también puede ayudar a aumentar la resistencia del cuero (o del cuero sintetico) al clima, los rayones y raspones

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El compuesto de betun de este invento se puede aplicar sobre articulos de cuero y cuero sintetico y puestos a secar Una vez seco, el compuesto deja una pelicula brillante en la superficie del articulo El articulo tratado podra ser pulido para aumentar el brillo, pero en la incorporacion preferida, no es necesario pulir para dar brillo al articulo tratado Por lo tanto, en esa incorporacion preferida, el compuesto de betun es auto-brillante Se cree que el silicato en capas es especialmente util en un compuesto de betun auto-brillante, pues se cree que el silicato proporciona una reologia con adelgazamiento por cortante al compuesto que ayuda a la formacion de una pelicula brillante sobre el articulo al aplicarlo

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El compuesto de betun de este invento se puede aplicar con esponja El compuesto de betun puede estar dentro de un tubo o, preferiblemente, en un frasco

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El compuesto de betun de este invento puede ser preparado mezclando al tiempo los componentes individuales del compuesto, por ejemplo, para formar una emulsion

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En una incorporación, el polimero que forma una pelicula y el silicato con capas se agregan a una emulsion acuosa de cera (s), preferiblemente, mezclando enérgicamente Preferiblemente, el silicato con capas (ej Silicato de magnesio sodio litio modificado con pirofosfato de sodio tera) se agrega a la emulsion de cera en la forma de solucion acuosa pre-formada

Adicionalmente al polímero que forma una pelicula y al silicato con capas, los componentes como la resina, colorante(s), surfactantes, emulsificadores y solventes también se pueden agregar a la emulsion de cera, preferiblemente mezclando continuamente Cuando se utilizan el surfactante

(ej éter poliglicol de ácido graso) y el solvente (ej Solvente de hidrocarburo) se pueden agregar como mezcla pre-formada. En una incorporación preferida un solvente de alcohol, como el alcohol isopropilo se agrega a la mezcla resultante en de manera continua para ayudar a crear la consistencia de gel

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La emulsion de cera se puede formar de manera preliminar, por ejemplo, deritiendo la (s) cera (s) a una temperatura elevada de por ejemplo entre 80 a 150°C, preferiblemente, entre 100 y 130°C, aun mejor, entre 120 y 125°C. En un recipiente separado, el agua se puede calentar a una temperatura de por ejemplo, entre 80 y 100°C, preferiblemente entre 90 y 95°C. La cera derretida se puede agregar luego al agua y la mezcla resultante se revuelve para formar una emulsion (ej emulsión de aceite en agua). Como opcion, se puede agregar a la cera derretida un emulsificador (p ej eteres poliglicoles de acidos grasos)) y/o un aditivo estabilizador (ej 2-amino-2-metil prompan-1-ol), por ejemplo, antes de que la cera derretida se mezcle con el agua. Una vez la cera derretida se mezcla con el agua, la mezcla resultante se enfria, por ejemplo, pasándolo a una temperatura de por ejemplo entre 10 y 50°C, por ejemplo entre 30 y 40°C

20 Ejemplo

El compuesto auto-brillante de la Tabla 1 se preparó calentando primero las ceras (ii y iii) con el componente (iv) a una temperatura de entre 120 y 125°C para formar una mezcla de cera derretida. Se agrego el componente (v) a la mezcla. La mezcla de cera derretida se agrego lentamente al agua caliente (entre 90 y 95°C) revolviendo vigorosamente. La mezcla resultante se enfrio rápidamente a 40°C para formar una emulsion de cera. Aproximadamente 75% del 46.58 peso/peso% agua del compuesto se utiliza para formar la emulsion de cera. El agua restante se mezcla con el componente (xi) para formar una dispersion (ver más abajo)

Luego se agregaron los componentes (xiv), (xii), (x) (ix) y (viii) a la emulsión de cera revolviendo vigorosamente. Luego, se agregó una mezcla del

componente (xi) y agua y se revolvió la mezcla restante durante otros 15 minutos

Una pre-mezcla de componentes (vi) y (vii) se agrego luego La mezcla
5 resultante se revolvió durante otros 20 minutos antes de que se agregara el
componente (xii) de manera continua

La formacion de una gel cremosa ocumo 1 hora despues de la adición
del componente (xii)

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Ejemplo comparativo

El procedimiento descrito haciendo referencia al Ejemplo anterior se
repitió para preparar el compuesto auto-brillante de la Tabla 2 Sin embargo, el
15 componente (xi), se omitió de la composición del Ejemplo Comparativo Por
ende, la totalidad del 49.16 p/p% agua de este Ejemplo Comparativo se utiliza
para formar la emulsion de cera

Los compuestos del Ejemplo y del Ejemplo Comparativo fueron
20 almacenados en frascos de vidrio sellados durante un mes Segun el ejemplo,
el compuesto fue estable durante el almacenamiento En contraposición, el
compuesto del Ejemplo Comparativo mostro sinéresis

Tabla 1

Componente	p/p%
(i) Agua (suave)	46 58
(ii) Ester de cera montana refinado (Licowax KSL, Clariant)	5 85
(iii) Cera de polietileno oxidado (Cera de polietileno PED 522, Clariant)	3 60
(iv) Mezcla de éteres poliglicol de ácidos grasos (Emulsificador 4106 Clariant)	1 80
(v) 2-amino-2-metil propano-1-ol (AMP 90, Angus Chemie)	0 90
(vi) Éter poliglicol de ácido graso (Genopol X060, Clariant)	3 00
(vii) Solvente de hidrocarburo con bajo contenido aromático (Exxsol D40, Exxon)	6 00
(viii) Copolímero de estireno acrílico (Vinacryl 7190, Vinacryl - 50% activos)	6 00
(ix) Copolímero de ésteres de ácido metacrílico (Mowilith DM 772, Clariant - 46% activos)	8 00
(x) Solución acuosa de resina de ácido maleínico modificado (NaOH Alresat solución de Resina 30%, Dick Peters)	6 00
(xi) Silicato de magnesio de sodio de litio modificado con pirofosfato de sodio tera (Laponite RDS, Rockwood)	0 50
(xii) alcohol isopropilo	10 00
(xiii) Colorante Negro 2 (Acid black 2) índice de color 504201 (Nigrosine WLF soluble en agua)	1 27
(xiv) Dispersión acuosa negro carbon (Colanyl Black PR 130)	0 50

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Tabla 2

Componente	p/p%
(i) Agua (suave)	49 18
(ii) Ester de cera montana refinado (Licowax KSL, Clariant)	5 46
(iii) Cera de polietileno oxidada (Cera de polietileno PED 522	3 36

Clariant)	
(iv) Mezcla de éteres poliglicol de ácido graso (Emulsificador 4106, Clariant)	1 68
(v) 2-amino-2-metil propano-1-ol (AMP 90 Angus Chemie)	0 84
(vi) Éter poliglicol de ácido graso (Genopol X060, Clariant)	3 00
(vii) Solvente de hidrocarburo con bajo contenido aromático (Exxsol D40, Exxon)	6 00
(viii) Copolímero de estireno acrílico (Vinacryl 7190, Vinacryl - 50% activos)	6 00
(ix) Copolímero de ésteres de ácido metacrílico (Mowilith DM 772, Clariant - 46% activos)	8 00
(x) Solución acuosa de resina de ácido maleínico modificado (NaOH Alresat solución de Resina 30%, Dick Peters)	6 00
(xi) alcohol isopropilo	10 00
(xiv) Dispersión acuosa negro carbón (Colanyl Black PR 130)	0 500

REVINDICACIONES

- 1 Un compuesto de betun para el tratamiento de articulos de cuero y/o
cuero sintetico, dicho compuesto incluye
- 5 agua,
por lo menos una cera
por lo menos un polimero que forma una pelicula, y
un silicato con capas que incluye un peptico inorganico
- 10 2 Un compuesto segun la Revindicacion 1, en el cual el péptico inorgánico
es un polifosfato inorganico
- 3 Un compuesto segun la Revindicacion 1 ó 2, en el cual la cera incluye
un ester de cera montana y cera de polietileno oxidado
- 15 4 Un compuesto segun cualquiera de las Revindicaciones precedentes,
en el cual el polimero que forma una pelicula se selecciona de por lo menos
uno de los siguientes: silicona, poliuretano y polimero acrilico
- 20 5 Un compuesto segun la Revindicación 4, en el cual el polímero que
forma una pelicula incluye una mezcla de copolimero de estireno acrílico y un
copolimero de éster de ácido metacrilico
- 6 Un compuesto segun cualquiera de las Revindicaciones precedentes,
que además incluye una resina alcalina soluble
- 25 7 Un compuesto segun la Revindicación 6, en el cual la resina alcalina
soluble es una resina de acido maleinico
- 30 8 Un compuesto segun cualquiera de las Revindicaciones precedentes,
que se encuentra en la forma de una emulsion de aceite en agua
- 9 Un compuesto segun cualquiera de las Revindicaciones precedentes, que
incluye

% de peso 1 a 20 de dicha cera,

% de peso 1 a 20 por lo menos de dicho un polimero que forma una película,

% de peso 0.01 a 5 de dicho silicato con capas

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10 Un compuesto segun cualquiera de las Reivindicaciones precedentes que además incluye un alcohol

11 Un compuesto segun la Reivindicación 10, en el cual el alcohol es un

10 alcohol isopropílico

12 Un compuesto segun cualquiera de las Reivindicaciones precedentes que es un compuesto de betun auto-brillante

15 13 Un método para la preparacion de un compuesto segun lo reivindicado en cualquiera de las Reivindicaciones 1 a 12, y dicho metodo incluye

20 la formacion de una emulsion acuosa de dicha cera, dicho polimero que forma una película y dicho silicato sintético con capas

14 Un método segun la Reivindicacion 15, que además incluye la adicion de un alcohol

25 15 Un metodo para el tratamiento de artículos de cuero y/o cuero sintético, que incluye la aplicacion de un compuesto segun lo reivindicado en cualquiera de las Reivindicaciones 1 a 12 a articulos de cuero y/o cuero sintético

30 16 Un metodo segun la Reivindicación 15, en el cual dicho compuesto se deja secar para dar un terminado brillante sin pulir

17 Uso de un silicato con capas sintético que incorpora un peptico inorganico en un compuesto de betun para reducir o evitar la sineresis del compuesto de betun

18 Uso según lo reivindicado en la Reivindicación 17, en el cual dicho compuesto de betún incluye agua, por lo menos una cera y por lo menos un polímero que forma una película

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19 Uso según lo reivindicado en la Reivindicación 18, en el cual dicho compuesto de betún es un compuesto de betún auto-brillante

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5 **Compendio**

Compuesto de Betún para Cuero o Cuero Sintético

- 10 Un compuesto de betún para el tratamiento de artículos de cuero y/o cuero sintético, dicho compuesto incluye agua, por lo menos una cera, por lo menos un polímero que forma una película y un silicato con capas que incluye un péptico inorgánico

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Mejoras en un Compuesto o relacionadas con este

Este invento hace referencia a un compuesto de betún para el tratamiento de artículos de cuero y/o cuero sintético. En particular este invento
5 hace referencia, aunque no exclusivamente, a compuestos de betún auto-brillantes.

Los compuestos de betún se utilizan frecuentemente para dar brillo a artículos de cuero y/o cuero sintético, tales como calzado. Los compuestos
10 tradicionales de betún incluyen típicamente cera y solventes orgánicos. Estos betunes se secan y dan un terminado opaco al artículo tratado. Se requiere pulir los artículos para darles un acabado brillante.

Los betunes auto-brillantes en presentación líquida fueron creados para
15 lograr brillo sin necesidad de pulir.

Recientemente fueron creados también otros compuestos auto-brillantes en gel o crema. Estos compuestos están fabricados a base de emulsiones acuosas de cera y polímeros acrílicos. Al aplicarlos a un artículo, los
20 compuestos se secan, dando un acabado brillante. Por lo general no se requiere pulir el artículo tratado para lograr el brillo deseado.

Hemos observado que los compuestos de betún auto-brillantes que
25 existen tienden a sufrir problemas con el almacenamiento. Cuando por ejemplo se almacenan durante períodos prolongados, el líquido se puede separar de los compuestos conocidos. La separación del líquido del resto del compuesto se conoce como sinéresis.

Según este invento, se proporciona un compuesto de betún para
30 el tratamiento de artículos de cuero y/o cuero sintético y dicho compuesto incluye

agua,

por lo menos una cera,

por lo menos un polímero que forma una película y
un silicato con capas que incluye un peptico inorgánico

Al incluir un silicato con capas en el compuesto, los problemas de
almacenamiento del compuesto se ven sustancialmente reducidos. De manera
particular, la utilización del silicato con capas puede reducir la probabilidad de
que el líquido se separe del compuesto aun después de largos periodos
almacenamiento. Por lo tanto, el silicato con capas puede ser utilizado en el
compuesto de betún para reducir o prevenir la sinéresis. El silicato con capas
también puede asegurar la preservación de las propiedades reológicas del
compuesto, por ejemplo, para asegurar la facilidad en la aplicación

De preferencia, el compuesto de este invento se puede mantener
estable durante su almacenamiento por un mínimo de 4 semanas, aun mejor
por 8 semanas, y más preferiblemente por un mínimo de 12 semanas

Idealmente, el silicato con capas es un silicato con capas sintético. El
silicato con capas puede ser un silicato de metal, tal como el silicato de un
metal alcalino y/o un metal alcalinotérreo. Algunos silicatos de metal alcalino
adecuados incluyen silicatos de litio, sodio y potasio. Algunos silicatos
alcalinotérreos incluyen silicatos de magnesio y calcio. Es preferible que el
silicato de metal sea un silicato de por lo menos un metal alcalino y por lo
menos uno alcalinotérreo. En una incorporación se utiliza el silicato de
magnesio de litio sódico

De preferencia, el silicato con capas tiene menos del % de peso 2
y aun mejor si es menos del % de peso 1, y todavía más si es menos del % de
peso 0.5, y lo ideal sería menos del % de peso 0.1 de sílice cristalino. En una
incorporación, el silicato con capas está prácticamente libre de sílice cristalino

El silicato con capas también puede tener un contenido de metal de baja
transición. Por ejemplo, el silicato con capas puede incluir un contenido de
metal de transición de menos del % de peso 2, de preferencia menos del % de
peso 1, aun mejor si es menos del % de peso 0.5, por ejemplo, menos del %

de peso 0.1. En una incorporación, el silicato con capas está prácticamente libre de metal de transición.

El silicato con capas incluye un peptico inorgánico. Es preferible que el peptico inorgánico sea un fosfato. Se puede utilizar cualquier peptico de fosfato adecuado. Sin embargo, son preferibles los fosfatos de metal tales como los metales alcalinos y/o fosfatos alcalinoterreos. Los fosfatos de metal alcalino considerados adecuados incluyen fosfatos de litio, sodio y potasio. Los fosfatos de metal alcalinoterreos adecuados incluyen fosfatos de magnesio y calcio.

Es preferible que el fosfato sea un poli-fosfato, como un pirofosfato. En una incorporación preferida, se utiliza el pirofosfato de sodio.

Un ejemplo de un silicato con capas adecuado es Laponite® RDS.

El silicato con capas se suministra preferiblemente de forma finamente dividida.

El silicato con capas puede estar presente en una cantidad de % de peso entre 0.01 y 5 de la totalidad del compuesto de betún. De preferencia, el silicato con capas se encuentra presente en una cantidad de % de peso entre 0.05 y 4, preferiblemente % de peso entre 0.1 y 3, por ejemplo % de peso entre 0.2 y 2. En una incorporación preferida, se utiliza % de peso entre 0.4 y 1, por ejemplo % de peso entre 0.5 y 0.7 de silicato con capas.

El compuesto de betún incluye por lo menos una cera. También se pueden utilizar mezclas de una o más ceras. Algunas ceras adecuadas incluyen ceras de insecto, como cera de abejas, ceras vegetales, como cera de carnauba y candelilla, ceras de mineral ester y ceras ácidas. De preferencia se utilizan ceras de mineral ester. Algunas ceras de mineral éster adecuadas incluyen cera montana (ozoquenta) (ej. Ester de cera montana). También se pueden utilizar ceras sintéticas, como cera de polietileno (ej. oxidada) y éter poliol/cera de éster. En una incorporación preferida el compuesto de betún

incluye un ester de cera montana y una cera sintetica, como una cera oxidada de polietileno En el caso de utilizar un éster de cera montana este puede ser un ester refinado de cera montana

- 5 La cera o mezcla de cera utilizada en el compuesto de betun de este invento preferiblemente tiene un numero de acidez de entre 5 y 50, idealmente entre 10 y 30

- 10 La cera o mezcla de cera utilizada en el compuesto de betun preferiblemente tiene un peso molecular de entre 500 y 5000, idealmente entre 1000 y 4000, por ejemplo, entre 2000 y 3000

- 15 La cantidad de cera en el compuesto de betun puede estar % de peso entre 1 y 20, preferiblemente, % de peso entre 2 y 15, aun mejor, % de peso entre 5 y 10 En una incorporacion preferida, el compuesto de betun tiene % de peso entre 1 y 6 (ej entre 2 y 4) de cera de polietileno oxidado y % de peso entre 2 y 10 (ej entre 3 y 8) ester de cera montana

- 20 El compuesto de betun incluye un polimero que forma una pelicula Se pueden incluir uno o mas polimeros que forman una pelicula en el compuesto de betun Algunos polímeros adecuados que forman una pelicula son polimeros acrilicos (ej Polimeros de acrílico modificado), poliuretano y siliconas

- 25 Algunos polimeros acrilicos adecuados incluyen polimeros de monomeros seleccionados de entre por lo menos uno de los siguientes, acido acrílico, ácido metacrilico y los esteres derivados Se pueden utilizar homopolimeros y copolimeros Algunos copolimeros adecuados incluyen copolimeros de estireno/acrílico, tales como copolímeros de ester ácido metacrílico y copolimero de estireno acrílico En una incorporacion se utiliza una mezcla de copolímero de ester ácido metacrílico y copolímero de estireno acrílico
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105

El polímero que forma una película puede estar presente en el compuesto de betún en una cantidad de % de peso entre 1 y 20, preferiblemente, % de peso entre 8 y 18, por ejemplo, % de peso entre 4 y 12 del compuesto total. En una incorporación, el compuesto de betún incluye % de peso entre 2 y 4 de copolímero de estireno acrílico y % de peso entre 2 y 4 de un copolímero de éster ácido metacrílico.

El compuesto de betún de este invento se encuentra de preferencia en presentación de gel o crema. Por ende, el compuesto de betún de este invento tiene preferiblemente una viscosidad de entre 50 y 100,000 centipoise.

El compuesto de betún incluye preferiblemente una resina alcalina soluble. Se utiliza preferiblemente una resina de ácido maleínico como resina alcalina soluble. Una resina maleínica adecuada se vende bajo la marca registrada ALRESAT®. La resina alcalina soluble puede aumentar el brillo y ayudar a dar la consistencia de gel al compuesto.

La resina alcalina soluble puede estar presente en una cantidad de % de peso entre 0.01 y 10, preferiblemente % de peso entre 0.5 y 8, por ejemplo, % de peso entre 1 y 5.

El compuesto de betún de este invento se encuentra preferiblemente en presentación como emulsión, por ejemplo, una emulsión de aceite en agua.

Puede haber agua en el compuesto de betún en una cantidad de % de peso entre 5 y 90, preferiblemente % de peso entre 10 y 75, aun mejor, % de peso entre 20 y 60, por ejemplo, % de peso entre 40 y 55.

El compuesto de betún incluye preferiblemente por lo menos un alcohol, como el alcohol entre C_1 y C_{10} . El alcohol puede ayudar a dar la consistencia de gel al compuesto. Algunos ejemplos de alcoholes adecuados incluyen metanol, etanol, propanol, butanol, pentanol, hexanol, heptanol, octanol, nonanol y decanol. De preferencia se utiliza un alcohol entre C_2 y C_6 , como el etanol, propanol, butanol, pentanol y/o hexanol. En una incorporación preferida,

105

se utiliza un alcohol C₃ o C₄, como el propanol o el butanol. Se prefiere el alcohol isopropilo. Los alcoholes pueden ser utilizados en una cantidad % de peso entre 1 y 30, preferiblemente, % de peso entre 5 y 20, aun mejor, % de peso entre 8 y 15. En una incorporacion preferenda, el compuesto de betun
5 contiene % de peso entre 8 y 15 de alcohol isopropilo.

Pueden estar presentes tambien otros solventes organicos en el compuesto de betun. Por ejemplo, el compuesto de betun puede incluir uno o más solventes de hidrocarburo. Sin pretender estar ligado a una teoria, el
10 solvente de hidrocarburo puede ayudar a estabilizar el compuesto, sobretodo si este se encuentra en forma de gel. Al utilizar solventes de hidrocarburo, se trata de preferencia al solvente de hidrocarburo para remover cualquier componente aromático. Existe un solvente de hidrocarburo adecuado bajo la marca registrada EXXSOL ® D40. Al utilizar un solvente de hidrocarburo, se
15 utiliza preferiblemente en una cantidad de % de peso entre 1 y 5.

El compuesto de betun de este invento tambien puede incluir como opcion un surfactante o emulsificador. Se prefieren surfactantes no ionicos como etoxilatos de alcohol graso. Se prefieren los etoxilatos de alcohol graso
20 derivados de la reaccion entre un alcohol entre C₁₂ y C₁₅ y oxido de etileno. De preferencia, cada molecula gramo de alcohol reacciona con entre 8 y 15 moleculas gramo de oxido de etileno. Algunos ejemplos de surfactantes y emulsificadores adecuados se venden bajo las marcas registradas Emulsifier 4106 (Clariant) y Genopol X060 (ex Clariant).

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Se pueden utilizar los emulsificadores o surfactantes en una cantidad de % de peso entre 0.1 y 10, preferiblemente, % de peso entre 1 y 10, por ejemplo, % de peso entre 2 y 5 del compuesto total.

30 El compuesto de betun puede incluir colorantes como opcion. Algunos colorantes adecuados incluyen ácido negro 2 (Acid black 2). En una incorporación, la dispersion de negro carbón se incluye en el compuesto de betun.

107

El (Los) colorante(s) pueden estar presentes en una cantidad de % de peso entre 0.01 y 10, por ejemplo % de peso entre 0.1 y 5

Otros componentes opcionales como perfumes y preservativos tambien
5 se pueden incluir en el compuesto de betun

El compuesto tambien puede incluir un aditivo estabilizador como 2-amino 2-metil propano-1-ol. Se cree que estos aditivos estimulan la estabilidad de la emulsion

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En una incorporacion, el compuesto de betun de este invento es una emulsion acuosa que incluye

agua (ej. En una cantidad de % de peso entre 20 y 60),

cera (ej. En una cantidad de peso entre 5 y 10),

15 un polimero que forma una pelicula (e.g. ej. en una cantidad de % de peso entre 8 y 20),

una resina alcalina soluble (ej. en una cantidad de % de peso entre 0.5 y 8),

alcohol (ej. en una cantidad de % de peso entre 5 y 20),

20 silicato con capas que incluye un polifosfato inorganico (ej. en una cantidad de % de peso entre 0.01 y 5) y, opcionalmente,

un solvente de hidrocarburo y/o surfactante

En la incorporacion previa, la cera es preferiblemente una mezcla de
25 cera ester montana y cera de polietileno oxidada, el polimero que forma una pelicula incluye preferiblemente por lo menos un polimero acrilico, la resina alcalina soluble es preferiblemente una resina de acido maleinico, y el alcohol es preferiblemente un alcohol isopropilo. Aun mejor, el polimero que forma una pelicula incluye un copolimero de esteres acidos metacrilicos y un copolimero
30 de estireno acrilico

El compuesto de betun de este invento es ideal para el tratamiento de articulos de cuero y cuero sintetico. Estos articulos incluyen articulos de

107

calzado, como zapatos, botas y sandalias, así como carteras, cinturones, guantes sillas para montar a caballo y muebles

De preferencia, el compuesto de betun de este invento proporciona un
5 acabado brillante al artículo tratado. El compuesto de betun también puede ayudar a aumentar la resistencia del cuero (o del cuero sintético) al clima, los rayones y raspones

El compuesto de betun de este invento se puede aplicar sobre artículos
10 de cuero y cuero sintético y puestos a secar. Una vez seco, el compuesto deja una película brillante en la superficie del artículo. El artículo tratado podrá ser pulido para aumentar el brillo, pero en la incorporación preferida, no es necesario pulir para dar brillo al artículo tratado. Por lo tanto, en esa incorporación preferida, el compuesto de betun es auto-brillante. Se cree que el
15 silicato en capas es especialmente útil en un compuesto de betun auto-brillante, pues se cree que el silicato proporciona una reología con adelgazamiento por cortante al compuesto que ayuda a la formación de una película brillante sobre el artículo al aplicarlo

20 El compuesto de betun de este invento se puede aplicar con esponja. El compuesto de betún puede estar dentro de un tubo o, preferiblemente, en un frasco

El compuesto de betun de este invento puede ser preparado mezclando
25 al tiempo los componentes individuales del compuesto, por ejemplo, para formar una emulsión

En una incorporación, el polímero que forma una película y el silicato con
30 capas se agregan a una emulsión acuosa de cera (s) preferiblemente, mezclando energicamente. Preferiblemente el silicato con capas (ej. Silicato de magnesio sodio lito modificado con pirofosfato de sodio tera) se agrega a la emulsión de cera en la forma de solución acuosa pre-formada

Adicionalmente al polímero que forma una película y al silicato con capas, los componentes como la resina colorante(s), surfactantes, emulsificadores y solventes también se pueden agregar a la emulsión de cera, preferiblemente mezclando continuamente. Cuando se utilizan el surfactante (ej. éter poliglicol de ácido graso) y el solvente (ej. Solvente de hidrocarburo) se pueden agregar como mezcla pre-formada. En una incorporación preferida, un solvente de alcohol, como el alcohol isopropílico se agrega a la mezcla resultante en de manera continua para ayudar a crear la consistencia de gel.

La emulsión de cera se puede formar de manera preliminar, por ejemplo, derretiendo la (s) cera (s) a una temperatura elevada de por ejemplo entre 80 a 150°C, preferiblemente, entre 100 y 130°C, aun mejor, entre 120 y 125°C. En un recipiente separado, el agua se puede calentar a una temperatura de por ejemplo, entre 80 y 100°C, preferiblemente entre, 90 y 95°C. La cera derretida se puede agregar luego al agua y la mezcla resultante se revuelve para formar una emulsión (ej. emulsión de aceite en agua). Como opción, se puede agregar a la cera derretida un emulsificador (p.ej. éteres poliglicólicos de ácidos grasos) y/o un aditivo estabilizador (ej. 2-amino-2-metil prompan-1-ol), por ejemplo, antes de que la cera derretida se mezcle con el agua. Una vez la cera derretida se mezcla con el agua, la mezcla resultante se enfría, por ejemplo, pasándolo rápidamente a una temperatura de por ejemplo entre 10 y 50°C, por ejemplo entre 30 y 40°C.

Ejemplo

El compuesto auto-brillante de la Tabla 1 se preparó calentando primero las ceras (ii y iii) con el componente (iv) a una temperatura de entre 120 y 125°C para formar una mezcla de cera derretida. Se agregó el componente (v) a la mezcla. La mezcla de cera derretida se agregó lentamente al agua caliente (entre 90 y 95°C) revolviendo vigorosamente. La mezcla resultante se enfrió rápidamente a 40°C para formar una emulsión de cera. Aproximadamente 75% del 46.58 peso/peso% agua del compuesto se utiliza para formar la emulsión de cera. El agua restante se mezcla con el componente (xi) para formar una dispersión (ver más abajo).

Luego se agregaron los componentes (xiv), (xiii), (x), (ix) y (viii) a la emulsion de cera revolviendo vigorosamente. Luego, se agrego una mezcla del componente (xi) y agua y se revolvió la mezcla restante durante otros 15 minutos

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Una pre-mezcla de componentes (vi) y (vii) se agregó luego. La mezcla resultante se revolvió durante otros 20 minutos antes de que se agregara el componente (xii) de manera continua

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La formacion de una gel cremosa ocurno 1 hora despues de la adición d l componente (xii)

Ej mplo comparativo

15 El procedimiento descrito haciendo referencia al Ejemplo anterior s repito para preparar el compuesto auto-brillante de la Tabla 2. Sin embargo, el componente (xi), se omitio de la composicion del Ejemplo Comparativo. Por ende, la totalidad del 49.16 p/p% agua de este Ejemplo Comparativo se utiliza para formar la emulsion de cera

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Los compuestos del Ejemplo y del Ejemplo Comparativo fueron almacenados en frascos de vidrio sellados durante un mes. Segun el ejemplo el compuesto fue estable durante el almacenamiento. En contraposicion, el compuesto del Ejemplo Comparativo mostro sineresis

Tabla 1

Componente	p/p%
(i) Agua (suave)	46 58
(ii) Ester de cera montana refinado (Licowax KSL, Clariant)	5 85
(iii) Cera de polietileno oxidado (Cera de polietileno PED 522, Clariant)	3 80
(iv) Mezcla de éteres poliglicol de ácido graso (Emulsificador 4106, Clariant)	1 80
(v) 2-amino-2-metil propano-1-ol (AMP 90, Angus Chemie)	0 90
(vi) Eter poliglicol de ácido graso (Genopol X060, Clariant)	3 00
(vii) Solvente de hidrocarburo con bajo contenido aromático (Exxsol D40, Exxon)	6 00
(viii) Copolímero de estireno acrílico (Vinacryl 7190, Vinacryl - 50% activos)	6 00
(ix) Copolímero de ésteres de ácido metacrílico (Mowilith DM 772, Clariant - 46% activos)	8 00
(x) Solución acuosa de resina de ácido maleínico modificado (NaOH Alresat solución de Resina 30%, Dick Peters)	6 00
(xi) Silicato de magnesio de sodio de litio modificado con pirofosfato de sodio tera (Laponite RDS, Rockwood)	0 50
(xii) alcohol isopropilo	10 00
(xiii) Colorante Negro 2 (Acid black 2) índice de color 504201 (Nigrosine WLF soluble en agua)	1 27
(xiv) Dispersión acuosa negro carbon (Colanyl Black PR 130)	0 50

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Tabla 2

Componente	p/p%
(i) Agua (suave)	49 16
(ii) Ester de cera montana refinado (Licowax KSL, Clariant)	5 46
(iii) Cera de polietileno oxidada (Cera de polietileno PED 522,	3 36

Clariant)	
(iv) Mezcla de eteres poliglicol de ácido graso (Emulsifier 4106, Clariant)	1 68
(v) 2-amino-2-metil propano-1-ol (AMP 90 Angus Chemie)	0 84
(vi) Éter poliglicol de ácido graso (Genopol X060, Clariant)	3 00
(vii) Solvente de hidrocarburo con bajo contenido aromatico (Exxsol D40, Exxon)	6 00
(viii) Copolimero de estireno acrílico (Vinacryl 7190, Vinacryl - 50% activos)	6 00
(ix) Copolímero de esteres de acido metacrilico (Mowilith DM 772, Clariant - 46% activos)	8 00
(x) Solucion acuosa de resina de ácido maleinico modificado (NaOH Alresat solucion de Resina 30%, Dick Peters)	6 00
(xi) alcohol isopropilico	10 00
(xiv) Dispersión acuosa negro carbón (Colanyl Black PR 130)	0 500

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REIVINDICACIONES

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1 Un compuesto de betun para el tratamiento de articulos de cuero y/o cuero sintetico, dicho compuesto incluye
agua,
por lo menos una cera,
15 por lo menos un polimero que forma una pelicula, y
un silicato con capas que incluye un peptico inorgánico

2 Un compuesto segun la Reivindicacion 1, en el cual el péptico inorgánico es un polifosfato inorganico

- 3 Un compuesto segun la Reivindicacion 1 ó 2, en el cual la cera incluye un ester de cera montana y cera de polietileno oxidado
- 5 4 Un compuesto segun cualquiera de las Reivindicaciones precedentes, en el cual el polimero que forma una pelicula se selecciona de por lo menos uno de los siguientes silicona, poliuretano y polimero acrílico
- 5 Un compuesto segun la Reivindicación 4, en el cual el polimero que
10 forma una pelicula incluye una mezcla de copolimero de estireno acrílico y un copolímero de éster de ácido metacrílico
- 6 Un compuesto segun cualquiera de las Reivindicaciones precedentes, que ademas incluye una resina alcalina soluble
15
- 7 Un compuesto segun la Reivindicacion 6, en el cual la resina alcalina soluble es una resina de ácido maleínico
- 8 Un compuesto segun cualquiera de las Reivindicaciones precedentes,
20 que se encuentra en la forma de una emulsion de aceite en agua
- 9 Un compuesto segun cualquiera de las Reivindicaciones precedentes que incluye
% de peso 1 a 20 de dicha cera,
25 % de peso 1 a 20 por lo menos de dicho un polimero que forma una pelicula,
% de peso 0.01 a 5 de dicho silicato con capas
- 10 Un compuesto segun cualquiera de las Reivindicaciones precedentes,
30 que ademas incluye un alcohol
- 11 Un compuesto segun la Reivindicacion 10, en el cual el alcohol es un alcohol isopropilo

12 Un compuesto segun cualquiera de las Reivindicaciones precedentes,
que es un compuesto de betun auto-brillante

5 13 Un metodo para la preparacion de un compuesto segun lo
revindicado en cualquiera de las Reivindicaciones 1 a 12, y dicho
metodo incluye

10 la formación de una emulsion acuosa de dicha cera, dicho polímero que
forma una pelicula y dicho silicato sintetico con capas

14 Un metodo segun la Reivindicacion 15, que además incluye la adicion de
un alcohol

15 15 Un metodo para el tratamiento de artículos de cuero y/o cuero sintetico,
que incluye la aplicación de un compuesto segun lo revindicado en cualquiera
de las Reivindicaciones 1 a 12 a articulos de cuero y/o cuero sintetico

20 16 Un metodo segun la Reivindicacion 15 en el cual dicho compuesto se
deja secar para dar un terminado brillante sin pulir

17 Uso de un silicato con capas sintético que incorpora un peptico
inorgánico en un compuesto de betun para reducir o evitar la sineresis del
compuesto de betun

25 18 Uso segun lo revindicado en la Reivindicación 17, en el cual dicho
compuesto de betun incluye agua, por lo menos una cera y por lo menos un
polímero que forma una pelicula

30 19 Uso segun lo revindicado en la Reivindicacion 18, en el cual dicho
compuesto de betun es un compuesto de betun auto-brillante

Compendio

Compuesto de Betún para Cuero o Cuero Sintético

Un compuesto de betun para el tratamiento de articulos de cuero y/o cuero sintetico, dicho compuesto incluye agua, por lo menos una cera, por lo menos un polimero que forma una pelicula y un silicato con capas que incluye un
5 peptico inorganico



US005837763A

United States Patent [19]

[11] Patent Number 5,837,763

Ferraro et al.

[45] Date of Patent. Nov 17, 1998

[54] COMPOSITIONS AND METHODS FOR
MANUFACTURING WAXES FILLED WITH
INTERCALATES AND EXFOLIATES
FORMED WITH OLIGOMERS AND
POLYMERS

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[21] Appl. No. 582,488

[22] Filed. Jan. 3, 1996

Related U.S. Application Data

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No. 5,721,306, which is a continuation-in-part of Ser. No.
488,264 Jun. 7 1995, Pat. No. 5,552,469, and a contin-
uation-in-part of Ser. No. 488,263, Jun. 7 1995, Pat. No.
5,698,624 and a continuation-in-part of Ser. No. 480,080,
Jun. 7, 1995, Pat. No. 5,578,672.

[51] Int. Cl.⁶ C08J 5/10 C08K 3/34,
C08L 29/00

[52] U.S. Cl. 524/449, 524/445 524/446;
524/447, 524/448, 524/377

[58] Field of Search 524/445, 446,
524/447 448, 449 789 792, 312, 376,
377, 277 523/202, 216

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[57] ABSTRACT

Compositions and methods that include a wax, in an amount of about 20% to about 99.95% by weight, containing an intercalate, or exfoliate thereof, in an amount of about 0.05% to about 80% by weight of the composition formed by contacting a layered phyllosilicate with an oligomer and/or polymer to sorb or intercalate the intercalant polymer or mixtures of intercalant polymers between adjacent phyllosilicate platelets. Sufficient intercalant polymer is sorbed between adjacent phyllosilicate platelets to expand the spacing between adjacent platelets (interlayer spacing) to a distance of at least about 5 Å, preferably to at least about 10 Å (as measured after water removal) and more preferably in the range of about 30–45 Å, so that the intercalate easily can be exfoliated, sometimes naturally without shearing being necessary.

30 Claims, 8 Drawing Sheets

116

115

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117

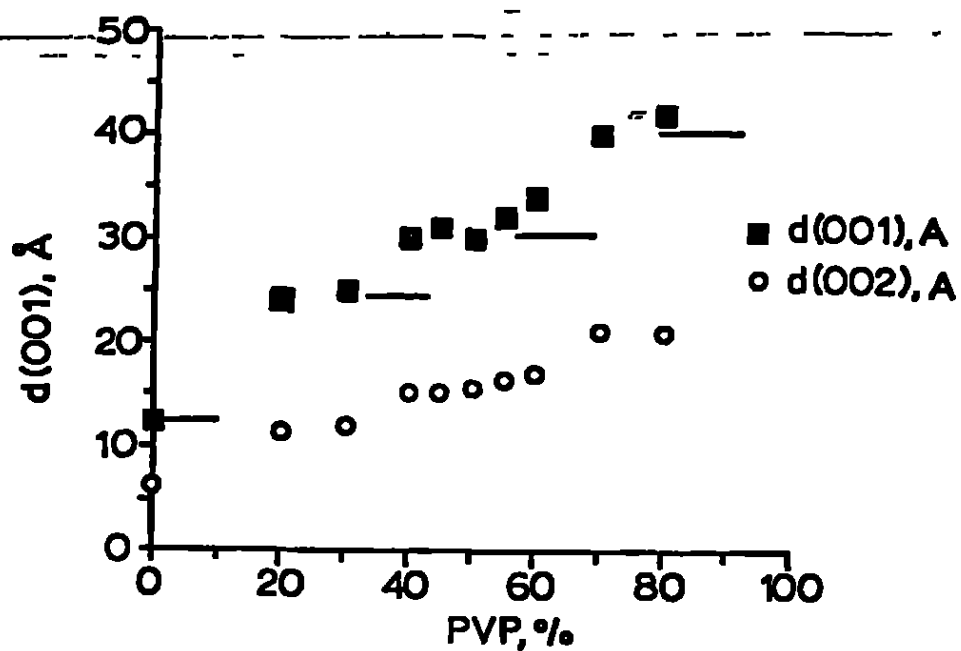


FIG. 1

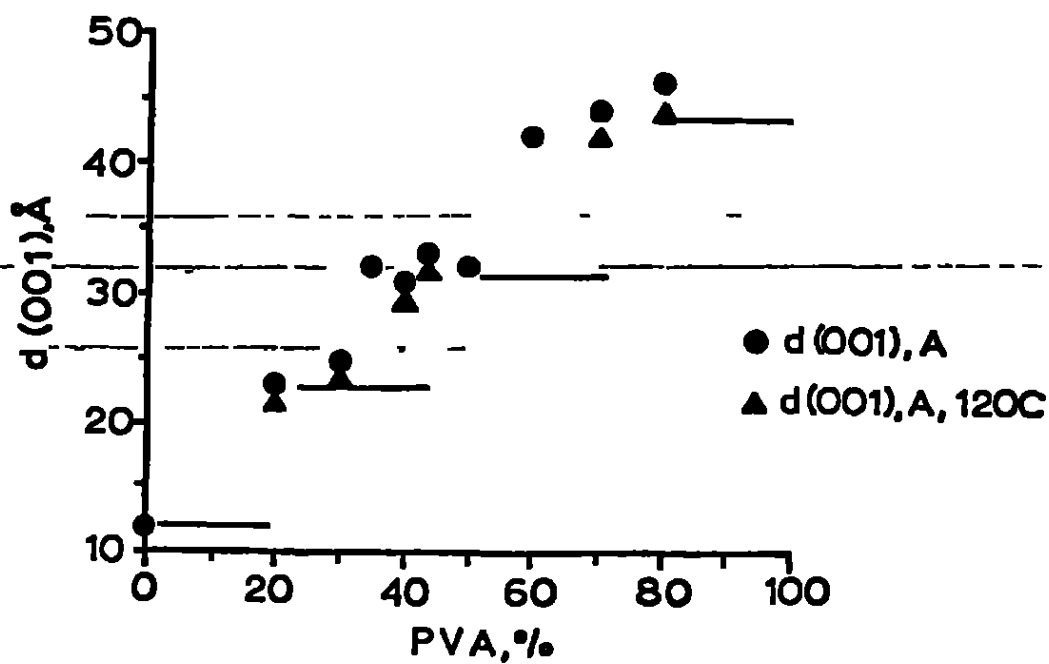


FIG. 2

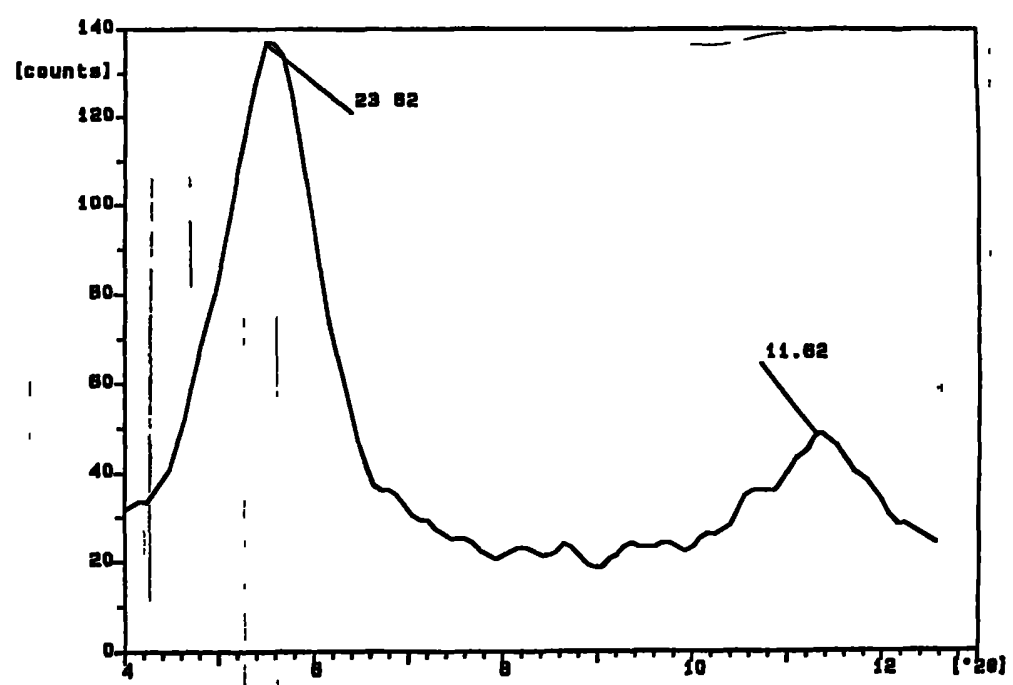


FIG. 3

118

U.S. Patent

Nov 17, 1998

Sheet 3 of 8

5,837,763

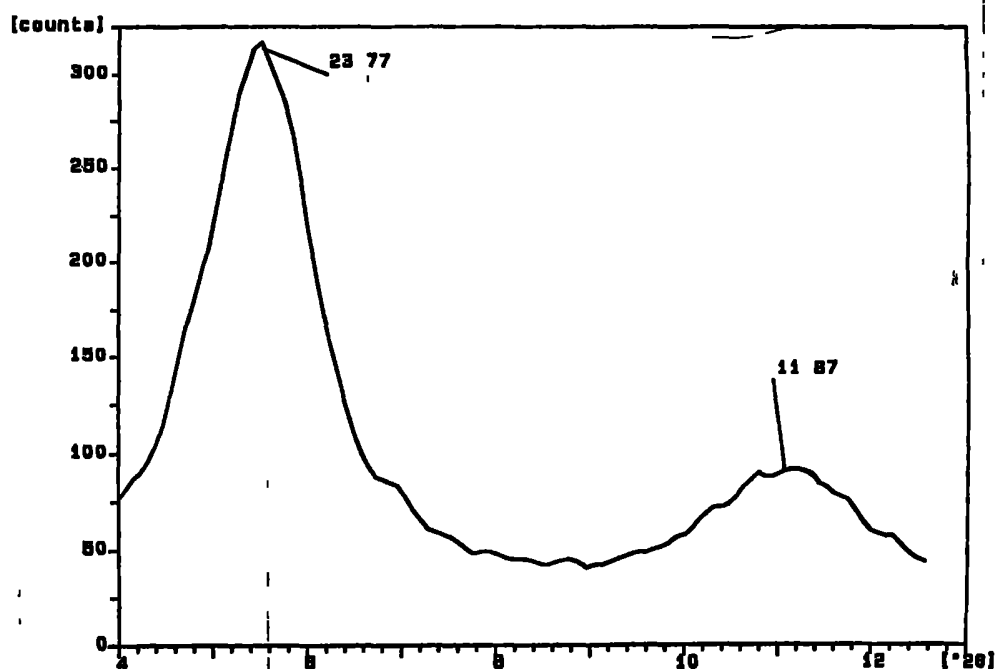


FIG. 4

11A

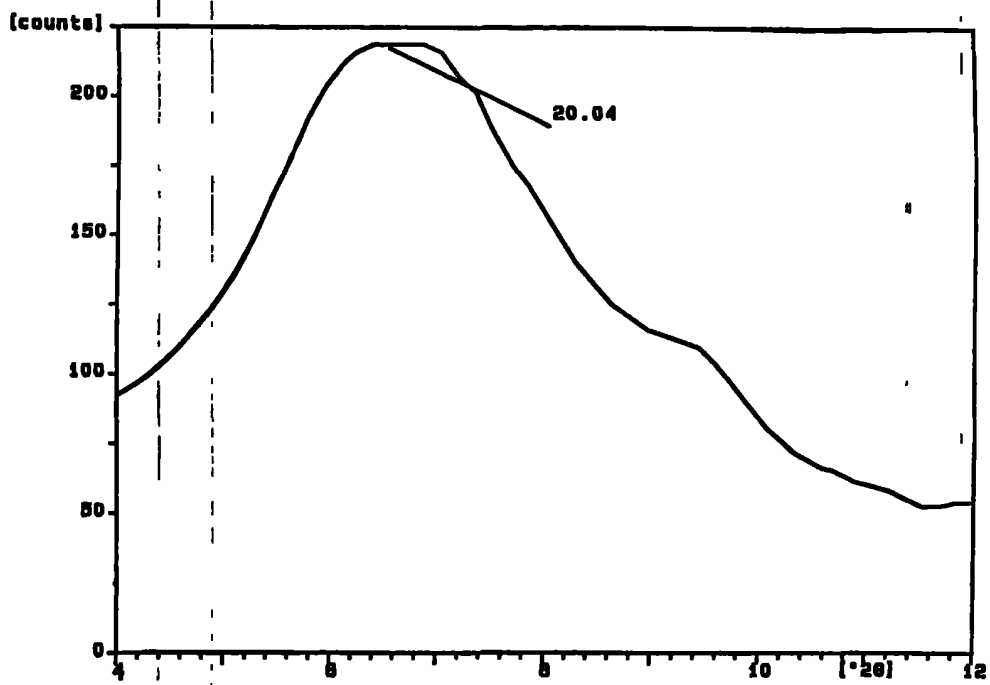


FIG. 5

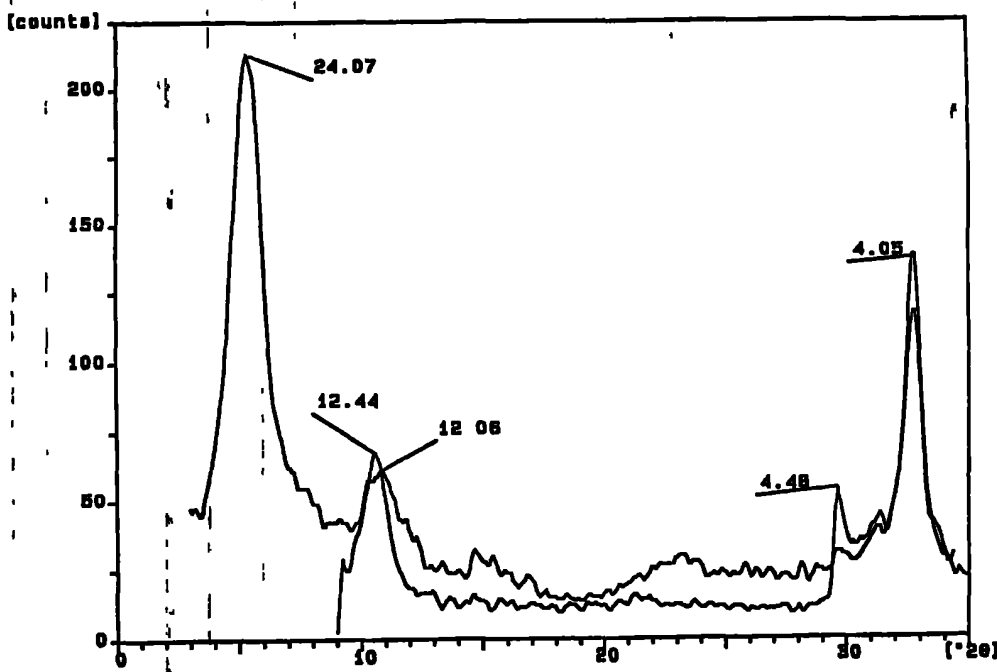


FIG. 6

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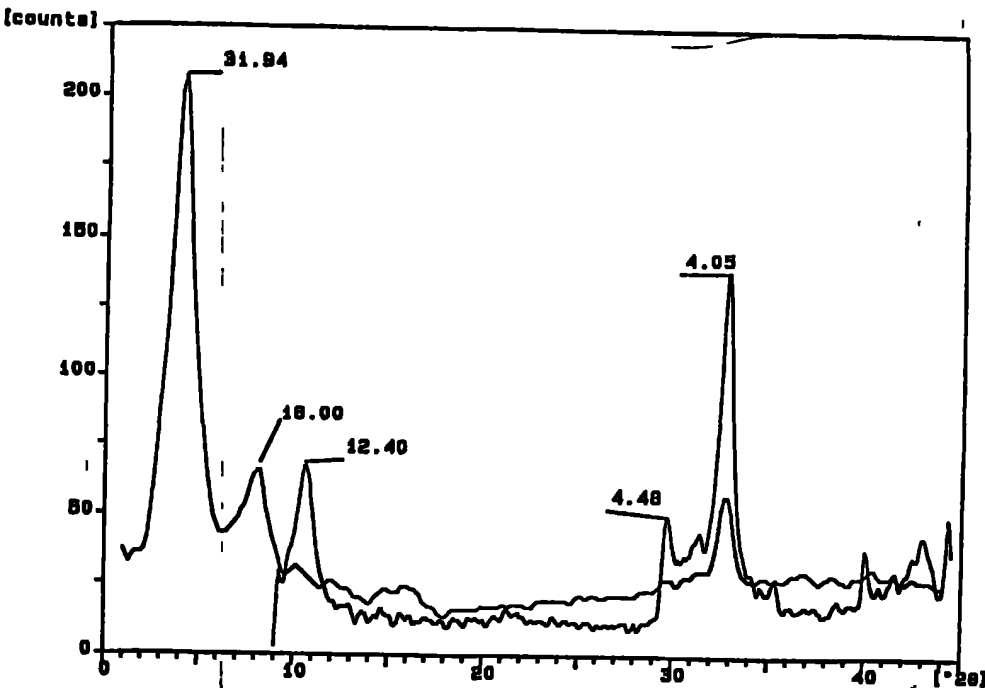


FIG. 7

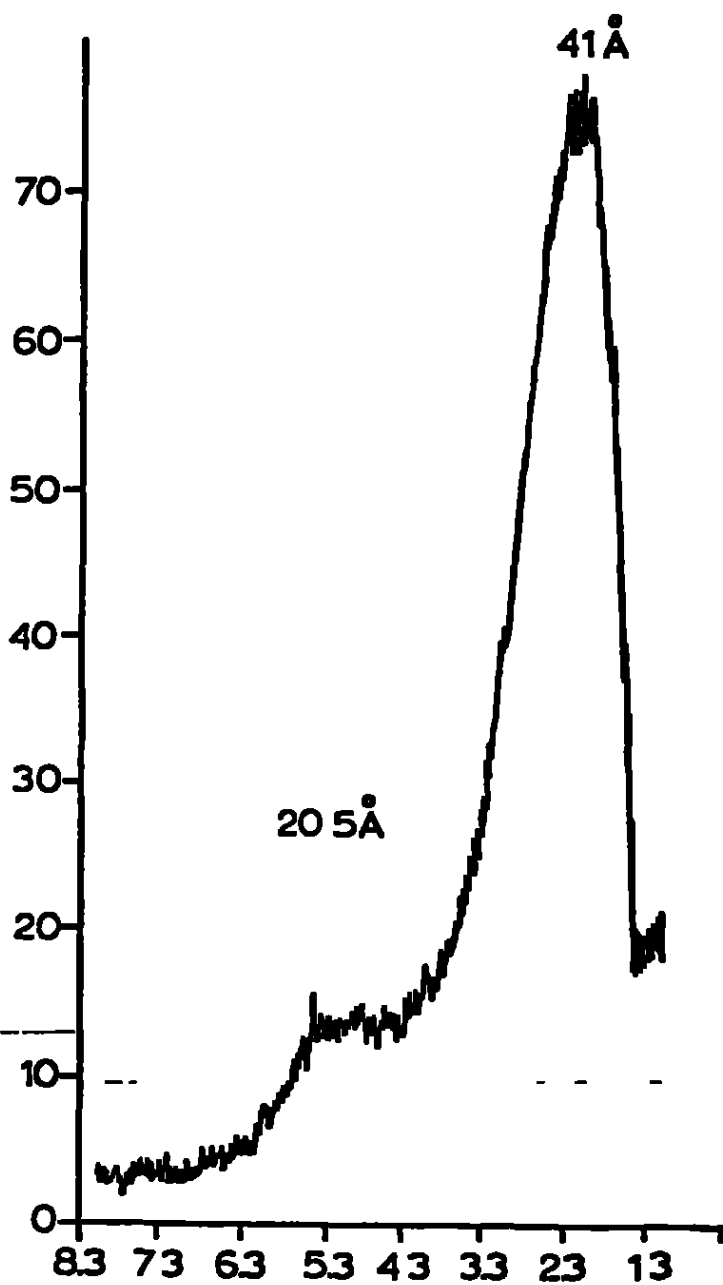


FIG. 8

FIG 9

 Na
  Mg
  Al
  O
  Si

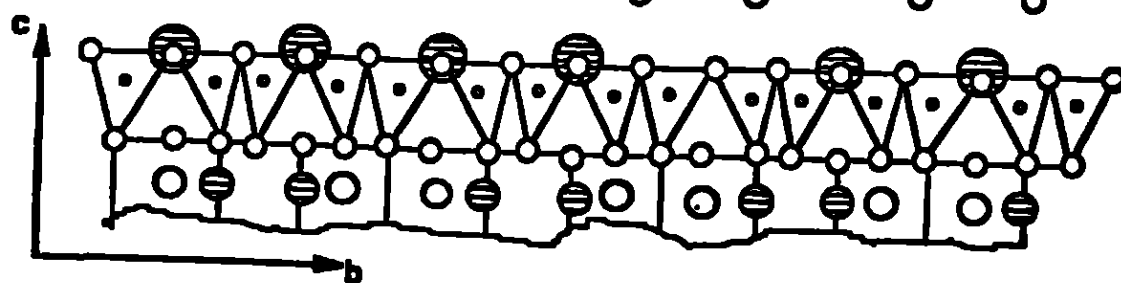
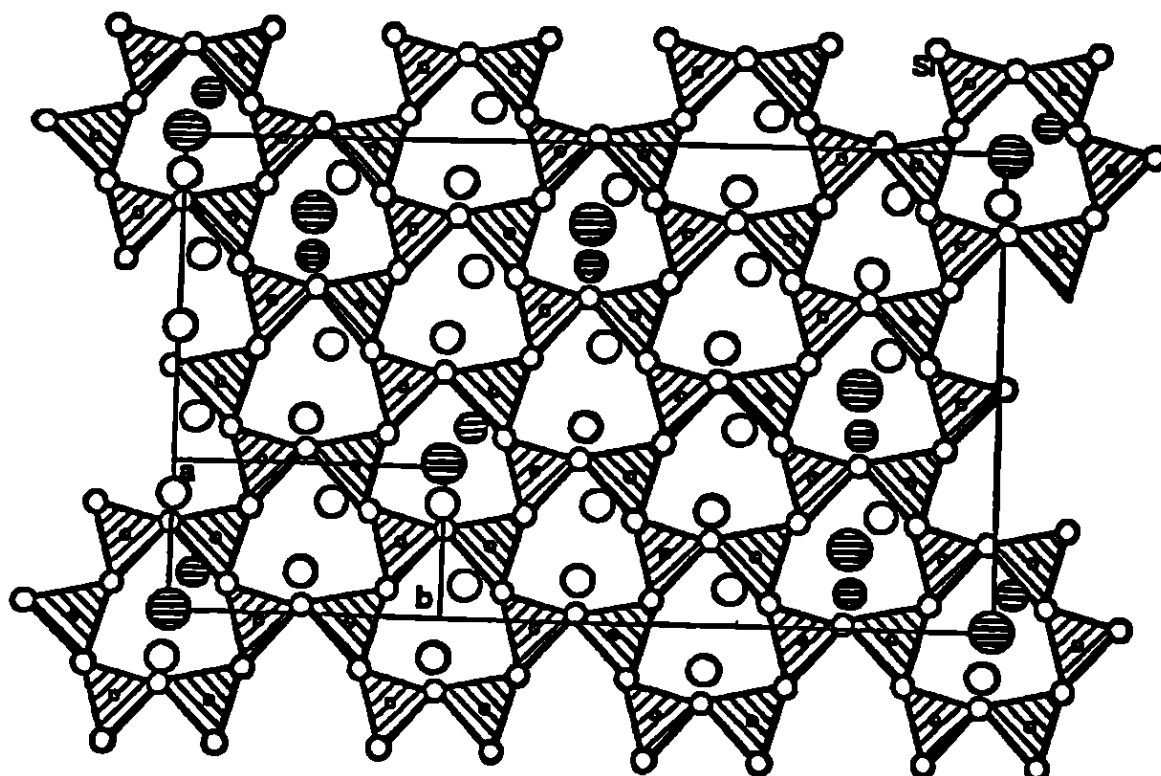


FIG 10

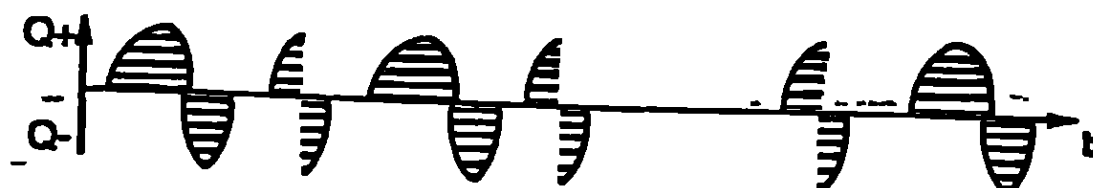


FIG. 11

COMPOSITIONS AND METHODS FOR MANUFACTURING WAXES FILLED WITH INTERCALATES AND EXFOLIATES FORMED WITH OLIGOMERS AND - POLYMERS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of application Ser. No. 08/525,416 filed Sep. 8, 1995 U.S. Pat. No. 5,721,306 which is a continuation in-part of application Ser. No. 08/488,264 U.S. Pat. No. 5,552,469 Ser. No. 08/480,080 U.S. Pat. No. 5,578,672 and Ser. No. 08/488,263 U.S. Pat. No. 5,698,624, all filed Jun. 7, 1995

FIELD OF THE INVENTION

The present invention is directed to waxes and wax objects filled with intercalated layered materials, and/or exfoliates thereof. The intercalates are manufactured by sorption (adsorption and/or absorption) of one or more oligomers or polymers between planar layers of a swellable layered material, such as a phyllosilicate or other layered material to expand the interlayer spacing of adjacent layers to at least about 5 Angstroms (Å) preferably to at least about 10 Å. More particularly, the present invention is directed to compositions and methods for manufacturing candles, wax novelty items, wax paper coating compositions, paraffin waxes, chlorinated paraffin waxes, and chlorinated naphthalenes used in electrical equipment, wax sizing compositions used in textile and leather sizing; wax compositions used for waterproofing; wax polish compositions; wax fruit and vegetable coating compositions, waxes used in cosmetic and pharmaceutical creams, waxes used in carbon paper printing ribbons and printing inks, waxes used in greases, lubricants and as mold release compositions; and the like. In accordance with the present invention, waxes useful for these industries are substantially and unexpectedly improved by incorporating into the wax about 0.05% to about 80% by weight, preferably about 0.1% to about 20% by weight, more preferably about 0.1% to about 10% by weight of one or more intercalates having at least two layers of oligomer and/or polymer molecules sorbed on the internal surfaces of adjacent layers of the planar platelets of a layered material such as a phyllosilicate, preferably a smectite clay. The oligomer or polymer is sorbed between the platelets of the layered material to expand the interlayer spacing to at least about 5 Å, preferably to at least about 10 Å, more preferably to at least about 20 Å, and most preferably to at least about 30–45 Å, up to about 100 Å, or disappearance of periodicity. The resulting intercalates are neither entirely organophilic nor entirely hydrophilic, but a combination of the two, and easily can be exfoliated for or during admixture with any wax material, to improve one or more properties of the wax particularly to reduce shrinkage and cracking when the wax is melted and cooled for solidification into a desired shape. The resulting compositions comprising a wax and an intercalate and/or an exfoliate thereof are useful wherever wax compositions are used, for example, as candles, shaped wax novelty items, in electrical equipment, coating compositions and the like, to decrease shrinkage of the wax, increase elasticity and temperature characteristics, such as melting point and increase the stability (reduction in separation of components upon standing and solidification) of the wax composition. Other advantages include increasing the opacity and dye receptivity and an increase in wax melt viscosity for wick flame control in candles, increasing

composition hardness without causing brittleness, improving the melt stability of the composition to make sure that the liquid composition remains homogeneous, without component separation, reducing or eliminating the need for purer more expensive wax components, such as microcrystalline wax and greatly reducing or eliminating the formation of exterior bubbles or pock marks that form upon reheating an upper portion of a candle when reducing the concave upper candle end formed upon initial solidification, and providing the capability of eliminating typical opacifying agents and viscosity increasing agents, e.g., ethylene vinylacetate copolymers, fatty acids, such as stearic acid, and the like with a much lower amount of the nanoscale platelet particles of the present invention. Additionally, the phyllosilicate platelets act as a good protector against deterioration of physical properties and color degradation caused by ultraviolet (UV) light so that UV protectors are unnecessary in the wax compositions of the present invention.

BACKGROUND OF THE INVENTION AND PRIOR ART

It is well known that phyllosilicates, such as smectite clays e.g. sodium montmorillonite and calcium montmorillonite, can be treated with organic molecules, such as organic ammonium ions, to intercalate the organic molecules between adjacent, planar silicate layers, thereby substantially increasing the interlayer (interlamellar) spacing between the adjacent silicate layers. The thus-treated, intercalated phyllosilicates, having interlayer spacing of at least about 10–20 Å and up to about 100 Å, then can be exfoliated, e.g., the silicate layers are separated, e.g., mechanically, by high shear mixing. The individual silicate layers, when admixed with a matrix polymer, before, after or during the polymerization of the matrix polymer, e.g., a polyamide—see U.S. Pat. Nos. 4,739,007, 4,810,734 and 5,385,776—have been found to substantially improve one or more properties of the polymer, such as mechanical strength and/or high temperature characteristics.

Exemplary of such prior art composites, also called "nanocomposites", are disclosed in published PCT disclosure of Allied Signal, Inc. WO 93/04118 and U.S. Pat. No. 5,385,776, disclosing the admixture of individual platelet particles derived from intercalated layered silicate materials, with a polymer to form a polymer matrix having one or more properties of the matrix polymer improved by the addition of the exfoliated intercalate. As disclosed in WO 93/04118, the intercalate is formed (the interlayer spacing between adjacent silicate platelets is increased) by adsorption of a silane coupling agent or an onium cation, such as a quaternary ammonium compound having a reactive group which is compatible with the matrix polymer. Such quaternary ammonium cations are well known to convert a highly hydrophilic clay, such as sodium or calcium montmorillonite, into an organophilic clay capable of sorbing organic molecules. A publication that discloses direct intercalation (without solvent) of polystyrene and poly(ethylene oxide) in organically modified silicates is *Synthesis and Properties of Two-Dimensional Nanostructures by Direct Intercalation of Polymer Melts in Layered Silicates*, Richard A. Vaia, et al. *Chem. Mater.*, 5:1694–1696(1993). Also as disclosed in *Adv. Materials*, 7, No. 2, (1985) pp. 154–156, *New Polymer Electrolyte Nanocomposites. Melt Intercalation of Poly(Ethylene Oxide) in Mica-Type Silicates* Richard A. Vaia, et al. poly(ethylene oxide) can be intercalated directly into Na-montmorillonite and Li-montmorillonite by heating to 80° C for 2–6 hours to achieve a d-spacing of 17.7 Å. The intercalation is accom-

121

120

panied by displacing water molecules, disposed between the clay platelets with polymer molecules. Apparently, however the intercalated material could not be exfoliated and was tested in pellet form. It was quite surprising to one of the authors of these articles that exfoliated material could be manufactured in accordance with the present invention.

Previous attempts have been made to intercalate polyvinylpyrrolidone (PVP), polyvinyl alcohol (PVA) and poly (ethylene oxide) (PEO) between montmorillonite clay platelets with little success. As described in Levy, et al., *Interlayer Adsorption of Polyvinylpyrrolidone on Montmorillonite*, Journal of Colloid and Interface Science, Vol. 50, No. 3, March 1975 pages 442-450, attempts were made to sorb PVP (40,000 average M W) between monomeric montmorillonite clay platelets (Na, K, Ca and Mg) by successive washes with absolute ethanol, and then attempting to sorb the PVP by contact with 1% PVP/ethanol/water solutions, with varying amounts of water, via replacing the ethanol solvent molecules that were sorbed in washing (to expand the platelets to about 17.7 Å). Only the sodium montmorillonite had expanded beyond a 20 Å basal spacing (e.g., 26 Å and 32 Å), at 5% H₂O, after contact with the PVP/ethanol/H₂O solution. It was concluded that the ethanol was needed to initially increase the basal spacing for later sorption of PVP and that water did not directly affect the sorption of PVP between the clay platelets (Table II, page 445), except for sodium montmorillonite. The sorption was time consuming and difficult and met with little success.

Further, as described in Greenland *Adsorption of Polyvinyl Alcohols by Montmorillonite*, Journal of Colloid Sciences, Vol. 18, pages 647-664 (1963), polyvinyl alcohols containing 12% residual acetyl groups could increase the basal spacing by only about 10 Å due to the sorbed polyvinyl alcohol (PVOH). As the concentration of polymer in the intercalant polymer-containing solution was increased from 0.25% to 4% the amount of polymer sorbed was substantially reduced, indicating that sorption might only be effective at polymer concentrations in the intercalant polymer-containing composition on the order of 1% by weight polymer or less. Such a dilute process for intercalation of polymer into layered materials would be exceptionally costly in drying the intercalated layered materials for separation of intercalants from the polymer carrier, e.g., water, and, therefore, apparently no further work was accomplished toward commercialization.

In accordance with one embodiment of the present invention, intercalates are prepared by contacting a phyllosilicate with a PVP polymer, preferably essentially alcohol-free, or a PVA intercalant polymer composition, wherein the PVA preferably contains 5% or less residual acetyl groups, more preferably fully hydrolyzed, containing 1% or less acetyl groups.

In accordance with an important feature of the present invention, best results are achieved using an oligomer (herein defined as a pre-polymer having 2 to about 15 recurring monomeric units, which can be the same or different) or polymer (herein defined as having more than about 15 recurring monomeric units, which can be the same or different) composition for intercalation having at least about 2% preferably at least about 5% by weight intercalant oligomer or intercalant polymer concentration, more preferably about 30% to about 80% by weight oligomer and/or polymer based on the weight of oligomer and/or polymer and carrier (e.g., water with or without another solvent for the intercalant oligomer or intercalant polymer) to achieve better sorption of the intercalant polymers between phyllo-

silicate platelets. Regardless of the concentration of intercalant polymer in liquid carrier of the intercalating composition, the intercalating composition should have a polymer:layered material weight ratio of at least about 1.20, preferably at least about 1.10, more preferably at least about 1.5 and most preferably about 1.4 to achieve efficient intercalation of the polymer between adjacent platelets of the layered material. The oligomer or polymer sorbed between and permanently bonded to the silicate platelets causes separation or added spacing between adjacent silicate platelets and, for simplicity of description, both the oligomers and polymers are hereinafter called the "intercalant" or "intercalant polymer" or "polymer intercalant". In this manner, the water-soluble oligomers or polymers will be sorbed sufficiently to increase the interlayer spacing of the phyllosilicate in the range of about 10 Å to about 100 Å, for easier and more complete exfoliation, in a commercially viable process, regardless of the particular phyllosilicate or intercalant polymer.

In accordance with the present invention, it has been found that a layered material, such as a phyllosilicate, e.g., a smectite clay can be intercalated sufficiently for subsequent exfoliation by sorption of polymers or oligomers that have functionalities, or aromatic rings to provide bonding of the polymer or oligomer to the internal surfaces of the layered material by a mechanism selected from the group consisting of ionic complexing, electrostatic complexing; chelation; hydrogen bonding; dipole/dipole; Van Der Waals forces, and any combination thereof. Such bonding is between two functional groups of one or two intercalant polymer molecules and the metal cations bonded to the inner surfaces of the phyllosilicate platelets. Sorption and metal cation electrostatic attraction or bonding of a platelet metal cation between two functional groups of the intercalant polymer molecules, or the electrostatic bonding between the interlayer cations in hexagonal or pseudohexagonal rings of the smectite layers and an intercalant polymer aromatic ring structure increases the interlayer spacing between adjacent silicate platelets or other layered material to at least about 5 Å, preferably at least about 10 Å, more preferably at least about 20 Å, and most preferably in the range of about 30 Å to about 45 Å. Such intercalated phyllosilicates easily can be exfoliated into individual phyllosilicate platelets before or during admixture with a wax material to form a wax/platelet composite material, or nanocomposite, having one or more of the wax properties substantially improved in comparison with the wax alone.

DEFINITIONS

Whenever used in this Specification, the terms set forth shall have the following meanings.

"Layered Material" shall mean an inorganic material, such as a smectite clay mineral, that is in the form of a plurality of adjacent, bound layers and has a maximum thickness, for each layer, of about 3 Å to about 50 Å, preferably about 10 Å.

"Platelets" shall mean individual layers of the Layered Material.

"Intercalate" or "Intercalated" shall mean a Layered Material that includes oligomer and/or polymer molecules disposed between adjacent platelets of the Layered Material to increase the interlayer spacing between the adjacent platelets to at least about 5 Å, preferably to at least about 10 Å.

"Intercalation" shall mean a process for forming an intercalate.

"Intercalant Polymer" or "Intercalant" shall mean an oligomer or polymer that is sorbed between Platelets of the Layered Material to form an Intercalate

"Intercalating Carrier" shall mean a carrier comprising water with or without an organic solvent used together with an Intercalant Polymer to form an Intercalating Composition capable of achieving Intercalation of the Layered Material.

"Intercalating Composition" shall mean a composition comprising an Intercalant, an Intercalating Carrier for the Intercalant, and a Layered Material.

"Exfoliate" or "Exfoliated" shall mean individual platelets of an Intercalated Layered Material so that adjacent platelets of the Intercalated Layered Material can be dispersed individually throughout a wax carrier material, such as paraffin wax used to form a candle.

"Exfoliation" shall mean a process for forming an Exfoliate from an Intercalate

SUMMARY OF THE INVENTION

In brief, the present invention is directed to compositions and methods that include a wax, in an amount of about 20% to about 99.95% by weight, containing an intercalate, or exfoliate thereof, in an amount of about 0.05% to about 80% by weight of the composition formed by contacting a layered phyllosilicate with an oligomer and/or polymer to sorb or intercalate the intercalant polymer or mixtures of intercalant polymers between adjacent phyllosilicate platelets. Sufficient intercalant polymer is sorbed between adjacent phyllosilicate platelets to expand the spacing between adjacent platelets (interlayer spacing) to a distance of at least about 5 Å, preferably to at least about 10 Å (as measured after water removal) and more preferably in the range of about 30–45 Å, so that the intercalate easily can be exfoliated, sometimes naturally without shearing being necessary. At times, the intercalate requires shearing that easily can be accomplished, e.g., when mixing the intercalate with the wax, either by extrusion or by mixing with a wax melt, to provide a wax/platelet composite material or nanocomposite—the platelets being obtained by exfoliation of the intercalated phyllosilicate

The intercalant polymer should have an affinity for the phyllosilicate so that it is sorbed between, and is maintained associated with the silicate platelets in the interlayer spaces, and after exfoliation in accordance with the present invention, the intercalant polymer can be water-soluble, water dispersible, or water-insoluble, so long as the polymer includes a functionality selected from the group consisting of carbonyl, hydroxyl, carboxyl, amine, amide, ether, ester, sulfate, sulfonate, sulfinate, sulfamate, phosphate, phosphonate, and/or phosphinate. Preferably, the intercalant polymer should be sufficiently water-soluble (herein defined as sufficiently soluble such that at least 0.1 gram of the polymer will dissolve per 100 grams of distilled water at 25° C). In accordance with the present invention, the intercalant polymer should include an aromatic ring and/or have a functionality selected from the group consisting of a carbonyl, carboxyl, hydroxyl, amine, amide, ether, ester, sulfate, sulfonate, sulfinate, sulfamate, phosphate, phosphonate, and/or phosphinate structures to be sufficiently bound by a mechanism selected from the group consisting of ionic complexing, electrostatic complexing, chelation, hydrogen bonding, dipole/dipole, Van Der Waals forces, and any combination thereof. Such bonding results from the metal cations of the phyllosilicate, bonded to the inner surfaces of the phyllosilicate platelets, sharing electrons with two functional groups of one or two intercalant polymer molecules.

Such intercalant polymers have sufficient affinity for the phyllosilicate platelets to maintain sufficient interlayer spacing for exfoliation, without the need for coupling agents or spacing agents, such as the onium ion or silane coupling agents disclosed in the above-mentioned prior art.

Sorption of the intercalant polymer should be sufficient to achieve expansion of adjacent platelets of the layered material (when measured dry) to an interlayer spacing of at least about 5 Å, preferably at least about 10 Å, more preferably a spacing of at least about 20 Å, and most preferably a spacing of about 30–45 Å. To achieve intercalates that can be exfoliated easily using the water-soluble polymer intercalants disclosed herein such as polyvinylpyrrolidone, polyvinyl alcohol, and mixtures thereof, the weight ratio of intercalant polymer to layered material in the intercalating composition contacting the phyllosilicate should be at least about 1:20, preferably at least about 1:10, more preferably at least about 1:5 and most preferably about 1:5 to 1:3. It is preferred that the concentration of intercalant polymer in the intercalating composition, based on the total weight of intercalant polymer plus intercalant carrier in the intercalating composition, is at least about 15% by weight, more preferably at least about 20% by weight intercalant polymer, for example about 20–30% to about 90% by weight intercalant polymer based on the weight of intercalant polymer plus intercalant carrier in the intercalant composition during intercalation.

It has been found that the intercalates of the present invention are increased in interlayer spacing step-wise. If the phyllosilicate is contacted with an intercalant polymer-containing composition containing less than about 16% by weight polymer, e.g., 10% to about 15% by weight polymer, based on the dry weight of the phyllosilicate, a monolayer width of polymer is sorbed (intercalated) between the adjacent platelets of the layered material. A monolayer of polymer intercalated between platelets increases the interlayer spacing to a distance in the range of about 5 Å to less than about 10 Å. When the amount of intercalant polymer is in the range of about 16% to less than about 35% by weight, based on the weight of the dry layered material, the intercalant polymer is sorbed in a bilayer thereby increasing the interlayer spacing to a distance in the range of about 10 Å to about 16 Å. At an intercalant polymer loading in the intercalating composition of about 35% to less than about 55% intercalant polymer, based on the dry weight of the layered material contacted, the interlayer spacing is increased to a distance in the range of about 20 Å to about 25 Å, corresponding to three layers of intercalant polymer sorbed between adjacent platelets of the layered material. At an intercalant polymer loading of about 55% to about 80% intercalant polymer based on the dry weight of the layered material in the intercalating composition, the interlayer spacing will be increased to a distance in the range of about 30 Å to about 35 Å, corresponding to 4 and 5 layers of intercalant polymer sorbed (intercalated) between adjacent platelets of the layered material.

Such interlayer spacings have never been achieved by direct intercalation of an oligomer or polymer molecule, without prior sorption of a swelling agent, such as an onium or silane coupling agent, and provides easier and more complete exfoliation for or during incorporation of the platelets into a thermoplastic or thermosetting matrix polymer. Such intercalates are especially useful in admixture with matrix thermoplastic or thermosetting polymers in the manufacture of polymeric articles from the polymer/platelet composite materials; and for admixture of the intercalates and exfoliated intercalates with polar solvents in modifying

rhology e.g., of cosmetics, oil-well drilling fluids, in the manufacture of oil and grease, and the like.

Once exfoliated, the platelets of the intercalate are predominantly completely separated into individual platelets and the originally adjacent platelets no longer are retained in a parallel, spaced disposition, but are free to move as predominantly individual platelets throughout a matrix polymer melt to act similar to a nanoscale filler material for the matrix polymer. Once the polymer/platelet composite material is set and hardened into a desired shape, the predominantly individual phyllosilicate platelets are permanently fixed in position and are randomly, homogeneously and uniformly dispersed, predominantly as individual platelets, throughout the matrix polymer/platelet composite material.

As recognized, the thickness of the exfoliated, individual platelets (about 10 Å) is relatively small compared to the size of the flat opposite platelet faces. The platelets have an aspect ratio in the range of about 200 to about 2,000. Dispersing such finely divided platelet particles into a wax composition provides a very large area of contact between wax and platelet particles, for a given volume of particles in the composite, and a high degree of platelet homogeneity in the composite material.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG 1 is a graph plotting interlayer space for polyvinylpyrrolidone (PVP) smectite clay complexes (intercalates) showing d(001) and d(002) spacing, in Angstroms, between smectite clay platelets versus percentage of PVP sorbed, based on the dry weight of the smectite clay;

FIG 2 is a graph plotting interlayer space for polyvinyl alcohol (PVA) smectite clay complexes (intercalates) showing d(001) spacing, in Angstroms, between smectite clay platelets versus percentage of PVA sorbed, based on the dry weight of the smectite clay;

FIG 3 is an x-ray diffraction pattern for a complex of PVP (weight average molecular weight of 10,000) sodium montmorillonite clay, in Angstroms, at a weight ratio of PVP:clay of 20:80;

FIG 4 is an x-ray diffraction pattern for a complex of PVP (weight average molecular weight of 40,000) sodium montmorillonite clay, in Angstroms, at a weight ratio of PVP:clay of 20:80;

FIG 5 is an x-ray diffraction pattern for a complex of PVA (weight average molecular weight of 15,000) sodium montmorillonite clay, in Angstroms, at a weight ratio of PVA:clay of 20:80;

FIG 6 is an x-ray diffraction pattern for a complex of PVP-sodium montmorillonite clay, in Angstroms, at a weight ratio of PVP:clay of 20:80 (upper pattern); and an x-ray diffraction pattern for ~100% sodium montmorillonite clay having a cristobalite impurity (lower pattern);

FIG 7 is an x-ray diffraction pattern for a complex of PVP-sodium montmorillonite clay, in Angstroms, at a weight ratio of PVP:clay of 50:50 (upper pattern), and an x-ray diffraction pattern for ~100% sodium montmorillonite clay having a cristobalite impurity (lower pattern);

FIG 8 is a portion of an x-ray diffraction pattern for PVP-sodium montmorillonite clay in Angstroms, at a PVP:clay ratio of 80:20, showing a PVP:clay complex peak or d(001) spacing of about 41 Å;

FIG 9 is a schematic representation of a top view of sodium montmorillonite clay showing the ionic charge distribution for the sodium montmorillonite clay top and inter-

layer surfaces showing Na⁺ ions as the largest circles as well as magnesium and aluminum ions and Si and oxygen (Ox) atoms disposed beneath the sodium ions;

FIG 10 is a side view (bc-projection) of the schematic representation of FIG 6, and

FIG 11 is a schematic representation of the charge distribution on the surfaces of sodium montmorillonite clay platelets showing the distribution of positive and negative charges on the clay platelet surfaces as a result of the natural disposition of the Na, Mg, Al, Si, and oxygen (Ox) atoms of the clay shown in FIGS 6 and 7

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

To form the intercalated materials useful in admixture with one or more waxes in accordance with the present invention, the phyllosilicate should be swelled or intercalated by sorption of an oligomer or polymer that includes an aromatic ring and/or a functionality selected from the group consisting of carbonyl, carboxyl, hydroxyl, amine, amide, ether, ester, sulfate, sulfonate, sulfinate, sulfamate, phosphate, phosphonate, phosphinate, or combinations thereof. In accordance with a preferred embodiment of the present invention, the intercalating composition should include at least about 4% by weight water, up to about 5000% by weight water, based on the dry weight of the phyllosilicate, preferably about 7% to about 100% water, more preferably about 25% to about 50% by weight water, prior to or during contact with the intercalant polymer to achieve sufficient intercalation for exfoliation. Preferably, the phyllosilicate should include at least about 4% by weight water before contact with the intercalating carrier for efficient intercalation. The amount of intercalant polymer in contact with the phyllosilicate from the intercalating composition, for efficient exfoliation, should provide an intercalant polymer/phyllosilicate weight ratio (based on the dry weight of the phyllosilicate) of at least about 1.20, preferably at least about 3.2:20, and more preferably about 4-14.20, to provide efficient sorption and complexing (intercalation) of the polymer between the platelets of the layered material, e.g., phyllosilicate, (preferably about 16 to about 70 percent by weight intercalant polymer, based on the dry weight of the layered silicate material).

The preferred polymer intercalants are water-soluble and are added to the intercalating composition in the form of a solid or liquid (neat or aqueous solution or dispersion, with or without a liquid organic solvent, e.g., alcohol) having an intercalant polymer concentration of at least about 2%, preferably at least about 5% by weight polymer, more preferably at least about 50% to about 100% by weight intercalant polymer in the intercalating composition, based on the dry weight of the layered material, for intercalant polymer sorption. The polymer can be added as a solid with the addition to the layered material/polymer blend of at least about 20% water, preferably at least about 30% water to about 5000% water or more, based on the dry weight of the layered material, with or without another solvent for the intercalant polymer. Preferably about 30% to about 50% water, more preferably about 30% to about 40% by weight water based on the dry weight of the layered material, is included in the intercalating composition, when extruding or pug milling, so that less water or solvent is sorbed by the intercalate, thereby necessitating less drying energy after intercalation. The intercalant polymer may be introduced into the spaces between every layer, nearly every layer, or at least a predominance of the layers of the layered material

such that the subsequently exfoliated platelet particles are preferably predominantly less than about 5 layers in thickness, more preferably, predominantly about 1 or 2 layers in thickness, and most preferably, predominantly single platelets.

Any swellable layered material that sufficiently sorbs the intercalant polymer to increase the interlayer spacing between adjacent phyllosilicate platelets to at least about 5 Å, preferably at least about 10 Å (when the phyllosilicate spacing is measured dry—having a maximum of about 5% by weight water) may be used in the practice of this invention. Useful swellable layered materials include phyllosilicates, such as smectite clay minerals, e.g., montmorillonite, particularly sodium montmorillonite, magnesium montmorillonite and/or calcium montmorillonite, nontronite, beidellite, volkonskoite, hectorite, saponite, saucornite, sobockite, stevensite, svinfordite, vermiculite, and the like. Other useful layered materials include micaceous minerals, such as illite and mixed layered illite/smectite minerals, such as rectorite, tarasovite, ledikite and admixtures of illites with the clay minerals named above.

Other layered materials having little or no charge on the layers may be useful in this invention provided they can be intercalated with the intercalant polymers to expand their interlayer spacing to at least about 5 Å, preferably to at least about 10 Å. Preferred swellable layered materials are phyllosilicates of the 2:1 type having a negative charge on the layers ranging from about 0.15 to about 0.9 charges per formula unit and a commensurate number of exchangeable metal cations in the interlayer spaces. Most preferred layered materials are smectite clay minerals such as montmorillonite, nontronite, beidellite, volkonskoite, hectorite, saponite, saucornite, sobockite, stevensite, and svinfordite.

As used herein the "interlayer spacing" refers to the distance between the internal faces of the adjacent dry layers as they are assembled in the layered material before any delamination (exfoliation) takes place. The interlayer spacing is measured when the layered material is "air dry" e.g., contains about 3–10% water preferably about 3–6% by weight water, based on the dry weight of the layered material. The preferred clay materials generally include interlayer cations such as Na^+ , Ca^{+2} , K^+ , Mg^{+2} , NH_4^+ and the like, including mixtures thereof.

The amount of intercalant polymer intercalated into the swellable layered materials useful in this invention in order that the intercalated layered material platelet surfaces sufficiently complex with the polymer molecules, such that the layered material may be easily exfoliated or delaminated into individual platelets, may vary substantially between about 10% and about 80%, based on the dry weight of the layered silicate material. In the preferred embodiments of the invention, amounts of polymer intercalants employed, with respect to the dry weight of layered material being intercalated, will preferably range from about 8 grams of intercalant polymer/100 grams of layered material (dry basis), preferably at least about 10 grams of polymer/100 grams of layered material to about 80–90 grams intercalant polymer/100 grams of layered material. More preferred amounts are from about 20 grams intercalant polymer/100 grams of layered material to about 60 grams intercalant polymer/100 grams of layered material (dry basis).

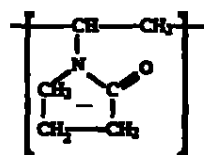
The polymer intercalants are introduced into (sorbed within) the interlayer spaces of the layered material in one of two ways. In a preferred method of intercalating, the layered material is intimately mixed, e.g., by extrusion or

pug milling, to form an intercalating composition comprising the layered material, in an intercalant polymer or intercalant polymer/water solution, or intercalant polymer water and an organic solvent. To achieve sufficient intercalation for exfoliation, the layered material/intercalant polymer blend contains at least about 8% by weight, preferably at least about 10% by weight intercalant polymer based on the dry weight of the layered material. The intercalating carrier (preferably water, with or without an organic solvent) can be added by first solubilizing or dispersing the intercalant polymer in the carrier or the dry intercalant polymer and relatively dry phyllosilicate (preferably containing at least about 4% by weight water) can be blended and the intercalating carrier added to the blend, or to the phyllosilicate prior to adding the dry intercalant polymer. In every case, it has been found that surprising sorption and complexing of intercalant polymer between platelets is achieved at relatively low loadings of intercalating carrier especially H_2O , e.g., at least about 4% by weight water based on the dry weight of the phyllosilicate. When intercalating the phyllosilicate in slurry form (e.g. 900 pounds water, 100 pounds phyllosilicate, 25 pounds polymer) the amount of water can vary from a preferred minimum of at least about 30% by weight water, with no upper limit to the amount of water in intercalating composition (the phyllosilicate intercalate is easily separated from the intercalating composition).

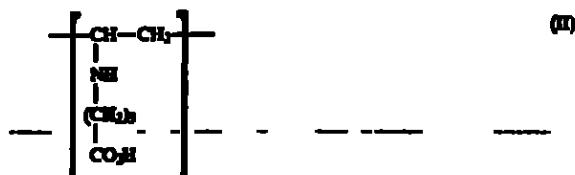
Alternatively, the intercalating carrier e.g. water with or without an organic solvent, can be added directly to the phyllosilicate prior to adding the intercalant polymer, either dry or in solution. Sorption of the polymer intercalant molecules may be performed by exposing the layered material to dry or liquid polymer intercalant compositions containing at least about 2% by weight, preferably at least about 5% by weight intercalant polymer, more preferably at least about 50% intercalant polymer based on the dry weight of the layered material. Sorption may be aided by exposure of the intercalating composition to heat, pressure, ultrasonic cavitation, or microwaves.

In accordance with another method of intercalating the intercalant polymer between the platelets of the layered material and exfoliating the intercalate, the layered material, containing at least about 4% by weight water, preferably about 10% to about 15% by weight water is blended with an aqueous solution of a water-soluble intercalant polymer in a ratio sufficient to provide at least about 8% by weight, preferably at least about 10% by weight intercalant polymer, based on the dry weight of the layered material. The blend then preferably is extruded for faster intercalation of the polymer with the layered material.

The preferred polymer intercalants are water-soluble, such as polyvinylpyrrolidone (PVP) having a monomeric structure (I) as follows.

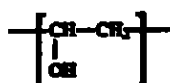


The water-solubility of PVP can be adjusted according to (1) the degree of hydrolysis of the polyvinyl-pyrrolidone, and (2) by forming a metal salt of PVP, such as sodium or potassium PVP can be hydrolyzed to the structure (II):



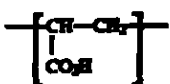
and the PVP, or copolymers of vinylpyrrolidone and a vinyl amide of γ -amine butyric acid, can be intercalated in the salt form, e.g., sodium or potassium polyvinylpyrrolidone polymers. Preferred PVP intercalants, and the following PVP derivatives, should have a weight average molecular weight in the range of about 100 to about 100,000 or more, more preferably about 1,000 to about 40,000.

Other suitable water-soluble vinyl polymers include poly (vinyl alcohol)



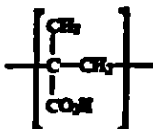
The polyvinyl alcohols function best when they are essentially fully hydrolyzed, e.g., 5% or less acetyl groups, preferably 1% or less residual acetyl groups. The lower molecular weight PVA's function best, e.g., a weight average molecular weight of about 2,000 to about 10,000, but higher molecular weights also function, e.g., up to about 100,000.

The polyacrylic acid polymers and copolymers and partially or fully neutralized salts, e.g., metal salts, are also suitable, having monomer units:

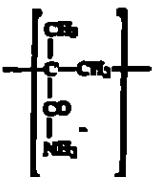


and are commercially available as CARBOPOL resins from B F Goodrich and PRIMAL resins from Rohm & Haas. Light cross-linking is acceptable, so long as water-solubility is retained. Weight average molecular weights, for the polyacrylic polymers and copolymers described above and below, of about 10,000 or less, e.g., 200-10,000, intercalate more easily, but higher molecular weights up to about 100,000 or more also function.

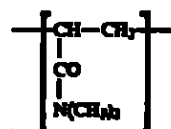
Other water-soluble derivatives of, and substituted, polyacrylic acids also are useful as intercalant polymers in accordance with the present invention, such as poly (methacrylic acid), (PMAA), having a monomeric structure



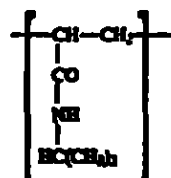
Similar water-soluble polymers and copolymers that are suitable in accordance with the present invention include poly(methacrylamide), or PMAAm, having a general monomeric structure.



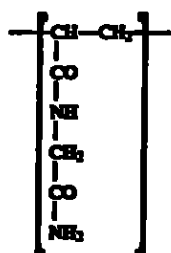
Poly(N,N-Dimethylacrylamide), having the general monomeric structure.



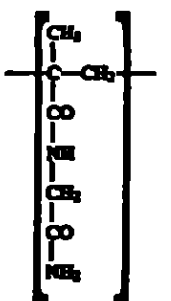
Poly(N Isopropylacrylamide), or PIPAAm, having the monomeric structure.



Poly(N-acetamidocrylamide), having a monomeric structure.

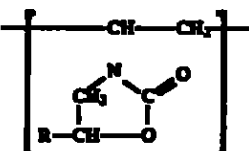


and Poly(N-acetamidomethacrylamide), having a monomeric structure



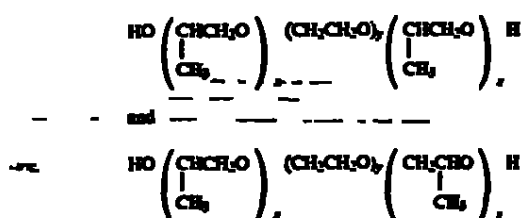
Water-soluble copolymers including any one or more of the above-described acrylic polymers also are useful in accordance with the principles of the present invention, including the acrylic interpolymers of polyacrylic acid and poly (methacrylic acid) polyacrylic acid with poly (methacrylamide), and polyacrylic acid with methacrylic acid.

Other suitable water-soluble polymers include polyvinylloxazolidone (PVO) and polyvinylmethyloxazolidones (PVMO), having the monomeric structures:



PVO: R = H
PVMO: R = CH₃

Also suitable are polyoxypropylene, polyoxyethylene block polymers that conform to the formulas.



wherein x and z are each an integer in the range of about 4 to about 30; and y is an integer in the range of about 4 to about 100, for example Meroxapol 105 Meroxapol 108, Meroxapol 171, Meroxapol 172, Meroxapol 174, Meroxapol 178, Meroxapol 251 Meroxapol 252, Meroxapol 254, Meroxapol 255, Meroxapol 258, Meroxapol 311, Meroxapol 312, and Meroxapol 314.

Other suitable water-soluble/water-dispersible intercalant polymers include polyacrylamide and copolymers of acrylamide, acrylamide/sodium acrylate copolymer; acrylate/acrylamide copolymer acrylate/ammonium methacrylate copolymer acrylate/diacetoneacrylamide copolymers, acrylic/acrylate copolymers, adipic acid/dimethylaminohydroxypropyl diethylenetriamine copolymer ammonium acrylate copolymers, ammonium styrene/acrylate copolymers, ammonium vinyl acetate/acrylate copolymers, AMP acrylate/diacetoneacrylamide copolymers, AMPD acrylate/diacetoneacrylamide copolymers, butyl benzoic acid/phthalic anhydride/trimethylolthane copolymer cornstarch/acrylamide/sodium acrylate copolymer diethylene glycolamine/epichlorohydrin/piperazine copolymer dodecanedioic acid/cetearyl alcohol/glycol copolymers, ethylene/vinyl alcohol copolymer ethyl ester of polyethyleneimines, such as hydroxyethyl/PEI 1000 and hydroxyethyl PEI-1500; isopropyl ester of PVM/MA copolymer melamine/formaldehyde resin, methacryloyl ethyl betaine/methacrylate copolymers, methoxy PEG-22/dodecyl glycol copolymer; octadecene/maleic anhydride copolymer; octylacrylamide/acrylate/butylaminoethyl methacrylate copolymers, octylacrylamide/acrylate copolymers, PEG/dodecyl glycol copolymers, polyethyleneimines, such as PEI-7, PEI 15 PEI-30; PEI-45, PEI-275 PEI-700, PEI-1000 PEI 1500; and PEI-2500; phthalic anhydride/glycerol/glycidyl decanoate copolymer metal salts of acrylic and polyacrylic acid, polyaminopropyl biguanide, polymeric quaternary ammonium salts, such as polyquaternum-1, polyquaternum-2, polyquaternum-4 polyquaternum-5, polyquaternum-6, polyquaternum 7 polyquaternum-8, polyquaternum 9; polyquaternum 10, polyquaternum 11, polyquaternum 12, polyquaternum-13, polyquaternum-14 and polyquaternum-15 polyvinyl imidazolium acetate potassium polyacrylate, sodium polyacrylate; metal salts of PVM/MA copolymers, e.g. Li, K, Na Ru, Ce salts, PVP/eicosene copolymers, PVP/ethyl methacrylate/methacrylic acid copolymer; PVP/hexadecene copolymer PVP/VA copolymer, PVP/vinyl acetate/itaconic acid copolymer; sodium acrylate/vinyl alcohol copolymers, sodium C₈-C₁₂, and other metal salts of olefin/maleic acid copolymers, sodium polymethacrylate, sodium polystyrene sulfonate, sodium styrene/acrylate/PEG 10 dimaleate copolymer; water-soluble esters and ethers of cellulose, sodium styrene/PEG-10 maleate/nonoxynol 10 maleate/acrylate copolymer; starch/acrylate/acrylamide copolymers, styrene/acrylamide copolymer; styrene/acrylate/ammonium methacrylate copolymer styrene/maleic anhydride copolymer; styrene/PVO copolymer, sucrose benzoate/sucrose acetate isobutyrate/butyl benzyl phthalate copolymer,

sucrose benzoate/sucrose acetate isobutyrate/butyl benzylphthalate/methyl methacrylate copolymer urea/formaldehyde prepolymers, urea/melamine/formaldehyde prepolymers, vinyl acetate/crotonic acid copolymers, and vinyl alcohol copolymers.

Other water-soluble polymeric polyols and polyhydric alcohols, such as polysaccharides, also are suitable as polymer intercalants.

Any wax is useful in the compositions of the present invention. The useful waxes may be natural or synthetic, or combinations thereof, and generally have melting points within the range of about 30° C to about 100° C., including animal waxes, mineral waxes, vegetable waxes, insect waxes, and synthetic waxes including beeswax, bayberry-myrtle candelilla, caranday carnauba, castor bean wax; esparto grass wax, Japan wax; montan crude wax; ouricury; relamo-cen numbu, shellac wax, spermaceti, sugar cane wax, and wool wax lanolin.

Of these waxes, the petroleum waxes and synthetic waxes are preferred for the compositions of the present invention. Synthetic waxes include the ester waxes made by esterifying acid waxes, such as montan wax, with alcohols and/or glycols. Paraffins and chlorinated paraffins also are of considerable interest as the wax components of the compositions of the present invention. Waxy film formers produced by the emulsion polymerization of ethylene, styrene, or acrylates (weight average molecular weights of about 10,000 to about 50,000) are of particular interest in the compositions of the present invention in the manufacture of polyolefin films, filled with intercalates and/or exfoliates, having increased gas impermeability. Oxidized hydrocarbon waxes, such as those manufactured from the Fisher-Tropach paraffins, and the microcrystalline petroleum waxes (ester-type waxes) also are useful in the compositions of the present invention, particularly for polishes and the like.

Other synthetic waxes of entirely different structure such as the fatty amides, imides, amides, and nitrates can be waxlike and very useful, particularly when special surface activity or coordinate solubilities are needed. The polyoxy ethylenes or carbowaxes are a unique and important group of waxes because of their water solubility and compatibility with fatty materials common to cosmetic and pharmaceutical formulations.

The petroleum waxes, particularly paraffin waxes but also the microcrystalline waxes are most useful for the manufacture of candles. Petroleum waxes can be sufficiently hardened together with an intercalate and/or exfoliate, in accordance with the present invention, for candle manufacture. The petroleum waxes are predominantly long chain (C₁₆-C₃₀) alkane compounds. The paraffins are mostly straight-chain molecules, but may have branched chains, but on average have less than one branched-chain carbon atom per molecule. The microcrystalline waxes range in molecular weight from about 400 to about 700 and have average molecules of about 40 to about 50 carbon atoms. The microcrystalline waxes have more branched-chain molecules than in paraffin waxes, containing an average of three carbon atoms per side chain. Oxidized microcrystalline waxes also are useful in the compositions of the present invention. Petroleum waxes contains both solid and liquid hydrocarbons with the liquid hydrocarbons held in discrete droplets within the petroleum wax. The paraffin waxes used in the compositions of the present invention may be crude scale wax and/or fully refined wax.

Synthetic paraffin waxes are mixtures of saturated straight-chain paraffinic hydrocarbons with short side chains (C₁-C₄). The weight average molecular weight is about 700 to about 800 or about 45-60 carbon atoms per molecule.

Synthetic paraffin wax serves as an opacifier in candle formulations and is used to improve the sun-check resistance of vulcanized rubber. For use in candle formulations and in vulcanized rubber, synthetic paraffin waxes are improved in accordance with the present invention by the addition of an

intercalate and/or exfoliate thereof. The amount of intercalated and/or exfoliated layered material included in the wax compositions of the present invention may vary widely depending on the intended use of the composition. For example, relatively higher amounts of intercalates, i.e. from about 40% to about 80% by weight of the total composition, are used in forming wax compositions for increasing crack resistance and lowering shrinkage upon solidification of the wax. However, smoothing of surface finish, as well as increased crack resistance and reduced shrinkage upon solidification also can be achieved with a relatively small concentration of intercalates and/or exfoliates thereof, e.g., 0.05% to about 10% by weight. It is preferred that the intercalate or platelet loading be less than about 10% by weight of the wax composition, preferably about 0.1% to about 5% by weight of the composition. Intercalate or platelet particle loadings may vary widely, e.g., within the range of about 0.05% to about 80% by weight, preferably about 0.01% to about 20%, more preferably about 0.5% to about 10%, and most preferably about 0.1% to about 5% of the total weight of the composition. The intercalates and/or exfoliates significantly increase the resistance of cracking, lowers shrinkage upon wax solidification of the wax compositions, and improves the surface finish of the wax compositions. In most compositions, the amount of intercalate and/or platelet particles incorporated into the wax compositions is less than about 20% by weight of the total composition, and preferably from about 0.05% to about 10% by weight of the composition, more preferably from about 0.05% to about 5% by weight of the composition.

In accordance with an important feature of the present invention, the intercalate and/or platelet/wax compositions of the present invention can be manufactured in a concentrated form e.g. as a master composition, e.g., having about 10-80%, preferably about 20-50% intercalate and/or exfoliated platelets of layered material and about 10-90%, preferably about 50-80% wax, e.g., paraffin wax. The master gel can be later diluted and mixed with additional wax and/or solvent to reduce the concentration of intercalate and/or exfoliated platelets in the composition. The intercalates, and/or exfoliates thereof are mixed with a wax composition to produce the compositions of the present invention.

Eventual exfoliation of the intercalated layered material should provide delamination of at least about 90% by weight of the intercalated material to provide particles substantially homogeneously dispersed therein. Some intercalates require a shear rate that is greater than about 10 sec^{-1} for such relatively thorough exfoliation. Other intercalates exfoliate naturally or by heating, or by applying low pressure, e.g., 0.5 to 60 atmospheres above ambient, with or without heating. The upper limit for the shear rate is not critical. In the particularly preferred embodiments of the invention, when shear is employed for exfoliation, the shear rate is from greater than about 10 sec^{-1} to about $20,000 \text{ sec}^{-1}$, and in the more preferred embodiments of the invention the shear rate is from about 100 sec^{-1} to about $10,000 \text{ sec}^{-1}$.

When shear is employed for exfoliation, any method which can be used to apply a shear to the intercalant/carryer composition can be used. The shearing action can be provided by any appropriate method, as for example by mechanical means, by thermal shock, by pressure alteration,

or by ultrasound, all known in the art. In particularly useful procedures, the composition is sheared by mechanical methods in which the intercalate, with or without the wax, is sheared by use of mechanical means, such as stators, Banbury® type mixers, Brabender® type mixers, long continuous mixers, and extruders. Another procedure employs thermal shock in which shearing is achieved by alternatively raising or lowering the temperature of the composition causing thermal expansions and resulting in internal stresses which cause the shear. In still other procedures, shear is achieved by sudden pressure changes in pressure alteration methods, by ultrasonic techniques in which cavitation or resonant vibrations which cause portions of the composition to vibrate or to be excited at different phases and thus subjected to shear. These methods of shearing are merely representative of useful methods, and any method known in the art for shearing intercalates may be used.

Mechanical shearing methods may be employed such as by extrusion, injection molding machines, Banbury® type mixers, Brabender® type mixers and the like. Shearing also can be achieved by introducing the layered material and intercalant polymer at one end of an extruder (single or double screw) and receiving the sheared material at the other end of the extruder. The temperature of the layered material/intercalant polymer composition, the length of the extruder, residence time of the composition in the extruder and the design of the extruder (single screw, twin screw, number of flights per unit length, channel depth, flight clearance, mixing zone, etc.) are several variables which control the amount of shear to be applied for exfoliation.

Exfoliation should be sufficiently thorough to provide at least about 80% by weight, preferably at least about 85% by weight, more preferably at least about 90% by weight, and most preferably at least about 95% by weight delamination of the layers to form individual platelet particles that can be substantially homogeneously dispersed in the wax composition. As formed by this process, the platelet particles dispersed in the wax composition have the thickness of the individual layers plus one to five monolayer thicknesses of complexed polymer, or small multiples less than about 10, preferably less than about 5 and more preferably less than about 3 of the layers, and still more preferably 1 or 2 layers. In the preferred embodiments of this invention, intercalation and delamination of every interlayer space is complete so that all or substantially all individual layers delaminate one from the other to form separate platelet particles for admixture with the wax composition. The compositions can include the layered material as all intercalate, completely without exfoliation, for later exfoliation during manufacture.

The effect of adding into a wax composition the nanoscale particulate dispersed platelet particles, derived from the intercalates formed in accordance with the present invention, typically is a decrease in cracking and shrinkage and an increase in stability (reduction in separation of components upon standing and solidification) of the wax composition. Other advantages include increasing the opacity and dye receptivity and an increase in wax melt viscosity for wick flame control in candles, increasing composition hardness without causing brittleness; improving the melt stability of the composition to make sure that the liquid composition remains homogenous, without component separation, reducing or eliminating the need for purer, more expensive wax components, such as microcrystalline wax; and greatly reducing or eliminating the formation of exterior bubbles or pock marks that form upon reheating an upper portion of a candle when reducing the concave upper candle end formed upon initial solidification, and providing the

capability of eliminating typical opacifying agents and viscosity increasing agents, e.g. ethylene vinylacetate copolymers, fatty acids, such as stearic acid, and the like, with a much lower amount of the nanoscale platelet particles of the present invention. Additionally the phyllosilicate platelets act as a good protector against deterioration of physical properties and color degradation caused by ultra violet (UV) light so that UV protectors are unnecessary in the wax compositions of the present invention.

The following specific clay-polymer complex preparations are presented to more particularly illustrate the invention and are not to be construed as limitations thereon.

Preparation of Clay-PVP Complexes (Intercalates)

Materials.

Clay—sodium montmorillonite,

PVP—molecular weights of 10,000 and 40,000.

To prepare Clay (sodium montmorillonite) - PVP complexes (intercalates) we used three different processes for polymer intercalation.

- 1 Mixture of the 2% PVP/water solution with the 2% clay/water suspension in a ratio sufficient to provide a polymer concentration of at least about 8% by weight, preferably at least about 10% by weight, based on the dry weight of the clay
- 2 Dry clay powder (about 8% by weight moisture) was gradually added to the 2% PVP/water solution in a ratio sufficient to provide a polymer concentration of at least about 8% by weight preferably at least about 10% by weight, based on the dry weight of the clay
- 3 Dry PVP was mixed with dry clay the mixture was hydrated with 25–50%, preferably 35–40% by weight water, based on the dry weight of the clay, and then extruded.

Mixtures 1 and 2 were agitated at room temperature during 4 hours.

The weight ratio Clay PVP was changed from 90:10 to 20:80.

These experiments show that all methods of preparation yielded the Clay - PVP complexes (intercalates), and the results of the intercalation do not depend on the method of preparation (1, 2, or 3) or molecular weight of the intercalant polymer (PVP), but do depend on the ratio of clay-PVP in the intercalating composition. In Table 1 the results of the X ray diffraction for Clay - PVP complexes with different ratios of components are demonstrated. The plot of these data is shown in FIG 1. From these data (Table 1, FIG 1) one can see the step character of intercalation while the polymer is being sorbed in the interlayer space between adjacent platelets of the montmorillonite clay. There are increasing $d(001)$ values from 12 Å for clay with no PVP sorbed to 24–25 Å spacing between adjacent platelets with sorption of 20–30% PVP. The next step to 30–32 Å spacing occurs when the sorbed PVP content is increased to 40–60%. Further increasing the sorbed PVP content to 70–80% increases the $d(001)$ values to 40–42 Å. There are $d(002)$ reflexes together with $d(001)$ reflexes in X-ray patterns of all complexes obtained (Table 1, FIG 1). This indicates the regularity of Clay - PVP complex structures.

TABLE 1

	PVP, %	$d(001)$, Å	$d(002)$, Å
1	0.0	12.4	6.2
2	10.0	17.3	8.6
3	30.0	24.0	11.4
4	30.0	25.0	12.0
5	40.0	30.0	15.2
6	45.0	31.0	15.5
7	50.0	30.0	15.3
8	55.0	32.0	16.3
9	60.0	34.0	17.0
10	70.0	40.0	21.0
11	80.0	42.0	21.0

Percent by weight, based on the dry weight of the clay plus polymer.

Preparation of Clay - PVA Complexes (Intercalates)

Materials.

Clay—sodium montmorillonite,

PVA—degree of hydrolysis 75–99%, —molecular weight of 10,000.

To prepare Clay (sodium montmorillonite) - PVA complexes (intercalates) we provided three different processes for polymer intercalation.

- 1 Mixture of the 2% PVA/water solution with the 2% clay/water suspension in a ratio sufficient to provide a polymer concentration of at least about 8% by weight, preferably at least about 10% by weight, based on the dry weight of the clay
- 2 Dry clay powder was gradually added to the 2% PVA/water solution in a ratio sufficient to provide a polymer concentration of at least about 8% by weight, preferably at least about 10% by weight, based on the weight of the clay

3 Dry clay was moisturized with PVA/water solution to a moisture content of 25%–80%, preferably about 35%–40% water, and then extruded.

The mixtures 1 and 2 were agitated at room temperature during 4 hours.

The weight ratio Clay-PVA was changed from 80:20 to 20:80.

Some of the exfoliates were studied by X-ray diffraction. These experiments show that all methods of preparation yielded the composite Clay - PVA complexes (intercalates), and the results of the intercalation do not depend on the method of preparation (1, 2, or 3), or molecular weight of the intercalant polymer (PVA), or degree of hydrolysis, but do depend on the ratio of clay-PVA in the intercalating composition. In Table 2 the results of the X-ray diffraction for Clay - PVA complexes with different ratios of components are demonstrated. The plot of these data is shown in FIG 2. From these data (Table 2, FIG 2) one can see the step character of increasing $d(001)$ values from 12 Å for clay with no sorbed PVA to 22–25 Å spacing between adjacent platelets with sorption of 20–30% PVA. The next step to 30–33 Å occurs when the sorbed PVA content increases to 35–50%. A further increase of the sorbed PVA content to 60–80% increases the $d(001)$ values to 40–45 Å.

Heating of samples at 120° C during 4 hours insignificantly changed the $d(001)$ values (Table 2, FIG 2).

125

124

TABLE 2

	PVA %*	d (001), Å	d (001), Å 120° C.
1	0.0	12.4	9.6
2	10.0	17.0	16.8
3	20.0	23.0	32.0
4	30.0	25.0	24.0
5	35.0	32.0	32.0
6	40.0	31.0	30.0
7	45.0	33.0	33.0
8	50.0	32.0	32.0
9	60.0	42.0	42.0
10	70.0	44.0	42.0
11	80.0	48.0	44.0

*Percent by weight, based on the dry weight of the clay plus PVA.

The graphs of FIGS 3 to 5 are x-ray diffraction patterns of blends of different water-soluble polymers with sodium bentonite clay. The pattern of FIGS 3 and 4 are taken from intercalated clay 20% by weight polyvinylpyrrolidone (weight average molecular weight=10,000 for FIG 3, 40,000 for FIG 4) and 80% by weight sodium bentonite clay. The blends were formed by mixing the PVP and clay from a 2% solution of PVP and a 2% dispersion of sodium bentonite in a 1:4 ratio, respectively. As shown, the PVP-clay complexed since no d(001) smectite peak appears at about 12.4 Å. Similar results are shown for 20% polyvinyl alcohol, 80% sodium bentonite, as shown in FIG 5, blended in the same way and in the same ratio. The d(001) peak of non-exfoliated (layered) sodium bentonite clay appears at about 12.4 Å, as shown in the x-ray diffraction pattern for sodium bentonite clay (containing about 10% by weight water) in the lower x-ray diffraction patterns of FIGS 6 and 7. The graphs of FIG 6 are x-ray diffraction patterns of sodium bentonite clay (montmorillonite) and a PVP:clay complex that was obtained by extrusion of a blend of 20% by weight polyvinylpyrrolidone (molecular weight 10,000) and 80% by weight sodium bentonite clay (containing a cristobalite impurity, having a d-spacing of about 4.05 Å) with 35% water based on the weight of dry clay plus polymer. As shown in FIG 6, the PVP:clay complexed since no d(001) smectite peak appears at about 12.4 Å. There are basal spacings with a d(001) peak of PVP:clay complex at about 24 Å and d(002) peak of PVP:clay complex at about 12 Å, that shows close to regular structure of this intercalated composite with a PVP:clay ratio equal to 1:4. The graphs of FIG 7 are x-ray diffraction patterns of sodium bentonite clay (montmorillonite) and PVP:clay complex that was obtained by extrusion of blend of 50% by weight polyvinylpyrrolidone (molecular weight 10,000) and 50% of sodium bentonite clay (containing a cristobalite impurity, having d-spacing of about 4.05 Å) with 35% water based on the weight of dry clay plus polymer. As shown in FIG 7, the PVP:clay complexed since no d(001) smectite peak appears at about 12.4 Å. There are basal spacings with a d(001) peak of the PVP:clay complex at about 32 Å and a d(002) peak of PVP:clay complex at about 16 Å that shows close to regular structure of this intercalated composite with a PVP:clay ratio equal to 1:1. When mechanical blends of powdered sodium bentonite clay (containing about 10% by weight water) and powdered polyvinylpyrrolidone (PVP) polymer were mixed with water (about 75% by weight water), the polymer was intercalated between the bentonite clay platelets, and an exothermic reaction occurred that, it is theorized, resulted from the polymer being bonded to the internal faces of the clay platelets sufficiently for exfoliation of the intercalated clay.

It should be noted, also, that exfoliation did not occur unless the bentonite clay included water in an amount of at

least about 4% by weight based on the dry weight of the clay preferably at least about 10% by weight water. The water can be included in the clay as received, or can be added to the clay prior to or during intercalant polymer contact.

It should also be noted that the exfoliation occurred without shearing—the layered clay exfoliated naturally after sufficient intercalation of polymer between the platelets of the layered bentonite—whether the intercalate was achieved by using sufficient water, e.g., at least about 20% by weight, preferably about 30% to about 100% by weight, or higher, based on the dry weight of the clay, for sufficient migration of the polymer into the interlayer spaces, and preferably also by extruding. When intercalating in a phyllosilicate slurry, it has been found that at least about 65% by weight water, based on the total weight of the intercalating composition, provides easier mixing and faster migration of the polymer into the spaces between platelets.

The x-ray diffraction pattern of FIG 8 shows that at a ratio of 80% PVP, 20% clay the periodicity of the intercalated composite, with a PVP:clay ratio equal to 4:1, is increased to about 41 Å.

EXAMPLE

A candle composition is prepared as follows:

Component	Weight %
petroleum-derived paraffin wax	94
microcrystalline wax	3
sodium bentonite platelets exfoliated from a PVP intercalate	3

The candle composition is solidified into a candle form and exhibits excellent stability (without separation of the platelets from the composition); excellent hardness without brittleness, significantly less shrinkage, without cracking; and the melt has ideal viscosity for good flow and flame control.

What is claimed is:

1 A composition consisting essentially of exfoliated platelets of a layered material formed from an intercalate, together with a wax composition, said intercalate formed by contacting a layered material, having a moisture content of at least about 4% by weight, with an intercalant polymer to form an intercalating composition containing at least about 16% by weight intercalant polymer based on the dry weight of the layered material, said intercalate having a weight ratio of polymer to layered material of about 16–90 grams of polymer per 100 grams of dry layered material to achieve sorption and complexing of the polymer between adjacent spaced layers of the layered silicate material, without prior sorption of an onium ion or silane coupling agent, to expand the spacing between a predominance of the adjacent platelets of said layered silicate material to at least about 5 Å, when measured after sorption of the intercalant polymer and drying to a maximum of 5% by weight water, and delaminating at least about 80% of the intercalated material into platelet particles having less than five platelet layers.

2 A composition in accordance with claim 1, wherein the concentration of intercalant polymer in said intercalating composition is at least about 0.1% by weight, based on the weight of water and polymer in the intercalating composition.

3 A composition in accordance with claim 2, wherein the concentration of intercalant polymer in said intercalating composition is at least about 1% by weight.

4 A composition in accordance with claim 3 wherein the concentration of intercalant polymer in said intercalating composition is at least about 2% by weight. — —

5 A composition in accordance with claim 1, wherein the concentration of intercalant polymer in said intercalating composition is in the range of about 10%–60% by weight

6 A composition in accordance with claim 4 wherein the concentration of intercalant polymer in said intercalating composition is at least about 15% by weight, based on the dry weight of layered material in the intercalating composition to achieve spacing of said adjacent platelets of at least about 10 Å.

7 A composition in accordance with claim 6, wherein the concentration of intercalant polymer in said intercalating composition is at least about 20% by weight, based on the dry weight of layered material in the intercalating composition, and wherein said intercalant polymer includes a functionality selected from the group consisting of an aromatic ring, a carboxyl, a hydroxyl, a carbonyl, an ether, an ester, an amine, an amide, an SOx, a POx, wherein x=2,3 or 4, and mixtures thereof.

8 A composition in accordance with claim 7, wherein the concentration of intercalant polymer in said intercalating composition is at least about 30% by weight, based on the dry weight of layered material in the intercalating composition.

9 A composition in accordance with claim 1 wherein the concentration of intercalant polymer in said intercalating composition is in the range of about 50% to about 90% by weight, based on the weight of polymer plus water

10 A composition in accordance with claim 9, wherein the concentration of intercalant polymer in said intercalating composition is in the range of about 50% to about 80% by weight.

11 A composition in accordance with claim 1, wherein the concentration of intercalant polymer in the intercalating composition is at least about 16% by weight, based on the dry weight of the layered material.

12 A composition in accordance with claim 11, wherein the concentration of intercalant polymer in the intercalating composition is in the range of about 16% to about 70% by weight, based on the dry weight of the layered material.

13 A composition in accordance with claim 1, wherein the weight ratio of intercalant polymer to layered material in the intercalating composition is in the range of about 1:20 to about 10:1

14 A composition in accordance with claim 11 wherein the weight ratio of intercalant polymer to layered material is at least 1:12.

15 A composition in accordance with claim 14, wherein the weight ratio of intercalant polymer to layered material in the intercalating composition is at least 1:5

16 A composition in accordance with claim 15, wherein the weight ratio of intercalant polymer to layered material in the intercalating composition is in the range of 1:5 to 1:3.

17 A composition in accordance with claim 1, wherein the intercalant polymer is selected from the group consisting of polyvinylpyrrolidone, polyvinyl alcohol, polyvinylimine, and mixtures thereof.

18 A composition in accordance with claim 17, wherein the intercalant polymer is polyvinyl alcohol.

19 A composition in accordance with claim 13, wherein the intercalant polymer is polyvinylpyrrolidone.

20 A composition in accordance with claim 18, wherein the intercalant polymer is polyvinyl alcohol having less than about 5% by weight acetal substituents in the polymer.

21 A composition in accordance with claim 17 wherein the intercalant polymer has a weight average molecular weight in the range of about 100 to about 100,000.

22 A composition in accordance with claim 17 wherein the intercalant polymer has a weight average molecular weight in the range of about 200 to about 40,000.

23 A composition in accordance with claim 22, wherein the intercalant polymer is polyvinylpyrrolidone.

24 A composition in accordance with claim 22, wherein the intercalant polymer is a polyvinyl alcohol.

25 A composition in accordance with claim 1, wherein the intercalant polymer is a homopolymer or copolymer of N-vinylpyrrolidone

26 A method of decreasing the shrinkage and increasing the crack resistance of a wax composition comprising combining said wax composition with an intercalate complex of a phyllosilicate and polymer to form a composition consisting essentially of said wax composition and said intercalate complex comprising:

contacting the phyllosilicate, having a water content of at least about 4% by weight, with an intercalant polymer to form an intercalating composition having at least about 16% by weight intercalant polymer based on the dry weight of the phyllosilicate, to form an intercalate having a weight ratio of polymer to phyllosilicate in the range of about 16–90 grams of polymer per 100 grams of dry phyllosilicate wherein intercalation of said polymer between said adjacent phyllosilicate platelets of said intercalate is achieved without prior sorption of an onium ion or silane coupling agent and sufficient to space said adjacent phyllosilicate platelets a distance of at least about 5 Å,

exfoliating said intercalate, and

combining said exfoliate with a material consisting essentially of said wax composition.

27 The method of claim 26, wherein said intercalating composition includes a water intercalating carrier comprising about 4% to about 5000% by weight water capable of dissolving said polymer, based on the dry weight of said phyllosilicate

28 The method of claim 27, wherein said intercalating composition includes water in an amount of about 30% to about 40% by weight.

29 The method of claim 28, wherein said water content of said intercalating composition comprises about 35% to about 40% by weight, based on the dry weight of said phyllosilicate

30 The method of claim 27 wherein said intercalating composition comprises about 5% to about 50% by weight water, based on the dry weight of said phyllosilicate.

31 The method of claim 27, wherein said intercalating composition includes water in an amount of about 7% to about 100% by weight, based on the dry weight of the phyllosilicate in the intercalating composition.

32 A composition consisting essentially of a wax having about 16 to about 60 carbon atoms per molecule, in an amount of about 0.5% to about 99.95% by weight of the composition and about 0.05% to about 80% by weight of the composition of an exfoliate of a phyllosilicate material, said exfoliate formed by contacting a phyllosilicate, having a water content of at least about 4% by weight, with an intercalant polymer in an amount of at least about 16% by weight intercalant polymer based on the dry weight of the phyllosilicate to form an intercalate having said intercalant polymer sorbed between adjacent spaced layers of the phyllosilicate and complexed on platelet surfaces of said phyllosilicate in an amount of about 16–90 grams of intercalant polymer per 100 grams of dry phyllosilicate material, without prior sorption of an onium ion or silane coupling agent, to expand the spacing between a predominance of the

adjacent phyllosilicate platelets to at least about 5 Å, when measured after sorption of the polymer and drying of the intercalate to a maximum water content of 5% by weight, and exfoliating at least about 80% of the intercalated material into platelet particles having less than five platelet layers.

33. The composition of claim 32, wherein the wax has about 18 to about 50 carbon atoms, and mixtures thereof

34. A composition in accordance with claim 32, wherein the intercalant composition has a weight ratio of intercalant polymer to phyllosilicate of at least about 1:20.

35. A composition in accordance with claim 34, wherein the weight ratio of intercalant polymer to phyllosilicate in said intercalating composition is at least about 1:12.

36. A composition in accordance with claim 35, wherein the weight ratio of intercalant polymer to phyllosilicate in said intercalating composition is at least about 1:10.

37. A composition in accordance with claim 36, wherein the weight ratio of intercalant polymer to phyllosilicate in said intercalating composition is at least about 1:5.

38. A composition in accordance with claim 37, wherein the weight ratio of intercalant polymer to phyllosilicate in said intercalating composition is in the range of about 1:5 to about 9:1.

39. A composition in accordance with claim 38, wherein the weight ratio of intercalant polymer to phyllosilicate in said intercalating composition is in the range of about 1:5 to about 1:3.

40. A composition in accordance with claim 34, wherein the concentration of intercalant polymer in the intercalating composition is at least about 16% by weight, based on the dry weight of the phyllosilicate.

41. A composition in accordance with claim 40, wherein the concentration of intercalant polymer in the intercalating composition is in the range of about 16% to about 70% by weight, based on the dry weight of the phyllosilicate.

42. A composition in accordance with claim 40, wherein the concentration of intercalant polymer in the intercalating composition is in the range of about 16% to less than about 35% by weight, based on the dry weight of the phyllosilicate.

43. A composition in accordance with claim 41, wherein the concentration of intercalant polymer in the intercalating composition is in the range of about 35% to less than about 55% by weight, based on the dry weight of the phyllosilicate.

44. A composition in accordance with claim 41, wherein the concentration of the intercalant polymer in the intercalating composition is in the range of about 55% to less than about 70% by weight, based on the dry weight of the phyllosilicate.

45. A composition in accordance with claim 32, wherein the wax has about 16 to about 40 carbon atoms per molecule

46. A method of manufacturing a wax composition consisting essentially of about 20% to about 99.95% by weight of a wax and about 0.05% to about 80% by weight of exfoliated platelets of an intercalated layered material, said intercalated layered material having a water-soluble polymer intercalated between and bonded to said platelet surfaces thereof through a bonding mechanism selected from the group consisting of ionic complexing; electrostatic complexing; chelation; hydrogen bonding; dipole/dipole, Van Der Waals forces, and any combination thereof, comprising:

contacting the layered material with a water-soluble intercalant polymer and water, without prior sorption of an onium ion or silane coupling agent to form an intercalating composition having at least about 16% by weight intercalant polymer based on the dry weight of the phyllosilicate to form an intercalate having said polymer intercalated between said adjacent platelets in an amount of about 16-90 grams of polymer per 100 grams of dry phyllosilicate;

combining the intercalate with said wax; and exfoliating the spaced platelets of said intercalate into at least about 80% by weight of platelet particles having less than three individual platelets.

47. The method of claim 46, wherein said layered material is a phyllosilicate and said intercalating composition is an aqueous solution comprising about 4% to about 5000% by weight water, based on the dry weight of said phyllosilicate in said intercalating composition.

48. The method of claim 47, wherein said intercalating composition comprises about 30% to about 50% water, based on the dry weight of the phyllosilicate.

49. The method of claim 48, wherein said intercalating composition comprises about 35% to about 45% by weight water.

50. A method of manufacturing a candle comprising wax and a phyllosilicate intercalate comprising:

contacting the phyllosilicate with an intercalating composition comprising the phyllosilicate, an intercalant polymer, and water, wherein the weight ratio of the intercalant polymer to phyllosilicate is at least 1 to about 20, and the concentration of said water-soluble intercalant polymer is at least about 5% up to about 900% polymer based on the dry weight of the phyllosilicate, to form an intercalate having said intercalant polymer intercalated between said adjacent phyllosilicate platelets in an amount sufficient to space said adjacent phyllosilicate platelets to a distance of at least about 5 Å, and

combining the intercalate with said wax and a wick held within said wax.

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127

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- [54] **POLISH**
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[52] **U.S. Cl.** _____ **106/3; 106/11**
[58] **Field of Search** _____ **106/3, 11**

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[57] **ABSTRACT**
A polish is provided for cleaning metallic and fiberglass surfaces, such as an automobile, truck and boat bodies, and for providing a protective film on the surface. The polish comprises water in an amount between about 40.0 to about 75.0 percent, a solvent in an amount between about 12.0 to about 35.0 percent, a rheological additive in an amount between about 0.30 to about 1.0 percent, an ultraviolet absorber in an amount between about 0.05 to about 0.50 percent, a dye in an amount between about 0.0005 to about 3.0 percent, a first silicate in an amount between about 5.0 to about 15.0 percent, dimethylpolysiloxane in an amount between about 0.50 to about 6.0 percent, a silicone resin solution in an amount between about 0.10 to about 3.0 percent, oleic diethanol amide in an amount between about 0.30 to about 2.0 percent, a second silicate in an amount between about 0.10 to about 3.0 percent, and a bactericide in an amount between about 0.05 to about 0.20 percent, by weight of the total polish.

16 Claims, No Drawings

126

POLISH

BACKGROUND OF THE INVENTION

The present invention relates generally to a polish and a method for formulating same and, more particularly, to a polish that is used to enhance the original color of the treated surface and provide longlasting high gloss polymer protection.

Polishes have been employed to clean dirt, dust and grime from a surface, such as an automobile, truck, boat and other metal and fiberglass surfaces. These polishes have not, however, been known to enhance the original or true color of the automobile's body. These polishes have merely added dye to an ordinary wax. Accordingly, as the wax wears off the treated surface so does the dye.

In recent years, there has been an increased concern over the damage done to surfaces that are exposed to the sun and ultraviolet rays. Compositions have been known to include ultraviolet ray resistant ingredients in their products, such as sunscreen lotions. Heretofore, few, if any, polishes have included sun and ultraviolet ray resistant properties. Furthermore, such polishes have not provided the adhesion to the surface and the enhancement of the surface's color as provided for by the present polish. Moreover, such polishes have not provided the high gloss polymer protective layer or film coat of the present polish.

SUMMARY OF THE INVENTION

Against the foregoing background, it is a primary object of the present invention to provide a polish for removing dirt, dust and grime from metallic and fiberglass surfaces.

It is another object of the present invention to provide such a polish that removes oxidation and restores original luster to dull or faded surfaces by the ability of the polish to blend with the color of the surface.

It is a further object of the present invention to provide such a polish that blends together with a wide range of different shades of colored surfaces.

It is a still further object of the present invention to provide such a polish that provides a unique blend of color absorbent and color reflective particles that improve the adherence of the polish to the surface and the ability of the polish to blend with a range of color shaded surfaces.

It is still yet a further object of the present invention to provide such a polish that provides a high gloss polymer protective layer on the polished or treated surface.

It is yet another object of the present invention to provide such a polish that is formulated in a three stage process in order to preserve the integrity of the formed polish.

To the accomplishments of the foregoing objects and advantages, the present invention, in brief summary, includes a polish for treating a surface and providing a high gloss polymer protective layer thereon. The polish comprises: water in an amount between about 40.0 to about 75.0 percent, a solvent, preferably petroleum naphtha, in an amount between about 12.0 to about 35.0 percent, a rheological additive in an amount between about 0.30 to about 1.0 percent, an ultraviolet absorber in an amount between about 0.05 to about 0.50 percent, dye in an amount between about 0.0005 to about 3.0 percent, a first silicate in an amount between about 5.0 to about 15.0 percent, dimethylpolysiloxane in an

amount between about 0.50 to about 6.0 percent, a silicone resin solution in an amount between about 0.10 to about 3.0 percent, oleic diethanol amide in an amount between about 0.50 to about 2.0 percent, a second silicate in an amount between about 0.10 to about 3.0 percent, and a bactericide in an amount between about 0.05 to about 0.20 percent, by weight of the total polish composition.

BRIEF DESCRIPTION OF THE PREFERRED EMBODIMENTS

The polish of the present invention is adapted for use on painted metallic and fiberglass surfaces. In particular, it is effective for automobile, trucks and boat bodies. Other applications for the polish are still being developed, but it is anticipated that the polish can be used on many types of painted metallic and fiberglass surfaces in order to improve the surface's color as well as the surface's resistance to ultraviolet rays.

It is known that the polish is effective in removing dirt, dust, grime and oxidation. Further, the polish leaves a film or high gloss polymer film layer on the treated surface. This film layer acts as a barrier to protect the surface from damage, such as discoloration, that normally results from the sun and, in particular, ultraviolet rays.

Significantly, the polish restores the original luster to the dull or faded surfaces by the interaction of the polish with the surface itself. It is believed that the polish removes oxidation on the surface and then adheres to the surface through polar bonding or entrapment due to the color absorbent particles in the polish.

The polish comprises: (1) water, (2) a solvent, (3) a rheological additive, (4) an ultraviolet or UV absorber, (5) a dye, (6) a first silicate, (7) dimethylpolysiloxane, (8) a silicone resin solution, (9) oleic diethanol amide, (10) a second silicate, and (11) a bactericide.

The water is the carrier of the polish composition. It is present in an amount between about 40.0 and about 75.0 percent by weight of the total composition. The water is preferably present in an amount about 66.9 percent by weight of the total preferred polish composition.

The solvent acts to mix ingredients, especially the rheological additive, while in solution. The solvent, preferably, is petroleum naphtha or as it is commonly known mineral spirits. It is a clear light colored liquid solvent with a hydrocarbon odor. The boiling range of this solvent is about 330 to about 390 degrees Fahrenheit, the vapor pressure is 16 mm. Hg., the vapor density is measured at 4.8 with air measured as 1 and the evaporation rate is measured as less than 0.01 with butyl acetate measured as 1.

The solvent is present in an amount between about 12.0 and about 35.0 percent by weight of the total polish composition. In the preferred polish composition, the solvent is petroleum naphtha and is present in an amount about 20.5 percent by weight.

The rheological additive provides the polish composition with the desired elasticity, viscosity and plasticity. The preferred rheological additive is an organophilic clay. The preferred organophilic clay is sold under the mark BENTONE 38 by NL Chemicals/NL Industries, Inc.

The organophilic clay or rheological additive should be present in the total polish composition in an amount between about 0.30 and about 1.0 percent by weight. In

the preferred polish composition, it is present in an amount about 0.50 percent by weight of the total preferred polish composition.

The ultraviolet or UV absorber is used to abate the adverse effects of ultraviolet rays on the treated surface. It can be made of any water soluble ultraviolet absorber. The preferred ultraviolet absorber is a 2-propenoic acid-2-cyano-3, 3-diphenyl-2-ethylhexyl ester. It is also known as 2-ethylhexyl 2-cyano-3, 3-diphenyl acrylate. The chemical formula is $C_{24}H_{27}NO_2$. This ultraviolet absorber is sold under the tradename UVI-NUL N-339 by BASF Corporation.

The ultraviolet absorber is present in an amount between about 0.05 and about 0.50 percent by weight of the total composition. In the preferred composition, it is present in an amount about 0.10 percent by weight.

The dye must be an oil soluble dye in order for the color of the dye to be retained in the present polish composition. It cannot be a water soluble dye. The three dye colors are each used in a different colored embodiment of the polish of the present application. Each colored embodiment can be used in a range of colored surfaces. In particular, a colored embodiment of the present application can be used in about five to about ten different shades. For example, the red colored embodiment can be used in about five to about ten different shades of a red surface.

The three preferred dyes are black, red and blue colorings. The black dye is preferably from the azine dye chemical family and is known as nigrosine base N or solvent black 7. The red dye is preferably from the bisazo dye chemical family and has the formula $C_{25}H_{22}N_4O$. The blue dye is preferably from the anthraquinone dyestuff chemical family and has the chemical formula $C_{20}H_{14}N_2O_2$.

The dye is present in an amount between about 0.0005 and about 3.0 percent by weight of the total polish composition. In the preferred polish composition, it is present in an amount about 0.50 percent by weight.

The first silicate is the unique color absorbent material that is provided to absorb the color of the surface. Basically, the first silicate cleans the oxidized paint from the surface, absorbs the color of the surface and spreads the dye of the polish evenly as it smooths the silicone layer. The first silicate finds its way into the surface. What makes this more unique is that hard particles usually do not absorb colors or other particles.

The first silicate is a magnesium aluminum silicate. It is also known as fullers earth or attapulgite, palygorskite. It has the chemical formula $5(Mg,Al)^+8SiO_2 \cdot 4H_2O \cdot 4H_2O$. The preferred magnesium aluminum silicate is sold under the name MIN-U-GEL 400 by Whitaker, Clark & Daniels, Inc.

The magnesium aluminum silicate is present in an amount between about 5.0 and about 15.0 percent by weight of the total polish composition. In the preferred composition, it is present in an amount about 6.0 percent by weight of the preferred polish composition.

The fluid is from the silicone siloxane fluid chemical family. It is used to provide gloss and, also, lubricity thereby providing easy application of the polish composition. The preferred fluid is dimethylpolysiloxane. The silicone siloxane fluid, preferably dimethylpolysiloxane, is present in an amount between about 0.50 and about 6.0 percent by weight of the total polish composition. It is preferred that dimethylpolysiloxane be present in about 2.8 percent by weight in the preferred polish composition.

The silicone resin solution is known as methylsiloxane resin in solvent. It is also known under the trade designation SR107 and is manufactured by General Electric Co. Silicone Products Division. It is used in the polish composition to form a clear, resilient protective film. The silicone resin solution is present in an amount between about 0.10 and about 3.0 percent by weight of the total polish composition. In the preferred composition, it is present in an amount about 1.1 percent by weight of the preferred polish composition.

The oleic diethanol amide is sold under the tradename WITCAMIDE 511 by the Witco Chemical. It is used in the polish composition to emulsify the water and oil solutions of the polish composition. The oleic diethanol amide is present in an amount between about 0.50 and about 2.0 percent by weight of the total polish composition. In the preferred composition, it is present in an amount about 1.0 percent by weight of the preferred polish composition.

The second silicate is used to buff the surface to be treated and, also, to leave a small residue in order to reflect entrapped dye. This material has been found to provide the unique reflective properties of the present polish. These reflective properties are attributed to the second silicate causing the color from the car or treated surface to blend with the selected dye in the present polish.

The second silicate is a potassium aluminum silicate. The preferred potassium aluminum silicate is sold under the name MICA by Whitaker, Clark & Daniels, Inc.

The potassium aluminum silicate or MICA is present in an amount between about 0.10 and about 3.0 percent by weight of the total polish composition. In the preferred composition, it is present in an amount about 0.50 percent by weight of the preferred polish composition.

A bactericide is used in the present polish composition to stabilize the emulsion or composition. It is soluble in or miscible with water and organic solvents. The preferred bactericide is from the substituted meta-dioxane chemical family. It has the chemical name 6-acetoxy-2,4-dimethyl-1,3-dioxane. It has the chemical formula $C_8H_{14}O_4$, and has a molecular weight of 174.2. The bactericide is commercially available under the trademark GIV-GARD DXN by Glavinian Corporation.

The bactericide, preferably the substituted meta-dioxane, is present in an amount between about 0.05 and about 0.20 percent by weight of the total polish composition. It should be present in an amount of about 0.10 percent by weight in the preferred polish composition.

It will be appreciated that the amount of each component will vary as discussed above. The preferred formula is:

Component	Amount (% weight)
Water	64.9
Parachloro naphtha	20.5
Organophilic clay	0.50
Water soluble UV absorber	0.10
Dye	0.50
Magnesium aluminum silicate	6.0
Dimethylpolysiloxane	2.8
Silicone resin solution	1.1
Oleic diethanol amide	1.0
Potassium aluminum silicate	0.50
6-acetoxy-2,4-dimethyl-1,3-dioxane	0.10

128

178

The preferred ultraviolet absorber is a 2-propenoic acid-2-cyano-3, 3-diphenyl-2-ethylhexyl ester

The polish should be formulated in the following manner in order to obtain maximum efficacy Using the preferred polish composition, in a first vessel or container, the solvent, preferably petroleum naphtha in an amount about 20.5 percent by weight is poured in and, then, the organophilic clay in an amount about 0.50 percent by weight is added. The two are agitated for fifteen minutes. The ultraviolet absorber in an amount about 0.10 percent by weight and the dye in an amount about 0.50 percent by weight are then added and the solution is agitated for another fifteen minutes. Next, the magnesium aluminum silicate in an amount about 6.0 percent by weight is added and the solution is then agitated for another fifteen minutes. Lastly, the dimethylpolysiloxane in an amount about 2.8 percent by weight and the oleic diethanol amide in an amount about 1.0 percent by weight are added and the solution is agitated for thirty minutes.

In a second vessel or container, the water in an amount about 66.9 percent by weight, the potassium aluminum silicate in an amount about 0.50 percent by weight and the bactericide, preferably 6-acetoxy-2,4-dimethyl-1,3-dioxane, in an amount about 0.10 percent by weight are poured into the vessel and agitated for fifteen minutes.

The contents of the second vessel are slowly added into the contents of the first vessel while the solution is being agitated. After pouring, the resultant solution is agitated for one hour.

The polish may be applied to the surface by hand using a clean, dry, soft cloth. The hand motion should be a firm circular motion.

An eight ounce bottle of polish will typically cover about two standard size vehicles. The polish, once applied, leaves a film or layer that serves as a sunscreen to block ultraviolet rays.

Having thus described the invention with particular reference to the preferred forms thereof, it will be obvious that various changes and modifications may be made therein without departing from the spirit and scope of the invention as defined by the appended claims.

Wherefore I claim:

1. A polish comprising:

water in an amount between about 40.0 and about 75.0 percent;

a petroleum naphtha in an amount between about 12.0 and about 35.0 percent;

a rheological additive in an amount between about 0.30 and about 1.0 percent;

an ultraviolet absorber in an amount between about 0.05 and about 0.50 percent;

an oil soluble dye in an amount between about 0.0005 and about 3.0 percent;

a first silicate in an amount between about 5.0 and about 15.0 percent;

a fluid from a silicone siloxane fluid chemical family in an amount between about 0.50 and about 6.0 percent;

a methylsiloxane resin in solvent in an amount between about 0.10 and about 3.0 percent;

an oleic diethanol amide in an amount between about 0.50 and about 2.0 percent;

a second silicate in an amount between about 0.10 and about 3.0 percent;

a bactericide in an amount between about 0.05 and about 0.20 percent, by weight of the polish, wherein the rheological additive is any rheological additive that provides the polish with elasticity, viscosity and plasticity needed for application to painted metallic and fiberglass surfaces.

2. The polish of claim 1, wherein the rheological additive is an organophilic clay.

3. The polish of claim 1, wherein the ultraviolet absorber is a 2-propenoic acid-2-cyano-3, 3-diphenyl-2-ethylhexyl ester.

4. The polish of claim 1, wherein the first silicate is a magnesium aluminum silicate.

5. The polish of claim 1, wherein the silicone siloxane fluid is dimethylpolysiloxane.

6. The polish of claim 1, wherein the second silicate is a potassium aluminum silicate.

7. The polish of claim 6, wherein the magnesium aluminum silicate is present in an amount about 6.0 percent, and wherein the potassium aluminum silicate is present in an amount about 0.50 percent.

8. The polish of claim 1, wherein the bactericide is from a substituted meta-dioxane chemical family.

9. The polish of claim 8, wherein the bactericide is 6-acetoxy-2,4-dimethyl-1,3-dioxane.

10. The polish of claim 1, wherein the petroleum naphtha is present in an amount about 20.5 percent by weight of the polish.

11. A polish comprising:

water in an amount about 66.9 percent;

a petroleum naphtha in an amount about 20.5 percent;

a organophilic clay in an amount about 0.50 percent;

a water soluble ultraviolet absorber in an amount about 0.10 percent;

an oil soluble dye in an amount about 0.50 percent;

a magnesium aluminum silicate in an amount about 6.0 percent;

a dimethylpolysiloxane in an amount about 2.8 percent;

a methylsiloxane resin in solvent in an amount about 1.1 percent;

an oleic diethanol amide in an amount about 1.0 percent;

a potassium aluminum silicate in an amount between about 0.50 percent; and

a bactericide in an amount about 0.10 percent, by weight of the polish.

12. The polish of claim 11, wherein the ultraviolet absorber is 2-propenoic acid-2-cyano-3, 3-diphenyl-2-ethylhexyl ester.

13. The polish of claim 11, wherein the bactericide is 6-acetoxy-2,4-dimethyl-1,3-dioxane.

14. A process for making a polish, the process comprising:

forming a first solution by

(a) blending together a petroleum naphtha and an organophilic clay;

(b) blending an ultraviolet absorber and an oil soluble dye to the blend of the petroleum naphtha and the organophilic clay;

(c) blending a magnesium aluminum silicate into a solution of step (b);

(d) blending a dimethylpolysiloxane and an oleic diethanol amide into a solution of step (c) to form the first solution;

forming a second solution by blending water, a potassium aluminum silicate and a bactericide; and

forming the polish by blending the second solution with the first solution.

15. The process of claim 14, further comprising the step of agitating each blend prior to the blending steps (b), (c) and (d) and during the steps of forming of the solution in the second vessel and the forming of the polish.

16. A polish comprising:

- water in an amount between about 40.0 and about 75.0 percent;
- a petroleum naphtha in an amount between about 12.0 and about 35.0 percent;
- a organophilic clay in an amount between about 0.30 and about 1.0 percent;
- a water soluble ultraviolet absorber in an amount between about 0.05 and about 0.50 percent;

- an oil soluble dye in an amount between about 0.0005 and about 3.0 percent;
- a first silicate in an amount between about 5.0 and about 15.0 percent;
- a fluid from a silicone siloxane fluid chemical family in an amount between about 0.90 and about 6.0 percent;
- a methylsiloxane resin in solvent in an amount between about 0.10 and about 3.0 percent;
- an oleic diethanol amide in an amount between about 0.50 and about 2.0 percent;
- a second silicate in an amount between about 0.10 and about 3.0 percent, and
- a bactericide in an amount between about 0.05 and about 0.20 percent, by weight of the polish.

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Die folgenden Angaben sind den vom Anmelder eingereichten Unterlagen entnommen

- ④ Bindemittelzusammensetzung zur Rollkleisterzubereitung
⑤ Die vorliegende Erfindung betrifft eine Zusammensetzung, mindestens enthaltend ein teichenförmiges retardiertes Polysaccharid und mindestens ein teichenförmiges natürliches oder synthetisches Schichtsilikat.

DE 102 27 871 A 1

129

[0001] Die vorliegende Erfindung betrifft eine Zusammensetzung, mindestens enthaltend ein teilchenförmiges retardiertes Polysaccharid und mindestens ein teilchenförmiges natürliches oder synthetisches Schichtsilikat.

5 [0002] Bindemittelzusammensetzungen, die ein natürliches oder synthetisches Polysaccharid und ein synthetisches Polymerisat enthalten, sind im wesentlichen bekannt. Derartige Bindemittelzusammensetzungen werden zum Kleben, Verfestigen oder Dichten eingesetzt. Konkrete Beispiele für derartige Anwendungen sind beispielsweise Kleister, Dispersionsklebstoffe, Grundierungen für mineralische Untergründe und dergleichen. Die obengenannten, aus dem Stand der Technik bekannten Bindemittelzusammensetzungen, insbesondere deren pulverförmige Zubereitungen, werden be-
10 sonders dann zur Herstellung der genannten Produkte eingesetzt, wenn eine Zubereitung der Produkte am Anwendungs-ort durch einfaches Vermischen mit Wasser möglich und insbesondere vom Anwender durchführbar und erwünscht ist. Der Einsatz solcher Bindemittel bei der Herstellung von Klebstoffen wird insbesondere dann bevorzugt, wenn die Ein-satzart der Klebstoffe die Verwendung von vom Anwender selbst zubereiteten Klebstoffen zuläßt.

[0003] Die Verwendung solcher Bindemittelzusammensetzungen spart in der Regel Transportkosten, da das Gewicht
15 des Wassers wegfällt. Häufig werden derartige Bindemittelzusammensetzungen zum flächigen Beschichten eines Unter-grunds mit Papier oder anderen Belägen eingesetzt. Eine besonders häufig anzutreffende Verwendung solcher Bindemittel sind Tapetenkleister, die bei der dekorativen Beschichtung von Wänden oder Decken in Innenräumen eingesetzt wer-den.

[0004] Die dabei üblicherweise eingesetzte Auftragstechnik trägt den in Innenräumen häufig vorherrschenden Unter-gründen Rechnung. Insbesondere beim Anbringen von Tapeten auf Wänden oder Decken herrschen saugfähige Unter-gründe vor, wobei die entsprechenden Untergründe in der Regel eine bestimmte Wassermenge aufnehmen. Andererseits werden jedoch durch die aufzubringenden Tapeten selbst üblicherweise große Wassermengen aufgenommen. Aus die-
20 sem Grund wird der zum Anbringen von Tapeten eingesetzte Klebstoff in der Regel zunächst auf die Tapeten aufgetra-gen, wobei nach dem Auftrag selbst eine bestimmte "Weichzeit" eingehalten werden muß, während der die Tapete durch die Aufnahme von Wasser durchfeuchtet wird. Dieser Auftragstechnik erlaubt das Verstreichen einer ausreichend großen Kleistermenge auf der Rückseite der Tapeten, so daß auch nach der Aufnahme von Wasser durch die Tapete einer ausre-
25 chend hohem Klebekraft zur Verfügung gestellt wird.

[0005] Tapetenkleister sollen üblicherweise durch die Verwendung eines Kleisterpinsels mit dem Tapetenkleister be-schichtbar sein. Diesem Erfordernis trägt die Gelstruktur des Tapetenkleisters üblicherweise dahingehend Rechnung, daß
30 ein Tapetenkleister für eine derartige Auftragstechnik ausreichend fließfähig ist. Da die Beschichtung der Tapete mit dem Kleister üblicherweise in waagerechter Position der Tapete auf einem Tapeziertisch erfolgt, treten hier in der Regel keine Probleme im Hinblick auf ein vorzeitiges Verlaufen (Zerfließen) des Kleisters auf.

[0006] In jüngerer Zeit werden jedoch häufig Tapeten angehten und eingesetzt, die nicht ausschließlich aus Papier be-
35 stehen sondern eingearbeitete Kunststofffasern enthalten. Derartige Tapeten weisen den Vorteil der Dimensionsstabilität auf. Dies bedeutet, daß sich solche Tapeten ohne Weichzeit auf die zu tapezierende Fläche auftragen lassen. Zwar läßt auch dieses Verfahren die oben bereits beschriebene Tapezierstechnik zu, es sind jedoch einfachere Möglichkeiten denk-bar. So wäre es beispielsweise für den Anwender mit einer großen Zeitersparnis verbunden, wenn die Tapete nicht auf der Tapetenrückseite mit Kleister beschichtet werden müßte sondern der Kleister direkt auf die Wand aufgetragen wer-den könnte. In diesem Fall könnte eine im wesentlichen beliebig große Wandfläche zunächst mit Kleister versehen wer-
40 den, wobei anschließend auf einfache Weise die Tapete angebracht werden könnte. Bei dieser Vorgehensweise würde darüber hinaus die mit dem Beschichten der Tapetenrückseite verbundenen Unannehmlichkeiten, beispielsweise der Aufbau eines Tapeziertisches und das Säubern solcher Tische aufgrund überschüssiger Kleistermengen, entfallen.

[0007] Problematisch wirkt sich bei der beschriebenen, vereinfachten Vorgehensweise jedoch aus, daß die aus dem Stand der Technik bekannten Tapetenkleister eine derartige Vorgehensweise nicht unterstützen. Aufgrund der Fließfä-higkeit der bekannten Kleister lassen sich diese an senkrechten Flächen nur in relativ dünnen Filmen auftragen, wobei die
45 Saugfähigkeit des Untergrunds in der Regel zu einem im Hinblick auf die oben beschriebene Vorgehensweise zu schnel-len Abtrocknen des Kleisters führt. Wenn ein Auftrag des Kleisters jedoch in Form eines dickeren Films erfolgen soll, so neigen die bekannten Kleister stark zum Abfließen an der damit versehenen Fläche. Darüber hinaus lassen sich die aus dem Stand der Technik bekannten Tapetenkleister in der Regel nur mittels eines speziellen Kleisterpinsels auftragen. Die
50 oben beschriebenen Vorgehensweise, die mit dem Beschichten größerer Flächen verbunden sein kann, ließe sich jedoch im Rollverfahren, wie es beim Anstreichen von Wänden mittels Schaumstoff oder Lammfellrollen üblicherweise prakti-ziert wird, zeitsparender und effizienter durchführen. Die derzeit bekannten Tapetenkleister lassen jedoch auch den Ein-satz von solchen Auftragsrollen in der Regel nicht zu.

[0008] Wenn zur Herstellung von Tapetenkleister geeignete Bindemittelzusammensetzungen vom Anwender selbst in
55 eine zur Anwendung geeignete Form gebracht werden sollen ist es darüber hinaus noch erforderlich, daß sie eine Reihe von Anforderungen erfüllen, die zum einen die Handhabbarkeit der Bindemittel und zum anderen eine möglichst kon-stante Produktqualität sowohl im Hinblick auf die Bindemittelzusammensetzungen selbst als auch auf die aus solchen Bindemittelzusammensetzungen herstellbaren Produkte betreffen. Derartige Anforderungen beziehen insbesondere das Lösungsverhalten der Bindemittelzusammensetzungen ein. Häufig neigen derartige Bindemittelzusammensetzungen
60 nämlich zum Verklumpen beim Einrühren in Wasser, wodurch entweder inakzeptabel hohe Zeiträume zur Beseitigung der Klumpen erforderlich sind oder aber die Klumpen sich überhaupt nicht auflösen. Bei der Verwendung eines solchen Klumpen enthaltenden Produkts ergeben sich jedoch Nachteile im Hinblick auf optische oder technische Störungen. Wenn beispielsweise ein Tapetenkleister solche Klumpen aufweist, kann es insbesondere bei der Verklebung von glatten, unstrukturierten Tapeten zu Störungen in der Oberflächenstruktur kommen.

[0009] Weiterhin ist eine möglichst schnelle Einsetzbarkeit eines mit Hilfe der genannten Bindemittel erhaltenen Pro-
65 dukts gefordert. Hierbei wird insbesondere auf eine möglichst schnelle Löslichkeit oder Dispergierbarkeit verbunden mit einem möglichst schnellen Viskositätsaufbau des Produkts Wert gelegt, wobei trotz eines möglichst schnellen Viskosi-tätsaufbaus noch eine klumpenfreie Auflösung oder Dispersion des Bindemittels erfolgen soll.

[0010] Es bestand daher ein Bedürfnis nach Bindemittelzusammensetzungen die in einer anwendbaren Zubereitung einen großflächigen Auftrag auch auf saugfähigen Untergründe erlauben. Weiterhin bestand ein Bedürfnis nach Bindemittelzusammensetzungen, die in anwendungsfertiger Zubereitung mittels üblicher Rollen großflächigen auf Untergründen auftragbar sind, wobei die aufgetragene Filme eine ausreichende Dicke aufweisen. Weiterhin bestand ein Bedürfnis nach Bindemittelzusammensetzungen die im Rahmenanwendung fertiger Zubereitungen mittels Rollen auf Untergründe aufgetragen werden können, wobei d-artige fertige Zubereitungen nur eine geringe Spritzneigung aufweisen.

[0011] Der vorliegenden Erfindung liegt daher die Aufgabe zugrunde, Bindemittelzusammensetzungen zur Verfügung zu stellen, welche die obengenannten Nachteile nicht aufweisen. Insbesondere liegt der vorliegenden Erfindung die Aufgabe zugrunde, Bindemittelzusammensetzungen zur Verfügung zu stellen die sich vom Anwender vor Ort mit Wasser zu Zubereitungen verarbeiten lassen, die insbesondere als Tapetenkleister geeignet sind und zumindest einen Teil der oben genannten Bedürfnisse erfüllen.

[0012] Gegenstand der vorliegenden Erfindung ist daher eine Bindemittelzusammensetzung, mindestens enthaltend mindestens 1 Gew.-% eines teilchenförmigen retardierten Polysaccharids oder eines Gemischs aus zwei oder mehr solcher teilchenförmigen retardierten Polysaccharide und mindestens 3 Gew.-% eines teilchenförmigen natürlichen oder synthetischen Schichtsilikats oder eines Gemischs aus zwei oder mehr natürlichen oder zwei oder mehr teilchenförmiger synthetischer Schichtsilikate oder ein Gemisch eines oder mehrerer natürlicher und eines oder mehrerer synthetischer Schichtsilikate.

[0013] Unter einem "Polysaccharid" wird im Rahmen des vorliegenden Textes eine polymere Verbindungen auf Basis sich wiederholender Zuckereinheiten verstanden. Im Rahmen der vorliegenden Erfindung geeignete Polysaccharide sind beispielsweise Polysaccharide auf Basis von Cellulose oder Stärke. Ein erfindungsgemäßes "Polysaccharid" kann beispielsweise ein Polysaccharid sein wie es in natürlicher Form vorliegt. Es ist jedoch im Rahmen der vorliegenden Erfindung ebenso möglich Polysaccharide einzusetzen die synthetisch hergestellt wurden oder Derivate von natürlichen oder synthetischen Polysacchariden. Im Rahmen der vorliegenden Erfindung besonders geeignet sind beispielsweise wasserlösliche oder wasserdispergierbare Stärkeether oder Celluloseether. Wenn im Rahmen des nachfolgenden Textes beispielsweise der Begriff Stärkeether oder Celluloseether benutzt wird so steht dieser Begriff jeweils Synonym für alle geeigneten Polysaccharide, die unter die obengenannte Definition fallen, sofern nicht ausdrücklich etwas anderes erwähnt wird.

[0014] Im Rahmen der vorliegenden Erfindung umfaßt der Begriff "wasserlöslich" solche Verbindungen, die sich in Wasser molekulardispers oder kolloidal lösen. Im Rahmen einer bevorzugten Ausführungsformen betrifft der Begriff "löslich" solche Verbindungen, die eine Löslichkeit von mehr als mindestens 0,01 g, bezogen auf 100 ml Wasser von 20°C, aufweisen. Vorzugsweise liegt die Löslichkeit von wasserlöslichen Verbindungen, wie sie im Rahmen des vorliegenden Textes aufgefaßt werden jedoch oberhalb dieses Wertes, beispielsweise bei 0,1 g oder 0,5 g oder 1 g bezogen auf 100 ml Wasser von 20°C. Die für die Wasserlöslichkeit genannten Werte müssen nicht sofort nach Einbringen des entsprechenden Stoffs in Wasser erreicht werden. Es kann beispielsweise ausreichend sein, wenn die entsprechenden Werte nach einem Zeitraum von etwa 10 oder etwa 20 Minuten oder mehr erreicht werden.

[0015] Der Begriff "wasserdispergierbar" umfaßt im Rahmen des vorliegenden Textes Verbindungen, die in Wasser keine monokulardisperse oder kolloidale Lösung ergeben sondern sich als disperse Phase im Wasser verteilen.

[0016] Im Rahmen einer ersten Ausführungsform der vorliegenden Erfindung enthalten die erfindungsgemäßen Bindemittelzubereitungen als beispielsweise wasserlösliche oder wasserdispergierbare retardierte Stärke und/oder Stärkederivate oder retardierte Cellulosederivate, insbesondere Celluloseether.

[0017] Wenn im Rahmen der erfindungsgemäßen Bindemittelzubereitungen retardierte Stärke eingesetzt wird, so wird im Rahmen einer bevorzugten Ausführungsform der vorliegenden Erfindung wasserlösliche bzw. wasserquellbare modifizierte Stärke eingesetzt. Geeignet sind beispielsweise partiell abgebaute Stärke oder Quellstärke. Wenn Stärkederivate eingesetzt werden so eignen sich beispielsweise Stärkeester oder Stärkeether, insbesondere carboxylierte oder die alkoxylierte Stärken. Als carboxylierte oder alkoxylierte Stärken eignen sich sämtliche entsprechend modifizierte natürlichen Stärketypen aus Kartoffeln, Mais, Weizen, Reis, Miso, Tapioka und dergleichen, wobei Stärkederivate auf Basis von Kartoffeln oder Maisstärke bevorzugt sind. Geeignete Stärkederivate weisen beispielsweise einen Carboxylierungsgrad von etwa 0,1 bis etwa 2,0 (DS) oder einen Alkoxylierungsgrad von 0,05 bis 1,5 (MS) auf. Die Stärkederivate können auch vernetzt sein. Als Vernetzungsmittel eignen sich beispielsweise difunktionelle Verbindungen wie sie aus der EP-B 0 311 873 bekannt sind.

[0018]—Als Celluloseether eignen sich insbesondere folgende Typen

Carboxymethylcellulose (CMC), Carboxymethylmethylcellulose (CMMC), Ethylcellulose (EC), Hydroxyethylcellulose (HBC), Hydroxybutylmethylcellulose (HBMC), Hydroxyethylcellulose (HEC), Hydroxyethylcarboxymethylcellulose (HECMC), Hydroxyethylethylcellulose (HEEC), Hydroxypropylcellulose (HPC), Hydroxypropylcarboxymethylcellulose (HPCMC), Hydroxypropylmethylcellulose (HPMC), Hydroxyethylethylcellulose (HEMC), Methylhydroxyethylcellulose (MHBC), Hydroxyethylmethylcellulose (HEMC), Methylhydroxyethylcellulose (MHBC), Methylcellulose (MC) und Propylcellulose (PC), wobei Carboxymethylcellulose, Methylcellulose, Methylhydroxyethylcellulose oder Methylhydroxypropylcellulose sowie die Alkalisalze der Carboxymethylcellulose sowie gegebenenfalls alkoxylierte, insbesondere ethoxylierte Methylcellulose bevorzugt sind.

[0019] Unter einem "retardierten" Polysaccharid wird im Rahmen der vorliegenden Erfindung ein Polysaccharid verstanden, das zur Einstellung seiner Löslichkeit in Wasser oder wässrigen Lösungen einer Oberflächenbehandlung, insbesondere einer oberflächlichen Vernetzung unterzogen wurde. Ein "retardiertes" Polysaccharid, wie es im Rahmen der vorliegenden Erfindung eingesetzt wird, weist gegenüber demselben Polysaccharid in nicht-retardierter Form eine verzögerte Löslichkeit auf d. h., bis zur Auflösung eines solchen "retardierten" Polysaccharids in Wasser oder einer wässrigen Lösung vergeht eine größere Zeitspanne als bei einem entsprechenden nicht retardierten Polysaccharid.

[0020] Erfindungsgemäß einsetzbare retardierte Celluloseether weisen nach einer solchen Behandlung eine verzögerte Wasserlöslichkeit auf. Im Rahmen des vorliegenden Textes bedeutet dies, daß die nach dem beschriebenen Verfahren vorliegenden Celluloseetherderivate sich im Vergleich zu ihrer ursprünglichen, vor Anwendung des beschriebenen Ver-

fahrens vorliegenden Form erst zu einem späteren Zeitpunkt in Wasser lösen. Gegebenenfalls kann dieser spätere Zeitpunkt durch den Verwender der Celluloseether oder der solche Celluloseether enthaltenden Zubereitungen bestimmt werden, indem er eine bestimmte Handlung durchführt, beispielsweise den pH-Wert verändert, es ist jedoch ebenso vorgesehen daß die erfindungsgemäß einsetzbaren Celluloseether ohne weitere Behandlung oder äußere Einflußnahme, beispielsweise in einer im wesentlichen pH-neutralen Umgebung, verzögert wasserlöslich sind.

[0021] Die Wasserlöslichkeit der im Rahmen der vorliegenden Erfindung zur Herstellung der erfindungsgemäßen eingesetzten retardierten Polysaccharide beispielsweise der eingesetzten retardierten Celluloseether beträgt in der Regel wenigstens etwa 0,5 Gewichtsteile pro 100 Gewichtsteile Wasser. Vorzugsweise liegt die Wasserlöslichkeit jedoch bei mindestens etwa 0,5 Gewichtsteilen pro 30 Gewichtsteilen Wasser.

[0022] Unter Stärke- oder Celluloseethern werden Stärke- oder Cellulosederivate verstanden, die durch partielle oder vollständige Substitution von Wasserstoffatomen der Hydroxygruppen der Stärke oder Cellulose durch Alkyl- und/oder (Ar)alkyl-Gruppen hergestellt werden. Die Alkyl- und/oder (Ar)alkyl-Gruppen tragen vorzugsweise zusätzlich nichtionische, anionische oder kationische Gruppen. Dabei sind die Einzelmoleküle in der Regel unterschiedlich substituiert, so daß ihr Substitutionsgrad ein Mittelwert ist. Außerdem kann die Substitution auch an während der Reaktion entstehenden "neuen" Hydroxylgruppen einsetzen, was z. B. beim Reaktionspartner Epoxid der Fall ist. Die im Rahmen der vorliegenden Erfindung eingesetzten wasserlöslichen Stärke- oder Celluloseether tragen jedoch mindestens eine OH-Gruppe.

[0023] Die Veretherung der Stärke oder Cellulose wird im allgemeinen durch Einwirkung von (Ar)alkylhalogeniden, beispielsweise Methyl-, Ethyl- und/oder Benzylchlorid, 2-Chlorethyl-diethylamin oder Chloressigsäure, und/oder Epoxiden, z. B. Ethylen-, Propylen- und/oder Butylenoxid, Glycidyltrimethylammoniumchlorid, und/oder aktiviertem Olefin, beispielsweise Acrylnitril, Acrylamid oder Vinylsulfonsäure, auf mit Basen, meist mit wäßriger Natronlauge, aktivierter Cellulose durchgeführt. Bevorzugt sind im Rahmen der vorliegenden Erfindung Carboxymethylcellulose, Methylcellulose, Ethylcellulose, Hydroxyalkylcellulose, insbesondere Hydroxyethylcellulose oder deren Mischether, wie Methylhydroxyethyl- oder -hydroxypropylcellulose, Carboxymethylhydroxyethylcellulose und/oder Ethylhydroxyethylcellulose.

[0024] Zur Herstellung von teilvernetzten wasserlöslichen Stärke oder Celluloseethern wird beispielsweise ein wasserlöslicher Celluloseether mit Glyoxal und/oder mit Polyglyoxal in Kontakt gebracht.

[0025] Zur Durchführung dieser Reaktion werden vorzugsweise wäßrige Lösungen von Glyoxal oder Polyglyoxal eingesetzt. Im Rahmen einer bevorzugten Ausführungsform der Erfindung werden wäßrige Glyoxallösungen eingesetzt, die einen Gehalt von etwa 0,1 bis etwa 60 Gew.-% beispielsweise etwa 2 bis etwa 50 Gew.-% an Glyoxal aufweisen. Besonders geeignet sind beispielsweise Glyoxallösungen, die einen Glyoxalgehalt von etwa 20 bis etwa 45, insbesondere etwa 30 bis etwa 40 Gew.-% aufweisen.

[0026] Werden zur Herstellung der erfindungsgemäß einsetzbaren Celluloseether wäßrige Lösungen von Polyglyoxal eingesetzt, so weisen diese vorzugsweise einen Gehalt an Polyglyoxal von etwa 70 bis etwa 90 Gew.-% auf. Vorzugsweise wird die im Handel erhältliche (Highlink 80, Hersteller Tromsø), etwa 80 gew.-%ige Form eingesetzt. Es ist im Rahmen der vorliegenden Erfindung ebenfalls möglich, Glyoxal und Polyglyoxal zusammen, d. h., gleichzeitig oder nacheinander zur Herstellung der retardierten Celluloseether einzusetzen.

[0027] Glyoxal und/oder Polyglyoxal werden, bezogen auf den wasserlöslichen Celluloseether, in der Regel in einem Anteil von etwa 0,05 bis etwa 8 Gew.-%, vorzugsweise etwa 0,1 bis etwa 5 Gew.-% und besonders bevorzugt in einem Anteil von etwa 0,5 bis etwa 3 Gew.-% eingesetzt. So kann das Polyglyoxal beispielsweise in einer Menge von > 1 Gew.-%, insbesondere in einer Menge von etwa 1,3 bis etwa 1,9 oder etwa 1,45 bis etwa 1,75 Gew.-%, bezogen auf wasserlöslichen Celluloseether, eingesetzt werden.

[0028] Das beschriebene Herstellungsverfahren für die retardierten Celluloseether kann beispielsweise nur mit einer einzigen Sorte von wasserlöslichem Celluloseether durchgeführt werden. Es ist im Rahmen der vorliegenden Erfindung jedoch auch vorgesehen, daß Gemische aus zwei oder mehr wasserlöslichen Celluloseethern eingesetzt werden, die der beschriebenen Behandlung unterzogen wurden.

[0029] Der wasserlösliche Celluloseether oder das Gemisch aus zwei oder mehr solcher Celluloseether sollte zur Durchführung der Retardierungsreaktion bevorzugt in trockener Form vorliegen, d. h. mit einem Wassergehalt von höchstens etwa 15 Gew.-%, vorzugsweise höchstens etwa 10 Gew.-%.

[0030] Die zur Behandlung vorgesehenen Celluloseether können dabei beispielsweise Wassergehalte von etwa 5 bis etwa 15 Gew.-%, oder etwa 6 bis etwa 9 Gew.-% aufweisen.

[0031] Ebenso möglich ist im Rahmen des Retardierungsverfahrens der Einsatz von feuchten, d. h. wasserhaltigen Celluloseethern, wie sie als Rohprodukte aus der Celluloseveretherung erhältlich sind. Die feuchten Celluloseether weisen in der Regel einen Wassergehalt von mehr als etwa 15 Gew.-% bis etwa 70 Gew.-%, vorzugsweise etwa 20 bis etwa 40 Gew.-% auf.

[0032] Die zur Behandlung vorgesehenen Celluloseether können beispielsweise in Pulverform eingesetzt werden. Die Celluloseether können dabei beispielsweise granular oder in Pulverform vorliegen. Werden pulverförmige Celluloseether eingesetzt, so weisen diese beispielsweise zu etwa 60%, besonders bevorzugt zu etwa 70% und insbesondere bevorzugt zu etwa 80% eine Teilchengröße von weniger als etwa 0,4 mm, bevorzugt weniger als etwa 0,3 mm und besonders bevorzugt weniger als etwa 0,2 mm (bestimmt nach DIN 4188) auf. Bevorzugt sind jedoch Celluloseether mit Teilchengrößen von wenigstens 0,1 mm Durchmesser.

[0033] Das Kontaktieren des wasserlöslichen Polysaccharide oder des Gemischs aus zwei oder mehr wasserlöslichen Polysacchariden mit Glyoxal oder mit Polyglyoxal oder deren Gemisch kann auf beliebige Weise erfolgen. Wird ein feuchter Celluloseether oder ein Gemisch aus zwei oder mehr feuchten Celluloseethern eingesetzt, so kann eine wäßrige Glyoxallösung beispielsweise durch Aufsprühen, Zutropfen oder jede geeignete andere Zugabeart zum Celluloseether oder zum Gemisch aus zwei oder mehr Celluloseethern erfolgen. Es ist ebenfalls möglich, eine wäßrige Lösung von Glyoxal oder Polyglyoxal oder deren Gemisch und den wasserlöslichen Celluloseether oder das Gemisch aus zwei oder mehr wasserlöslichen Celluloseethern in einer Knetvorrichtung, beispielsweise in einem Extruder, zu vermischen. Auch jede andere Mischvorrichtung ist geeignet, beispielsweise Rotor-Stator Mischvorrichtungen.

[0034] Zur Herstellung der erfindungsgemäß einsetzbaren retardierten Polysaccharide kann die Retardierungsreaktion

bei Umgebungstemperatur, d. h. bei einer Temperatur von etwa 10 bis etwa 30°C durchgeführt werden. Es ist jedoch ebenfalls möglich, die Retardierungsreaktion bei einer höheren Temperaturen durchzuführen beispielsweise bei einer Temperatur von etwa 30 bis etwa 60°C. Gegebenenfalls kann die Retardierungsreaktion auch bei noch höheren Temperaturen durchgeführt werden, beispielsweise bei etwa 60 bis etwa 100°C bzw. dem Siedepunkt der eingesetzten Glyoxal- oder Glyoxallösung falls eine solche verwendet wird.

[0035] Im Anschluß an die hier beschriebene Retardierungsreaktion kann das Polysaccharid oder das Gemisch aus zwei oder mehr Polysacchariden und Glyoxal und/oder Polyglyoxal gelagert werden. Eine solche Lagerung kann beispielsweise in einem Behälter durchgeführt werden, der bereits zur Durchführung der Retardierungsreaktion eingesetzt wurde.

[0036] Die im Rahmen der Retardierungsreaktion behandelten Gemische können während der Lagerung einer weiteren Vermischung unterzogen werden, beispielsweise durch Lagerung in einem entsprechenden Mischgerät, beispielsweise einem beheizten Pflugscharmscher oder einer beheizten rotierenden Trommel.

[0037] Die Lagerung wird vorzugsweise bei einer Temperatur von mindestens etwa 70°C durchgeführt. Im Rahmen einer weiteren bevorzugten Ausführungsform der vorliegenden Erfindung liegt die Temperatur während der Lagerung jedoch höher, beispielsweise bei mindestens etwa 75 oder mindestens etwa 80°C. Es hat sich gezeigt, daß die Lagerung auch bei noch höheren Temperaturen, beispielsweise bei 85, 90, 95 oder sogar 100°C durchgeführt werden kann. Die Obergrenze für die bei der Durchführung der Lagerung herrschende Temperatur stellt in der Regel der Siedepunkt des im Gemisch vorliegenden Wasseranteils bzw. der wässrigen Lösung von Glyoxal und/oder Polyglyoxal dar.

[0038] Die im Rahmen der vorliegenden Erfindung als Bestandteil der erfindungsgemäßen Bindemittelzusammensetzungen eingesetzten etablierten Polysaccharide liegen in den erfindungsgemäßen Bindemittelzusammensetzungen in Teilchenform vor. Der Begriff "teilchenförmig" betrifft dabei den tatsächlich innerhalb der Bindemittelzusammensetzung herrschenden Teilchenzustand der etablierten Polysaccharide. Es ist dabei im Rahmen der vorliegenden Erfindung möglich, daß ein Polysaccharidteilchen wie es im Rahmen der vorliegenden Erfindung als "teilchenförmig" bezeichnet wird, ein Agglomerat aus verschiedenen Partikeln mit einer Partikelgröße, die unterhalb der Teilchengröße liegt, besteht (beispielsweise Primärpartikel). Begriff "teilchenförmig" wie er im Rahmen des nachfolgenden Textes benutzt wird, bezieht sich auf innerhalb der Bindemittelzusammensetzung vorliegenden Teilchen, wie sie durch übliche Methoden zur Klassifizierung von Teilchengrößen, beispielsweise durch Siebverfahren, elektronenmikroskopische oder Lichtstreuung, ohne weitere Zerkleinerung meßbar sind. Es ist dabei unerheblich, ob ein in einem erfindungsgemäßen Bindemittel vorliegendes Teilchen als Agglomerat aus Primärpartikeln vorliegt oder das Teilchen selbst ein Primärpartikel ist.

[0039] Im Rahmen einer bevorzugten Ausführungsform der vorliegenden Erfindung weisen die Polysaccharid Teilchen in einer erfindungsgemäßen Bindemittelzusammensetzung eine Teilchengrößen Zusammensetzung auf, bei der höchstens 8 Gew.-%, vorzugsweise jedoch weniger als 8 Gew.-% der Teilchen eine Größe von mehr als 200 µm aufweisen. Vorzugsweise weisen etwa 40 bis etwa 95 Gew.-%, insbesondere etwa 60 bis etwa 90 Gew.-% oder etwa 75 bis etwa 85 Gew.-% der Polysaccharid Teilchen eine Teilchengröße von etwa 0,1 µm auf.

[0040] Vorzugsweise wird im Rahmen der vorliegenden Erfindung ein detailliertes Polysaccharid eingesetzt, daß als 2 gew.-%ige Lösung in Wasser eine Viskosität von etwa 2000 bis etwa 10 000 mPa s, insbesondere etwa 4000 bis etwa 7000 oder etwa 5000 bis etwa 6000 mPa s aufweist.

[0041] Im Rahmen einer weiteren Ausführungsform der vorliegenden Erfindung weisen die teilchenförmigen retardierten Polysaccharide oder das Gemisch aus zwei oder mehr teilchenförmigen retardierten Polysacchariden ein Lösungsverhalten in Wasser oder wässrigen Lösungen auf, bei dem nach höchstens etwa 60 Minuten, insbesondere jedoch nach 30 Minuten oder weniger, beispielsweise nach weniger als etwa 30, 15 oder 10 Minuten mindestens etwa 40% der maximalen Viskosität, d. h. der Viskosität wie sie sich beispielsweise bei einer entsprechenden Lösung nach etwa 3 bis etwa 10 Stunden einstellt, erreicht werden. Vorzugsweise erreichen die erfindungsgemäß eingesetzten, etablierten Polysaccharid Teilchen nach etwa 5 bis etwa 10 Minuten mindestens etwa 50% der maximalen Viskosität, vorzugsweise mindestens etwa 60 Prozent.

[0042] Die erfindungsgemäßen Bindemittelzusammensetzungen enthalten das retardierte Polysaccharid oder das Gemisch aus zwei oder mehr retardierten Polysacchariden in einer Menge von mindestens etwa 10 Gew.-%. Einer bevorzugten Ausführungsform der vorliegenden Erfindung beträgt der Anteil an retardierten Polysacchariden etwa 20 bis etwa 60 Gew.-%, insbesondere etwa 30 bis etwa 80 Gew.-%, beispielsweise etwa 40 bis etwa 70 Gew.-% oder etwa 45 bis etwa 60 Gew.-%.

[0043] Die erfindungsgemäße Bindemittelzusammensetzung kann die oben genannten Polysaccharide bzw. Polysaccharidderivate jeweils alleine enthalten. Es ist jedoch ebenso möglich und im Rahmen der vorliegenden Erfindung vorgesehen, daß eine erfindungsgemäße Bindemittelzusammensetzung ein Gemisch aus zwei oder mehr der oben genannten Polysaccharide oder Polysaccharidderivate, beispielsweise 3, 4, 5, 6, 7, 8, 9 oder 10 oder mehr unterschiedliche Polysaccharidderivate enthält. Es ist dabei erfindungsgemäß vorgesehen, daß eine Bindemittelzusammensetzung mindestens ein retardiertes Polysaccharid enthalten muß. Es ist jedoch erfindungsgemäß ebenso möglich, daß eine erfindungsgemäße Bindemittelzusammensetzung eine retardiertes Polysaccharid oder ein Gemisch aus mehreren retardierten Polysacchariden zusammen mit einem oder mehreren nicht retardierten Polysacchariden, wie sie obengenannt worden sind, enthält.

[0044] Als weiteren Bestandteil enthalten die erfindungsgemäßen Bindemittelzusammensetzungen noch mindestens 3 Gew.-% eines teilchenförmigen natürlichen oder synthetischen Schichtsilikats oder eines Gemisches aus zwei oder mehr natürlichen oder zwei oder mehr teilchenförmiger synthetischer Schichtsilikate oder ein Gemisch eines oder mehrerer natürlicher und eines oder mehrerer synthetischer Schichtsilikate.

[0045] Geeignete Schichtsilikate sind beispielsweise Sepiolite, Montmorillonite, Hectorite oder Smektit, wobei Hectorit oder Smektit, insbesondere Hectorit bevorzugt ist.

[0046] Die Schichtsilikate, wie sie als Bestandteil der erfindungsgemäßen Bindemittelzusammensetzungen im Rahmen der vorliegenden Erfindung eingesetzt werden können, können natürlichen oder synthetischen Ursprungs sein. Im Rahmen einer bevorzugten Ausführungsform der vorliegenden Erfindung werden als Schichtsilikate synthetischer Schichtsilikate, insbesondere synthetischer Hectorit eingesetzt. Geeignete synthetischer Schichtsilikate sind beispiels-

weise unter der Bezeichnung Laponite von Solvay Alkali erhältlich.

[0047] Im Rahmen einer bevorzugten Ausführungsform der vorliegenden Erfindung werden als Bestandteil der erfindungsgemäßen Bindemittelzusammensetzungen Schichtsilikate eingesetzt, die in Wasser oder wäßrigen Lösemitteln einen Viskositätsanstieg hervorrufen. Der Viskositätsanstieg sollte im Hinblick auf die zum Viskositätsanstieg benötigte Zeit so bemessen sein, daß das Verhältnis von Viskosität zu einem bestimmten Zeitpunkt zur maximalen Viskosität für das Schichtsilikat und das Polysaccharid innerhalb eines Verhältnisses von etwa 10 : 1 bis etwa 1 : 10, insbesondere etwa 1 : 5 bis etwa 5 : 1 oder etwa 1 : 2 bis etwa 2 : 1 liegt.

[0048] Im Rahmen einer bevorzugten Ausführungsform der vorliegenden Erfindung werden als Bestandteil der erfindungsgemäßen Bindemittelzusammensetzungen Schichtsilikate eingesetzt, die an der Kristalloberfläche eine negative Ladung von mindestens etwa 30 mmol pro 100 Gramm, vorzugsweise etwa 50 bis etwa 80 mmol pro 100 Gramm und beispielsweise etwa 50 bis etwa 60 mmol pro 100 Gramm aufweisen.

[0049] Die Teilchengröße der im Rahmen der vorliegenden Erfindung eingesetzten Schichtsilikate wird vorzugsweise so bemessen, daß die zum Viskositätsanstieg benötigte Zeit, wie oben beschrieben, innerhalb der obengenannten Relationen zum Viskositätsanstieg der Polysaccharide liegt. Vorzugsweise werden im Rahmen der vorliegenden Erfindung Schichtsilikate eingesetzt, deren Teilchengröße innerhalb eines Bereichs von etwa 1 bis etwa 500 µm, insbesondere etwa 20 bis etwa 200 µm liegt, beispielsweise bei etwa 30 bis etwa 80 nm oder etwa 40 bis etwa 60 nm.

[0050] Bei den hier genannten Teilchengrößen handelt es sich im wesentlichen um diejenigen Teilchengrößen, wie sie beispielsweise bei einer Vermahlung der Schichtsilikate auf eine bestimmte Größe einstellbar sind. Die beispielsweise nach einer Vermahlung durch die üblichen, oben bereits angegebene Meßmethoden meßbaren Teilchengrößen beziehen sich in diesem Fall auf Agglomerate, die aus einzelnen, ebenfalls agglomerierten Primär oder Sekundärteilchen bestehen. Erfindungsgemäß bevorzugt eingesetzte Schichtsilikate weisen in der Regel zunächst agglomerierte Teilchenstapel auf. Bei einem Zusatz von Schichtsilikat zu Wasser zerfällt zunächst ein agglomeriertes Teilchen in einzelne immer noch agglomerierte Teilchenstapel. Bei einer Dispergierung in Wasser werden zunächst die agglomerierten Teilchenstapel in einzelnen Teilchenstapel aufgelöst. Diese Teilchenstapel Quellen innerhalb einer bestimmten Zeit in Wasser auf, wobei eine Trennung der einzelnen Teilchenstapel in die einzelnen am Teilchenstapel beteiligten Primärteilchen erfolgt. Im Rahmen einer weiteren bevorzugten Ausführungsform der vorliegenden Erfindung werden Schichtsilikate eingesetzt, deren Primärteilchen innerhalb der Teilchenstapel eine Größe von weniger als 1 µm, insbesondere weniger als 500 nm und bevorzugt von weniger als etwa 100 nm aufweisen.

[0051] Im Rahmen einer bevorzugten Ausführungsform der vorliegenden Erfindung wird als Schichtsilikat ein Hectorit eingesetzt, beispielsweise der unter dem Namen Laponite RD erhältliche synthetische Hectorit (Vertrieb Solvay Alkali GmbH).

[0052] Im Rahmen einer bevorzugten Ausführungsform der vorliegenden Erfindung beträgt das Verhältnis der durchschnittlichen Teilchengrößen der Polysaccharide und der Schichtminerale etwa 5 : 1 bis etwa 1 : 5 beispielsweise etwa 3 : 1 bis etwa 1 : 3 oder etwa 2 : 1 bis etwa 1 : 2.

[0053] Die erfindungsgemäße Bindemittelzusammensetzung enthält das Schichtsilikat vorzugsweise in einer Menge von etwa 3 bis etwa 30 Gew.-%, insbesondere etwa 3,5 bis etwa 20 oder etwa 4 bis etwa 10 Gew.-%, beispielsweise etwa 5 bis etwa 8 Gew.-%.

[0054] Neben den bereits beschriebenen Verbindungen d. h. neben dem teilvernetzten, wasserlöslichen Celluloseether oder einem Gemisch aus zwei oder mehr solcher Celluloseether und gegebenenfalls einer wasserlöslichen oder wasserdispersiblen Verbindung können die erfindungsgemäßen, wasserlöslichen Zubereitungen noch ein Polymerisat enthalten. Derartige Polymerisate können der wasserlöslichen Zubereitung beispielsweise zur Klebkraftverstärkung zugegeben werden. Als Polymerisate eignen sich beispielsweise wasserdispersierbare Polymere wie Vinylpyrrolidon, Polyacrylamid, Polyvinylalkohol oder Ester oder Salze der Polyacrylsäure oder Polymethacrylsäure oder Gemische aus zwei oder mehr der genannten Polymeren. Im Rahmen einer bevorzugten Ausführungsform der Erfindung werden als Polymerisate Polyacrylate oder Polymethacrylate, das heißt, Polymerisate der Ester der Acrylsäure oder Methacrylsäure mit 1 bis etwa 8 C-Atomen in der Alkohol Komponente sowie Vinylpolymere, insbesondere Polyvinylacetat, eingesetzt.

[0055] Weiterhin können als Polymerisate redispersierbare Dispersionspulver von Polymerisationen eingesetzt werden. Hierbei handelt es sich beispielsweise um die Homo- oder Copolymerisate der Vinylester, von Styrol, Acrylsäure- oder Methacrylsäureestern oder von Vinylchlorid. Geeignete Vinylesterpolymerisate sind beispielsweise Vinylacetat-Homopolymere, Copolymere des Vinylacetats mit Ethylen oder Vinylchlorid oder weiteren Vinylestern wie Vinylalanat, Versäuerungvinylester, Vinylpivalat oder Ester von Maleinsäure oder Fumarsäure oder Homopolymerisate von Vinylestern von gesättigten C3- bis C8-Alkylcarbonsäuren oder deren Copolymerisate mit Ethylen, Vinylchlorid oder weiteren Vinylestern oder Copolymerisate die ein Gemisch aus zwei oder mehr der genannten Monomeren aufweisen oder Gemische aus zwei oder mehr der genannten Homo- oder Copolymerisate.

[0056] Wenn als Polymerisate Verbindungen eingesetzt werden die sich von Acrylsäure oder Methacrylsäure oder Styrol ableiten, so werden vorzugsweise Polymere eingesetzt, die sich aus der Polymerisation von Styrol oder Estern der Acrylsäure oder Methacrylsäure mit linearen oder verzweigten oder cyclischen aliphatischen Alkoholen mit 1 bis 20 C-Atomen erhalten lassen. Ebenfalls geeignet sind Copolymerisate des Styrols, beispielsweise Styrol-Butadien-Copolymere. Ebenfalls geeignet sind Vinylchlorid-Polymerisate, beispielsweise Vinylchlorid-Ethylencopolymere.

[0057] Im Rahmen einer bevorzugten Ausführungsform der Erfindung werden als Polymerisate Homopolymere des Vinylacetats, Vinylacetat-Ethylen-Copolymere oder Copolymere von Vinylestern von gesättigten C3- bis C8-Alkylcarbonsäuren und Ethylen mit einem Ethylengehalt von 1 bis etwa 40 Gew.-% und 0 bis etwa 40 Gew.-% weiterer Vinylester aus der Gruppe der Vinylester von gesättigten C3- bis C8-Alkylcarbonsäuren oder Vinylchlorid, Copolymere von Styrol und Estern der Acrylsäure oder Methacrylsäure wie Styrol-Butylacrylat- oder Styrol-Ethylhexylacrylat-Copolymere mit einem Styrolgehalt von 1 bis etwa 70 Gew.-%. Derartige redispersierbare Polymerisate werden beispielsweise durch Sprühtrocknung von Polymerdispersionen in Sprühtürmen hergestellt. Es ist im Rahmen der vorliegenden Erfindung vorgesehen, daß die oben genannten Polymerisate in den erfindungsgemäßen wasserlöslichen Zubereitungen einzeln oder als Gemische aus zwei oder mehr davon eingesetzt werden.

[0058] Gegenstand der vorliegenden Erfindung sind daher auch Bindemittelzubereitungen, die neben den obengenannten retardierten Polysacchariden und einem Schichtsilikat noch mindestens ein synthetisches wasserlösliches oder wasserdispersierbares Polymerisat enthalten

[0059] Die erfindungsgemäßen Bindemittelzubereitungen können gegebenenfalls Zusatzstoffe enthalten, die eine Alkalisierung des durch Auflösen der erfindungsgemäßen wasserlöslichen Zubereitungen herstellbaren Klebstoffs bewirken. Hierzu zählen beispielsweise Ammonium-, Alkali- und/oder Erdalkalimetallhydroxide, die wasserlöslichen vorzugsweise pulverförmigen Alkalimetallsilikate (Wasserglas), insbesondere Na- oder K-Wasserglas sowie Ammoniak und Amine oder basische Salze und Neutralsalze, die sie von starken und schwachen Säuren ableiten. Hierzu gehören beispielsweise die Alkalisalze der Kohlensäure oder der Carbonsäuren oder der tertiären Phosphate. Die genannten Verbindungen können alleine oder als Gemisch aus zwei oder mehr davon eingesetzt werden. Wenn im Rahmen der Auflösung der erfindungsgemäßen wasserlöslichen Zubereitungen eine Alkalisierung erfolgen soll, dann beträgt der Anteil der obengenannten Zusatzstoffe an der gesamten erfindungsgemäßen Bindemittelzubereitung im allgemeinen etwa 0,1 bis etwa 2 Gew.-%

[0060] Im Rahmen einer weiteren Ausführungsform der vorliegenden Erfindung enthält die wasserlösliche Zubereitung Füllstoffe. Geeignete Füllstoffe sind beispielsweise Carbonate (insbesondere Calciumcarbonat), Silikate (beispielsweise Talk, Ton, Glimmer), Kieselerde, Sulfate wie Calcium- oder Bariumsulfat, Aluminiumhydroxid sowie Cellulosefasern, Glasfasern oder Glaskugeln. Derartige Füllstoffe können in der erfindungsgemäßen wasserlöslichen Zusammensetzung beispielsweise in einer Menge von bis zu etwa 20, vorzugsweise von etwa 0,1 bis etwa 10 Gew.-%, bezogen auf die gesamte wasserlösliche Zubereitung, enthalten sein.

[0061] Derartige synthetische Polymerisate werden beispielsweise zur Verstärkung der Klebkraft bzw. zur Verbesserung der Wasserfestigkeit eines unter Verwendung eines aus einem erfindungsgemäßen Bindemittelagglomerat erhältlichen Produkts erhaltenen Endprodukts zu gewährleisten. Als synthetische Polymerisate eignen sich im Rahmen der vorliegenden Erfindung insbesondere redispersierbare Dispersionspulver von vollen synthetischen Polymeren (Basispolymerisate).

[0062] Grundsätzlich handelt es sich dabei um Homo- und Copolymerisate von Vinylestern, Styrol, Acrylsäureestern und Vinylchlorid.

[0063] Als Basispolymerisat geeignete Vinylesterpolymerisate sind beispielsweise Vinylacetat-Homopolymere, Copolymere des Vinylacetats mit Ethylen- und/oder Vinylchlorid und/oder weiteren Vinylestern wie Vinylacrylat, Versäuerungvinylestern, Vinylpivalat oder Estern von Maleinsäure oder Fumarsäure oder Copolymere aus zwei oder mehr der genannten Monomeren oder Homopolymerisate von Vinylestern von gesättigten C₃₋₈-Alkylcarbonsäuren oder deren Copolymerisate mit Ethylen, Vinylchlorid oder weiteren Vinylestern.

[0064] Die obengenannten Acrylsäureester, Methacrylsäureester oder Styrolpolymerisate leiten sich aus der Polymerisation von Styrol oder Estern der Acrylsäure oder Methacrylsäure ab. Als Ester der Acrylsäure oder Methacrylsäure werden vorzugsweise Ester mit geradketigen oder verzweigten oder cyclischen aliphatischen Alkoholen mit 1 bis 20 C-Atomen eingesetzt. Weitere Styrolpolymerisate können beispielsweise Copolymerisate von Styrol mit einem oder mehreren weiteren Monomeren sein. Geeignet sind beispielsweise Styrol-Butadiencopolymerisate. Als Vinylchlorid-Polymerisate sind Vinylchlorid-Ethylen Copolymere geeignet.

[0065] Vorzugsweise werden im Rahmen der vorliegenden Erfindung als Redispersionspulver Vinylacetat-Homopolymere, Vinylacetat-Ethylen-Copolymere oder Copolymere von Vinylestern von gesättigten Alkylcarbonsäuren und Ethylen mit einem Ethylengehalt von 1 bis etwa 40 Gew.-% Ethylen und 0 bis etwa 40 Gew.-% weiteren Vinylestern aus der Gruppe der Vinylester von gesättigten C₃₋₈-Alkylcarbonsäuren oder Vinylchlorid oder Gemischen aus zwei oder mehr davon, Styrolacrylate wie Styrol-Butylacrylat oder Styrol-Ethylhexylacrylat mit einem Styrolgehalt von 1 bis etwa 70 Gew.-% eingesetzt. Diese redispersierenden Polymerisate werden üblicherweise durch Sprühtrocknung von Polymerdispersionen in Sprühtürmen hergestellt.

[0066] Besonders geeignet sind beispielsweise Vinylester-Homo- oder -Copolymere, beispielsweise mit Ethylen, deren monomerer Grundbaustein ein Vinylester einer linearen oder verzweigten Carbonsäure mit etwa 2 bis etwa 44, beispielsweise etwa 3 bis etwa 15 C-Atomen darstellt. Als Monomere für diese homo- oder polymeren Polyvinylester kommen Vinylformiat, Vinylacetat, Vinylpropionat, Vinylisobutyrat, Vinylpivalat, Vinyl-2-ethylhexanoat, Vinylester von gesättigten verzweigten Monocarbonsäuren mit 9 bis etwa 15 C-Atomen im Säurerest, Vinylester von längerketigen gesättigten oder ungesättigten Fettsäuren wie Vinylacrylat, Vinylstearat oder Vinylester der Benzoesäure und substituierter Derivate der Benzoesäure wie Vinyl-p-tert-butylbenzoat in Frage. Die genannten Vinylester können jeweils einzeln oder als Gemische aus zwei oder mehr der genannten Vinylester im Vinylester Polymeren vorliegen.

[0067] Es kann zweckmäßig sein, wenn im Rahmen der vorliegenden Erfindung die erfindungsgemäßen Bindemittelagglomerate zwei oder mehr der genannten synthetischen Polymerisate enthalten.

[0068] Im Rahmen einer weiteren bevorzugten Ausführungsform der vorliegenden Erfindung werden als Polymerisatteilchen Gemische aus einem Homopolymerisat und einem Copolymerisat eingesetzt. Als Homopolymerisat geeignet sind die bereits obengenannten Homopolymerisate, insbesondere jedoch Homopolymerisate von Vinylestern, vorzugsweise Polyvinylacetat. Als Copolymerisate sind ebenfalls die obengenannten Copolymerisate geeignet. Im Rahmen einer bevorzugten Ausführungsform werden in den genannten Gemischen von zwei oder mehr Polymerisatteilchen jedoch Copolymere von Ethylen und Vinylacetat, Vinylacetat und Vinylversat oder Terpolymere, insbesondere Ethylen-Vinylacetat-Acrylat-Terpolymere eingesetzt.

[0069] Der Anteil an Homopolymerisaten in derartigen Gemischen von Polymerisatteilchen beträgt vorzugsweise mindestens etwa 20 Gew.-%, vorzugsweise jedoch 40 Gew.-% oder mehr, beispielsweise mindestens etwa 50 Gew.-%. Geeignete Mischungsverhältnisse von Homopolymerisaten und Copolymerisaten sind beispielsweise etwa 75 : 25 oder etwa 80 : 20.

[0070] Die erfindungsgemäßen Bindemittelagglomerate können neben den genannten Inhaltsstoffen, nämlich mindestens einem natürlichen oder synthetischen Polysaccharid und mindestens einem synthetischen Polymerisat noch weitere Zusatzstoffe enthalten.

[0071] Geeignete Zusatzstoffe sind beispielsweise Verbindungen, die eine Alkalisierung des durch Auflösen der erfindungsgemäßen wasserlöslichen Zubereitungen herstellbaren Klebstoffs bewirken. Hierzu zählen beispielsweise Ammonium-, Alkali- und/oder Erdalkalimetallhydroxide, die wasserlöslichen, vorzugsweise pulverförmigen Alkalimetallalkate (Wasserglas), insbesondere Natrium- oder Kaliumwasserglas sowie Ammoniak und Amine oder basische Salze und

5 Neutralsalze, die sich von starken und schwachen Säuren ableiten. Hierzu gehören beispielsweise die Alkalisalze der Kohlensäure oder der Carbonsäuren oder der tertiären Phosphate. Die genannten Verbindungen können alleine oder als Gemisch aus zwei oder mehr davon eingesetzt werden.

[0072] Wenn im Rahmen der Auflösung der erfindungsgemäßen wasserlöslichen Zubereitungen eine Alkalisierung erfolgen soll, dann beträgt der Anteil der obengenannten Zusatzstoffe an der gesamten erfindungsgemäßen wasserlöslichen

10 Zubereitung im allgemeinen etwa 0,1 bis etwa 2 Gew.-%.

[0073] Weiterhin als Zusatzstoffe geeignet sind Hilfs- oder Füllstoffe, Netz- und Konservierungsmittel, Konsistenzbildner und Zusatzkomponenten mit Klebkraft wie Dextrine oder ionogene Celluloseether.

[0074] Im Rahmen einer weiteren Ausführungsform der vorliegenden Erfindung enthält die wasserlöslichen Zubereitung Hilfs- oder Füllstoffe. Geeignete Hilfs- oder Füllstoffe sind beispielsweise Carbonate (insbesondere Calciumcarbonat), Silikate (beispielsweise Talk, Ton, Glimmer), Kiesel Erde, Sulfate wie Calcium- oder Bariumsulfat, Aluminiumhydroxid sowie Glasfasern oder Glaskugeln. Derartige Hilfs- oder Füllstoffe können in der erfindungsgemäßen wasserlöslichen Zusammensetzung beispielsweise in einer Menge von bis zu etwa 30, vorzugsweise von etwa 0,1 bis etwa

20 20 Gew.-% bezogen auf die gesamte wasserlöslichen Zubereitung enthalten sein.

[0075] Weiterhin kann eine erfindungsgemäße Bindemittelzusammensetzung noch Additive enthalten. Als Additive eignen sich insbesondere wasserlösliche ionische oder nichtionische Polymere aus der Gruppe der Polyvinylpyrrolidone, Vinylpyrrolidon/Vinylester-Copolymere, wasserlösliche amphotere Polymere aus der Gruppe der Alkylacrylamid/Acrylsäure-Copolymere, Alkylacrylamid/Methacrylsäure-Copolymere, Alkylacrylamid/Methylmethacrylsäure-Copolymere, Alkylacrylamid/Acrylsäure/Alkylaminoalkyl(meth)acrylsäure-Copolymere, Alkylacrylamid/Methacrylsäure/Alkylaminoalkyl(meth)acrylsäure-Copolymere,

25 Alkylacrylamid/Methylmethacrylsäure/Alkylaminoalkyl(meth)acrylsäure-Copolymere, Alkylacrylamid/Alkylmethacrylat/Alkylaminoethylmethacrylat/Alkylmethacrylat-Copolymere, Copolymere aus ungesättigten Carbonsäuren, kationisch derivatisierten ungesättigten Carbonsäuren, gegebenenfalls weiteren ionischen oder nichtionogenen Monomeren, wasserlösliche zwitterionische Polymere aus der Gruppe der Acrylamidoalkyltrialkylammoniumchlorid/Acrylsäure-Copolymere sowie deren Alkali- und Ammoniumsalze, Acrylamidoalkyltrialkylammoniumchlorid/Methacrylsäure-Copolymere sowie deren Alkali- und Ammoniumsalze.

30 Methacrylolethylbetain/Methacrylat-Copolymere, wasserlösliche anionische Polymere aus der Gruppe der Vinylacetat/Crotonsäure-Copolymere, Vinylpyrrolidon/Vinylacrylat-Copolymere, Acrylsäure/Bihylacrylat/N-tert-Butylacrylamid-Terpolymere, Pfropfpolymeren aus Vinylestern, Estern von Acrylsäure oder Methacrylsäure allein oder im Gemisch copolymerisiert mit Crotonsäure, Acrylsäure oder Methacrylsäure mit Polyalkylenoxiden und/oder Polyalkylen-

35 glycolen, gepfropfte und vernetzte Copolymere aus der Copolymerisation von mindestens einem Monomeren vom nichtionischen Typ, mindestens einem Monomeren vom ionischen Typ, von Polyethylenglycol und einem Vernetzer durch Copolymerisation mindestens eines Monomeren jeder der drei folgenden Gruppen erhaltenen Copolymere, Ester ungesättigter Alkohole und kurzkettiger gesättigter Carbonsäuren und/oder Ester kurzkettiger gesättigter Alkohole und ungesättigter Carbonsäuren, ungesättigte Carbonsäuren, Ester langkettiger Carbonsäuren und ungesättigter Alkohole und/oder Ester aus den Carbonsäuren der Gruppe mit gesättigten oder ungesättigten, geradkettigen oder verzweigten C₂-12-

40 Alkoholen, Terpolymere aus Crotonsäure, Vinylacetat und einem Allyl- oder Methallylester, Tetra- und Pentapolymere aus Crotonsäure oder Allyloxycarbonsäure, Vinylacetat oder Vinylpropionat, verzweigten Allyl- oder Methallylestern, Vinyllethern, Vinylestern oder geradkettigen Allyl- oder Methallylestern. Crotonsäure-Copolymere mit einem oder mehreren Monomeren aus der Gruppe Ethylen, Vinylbenzol, Vinylmethylether, Acrylamid und deren wasserlöslicher Salze, Terpolymere aus Vinylacetat, Crotonsäure und Vinylestern einer gesättigten aliphatischen in α - β - oder γ -Stellung ver-

45 zweigten Monocarbonsäure, wasserlöslichen kationische Polymeren aus der Gruppe der quaternierten Cellulose-Derivate, Polysiloxane mit quaternären Gruppen, kationischen Guar-Derivate, polymeren Dimethyldiallylammoniumsalzen und deren Copolymere mit Estern und Amidn von Acrylsäure und Methacrylsäure, Copolymere des Vinylpyrrolidons mit quaternierten Derivaten des Dialkylaminoacrylats und -methacrylats, Vinylpyrrolidon-Methionimidazoliumchlorid-Copolymere, quaternierter Polyvinylalkohol, unter den INCI-Bezeichnungen Polyquaternium 2, Polyquaternium 17, Polyquaternium 18 und Polyquaternium 27 angegebenen Polymere.

50 [0076] Ebenfalls als Additive geeignet sind wasserlösliche Polymere, wie sie durch Pfropfcopolymerisation erhältlich sind. Als Pfropfgrundlage eignen sich beispielsweise Polyalkylenglykole, insbesondere Polyethylenglykol, mit einem Molekulargewicht von etwa 100 bis etwa 50 000, insbesondere etwa 1000 bis etwa 10 000 zur Herstellung der Pfropfstoffe können grundsätzlich alle auf Polyalkylenglykole pfropfbaren Verbindungen mit mindestens einer olefinisch ungesättigten Doppelbindung eingesetzt werden. Vorzugsweise werden zur Herstellung der Pfropfstoffe jedoch Ester des Vinylalkohols mit linearen oder verzweigten, gesättigten Monocarbonsäuren mit 2 bis 24 C-Atomen, insbesondere 2 bis etwa 18 C-Atomen eingesetzt. Derartige Vinylester wurden im Rahmen des vorliegenden Textes bereits oben beschrieben. Be-

55 spielsweise können Pfropfcopolymere eingesetzt werden, die einen Gehalt an Pfropfgrundlage von etwa 10 bis etwa 90 Gew.-% und einen Gehalt an Pfropfstoffen von etwa 90 bis etwa 10 Gew.-% aufweisen. Das Verhältnis von Pfropfgrundlage zu Pfropfstoffen wird vorzugsweise so gewählt, daß die Pfropfcopolymeren wasserlöslich sind, wobei die Wasserlöslichkeit bei 20°C mindestens etwa 1 g/l, vorzugsweise jedoch mehr, beispielsweise etwa 2, 5 oder 10 g/l, betragen sollte.

[0077] Als Additiv kann beispielsweise ein Pfropfcopolymeres eingesetzt werden, das etwa 40 Gew.-% eines Polyethylenglykols (PEG) mit einem Molekulargewicht (M_w) von etwa 6000 als Pfropfgrundlage und etwa 60 Gew.-% Polyvinylacetat als Pfropfstoffe trägt.

60 [0078] Die genannten Additive können in einer Menge von etwa 0,1 bis etwa 10 Gew.-%, beispielsweise etwa 1 bis etwa 7 Gew.-% in den erfindungsgemäßen Bindemittelzusammensetzungen vorliegen.

[0079] Im Rahmen einer weiteren Ausführungsform der vorliegenden Erfindung kann eine erfindungsgemäße Binde-

mittelzusammensetzung mindestens eine quaternäre Ammoniumverbindung enthalten. Unter einer "quaternären Ammoniumverbindung" wird im Rahmen des vorliegenden Textes eine Stickstoffverbindung verstanden, die mindestens ein Stickstoffatom aufweist, das 3 oder 4 organische Reste trägt. Als eigenständige organische Reste werden im Rahmen der vorliegenden Erfindung auch solche Reste gezählt, wie sie sich aus der Einbindung des entsprechenden Stickstoffatoms in eine cyclische Struktur ergeben.

[0080] Im Rahmen einer bevorzugten Ausführungsform der vorliegenden Erfindung werden als quaternäre Ammoniumverbindungen Verbindungen eingesetzt, die 1 Stickstoffatom oder 2 Stickstoffatome aufweisen wobei mindestens eines der Stickstoffatome die oben genannte Eigenschaft erfüllt. Im Rahmen einer weiteren bevorzugten Ausführungsform der vorliegenden Erfindung werden quaternäre Ammoniumverbindungen eingesetzt, die nur 1 Stickstoffatom aufweisen. Grundsätzlich können die im Rahmen der vorliegenden Erfindung einsetzbaren quaternären Ammoniumverbindungen am Stickstoffatom beliebige organische Reste tragen. Im Rahmen einer bevorzugten Ausführungsform der vorliegenden Erfindung werden jedoch quaternäre Ammoniumverbindungen eingesetzt, die am Stickstoffatom 4 organische Reste ausgewählt aus der Gruppe bestehend aus linearen oder verzweigten, gesättigten oder ungesättigten Alkylresten mit 1 bis 4 C-Atomen, gesättigten oder ungesättigten Cycloalkylresten mit 4 bis 24 C-Atomen oder Arylresten mit 6 bis 24 C-Atomen ausgewählt sind. Die genannten Reste können gegebenenfalls unabhängig voneinander einen oder mehrere Substituenten aufweisen.

[0081] Im Rahmen einer weiteren bevorzugten Ausführungsform der vorliegenden Erfindung werden quaternäre Ammoniumverbindungen eingesetzt, bei denen die mit dem Stickstoffatom verbundenen organischen Reste eine unterschiedliche Zahl an C-Atomen aufweisen. So ist es beispielsweise möglich, quaternäre Ammoniumverbindungen einzusetzen, bei denen zwei Arten unterschiedlicher organischer Reste mit dem Stickstoffatom verbunden sind, wobei von dem am Stickstoffatom befindlichen organischen Resten beispielsweise jeweils zwei oder drei identisch sein können. Es ist darüber hinaus ebenfalls möglich, quaternäre Ammoniumverbindungen einzusetzen, bei denen drei unterschiedliche Reste oder vier unterschiedliche Reste mit dem Stickstoffatom verbunden sind.

[0082] Im Rahmen einer weiteren bevorzugten Ausführungsform der vorliegenden Erfindung werden als quaternäre Ammoniumverbindungen Verbindungen eingesetzt, die 3 oder mehr, insbesondere 10 oder mehr quaternäre Stickstoffatome aufweisen. Beispiele für derartige Verbindungen sind Polymere, die über quaternisierte Aminofunktionen verfügen. Geeignete Polymere sind beispielsweise Polyacrylate oder Polymethacrylate mit Dialkylaminogruppen, die entweder protoniert oder mit entsprechenden Quaternisierungsmitteln quaternisiert wurden. Ebenfalls geeignet sind entsprechende Polymere, welche die Stickstoffatome in einem cyclischen Strukturelement beinhalten, beispielsweise Polyvinylpyrrolidon.

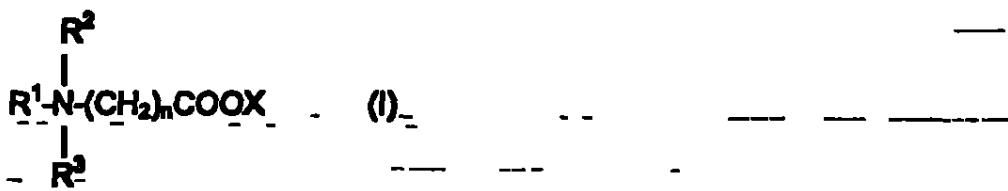
[0083] Geeignete quaternäre Ammoniumverbindungen können ein- oder mehrwertige Gegenionen aufweisen. Geeignete Gegenionen sind beispielsweise Halogenidionen wie Fluorid, Chlorid, Bromid oder Jodid, Ebenfalls geeignet sind Carboxylate, Sulfate oder Phosphate als Gegenionen.

[0084] Im Rahmen einer weiteren bevorzugten Ausführungsform der vorliegenden Erfindung werden als quaternäre Ammoniumverbindungen beispielsweise N,N-Didecyl-N,N-dimethylammoniumchlorid, N,N-Didecyl-N,N-dimethylammoniumpropionat, N,N-Didecylmethoxyethylammoniumchlorid, N,N-Didecylmethoxyethylammoniumpropionat, Cetyltrimethylammoniumchlorid, Distearyltrimethylammoniumchlorid, Lauryldimethylbenzylammoniumchlorid, Lauryltrimethylammoniumchlorid oder Oxyethylalkylammoniumphosphate eingesetzt. Ebenfalls geeignet sind beispielsweise Verbindungen wie Dioctyldimethylammoniumchlorid, Didecylmethylpoly(oxyethyl)ammoniumpropionat, Benzalkoniumchloride wie Benzethoniumchlorid, Alkylaminooktylglycinalkylamine, Polyhexamethylenbiguanidhydrochlorid oder Alkylpropylenbiguanidinium.

[0085] Im Rahmen einer weiteren Ausführungsform der vorliegenden Erfindung können in den erfindungsgemäßen Bindemittelzusammensetzungen als Zusatzstoffe noch Verbindungen eingesetzt werden, die mindestens eine saure und eine basische Gruppe aufweisen. Verbindungen die mindestens eine saure und eine basische Gruppe aufweisen, werden häufig als zwitterionische Verbindungen bezeichnet. Unter den zwitterionischen Verbindungen sind beispielsweise die Betaine geeignet.

[0086] Betaine stellen bekannte Verbindungen dar, die überwiegend durch Carboxyalkylierung, vorzugsweise Carboxymethylierung von aminischen Verbindungen hergestellt werden. Vorzugsweise werden die Ausgangsstoffe mit Halogencarbonsäuren oder deren Salzen, insbesondere mit Natriumchloracetat kondensiert, wobei pro Mol Betain ein Mol Salz gebildet wird. Ferner ist auch die Anlagerung von ungesättigten Carbonsäuren wie beispielsweise Acrylsäure möglich. Überichten zu diesem Thema finden sich beispielsweise von A. O'Lennick et al. in HAPPI, Nov. 70 (1986), S. Holzman et al. in Tens. Det. 23, 309 (1986), R. Bibo et al. in Soap Cosm. Chem. Spec. Apr. 46 (1990) und P. Ellis et al. in Euro. Cosm. 1, 14 (1994).

[0087] Beispiele für geeignete Betaine stellen die Carboxyalkylierungsprodukte von sekundären und insbesondere tertiären Aminen dar, die der Formel (I) entsprechen,



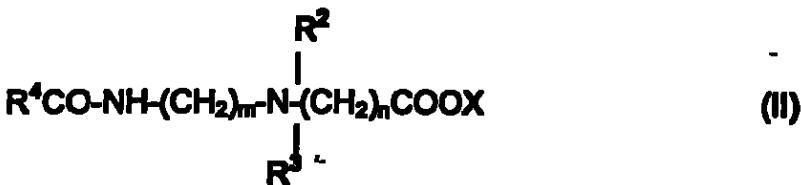
in der R^1 für Alkyl- und/oder Alkenylreste mit 6 bis 22 Kohlenstoffatomen, R^2 für Wasserstoff oder Alkylreste mit 1 bis 4 Kohlenstoffatomen, R^3 für Alkylreste mit 1 bis 4 Kohlenstoffatomen, n für Zahlen von 1 bis 6 und X für ein Alkali- und/oder Erdalkalimetall oder Ammonium steht.

[0088] Typische Beispiele sind die Carboxymethylierungsprodukte von Hexylmethylamin, Hexyldimethylamin, Oc-

DE 102 27 871 A 1

Iridumethylamin, Decylidimethylamin, Dodecylidimethylamin, Dodecylethylidimethylamin, C_{12/14}-Kokosalkylidimethylamin, Myristylidimethylamin, Cetylidimethylamin, Stearylidimethylamin, Stearylethylidimethylamin, Oleylidimethylamin, C_{16/18}-Talgalkylidimethylamin sowie deren technische Gemische.

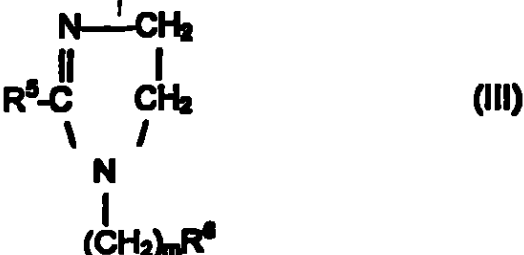
[0089] Weiterhin kommen als Betaine auch Carboxyalkylierungsprodukte von Ammonoaminen in Betracht, die der Formel (II) folgen,



In der R⁴CO für einen aliphatischen Acylrest mit 6 bis 22 Kohlenstoffatomen und 0 oder 1 bis 3 Doppelbindungen, m für Zahlen von 1 bis 3 steht und R², R³, n und X die oben angegebenen Bedeutungen haben.

[0090] Typische Beispiele sind Umsetzungsprodukte von Fettsäuren mit 6 bis 22 Kohlenstoffatomen, namentlich Capronsäure, Caprylsäure, Caprinsäure, Laurinsäure, Myristinsäure, Palmitinsäure, Palmoleinsäure, Stearinsäure, Isosteirinsäure, Ölsäure, Elaidinsäure, Petroselinssäure, Linolsäure, Linolensäure, Elaeostearinsäure, Arachinsäure, Gadoleinsäure, Behensäure und Erucasäure sowie deren technische Gemische, mit N,N-Dimethylamino-ethylamin, N,N-Dimethylaminopropylamin, N,N-Diethylaminoethylamin und N,N-Diethylaminopropylamin, die mit Natriumchloracetat kondensiert werden. Bevorzugt ist der Einsatz eines Kondensationsproduktes von C_{12/14}-Kokosfettsäure-N,N-dimethylaminopropylamid mit Natriumchloracetat.

[0091] Weiterhin kommen als geeignete Ausgangsstoffe für die im Sinne der Erfindung einzusetzenden Betaine auch Imidazoline in Betracht, die der Formel (III) folgen,



In der R⁵ für einen Alkylrest mit 5 bis 21 Kohlenstoffatomen, R⁶ für eine Hydroxylgruppe, einen OCOR⁵- oder NHCOR⁵-Rest und m für 2 oder 3 steht. Auch bei diesen Substanzen handelt es sich um bekannte Stoffe, die beispielsweise durch cyclisierende Kondensation von 1 oder 2 Mol Fettsäure mit mehrwertigen Aminen wie beispielsweise Azinoethyl ethanolamin (AEEA) oder Diethylentriamin erhalten werden können. Die entsprechenden Carboxyalkylierungsprodukte stellen Gemische unterschiedlicher offenkettiger Betaine dar.

[0092] Typische Beispiele sind Kondensationsprodukte der oben genannten Fettsäuren mit AEEA, vorzugsweise Imidazoline auf Basis von Laurinsäure oder wiederum C_{12/14}-Kokosfettsäure, die anschließend mit Natriumchloracetat betainisiert werden.

[0093] Die erfindungsgemäßen Bindemittelzusammensetzungen können die zwitterionischen Verbindungen jeweils einzeln, d. h. nur eine zwitterionische Verbindung, oder im Gemisch aus zwei oder mehr zwitterionischen Verbindungen enthalten.

[0094] Die erfindungsgemäßen Bindemittelzusammensetzungen enthalten die quaternären Ammoniumverbindungen oder die zwitterionischen Verbindungen oder ein Gemisch aus zwei oder mehr davon in einer Menge von mehr als 4 Gew. %. Die Obergrenze für den Gehalt an quaternären Ammoniumverbindungen oder die zwitterionischen Verbindungen oder Gemischen aus zwei oder mehr davon liegt bei etwa 40 Gew. %. Im Rahmen einer bevorzugten Ausführungsform enthält eine erfindungsgemäße Bindemittelzusammensetzung mindestens etwa 5, 6, 7, 8, 9 oder mindestens etwa 10 Gew. % an quaternären Ammoniumverbindungen oder die zwitterionischen Verbindungen oder Gemischen aus zwei oder mehr davon. Geeignete Mengen liegen beispielsweise in einer Größenordnung von etwa 8% bis etwa 30%, beispielsweise etwa 9% bis etwa 25% oder etwa 15% oder weniger bis etwa 20%. Die obengenannten Prozentangaben beziehen sich auf das Gewicht an quaternären Ammoniumverbindungen oder die zwitterionischen Verbindungen oder Gemischen aus zwei oder mehr davon.

[0095] Grundsätzlich können die erfindungsgemäßen Bindemittelzusammensetzungen die oben aufgezählten Verbindungen jeweils einzeln oder als Gemisch aus zwei oder mehr der jeweiligen Verbindungstypen enthalten. Es ist jedoch im Rahmen der vorliegenden Erfindung ebenso vorgesehen, daß die erfindungsgemäßen Bindemittelzusammensetzungen ein Gemisch aus zwei oder mehr unterschiedlichen Verbindungen unterschiedlicher Verbindungstypen enthalten.

[0096] Als weitere Zusatzstoffe kann eine erfindungsgemäße Bindemittelzusammensetzung beispielsweise Biozide, Farbstoffe, Pigmente, Dispergiermittel, Netzmittel und/oder Tenside, Glykole oder Rheologiehilfsmittel enthalten.

[0097] Als Biozide eignen sich beispielsweise quaternäre Ammoniumverbindungen, Aldehyde, vorzugsweise Formaldehyd, Isothiazolone oder Benzisothiazolone oder Gemische aus zwei oder mehr davon.

[0098] Als Farbstoffe und Pigmente sind beispielsweise Kreide, Ruß, Ruß und dergleichen anorganische Farbstoffe und Pigmente sowie organische Farbstoffe und Pigmente wie Azofarbstoffe oder Anilinfarbstoffe geeignet.

[0099] Als Dispergiermittel bzw. Netzmittel und/oder Tenside sind amomische, kationische oder nichtionische Tenside geeignet.

[0100] Typische Beispiele für amomische Tenside sind weniger als zwei Säuregruppen aufweisende Alkylbenzolsulfo-

ate, Alkansulfonate, Olefinsulfonate, Alkylethersulfonate, Glycerinethersulfonate, Methylstersulfonate, Sulfosulfuren, Alkylsulfate, Fettalkobol ethersulfate, Glycerinethersulfate, Hydroxymischethersulfate, Monoglycend(ether)sulfate, Fettsäureamid(ether)sulfate, Mono- und Dialkylsulfosuccinate, Mono- und Dialkylsulfosuccinamate, Sulfotri-glycende, Amidseifen, Eiherscarbonsäuren und deren Salze, Fettsäuremethionate, Fettsäuresarcosinate, Fettsäuretauride, Acyl-lactate, Alkyloligoglucosidsulfate, Proteinfettsäurekondensate (insbesondere pflanzliche Produkte auf Sojabasis) und Alkyl(ether)phosphate. Sofern die anionischen Tenside Polyglykoletherketten enthalten, können sie eine konventionelle, vorzugsweise jedoch eine eingeezte Homologenverteilung aufweisen.

[0101] Weiterhin im Rahmen der vorliegenden Erfindung geeignete sind nichtionische Tenside, die nicht auf Cellulosebasis aufgebaut sind.

[0102] Typische Beispiele für derartige nichtionische Tenside sind Fettalkoholpolyglykolether, Alkylphenolpolyglykolether, Fettsäurepolyglykolester, Fettsäureamidpolyglykolether, Fettamunpolyglykolether, alkoxylierte Triglycende, Alk(en)yloligoglucoside, Fettsäure-N-alkylglucanide, Proteinhydrolysate (insbesondere pflanzliche Produkte auf Sojabasis), Polyolfettsäureester, Zuckerester, Sorbitanester und Polysorbate. Sofern die nichtionischen Tenside Polyglykoletherketten enthalten, können sie eine konventionelle, vorzugsweise jedoch eine eingeezte Homologenverteilung aufweisen. Vorzugsweise enthalten die erfindungsgemäßen Mittel als weitere Komponente nichtionische Tenside wie beispielsweise Anlagerungsprodukte von durchschnittlich 15 bis 30 Mol Ethylenoxid an Fettalkohole mit 8 bis 18 Kohlenstoffatomen.

[0103] Im Rahmen einer bevorzugten Ausführungsform der vorliegenden Erfindung werden als Bestandteil der erfindungsgemäßen Polysaccharidsuspension nichtionische, schaumarme Tenside eingesetzt, insbesondere EO/PO-Mischether, die etwa 5 EO- und 5 PO-Einheiten aufweisen.

[0104] Als Glykole sind im Rahmen der vorliegenden Erfindung insbesondere die niedermolekularen Glykole oder Oligoglykolether wie Ethylenglycol, Propylenglycol, Butylenglycol, Diethylenglycol, Dipropylenglycol und dergleichen geeignet.

[0105] Als Rheologiehilfsmittel eignen sich im Rahmen der vorliegenden Erfindung insbesondere Xanthan-Gum oder Kieselsäure oder Gemische aus zwei oder mehr davon.

[0106] Eine erfindungsgemäße Bindemittelzusammensetzung weist beispielsweise folgende Bestandteile auf:

- etwa 20 bis etwa 80 Gew.-% retardierter Celluloseether
- etwa 0,2 bis etwa 1 Gew.-% Natriumcarbonat
- etwa 10 bis etwa 50 Gew.-% eines Polyvinylacetat-Homopolymeren
- etwa 2 bis etwa 8 Gew.-% Kreide
- etwa 4 bis etwa 15 Gew.-% Schichtsilikat, insbesondere Lapomte RD
- etwa 0,2 bis etwa 2 Gew.-% einer quaternären Ammoniumverbindung.

[0107] Die erfindungsgemäßen Bindemittelzusammensetzungen können vom Anwender vor Ort durch Vermischen der Bindemittelzusammensetzung mit Wasser oder wässrigen Lösemitteln zu einer gebrauchsfertigen wässrigen Klebstoffzubereitung vermischt werden.

[0108] Gegenstand der vorliegenden Erfindung ist daher auch ein Verfahren zur Herstellung einer erfindungsgemäßen Klebstoffzubereitung, bei dem eine erfindungsgemäße Bindemittelzusammensetzung mit Wasser vermischt wird.

[0109] Gegenstand der vorliegenden Erfindung ist weiterhin auch eine Klebstoffzubereitung, mindestens enthaltend 20 Gew.-% Wasser und mindestens 1 Gew.-%, beispielsweise etwa 2 bis etwa 20 Gew.-% oder etwa 5 bis etwa 10 Gew.-% einer erfindungsgemäßen Bindemittelzusammensetzung. Im Rahmen einer bevorzugten Ausführungsform der vorliegenden Erfindung enthält eine erfindungsgemäße Klebstoffzubereitung mindestens etwa 30 Gew.-%, insbesondere jedoch mindestens etwa 40 Gew.-% oder mindestens etwa 60 Gew.-%, beispielsweise mindestens etwa 70 oder mindestens etwa 80 oder mindestens etwa 90 Gew.-% Wasser.

[0110] Die erfindungsgemäße Klebstoffzubereitung wird beispielsweise durch Eintrag einer erfindungsgemäßen Bindemittelzusammensetzung in Wasser in einem Gewichtsverhältnis von etwa 1 : 10 bis etwa 1 : 25, beispielsweise etwa 1 : 15 bis etwa 1 : 22, insbesondere etwa 1 : 20, (Gewichtsverhältnisse) hergestellt.

[0111] Eine erfindungsgemäße Klebstoffzubereitung weist in einem Zeitraum von etwa 1 bis etwa 5 Minuten nach ihrer Zubereitung vorzugsweise eine Brookfield-Viskosität (RVT, 20°C) von etwa 1000 bis etwa 3000 mPa · s auf. Im Rahmen einer weiteren bevorzugten Ausführungsform der vorliegenden Erfindung weist eine erfindungsgemäße Klebstoffzubereitung etwa 20 bis etwa 40 Minuten, insbesondere nach etwa 25 bis etwa 35 Minuten nach ihrer Zubereitung eine Brookfield-Viskosität (RVT, 20°C) von etwa 10 000 bis etwa 20 000, insbesondere etwa 11 000 bis etwa 16 000 mPa · s auf.

[0112] Der pH-Wert einer erfindungsgemäßen Klebstoffzubereitung beträgt im Rahmen der vorliegenden Erfindung mindestens etwa 6. Im Rahmen einer bevorzugten Ausführungsform der vorliegenden Erfindung beträgt der pH-Wert einer erfindungsgemäßen Klebstoffzubereitung mindestens etwa 7, beispielsweise etwa 7,1 bis etwa 10, insbesondere etwa 8 bis etwa 9.

[0113] Die Herstellung der erfindungsgemäßen Klebstoffzubereitungen erfolgt vor Ort durch den Anwender durch einfaches Vermischen der oben beschriebenen Bindemittelzubereitungen mit Wasser. Das Vermischen selbst kann im wesentlichen auf beliebige Weise geschehen. So eignen sich beispielsweise einfache Vorrichtungen wie ein Gefäß und ein Rührpatel, wobei das Wasser vorgelegt und die erfindungsgemäße Bindemittelzubereitung zügig in das Wasser eingeführt wird. Es ist jedoch im Rahmen der vorliegenden Erfindung ebenso möglich und vorgesehen, die erfindungsgemäße Klebstoffzubereitung unter Zuhilfenahme beispielsweise angetriebener Rührvorrichtungen herzustellen.

[0114] Die Erfindung wird nachfolgend durch Beispiele näher erläutert.

Beispiele

Folgende Beispielrezepturen wurden hergestellt:

DE 102 27 871 A 1

Rezeptur 1

54,0 Gew.-% MHEC 6000 PR
30,0 Gew.-% PVAc-Dispersionspulver
5 7,0 Gew.-% Cellulosefasern
6,0 Gew.-% Lapomts RD
0,5 Gew.-% Soda
0,2 Gew.-% Dimethyldidodecylammoniumchlorid
2,3 Gew.-% kristalline Kreide

Rezeptur 2

54,0 Gew.-% MHEC 6000 PR
30,0 Gew.-% PVAc-Dispersionspulver
15 7,0 Gew.-% Cellulosefasern
6,0 Gew.-% Bentonit (Bentone BW)
0,5 Gew.-% Soda
0,2 Gew.-% Dimethyldidodecylammoniumchlorid
2,3 Gew.-% kristalline Kreide

Rezeptur 3

54,0 Gew.-% MHEC 6000 PR
30,0 Gew.-% PVAc-Dispersionspulver
25 7,0 Gew.-% Cellulosefasern
6,0 Gew.-% Smectit (Tixogel CD)
0,5 Gew.-% Soda
0,2 Gew.-% Dimethyldidodecylammoniumchlorid
2,3 Gew.-% kristalline Kreide

Rezeptur 4

54,0 Gew.-% MHEC 6000 PR
30,0 Gew.-% PVAc-Dispersionspulver
35 7,0 Gew.-% Cellulosefasern
0,5 Gew.-% Soda
0,2 Gew.-% Dimethyldidodecylammoniumchlorid
8,3 Gew.-% kristalline Kreide

Rezeptur 5

Handelsüblicher Kleister Metylan Spezial.

[0115] Die Zusammensetzungen gemäß den oben angegebenen Rezepturen wurden im Ansatzverhältnis von 1 20
(Gewichtsverhältnis) zügig mit Wasser vermischt. Nach 15 Minuten wurden die entstandenen Kleisterzusammensetzungen
45 gen mit einer handelsüblichen Lammfellrolle auf Neuputz aufgetragen. Spritzneigung und aufgetragene Kleistermenge
wurden visuell beurteilt. Die Ergebnisse sind in der nachfolgenden Tabelle aufgeführt.

Rezept ur	Spritzneigung	Kleistermenge
1	++++	++++
2	++	++
3	++	++
4	+	+
5	+	+

Dabei steht +++++ für sehr wenige Spritzer/satten Auftrag, hohe Auftragsmenge
 +++ für einige Spritzer/guten Auftrag, brauchbare Auftragsmenge
 ++ für mäßig viele Spritzer/mäßigen Auftrag
 + für viele Spritzer/schlechten Auftrag, geringe Auftragsmenge

Patentansprüche

- 1 Bindemittelzusammensetzung, mindestens enthaltend mindestens 10 Gew.-% eines teilchenförmigen retardierten Polysaccharids oder eines Gemischs aus zwei oder mehr solcher teilchenförmigen retardierten Polysaccharide und mindestens 3 Gew.-% eines teilchenförmigen natürlichen oder synthetischen Schichtsilikats oder eines Gemischs aus zwei oder mehr natürlicher oder zwei oder mehr teilchenförmiger synthetischer Schichtsilikate oder ein Gemisch eines oder mehrerer natürlicher und eines oder mehrerer synthetischer Schichtsilikate.
- 2 Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß sie als retardiertes Polysaccharid mindestens einen Celluloseether enthält.
- 3 Zusammensetzung nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß sie noch mindestens ein synthetisches Polymeresat enthält.
- 4 Zusammensetzung nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß sie als Schichtsilikat ein Schichtsilikat vom Hectorit-Typ enthält.
- 5 Zusammensetzung nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß das Schichtsilikat ein synthetisches Schichtsilikat ist.
- 6 Zusammensetzung nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß das Gewichtsverhältnis von Polysaccharid oder Polysacchariden zu Schichtsilikat oder Schichtsilikaten 1 : 4 bis 4 : 1 beträgt.
- 7 Zusammensetzung nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß 8 Gew.-% oder weniger des teilchenförmigen retardierten Polysaccharids eine Teilchengröße von mehr als 200 µm aufweisen.
- 8 Zusammensetzung nach einem der Ansprüche 1 bis 7, dadurch gekennzeichnet, daß 80 Gew.-% oder mehr des teilchenförmigen retardierten Polysaccharids eine Teilchengröße von 0,125 bis 0,2 µm aufweisen.
- 9 Zusammensetzung nach einem der Ansprüche 1 bis 8, dadurch gekennzeichnet, daß das Verhältnis der Teilchengrößen des retardierten Polysaccharids zur Teilchengröße des Schichtsilikats 10 : 1 bis 1 : 10 beträgt.
- 10 Zusammensetzung nach einem der Ansprüche 1 bis 9, dadurch gekennzeichnet, daß sie 0,05 bis 3 Gew.-% einer wasserlöslichen Base enthält.
- 11 Klebstoffzubereitung, mindestens enthaltend 20 Gew.-% Wasser und mindestens 1 Gew.-% einer Zusammensetzung gemäß einem der Ansprüche 1 bis 10.
- 12 Klebstoffzubereitung nach Anspruch 11, dadurch gekennzeichnet, daß sie mindestens 40 Gew.-% Wasser enthält.
- 13 Verfahren zur Herstellung einer Klebstoffzubereitung bei dem eine Bindemittelzusammensetzung nach einem der Ansprüche 1 bis 10 mit Wasser vermischt wird.
- 14 Verwendung einer Zusammensetzung gemäß einem der Ansprüche 1 bis 10 zur Herstellung von Klebstoffen.

- Leerserte -

United States Patent [19]
Varga et al

[11] Patent Number 4,497,919
[45] Date of Patent: Feb 5, 1985

[54] EMULSION POLISH COMPOSITIONS

- [36]

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[75] Inventors Stephen L. Varga, Evanston Donald
P. Mattz, Chicago, both of Ill.

[73] Assignee: Turtle Wax, Inc., Chicago, Ill.

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[51] Int. Cl.³ C09G 1/04; C09G 1/08,
C09G 1/10; C09G 1/12

[52] U.S. CL. 524/10; 252/8 57,
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524/313, 524/339; 524/444, 524/456

[58] Field of Search .. . 524/42 276, 10, 277
524/221, 72, 313, 339, 37 45 46, 444, 456, 506,
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Primary Examiner—Allan M. Lieberman

[57]

ABSTRACT

A water-in-oil emulsion polish composition suitable for treating natural and synthetic leather articles comprises a wax mixture, a film forming agent, a film-modifying agent, a nonionic emulsifying agent, a dispersing agent, a thickening agent, a solvent, and a preservatives in water. The composition is substantially self polishing and provides a durable natural looking high gloss.

18 Claims, No Drawings

137

136

EMULSION POLISH COMPOSITIONS

TECHNICAL FIELD

This invention relates to emulsion polish compositions suitable for treating natural and synthetic leather articles. More particularly, the compositions are water-in-oil emulsions suitable for use as shoe cream polish compositions for providing a durable finish and gloss with a minimum of buffing required.

BACKGROUND OF THE INVENTION

A great number of finished leather products require maintenance polishes to preserve, clean and water-proof them. Footwear, in particular, requires a leather-care product that helps prevent the leather from drying out and forming unsightly cracks in the creases of the shoe uppers. Shoe polishes, therefore, are used to impart a high gloss, maintain the supple hand of the leather, and increase the leather's resistance to weathering, scuffing and scratching.

One of the problems of conventional shoe polishes is providing, on a flexible surface, a protective finish which is both lustrous, durable, and water-resistant. The majority of shoe polishes are of the solvent paste type based on solvents and waxes. While solvent pastes clean the shoe well while the paste is being applied, the resulting film dries to a dull finish and must be buffed to produce a high natural shine. A further disadvantage of the solvent paste polishes is that the protective effect they produce is only temporary. Consequently, they must be applied frequently in order to properly protect the footwear leather.

Another disadvantage of a wax-based shoe polish is that the finish tends to deluster on exposure to moisture from rain, water splashing or puddles. Additionally, layers of wax can build up on the leather surface. This resulting buildup resists subsequent reapplications of polish, thus extensive buffing is required in order for a new layer of polish to properly "take" on the leather.

Some attempts have been made to overcome the drawbacks of solvent paste polishes by formulating emulsion cream polishes. These polishes are emulsions of waxes, solvents and water. However, the finish produced suffers from the same drawbacks as those obtained from other wax based polishes.

Further attempts to overcome the drawbacks of wax-based polishes include the formulation of self-polishing or dry bright liquids. Self-polishing liquids are generally comprised of a blend of a fairly soft acrylic polymer emulsion, a resin adduct leveling resin, a wax emulsion (frequently a low molecular weight polyethylene emulsion) and modifiers, such as a leveling plasticizer and a coalescing solvent. The ratio of polymer/resin/wax is varied depending on the degree of buffability desired. Usually, a higher wax content gives the polish better buffing properties. The liquid polishes clean the shoes well, particularly when they are applied with foam sponge applicators which provide abrasive cleaning. The emulsions apply a film of glossy polish that, in most cases, does not require buffing to obtain a high shine. However, the shine produced tends to have an unnatural plastic-like appearance.

Thus, there is a need for self polishing liquids and emulsion cream products that provide a flexible finish coating having a natural high gloss that is durable and scuff-proof.

SUMMARY OF THE INVENTION

This invention contemplates an emulsion-type polish composition suitable for treating natural and synthetic leather articles that provides a durable high-gloss finish that is substantially self-polishing. More particularly, the present polish composition is a water in-oil (w/o) emulsion comprising a wax mixture, a film forming agent, a film modifying agent, a nonionic emulsifying agent, an anionic dispersing agent, a thickening agent, a solvent, a preservative and water. The composition can also contain pigments and dyes to provide a coloring shoe polish.

The composition is substantially a drip-free emulsion cream. Surprisingly the composition retains the natural, mirror like sheen benefits traditionally associated with wax polishes without the corresponding drawbacks previously described. Further, the composition provides the benefits of flexible, durable films associated with appropriately plasticized polymer and resin films as disclosed herein, while providing a natural-looking, durable high gloss on the treated leather surface.

The term "leather" as used herein includes natural animal leather and any of the synthetic leather-like materials used by those skilled in the art for covering shoes, boots and like footwear. In its presently preferred use, the composition is applied to footwear but is not meant to be so limited. It is to be understood that the present composition can be used to treat such leather articles as handbags, belts, chair seats, gloves, saddles, bridles, book bindings, artwork trappings, suitcases, briefcases, and the like, having a glossy finish. The term "self-polishing" as used herein means that the composition produces a highly glossy film on air drying. The treated leather can be lightly buffed to speed up the drying process, but buffing is not necessary. It is to be understood that the term "buffing" and its various grammatical forms refers to the use of cloth, sponges, brushes and the like commonly used by consumers to rub leather articles to a high sheen finish.

Still further benefits and advantages will become apparent to those who are skilled in the art from the detailed description of the invention, the examples, and the claims which follow.

DESCRIPTION OF PREFERRED EMBODIMENTS

The polish composition of this invention is a water-in-oil (w/o) emulsion constituted by:

(a) a wax mixture of about 1 part by weight mineral ester wax having an acid value of about 0 to about 55, about 4 parts by weight partly saponified mineral ester wax having an acid value of about 10 to about 45, about 1.5 parts by weight insect wax having an acid value of about 0.2 to about 24;

(b) a film forming agent that is a curable material selected from the group consisting of a curable emulsion polymer, a curable resin, a curable aminofunctional silicone, and mixtures thereof;

(c) a film modifying agent that is a surfactant selected from the group consisting of a surface-active aminofunctional silicone, a linear arylalkyl modified polydialkyl siloxane, a linear alkylated copolymer of vinylpyrrolidone with a long chain (C₁₂ to C₂₂) alpha olefin, and mixtures thereof;

(d) a nonionic emulsifying agent having an HLB* value of about 10 to about 15 and selected from the group consisting of an oil-soluble polyglycerol ester of

a hydrophobic fatty acid capable of forming a w/o emulsion, a water-soluble C_8 to C_{18} alkylphenol ether with ethylene oxide having an average number of ethylene oxide units of about 5 to about 70, and mixtures thereof;

"HLB-hydrophile-lipophile balance.

(e) an effective amount of an anionic water-soluble dispersing agent;

(f) a thickening agent selected from the group consisting of a colloidal alkali metal or alkaline earth metal aluminum silicate, a water-soluble nonionic or anionic ester or ether of cellulose, and mixtures thereof;

(g) an organic solvent selected from the group consisting of a liquid aliphatic hydrocarbon, a liquid aromatic hydrocarbon, and an oleochemical liquid having an average kauri butanol value above 50, and mixtures thereof;

(h) an effective amount of a preservative; and

(i) deionized water

The composition can further include a C_8 to C_{12} alkylolamide that is the reaction product of about 2 moles of C_8 to C_{12} alkanolamine and about 1 mole of C_8 to C_{20} fatty acid, and effective amounts of a dye. The term "dye" as used herein includes water-soluble dyes, oil-soluble dyes, pigments and mixtures thereof capable of producing a coloring shoe polish.

"Wax mixture" as used herein refers to the above ratio of waxes in combination present in the final product. Thus, the waxes can be either premixed and then added to the composition during manufacture, or the individual waxes can be added sequentially to provide the aforementioned ratio in the final product. A particularly preferred embodiment of this invention comprises a wax mixture present in an amount of about 6 to about 7 weight percent, preferably above 6.2 to about 6.8 weight percent, in the composition.

Waxes which can be employed in the polish compositions of this invention are well known to those skilled in the art. Examples of suitable mineral ester waxes include montan, ozocerite (ceresin), paraffin (oxidized), microcrystalline (oxidized) and synthetic waxes such as ethylenic polymers (oxidized polyethylene), polyol ether-esters and mixtures thereof. A particularly preferred montan wax is commercially available from the American Hoechst Corporation, Industrial Chemicals Division sold under the trademark Hoechst Wax E, F, KPS, KSL, RT, KST ester wax series. Particularly preferred is Hoechst Wax F having an acid value of 6 to 10.

Acid value is the measure of the free fatty acidity, and represents the number of milligrams of potassium hydroxide that are required to neutralize the free fatty acid contained in one gram of an oil or fat. The analytical methods for determining acid value are well known in the art and need not be described herein.

Suitable mineral ester waxes that are partly saponified are available commercially from the American Hoechst Corporation, Industrial Chemicals Division as the montan-based series marketed under the trademark Hoechst Wax OP, O OM FL. Particularly preferred is Hoechst Wax OM having an acid value of 20 to 25. Examples of suitable insect waxes include beeswax, Chinese insect wax and shellac wax. Particularly preferred is natural beeswax having an acid value of about 17 to about 24.

It is to be understood that synthetic wax substitutes having the same physical-chemical constants as the corresponding natural wax can be used in the composition in place of the natural wax for economic considerations and are intended to fall within the scope of this

invention. It is further to be understood that the properties of the composition can be varied, as desired, by including animal waxes such as spermaceti and its synthetic substitutes, mink oil, lanolin and the like; vegetable waxes such as carnauba, candelilla, bayberry, jojoba oil, hydrogenated jojoba oil and its synthetic substitutes, and sugar cane wax.

In a preferred embodiment of the invention, the wax mixture comprises about 1 part by weight of a mineral ester wax having an acid value of about 6 to about 10, about 4 parts by weight of a partly saponified mineral ester wax having an acid value of about 20 to about 25, about 1.5 parts by weight insect wax having an acid value from about 17 to about 24. Particularly preferred is a wax mixture comprising about 1 part by weight montan wax having an acid value of about 6 to about 10, about 4 parts by weight partly saponified montan based wax having an acid value of about 20 to about 25, and about 1.5 parts by weight beeswax having an acid value of about 17 to about 24.

The w/o emulsion of this invention can be prepared by conventional techniques well known in the art. An appropriate procedure is described below in Example 1. Persons skilled in the art will appreciate that the amount of water present can vary in a range of about 25 to 75 weight percent as required for the product form desired. The compositions of this invention have exceptionally good product performance with respect to speed of application, quality of gloss, and durability of the finish.

It is believed that the excellent product performance results from the combination of the various individual components as disclosed herein. Specifically it is believed that the product performance is partly due to the wax mixture as disclosed herein in combination with nonionic emulsifying agents selected from the group consisting of oil-soluble polyglycerol esters of hydrophobic fatty acids, water-soluble alkylphenol ethers having an average number of ethylene oxide units of about 5 to about 70 and mixtures thereof the oil-soluble emulsifying agent being capable of forming a w/o emulsion. It is to be understood that the term "fatty acids" includes fatty acids derived from animal fats, and vegetable oils as well as free fatty acids. It is to be understood further that the term "hydrophobic fatty acids" includes the aforementioned acids, as well as resin acids, naphthenic acids and mixtures thereof. See, for example, Schwartz and Perry, *Surface-Active Agents*, published by Interscience Publishers, Inc., 1949.

A preferred embodiment comprises about 0.5 to about 2.5 weight percent, preferably about 0.5 to about 2.0 weight percent, nonionic emulsifying agent selected from the group consisting of an ester of an unsaturated C_{18} fatty acid with a glycerin polymer containing an average of 4 glycerin units, and a C_8 to C_9 alkylphenol ether having an average number of ethylene oxide units of about 12 to about 13, and mixtures thereof. A particularly preferred w/o emulsifying agent is Witconol 14, described by Material Number 18 in the glossary below, preferably present in amounts of about 1 to about 2 weight percent, more preferably in the range of about 1.4 to about 1.6 weight percent.

It is also believed that the product performance is due in part to the combination of emulsion polymer film-forming agents and surface-active polymeric film-modifying agents described herein. The exact interaction between the components and the proportions present in

the formula is not fully understood. However, the film-modifying agents are believed to function not only as plasticizers for the film forming agents but as auxiliary film forming agents as well.

In a preferred embodiment, the film forming agents comprise about 0.2 to about 8 solids weight percent, preferably about 7.2 to about 7.5 solids weight percent, selected from the group consisting of cyclized rubbers, acrylic ester polymers, drier modified alkyd resins, aminofunctional silicone resins and mixtures thereof. Examples of particularly preferred commercially available film forming agents are described in the glossary below by material numbers 1, 2, 11, 12, 13 and 14.

In another preferred embodiment, the film-modifying agent comprises about 0.05 to about 0.5 solids weight percent, preferably from about 0.05 to about 0.4 solids weight percent, selected from the group consisting of a surface active aminofunctional silicone, a nonreactive, linear arylalkyl modified polydi(C₁ to C₄ alkyl)siloxane, a linear alkylated copolymer of vinylpyrrolidone with a long chain (C₁₂ to C₁₆) alpha olefin, and mixtures thereof. Particularly preferred film-modifying agents are the C₁₆ alkylated vinylpyrrolidone copolymers having an average molecular weight ranging from about 7,300 to about 8,600 and commercially available under the trademark Ganex®. Specifically preferred film-modifying agents are described in the glossary below by Material Number 7 and Material Number 15.

Dispersing agents are commonly used in polish compositions and such ingredients are well known to the skilled artisan. For the compositions of this invention, however, anionic dispersing agents that are water-soluble and hydrocarbon insoluble are preferred, present in an amount in the range of about 0.05 to about 0.15 weight percent, preferably about 0.08 to about 0.12 weight percent. A specifically preferred dispersing agent is illustrated in the glossary below by Material Number 6.

In the presently preferred embodiment, the viscosity of the composition is controlled by means of thickening agents included in amounts of about 0.01 to about 0.5 weight percent, preferably about 0.15 to about 0.35 weight percent, selected from the group consisting of a colloidal alkaline earth metal aluminum silicate, a water-soluble nonionic ether of cellulose, a water-soluble anionic ester of cellulose and mixtures thereof. Suitable examples of thickening agents are described in the glossary below by Material Number 4, Material Number 10, and Material Number 17. Such thickeners are well known in the art as being capable of forming thixotropic, non-dripping liquids, creams, and pastes.

The viscosity of the present compositions can be further increased by including nonionic wetting agents commonly known as high activity alkylolamides that are the reaction product of 2 moles of a C₈ to C₁₂ alkylolamine and 1 mole C₈ to C₂₀ fatty acid or fatty acid oil, present in an amount of about 0.3 to about 0.7 weight percent. A particularly preferred alkylolamide is a reaction product of 2 moles diethanolamine and 1 mole coconut oil and is illustrated in the glossary below by Material Number 5.

Suitable organic solvents commonly employed in polish formulations are well known in the art. In a preferred embodiment, a solvent that is a member of the group consisting of an aliphatic liquid hydrocarbon, an aromatic liquid hydrocarbon and an oleo-resinous liquid having an average kauri-butanol value above 50 are preferably present in an amount of about 4 to about 20

weight percent, preferably about 12 to about 20 weight percent.

The solvent power of hydrocarbons is expressed in terms of kauri-butanol values, a term well-known to those skilled in the art. Methods of determining the kauri-butanol values are also well known and need not be described herein. Exemplary organic solvents include aliphatic hydrocarbon liquids such as mineral spirits and dipentene; aromatic hydrocarbon liquids such as toluene, xylene, and naphtha; oleo-resinous liquids such as pine oil and turpentine; and halogenated hydrocarbons, such as methylene chloride and perchloroethylene. See, for example, Kirk-Othmer, *Encyclopedia of Chemical Technology*, Volume 21 third edition, Chapter on Industrial Solvents, published by the Interscience Encyclopedia, Inc. and Scheffler and Jacobs, *The Handbook of Solvents*, published by D. Van Nostrand Co. in 1953. A particularly preferred solvent is an oleo-resinous solvent, such as steam-distilled turpentine having a kauri-butanol value of about 56.

The composition can also contain abrasives, corrosion inhibitors, alcoholic co-solvents, fragrance and other ingredients normally used in making polishes selected for their purposes well known to the skilled artisan. It should also be noted that although the compositions of this invention have been described in connection with liquids, creams and paste forms, it is not necessarily so limited. It is to be understood that the compositions can be prepared as pressurized products for use as aerosol polishes in combination with the appropriate propellant mixture and dispenser valve. It is further to be understood that pigments can be included to provide opaque hiding power particularly for use in polishes for children's shoes.

This invention is further illustrated in the following examples, which are not intended to be limited.

BEST MODES FOR CARRYING OUT THE INVENTION

A. Glossary of Materials

In the examples which follow, certain components of the composition are referred to, for easy reference and convenience, by their commercial trademark designation, common name or CIPA name as provided immediately here below. CIPA names are defined in the CIPA Cosmetic Ingredient Dictionary, Third Edition, published by Cosmetic, Toiletry and Fragrance Association, Inc. incorporated herein by reference.

1. Acryloid B-67MT. An acrylic ester polymer dispersed in mineral thinner, sold by Rohm & Haas Company, Inc., Philadelphia, Pa.

2. Alper C-8415. A cyclized rubber, sold by the American Hoechst Corporation, Somerville, N.J.

3. Beeswax. Purified wax rendered from the honeycomb of the Apidae (honeybee), having an acid value of about 17 to about 24 and a melting point of about 62 to about 65 degrees C.

4. Cellulose gum. CIPA name for an anionic sodium salt of the polycarboxymethyl ester of cellulose (CAS #9004-32-4), such as the CMC series, sold by Hercules, Inc., Wilmington, Del.

5. Cocamide DEA. CIPA name for a mixture of ethanolamides of coconut oil (CAS #61791-31-9; 68603-42-9), such as the high activity alkylolamides, sold by the Stepan Company, Northfield, Ill., under the NINOL® trademark, Series AA-62 EXTRA, 2012 EXTRA, P621 and 1128 EXTRA.

6. Darvan #2. A sodium salt of polysulfonated lignin (CAS #8061-31-6), sold by the R. T. Vanderbilt Company, Inc., Norwalk, Conn.

7 Ganex @V 216. A linear alkylated copolymer of vinylpyrrolidone and a C₁₆ alpha olefin having an average molecular weight of about 7,300 dispersed in toluene, sold by the GAF Corporation, New York, N Y CTFA name PVP/Hexadecene copolymer

8 Hoechst Wax F. A montan wax obtained by extraction of lignite having an acid value of about 6 to about 10, sold by the Industrial Chemicals Division of American Hoechst Corporation, Somerville, N.J

9 Hoechst Wax OM. A partly saponified montan-based wax having a saponification value of about 110 to about 125 and an acid value of about 20 to about 25, sold by the Industrial Chemicals Division of American Hoechst Corporation, Somerville, N.J

10. Methocel J 75 MS. A propylene glycol ether of methyl cellulose having an average propylene glycol ether molar substitution of 0.7 to 1.0 percent, sold by Dow Chemical Co. USA, Midland, Mich. (CAS #9004-65-3).

11 Silicone Alkyd Resin 6260. A 30% silicone-modified air dry soya alkyd resin dispersion in mineral spirits, sold by the Chemical Products Division of Cargill, Carpentersville, Ill.

12. Silicone 803 Resin. An aminofunctional silicone resin dispersion in xylene, sold by the Dow Corning Corporation, Midland, Mich.

13 Silicone 2059 Emulsion. An aqueous cationic emulsion of an aminofunctional silicone polymer, sold by the Silicone Products Department, General Electric Company, Waterford, N Y

14. Silicone 2079 Emulsion. An aqueous high viscosity aminofunctional silicone polymer emulsion, sold by the Silicone Products Department, General Electric Company, Waterford, N Y

15 Silicone L-42. A surfactant that is a trimethylsiloxy end-blocked copolymer of phenylethyl methylsiloxy groups and dimethylsiloxy groups in the form of a clear liquid having a viscosity at 25° C. of 400±200 centistokes, specific gravity 25/25° C. of 1.020-1.040, melting point of -64° C., flash point of 250° F minimum, surface tension of 25° C. of 22.0 dynes/cm and 15% maximum volatility at 150° C., 24 hours. This is a nonreactive, organomodified silicone fluid containing pendant aralkyl moieties linked to silicon via Si-C bonds, sold by the Union Carbide Corporation, Sisterville, W Va.

16. Triton X 102. A nonionic polyoxyethylene (13) octylphenyl ether (CAS #9002 93-1 9004-87-9, 9036-19-5) having an average of 12 to 13 ethylene oxide units and an HLB value of 14.6, sold by the Rohm & Haas Company, Inc. Philadelphia, Pa.

17 Veegum @T. A complex colloidal magnesium aluminum silicate, sold by the R. T. Vanderbilt Company, Inc. Norwalk, Conn.

18 Witconol 14. A nonionic, oil-soluble ester of oleic acid with a glycerin polymer containing an average of 4 glycerin units, sold by the Organics Division of Witco Chemical Co., Inc., New York, N Y

EXAMPLE 1 CREAM POLISH EMULSION

This example demonstrates a preferred composition for an unpigmented cream polish emulsion. The composition had the following formulation.

Ingredient		Weight Percent (as is basis)
Phase I		
Acrylon 867MT (43%)		0.500 ^(a)
Alpen C-8415		1.300
Beeswax		1.500
Ganex @ V-216 (94%)		0.300 ^(a)
Hoechst Wax F		1.000
Silicone Alkyd Resin #6260 (80%)		0.300 ^(a)
Silicone 803 Resin (30%)		1.00 ^(a)
Silicone L-42 (13%)		0.100 ^(a)
Triton X-102		0.800
Turpentine, steam distilled		12.900
Witconol 14		1.300
1,2-dibromo-3,4-dicyanobutane (25% in H ₂ O)		0.030
Phase II		
Cellulose Gum		0.02
Darvan #2		0.10
Methocel J75MS		0.225
Veegum @ T		0.010
1,2-dibromo-3,4-dicyanobutane (25% in H ₂ O)		0.010
Water Deionized		45.713
Phase III		
Silicone 2079 Emulsion (80%)		7.650 ^(a)
Silicone 2059 Emulsion (60%)		0.850 ^(a)

^(a)Weight percent actual resin solids = 0.223
^(b)Weight percent actual polymer solids = 0.288
^(c)Weight percent actual resin solids = 0.800
^(d)Weight percent actual resin solids = 0.930
^(e)Weight percent actual polymer solids = 0.085
^(f)Weight percent actual polymer solids = 4.390
^(g)Weight percent actual polymer solids = 0.510

The cream polish was prepared using the following emulsification technique for preparing w/o emulsions. The solid ingredients of Phase I were charged into the first master vessel with solvent and heated to about 190° F ± 5° F with stirring until the waxes melted and the phases became clear. The liquid portions of Phase I were then added with agitation. The resulting temperature of the oil phase cooled to 165° F ± 5° F. The thickener, Phase II, was separately prepared in a second vessel. The water of Phase II was charged into the vessel at 130° F ± 5° F and the preservative was gradually added to the vessel with agitation. The remaining ingredients of Phase II were then slowly added to the vessel and vigorously stirred until homogeneous. The resulting composition of Phase II was subsequently run through a suitable homogenizer, such as a Manton-Gaulin Homogenizer, at 1500 psi and filtered through a #800 filter bag (800 microns).

The cream polish emulsion composition was packaged in glass jars and in cans for storage. If desired, the composition can be packed in tubes, in plastic bottles fitted with appropriate sponge or cloth applicators, and in pressurized aerosol cans charged with appropriate compatible propellants and fitted with an appropriate dispenser valve.

The composition provided the desirable advantages of leather preservation compositions, particularly suitable for leather shoe uppers. The polish was easy to apply for leather articles, spread easily and provided a durable, natural looking high gloss on drying with minimal or no buffing needed.

The composition of this invention enhances the gloss on new leather shoes. Scuffs absorb the dye and are covered by the composition to form a uniform gloss. Leather shoes that have been waxed previously accept the composition and develop a quality gloss. Heavy prior wax buildup is not dissolved. This composition is

water repellent, however prolonged exposure to water does degrade water repellency. The finish does not water spot. Gloss retention in shoe creases is equivalent to conventional polishes.

EXAMPLE 2 BROWN SHOE POLISH

This example demonstrates a pigment-containing brown shoe polish cream. The cream had the following composition.

Ingredient	Weight Percent (as is basis)
Emulsion composition of Example 1	98.7
Oil-soluble brown dye	0.8
Cocamide DEA	0.5
	100.0

The composition was prepared by charging each ingredient into the vessel in sequence stirring in each ingredient until the composition is homogeneous. The procedure was carried out at substantially ambient room temperature conditions by using a liquid cocamide DEA, such as NINOL®2012 EXTRA described in the glossary above.

Alternatively the composition can be prepared by following the method of Example 1 and incorporating the dye and cocamide DEA with the ingredients of phase I.

The polish provided a durable, natural looking high gloss to brown leather shoes that required minimal buffing. Also, less color ruboff as compared to conventional shoe polishes is experienced.

The present invention has been described with respect to preferred embodiments. It will be clear to those skilled in the art that modifications and/or variations of the disclosed compositions and methods can be made without departing from the scope of the invention set forth herein. The invention is defined by the claims that follow.

We claim:

1. A water-in-oil emulsion composition suitable for treating natural and synthetic leather articles comprising:

(a) a wax mixture of about 1 part by weight mineral ester wax having an acid value of about 0 to about 55, about 4 parts by weight partly saponified mineral ester wax having an acid value of about 10 to about 45, about 1.5 parts by weight insect wax having an acid value of about 0.2 to about 24;

(b) a film forming agent that is a curable material selected from the group consisting of a cyclized rubber, an acrylic ester polymer, a drier-modified alkyl resin, an aminofunctional silicone, and mixtures thereof;

(c) a film modifying agent that is a surfactant selected from the group consisting of a surface-active aminofunctional silicone resin, a linear arylalkyl modified polydialkyl siloxane, a linear alkylated copolymer of vinylpyrrolidone with a long chain C₁₂ to C₂₁ alpha olefin, and mixtures thereof;

(d) a nonionic, emulsifying agent having an HLB value of about 10 to about 15 and selected from the group consisting of an oil-soluble polyglycerol ester of a hydrophobic fatty acid capable of forming a water-in-oil emulsion, a water-soluble C₈ to C₁₈ alkylphenol ether with ethylene oxide having

an average number of ethylene oxide units of about 5 to about 70, and mixtures thereof,

(e) about 0.05 to about 0.15 weight percent of an effective amount of an anionic, water-soluble and hydrocarbon insoluble dispersing agent;

(f) about 0.01 to about 0.5 weight percent of a thickening agent selected from the group consisting of a colloidal alkali metal aluminum silicate, a colloidal alkaline earth metal aluminum silicate, a water-soluble nonionic ester of cellulose, a water-soluble anionic ester of cellulose, a water-soluble nonionic ether of cellulose, a water-soluble anionic ether of cellulose, and mixtures thereof;

(g) about 4 to about 20 weight percent of an organic solvent selected from the group consisting of a liquid aliphatic hydrocarbon, a liquid aromatic hydrocarbon, and an oleoresinous liquid, said solvent having an average kauri-butanol value about 50, and mixtures thereof,

(h) an effective amount of a preservative; and

(i) about 25 to 75 weight percent of deionized water; wherein the wax mixture, the film-forming agent, the film-modifying agent and the nonionic emulsifying agent are present in amounts effective to produce a high gloss that is substantially self-polishing.

2. The composition of claim 1 wherein the composition further includes a C₈ to C₃₁ alkylolamide that is the reaction product of about 2 moles C₂ to C₁₂ alkanolamine and about 1 mole C₈ to C₂₀ fatty acid and effective amount of a dye, said dye being constituted by dyes selected from the group consisting of a water-soluble dye, an oil-soluble dye, a pigment, and mixtures thereof and being capable of producing a coloring shoe polish.

3. The composition of claim 2 wherein the alkylolamide is the reaction product of 2 moles diethanolamine and 1 mole coconut fatty acid.

4. The composition of claim 1 wherein the wax mixture comprises about 1 part by weight mineral ester wax having an acid value of about 6 to about 10, about 4 parts by weight partly saponified mineral ester wax having an acid value of about 20 to about 25, about 1.5 parts by weight insect wax having an acid value of about 17 to about 24.

5. The wax mixture of claim 1 wherein the mineral ester wax is montan wax.

6. The wax mixture of claim 1 wherein the partly saponified mineral ester wax is montan-based.

7. The wax mixture of claim 1 wherein the insect wax is beeswax.

8. The wax mixture of claim 4, wherein the mineral ester wax is montan wax, the partly saponified mineral ester wax is montan-based, and the insect wax is beeswax.

9. The composition of claim 8 wherein the alkyd resin is an about 30 percent silicone-modified air dry soya alkyd resin.

10. The composition of claim 1 wherein the nonionic emulsifying agent is selected from the group consisting of an ester of oleic acid and a glycerin polymer containing an average 4 glycerin units, a C₈ to C₉ alkylphenol ester having an average number of ethylene oxide units of about 12 to about 13, and mixtures thereof.

11. The composition of claim 1 wherein the dispersing agent is a complex polymerized alkali metal salt of a polysulfonated lignin.

12. The composition of claim 1 wherein the thickening agent is selected from the group consisting of a

11

magnesium aluminum silicate, carboxy-, alkyl-, and hydroxy-substituted cellulose, and mixtures thereof

13. A self-polishing shoe cream polish composition comprising:

about 6 to about 7 weight percent of a wax mixture comprised of about 1 part by weight mineral ester wax having an acid value of about 6 to about 10, about 4 parts by weight partly saponified mineral ester wax having an acid value of about 20 to about 25, and about 1.5 parts by weight insect wax having an acid value of about 17 to about 24;

about 0.2 to about 8 solids weight percent of a film-forming agent selected from the group consisting of a cyclized rubber, an acrylic ester polymer, a silicone-modified soya alkyd resin, an aminofunctional silicone resin and mixtures thereof;

about 0.05 to about 0.4 solids weight percent of a film-modifying agent selected from the group consisting of a surface active aminofunctional silicone, a linear arylalkyl modified polydialkyl siloxane, a linear alkylated copolymer of vinylpyrrolidone with a C₁₆ alpha olefin, and mixtures thereof;

about 0.5 to about 2.5 weight percent of a nonionic emulsifying agent selected from the group consisting of an ester of a hydrophobic C₁₂ to C₂₀ fatty acid and a glycerin polymer containing an average of 4 glycerin units, a C₈ to C₉ alkylphenol ether with ethylene oxide having an average number of ethylene oxide units of about 12 to 13, and mixtures thereof;

about 0.05 to about 0.15 weight percent of a water soluble and hydrocarbon insoluble anionic dispersing agent;

about 0.01 to about 0.5 weight percent of a thickening agent selected from a group consisting of a colloidal magnesium aluminum silicate, a water-soluble nonionic ether of cellulose, a water-soluble anionic ester of cellulose, and mixtures thereof;

about 4 to about 20 weight percent of an organic solvent selected from the group consisting of a liquid aliphatic hydrocarbon, a liquid aromatic hydrocarbon and an oleoresinous liquid having a kauri-butanol value above 50, and mixtures thereof; an effective amount of preservative; and

about 25 to 75 weight percent of deionized water

14. The composition of claim 13 further including about 0.3 to about 0.7 weight percent of an alkylolamide that is the reaction product of about 2 moles diethanolamine and about 1 mole coconut fatty acid, and about 0.5 to about 1 weight percent of a dye.

15. A self polishing shoe cream polish composition comprising:

about 6.2 to about 6.8 weight percent of a wax mixture comprised of about 1 part by weight montan wax having an acid value of about 6 to about 10, about 4 parts by weight partly saponified montan-based wax having an acid value of about 20 to about 25, and about 1.5 parts by weight beeswax having an acid value of about 17 to about 24;

about 7.2 to about 7.5 solids weight percent of a film-forming agent selected from the group consisting of a cyclized rubber, an acrylic ester polymer, a silicone-modified soya alkyd resin, an aminofunctional silicone resin and mixtures thereof;

about 0.8 to about 0.9 solids weight percent of a film modifying agent selected from the group consisting of a surface active aminofunctional silicone, a linear arylalkyl modified polydialkyl siloxane, a linear

12

copolymer of vinylpyrrolidone with a C₁₆ alpha olefin, and mixtures thereof,

about 0.5 to about 2.0 weight percent of a nonionic emulsifying agent selected from the group consisting of an ester of unsaturated C₁₈ fatty acid with a glycerin polymer containing an average of 4 glycerin units, a C₈ alkyl phenol ether with ethylene oxide having an average number of ethylene oxide units of about 12 to about 13, and mixtures thereof, about 0.08 to about 0.12 weight percent of a water-soluble and hydrocarbon insoluble anionic dispersing agent;

about 0.15 to about 0.35 weight percent of a thickening agent selected from the group consisting of a colloidal magnesium aluminum silicate, a water-soluble nonionic ether of cellulose, a water-soluble anionic ester of cellulose, and mixtures thereof,

about 12 to about 20 weight percent of an organic solvent selected from the group consisting of a liquid aliphatic hydrocarbon, a liquid aromatic hydrocarbon and an oleoresinous liquid having a kauri-butanol value above 50, and mixtures thereof, an effective amount of a preservative; and

about 25 to 75 weight percent of deionized water

16. The composition of claim 15 further including about 0.3 to about 0.7 weight percent of an alkylolamide that is the reaction product of about 2 moles diethanolamine and about 1 mole coconut fatty acid and about 0.5 to about 1 weight percent of a dye.

17. The composition of claim 1 wherein the composition is in the form of a thixotropic liquid, cream, paste, or aerosol spray

18. A water-in-oil emulsion composition suitable for treating natural and synthetic leather articles comprising:

(a) about 6 to 7 weight percent of a wax mixture of about 1 part by weight mineral ester wax having an acid value of about 6 to about 10, about 4 parts by weight partly saponified mineral ester wax having an acid value of about 20 to about 25, and about 1.5 parts by weight insect wax having an acid value of about 17 to about 24;

(b) about 0.2 to 8 weight percent of a film-forming agent that is a curable material selected from the group consisting of a cyclized rubber, an acrylic ester polymer, a drier-modified alkyl resin, an aminofunctional silicone resin, and mixtures thereof;

(c) about 0.05 to 0.5 solids weight percent of a film-modifying agent that is a surfactant selected from the group consisting of a surface-active aminofunctional silicone, a linear arylalkyl modified polydialkyl siloxane, a linear alkylated copolymer of vinylpyrrolidone with a long chain C₁₂ to C₂₂ alpha olefin, and mixtures thereof;

(d) about 0.5 to about 2.5 weight percent of a non-ionic, emulsifying agent having an HLB value of about 10 to about 15 and selected from the group consisting of an oil-soluble polyglycerol ester of a hydrophobic fatty acid capable of forming a water-in-oil emulsion, a water-soluble C₈ to C₁₈ alkyl phenol ether with ethylene oxide having an average number of ethylene oxide units of about 5 to about 70, and mixtures thereof;

(e) about 0.05 to about 0.15 weight percent of an effective amount of an anionic, water-soluble and hydrocarbon insoluble dispersing agent,

13

(f) about 0.01 to about 0.5 weight percent of a thickening agent selected from the group consisting of a colloidal alkali metal aluminum silicate, a colloidal alkaline earth metal aluminum silicate, a water-soluble nonionic ester of cellulose, a water-soluble anionic ester of cellulose, a water-soluble nonionic ether of cellulose, a water-soluble anionic ether of cellulose, and mixtures thereof;

14

(g) about 4 to about 20 weight percent of an organic solvent selected from the group consisting of a liquid aliphatic hydrocarbon, a liquid aromatic hydrocarbon and an oleoresinous liquid, said solvent having an average kauri-butanol value about 50, and mixtures thereof,

(h) an effective amount of a preservative; and

(i) about 25 to 75 weight percent of deionized water

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Lederpflegemittel

(57)

Beschrieben wird ein Lederpflegemittel, das im Wesentlichen frei von flüchtigen organischen Lösungsmitteln ist und eine Emulsion von Wachs, Wasser und Emulgator umfasst, dadurch gekennzeichnet, dass es bei einer Temperatur von 23 °C bei 5-minütiger Einwirkung einer Schubspannung von 750 Pa eine maximale Deformation von 0,1 oder weniger und nach 5-minütiger Relaxation eine bleibende Deformation von 50 % der maximalen Deformation oder weniger aufweist. Das Lederpflegemittel umfasst vorzugsweise

- (a) 0,1 bis 15 Gew.-% eines oder mehrerer Wachse eines Tropfpunkts von 95 bis 140 °C,
(b) 0,2 bis 60 Gew.-% eines oder mehrerer Wachse eines Tropfpunkts von 45 bis 90 °C,
(c) 1 bis 15 Gew.-% Emulgator,
(d) 0 bis 20 Gew.-% fakultative Bestandteile und
(e) Differenz auf 100 Gew.-% Wasser

Fakultative Bestandteile sind z. B. Silicone, Minerale und Farbstoffe.

Beschreibung

[0001] Die vorliegende Erfindung betrifft ein Lederpflegemittel, das im Wesentlichen frei von flüchtigen organischen Lösungsmitteln ist, und ein Verfahren zu seiner Herstellung.

[0002] Lederpflegemittel sind farblose oder mit Farbmitteln gefärbte wachshaltige Pasten oder Flüssigkeiten, die nach dem Auftragen auf glattes Leder, z. B. Schuhwerk, durch Polieren des entstandenen Wachsfilms einen hohen Glanz hervorrufen. Man unterscheidet zwischen den sog. Ölwaren und Waren auf wässriger Basis, den sog. Emulsionswaren.

[0003] Zu den Ölwaren gehören die herkömmlichen Schuhcremes. Diese bestehen aus einem Gemisch von Wachsen, z. B. Montanwachs-Derivaten, Mikrowachsen, Ceresin, Carnauba-, Candelillawachs, Stearin, synthetischen Wachsen Paraffinen und Lösungsmittelgemischen, z. B. Testbenzin, Terpentinöl usw. Die Ölware besitzt eine relativ harte, gut verteilbare Konsistenz und wird meist in Dosen abgefüllt. Die Konsistenz der Ölware ist durch ein bestimmtes rheologisches Verhalten gekennzeichnet, das bisweilen als Schollenbruch bezeichnet wird. Unter "Schollenbruch" wird verstanden, dass das Mittel bei der Entnahme aus der Dose bricht und dabei typische Schollen bildet. Diese Erscheinung beruht vermutlich darauf, dass das Mittel bei Einwirkung kleiner Kräfte zunächst elastisch verformt wird und bei Einwirkung größerer Kräfte schließlich bricht, wobei die erhaltenen Bruchstücke ihre ursprüngliche Ausdehnung wieder annehmen. Die Bruchstücke sehen daher wie Schollen aus.

[0004] Ware auf wässriger Basis wird als pastöse Emulsion in Tüben oder als Flüssigkeit in Flaschen angeboten. Es sind auch verdickte Emulsionen bekannt, die in Dosen abgefüllt werden können. Aus der DE-OS 35 41 434 ist eine Lederpflegeemulsion bekannt, die Wachs, Emulgator Wasser und ein anionisches Polysaccharid als Coemulgator enthält. Diese bekannte lösungsmittelfreie Schuhcreme auf Emulsionsbasis weist eine cremeartige Konsistenz auf, die als "löffelbar" bezeichnet werden kann, d. h. bei Entnahme von Produkt mit einem Löffel bleibt ein "Negativabbild" des Löffelrückens erkennbar. Die Firmendruckschrift "Die Ökologie braucht das Know-How" der Hoechst AG, Deutschland, beschreibt z. B. eine Lederpflegerezeptur auf der Basis von Wasser Säurewachs, Paraffin, Kolophonium, Emulgator und Kaliumhydroxid. Das nach dieser Rezeptur erhältliche Erzeugnis zeigt eine gewisse Verbesserung hinsichtlich der Auftragbarkeit. Das für Ölware typische "Schollenbruch"-Verhalten beobachtet man bei den bekannten Produkten nicht.

[0005] Lösungsmittelhaltige Lederpflegemittel werden von den Verbrauchern zunehmend aufgrund des meist unangenehmen Geruchs der eingesetzten Lösungsmittel und steigender Umweldiskussionen abgelehnt. Andererseits ist es bislang nicht gelungen, mit lösungsmittelfreien Emulsions-Lederpflegemitteln

die Konsistenz und die gute Verteilbarkeit lösungsmittelhaltiger Dosenschuhcreme nachzuahmen. Aus Marktuntersuchungen ist bekannt, dass bestimmte Verbraucherkreise nach einem Produkt verlangen, das die typische, durch den Schollenbruch gekennzeichnete Konsistenz der Ölware aufweist. Produkte mit cremeartiger Konsistenz werden abgelehnt. Die durch Schollenbruch gekennzeichnete Konsistenz weist den Vorteil auf, dass mit einem geeigneten Auftragsgerät, z. B. einer Schuhbürste oder einem Lappen, beim Eintauchen in die Dose oder den Tiegel des Lederpflegemittels stets die gewünschte Menge entnommen werden kann, während bei Produkten mit cremeartiger Konsistenz meist unbeabsichtigt eine zu große Menge Produkt entnommen wird. Die cremeartige Konsistenz bedingt außerdem einen kalten Fluss. Dieses Verhalten ist deswegen unerwünscht, da die mit dem Produkt gefüllten flachen Dosen, z. B. in einem Verkaufregal häufig schräg oder hochkant aufgestellt werden, um eine größere Schaufläche zu bieten. Ein Mittel, das kalten Fluss zeigt, verläuft unter diesen Bedingungen und haftet am Deckel der Dose, was der Verbraucher beim Öffnen der Dose als lästig empfindet.

[0006] Der vorliegenden Erfindung liegt daher die Aufgabe zugrunde, ein von flüchtigen organischen Lösungsmitteln im Wesentlichen freies Lederpflegemittel bereitzustellen, das eine Konsistenz aufweist, die derjenigen der herkömmlichen Ölware vergleichbar ist. Insbesondere sollte das erfindungsgemäße Lederpflegemittel das für Ölware charakteristische Schollenbruch-Verhalten zeigen. Das Lederpflegemittel soll außerdem keinen kalten Fluss zeigen.

[0007] Erfindungsgemäß wird diese Aufgabe durch ein Lederpflegemittel gelöst, das im Wesentlichen frei von flüchtigen organischen Lösungsmitteln ist, eine Emulsion von Wachs, Wasser und Emulgator umfasst, und jeweils bei einer Temperatur von 23 °C bei 5-minütiger Einwirkung einer Schubspannung von 750 Pa eine maximale Deformation γ von 0,1 oder weniger und nach 5-minütiger Relaxation eine bleibende Deformation von 50 % der maximalen Deformation oder weniger aufweist.

[0008] Die maximale Deformation und die bleibende Deformation werden anhand einer Kriech-/Rückverformungsmessung (Creep-Recovery-Messung) ermittelt. Diese Messung gestattet eine Unterscheidung zwischen dem viskosen Anteil und dem elastischen Anteil bei rheologischen Phänomenen. In der Kriechphase wird auf eine zu messende Probe eine konstante Schubspannung ausgeübt und die auftretende Deformation aufgezeichnet. In der Rückverformungsphase (Relaxationsphase) entfällt die Schubspannung und die gegebenenfalls auftretende Rückverformung der Probe wird aufgezeichnet. Bei einer ideal-elastischen Probe wird in der Kriechphase eine zeitunabhängige, zur aufgewandten Schubspannung proportionale Deformation erhalten. Bei Entlastung verschwindet die Deformation sofort und vollkommen und der Probekörper erlangt

seine ursprüngliche Form vollständig zurück. Bei einer ideal-viskosen Probe stellt die Deformationskurve in der Kriechphase eine mit konstantem Winkel ansteigende Gerade dar. In der Relaxationsphase bleibt der erreichte Wert der Deformation erhalten.

[0009] Viskoelastische Fluide zeigen ein rheologisches Verhalten das zwischen den Grenzfällen der ideal elastischen und ideal-viskosen Proben liegt. In der Kriechphase nimmt die Deformation zunächst rasch zu. Danach flacht die Deformationskurve ab und nähert sich asymptotisch einer Gerade mit konstanter Steigung. Die in der Kriechphase (bei gegebener Schubspannung und Dauer der Kriechphase) erreichte maximale Deformation ist ein Maß für die Summe der viskosen und elastischen Anteile des rheologischen Verhaltens. In der Rückverformungsphase können der viskose und der elastische Anteil voneinander unterschieden werden. Die nach der Entlastung der Probe nach einer angemessenen Rückverformungszeit bestimmte bleibende Deformation ist auf ein viskoses, irreversibles Fließen zurückzuführen. Somit gestattet die Angabe der in der Kriechphase erreichten maximalen Deformation und der bleibenden Deformation nach der Relaxationsphase (bei gegebener Schubspannung und Dauer der Kriech- und Relaxationsphase) eine hinreichend charakteristische Beschreibung des rheologischen Verhaltens eines realen Fluids.

[0010] Die Deformation ist eine dimensionslose Zahl, die die Verschiebung dividiert durch die Probenhöhe, angibt. Die Messungen für die Zwecke der vorliegenden Erfindung erfolgen bei einer Temperatur von 23 °C, einer Schubspannung von 750 Pa, einer Kriechzeit von 5 Minuten und einer Relaxationszeit von 5 Minuten. Zur Durchführung der Messungen ist ein Haake Rheometer mit CS-Modus und einem Mess-Sensor PP 35 TI bei einem Messabstand von 1 mm geeignet. Das Messprinzip beruht auf einer Torsionsmessung mit parallelen Platten.

[0011] Das erfindungsgemäße Lederpflegemittel zeigt bei 5-minütiger Einwirkung einer Schubspannung von 750 Pa eine maximale Deformation von 0,1 oder weniger vorzugsweise 0,05 oder weniger insbesondere 0,01 oder weniger. Nach der Relaxationsphase beträgt die bleibende Deformation gleich 50 % oder weniger vorzugsweise gleich 40 % oder weniger insbesondere gleich 30 % oder weniger der maximalen Deformation in der Kriechphase. Die bleibende Deformation kann bis hinunter zu 0 % oder z. B. bis hinunter zu 5 % der maximalen Deformation betragen.

[0012] Fig 1 zeigt ein unter den vorstehenden Bedingungen gemessenes Kriech-/Rückverformungsdiagramm eines erfindungsgemäßen Lederpflegemittels (dreieckige Symbole) im Vergleich zu einer handelsüblichen Lösungsmittelhaltigen Dosenschuhcreme (rautenförmige Symbole). Es ist ersichtlich, dass in der Kriechphase die Deformation beider Proben zunächst steil ansteigt und sich dann einer flach ansteigenden Geraden annähert. Die erreichte maximale

Deformation in der 5-minütigen Kriechphase beträgt etwa 0,003 für das erfindungsgemäße Lederpflegemittel und etwa 0,0022 für die handelsübliche Dosenschuhcreme. In der Relaxationsphase geht die Deformation in beiden Fällen zunächst rasch zurück, wobei im Fall der handelsüblichen Dosenschuhcreme eine vollständige Formwiedererlangung zu beobachten ist und die bleibende Deformation im Fall des erfindungsgemäßen Lederpflegemittels etwa 0,0005 beträgt.

[0013] In Fig 2 ist ein Kriech-/Rückverformungsdiagramm (Bedingungen wie vorstehend) einer pastenförmigen Lederpflegeemulsion des Standes der Technik wiedergegeben (quadratische Symbole). Das Verhalten des erfindungsgemäßen Lederpflegemittels (dreieckige Symbole) ist zum Vergleich nochmals mit dargestellt. Die bekannte Lederpflegeemulsion zeigt in der Kriechphase einen nahezu linearen Anstieg der Deformation mit der Zeit. Die maximale Deformation beträgt 4,75. In der Relaxationsphase bleibt die Deformation vollständig erhalten, es erfolgt keine Rückverformung.

[0014] Unter "flüchtigen organischen Lösungsmitteln" werden organische Lösungsmittel mit einem Siedepunkt unter 200 °C verstanden, wie Benzin, Terpenin oder Isopropanol. Das erfindungsgemäße Lederpflegemittel enthält weniger als 5 Gew.-%, vorzugsweise weniger als 3 Gew.-% derartiger Lösungsmittel.

[0015] Die Erfindung betrifft ferner ein Lederpflegemittel, welches enthält:

- (a) 0,1 bis 15 Gew.-% eines oder mehrerer Wachse eines Tropfpunkts von 95 bis 140 °C,
- (b) 0,2 bis 60 Gew.-% eines oder mehrerer Wachse eines Tropfpunkts von 45 bis 90 °C,
- (c) 1 bis 15 Gew.-% Emulgator,
- (d) 0 bis 20 Gew.-% fakultative Bestandteile und
- (e) Differenz auf 100 Gew.-% Wasser

[0016] Soweit nicht anders angegeben, beziehen sich Mengenangaben in Gew.-% auf das Gesamtprodukt. Das Lederpflegemittel der vorstehenden Zusammensetzung zeigt vorteilhafterweise das oben angegebene rheologische Verhalten. Im Allgemeinen enthält das erfindungsgemäße Lederpflegemittel 8 bis 25 Gew.-% Wachs und 50 bis 92 Gew.-%, vorzugsweise 60 bis 85 Gew.-% Wasser. Vorzugsweise beträgt das Gewichtsverhältnis von Emulgator zu Wachs im erfindungsgemäßen Lederpflegemittel 1:3 bis 1,5:1, insbesondere 1:2,5 bis 1:1,1, besonders bevorzugt 1:2 bis 1:1.

[0017] Die Wachsephase des erfindungsgemäßen Lederpflegemittels besteht vorzugsweise zu 0,1 bis 15 Gew.-%, insbesondere 5 bis 15 Gew.-%, aus einem oder mehreren Wachsen eines Tropfpunkts von 95 bis 140 °C (im Folgenden als "Hartwachskomponente" bezeichnet). Die Hartwachskomponente bildet im erfindungsgemäßen Lederpflegemittel bei Raumtemperatur vermutlich ein Gefüge feiner Kristalle, das als

grobmächtige elastische Netzwerkstruktur wirkt.

[0018] Neben der Hartwachskomponente enthält das erfindungsgemäße Lederpflegemittel vorzugsweise 0,2 bis 60 Gew.-%, insbesondere 5 bis 30 Gew.-%, eines oder mehrerer Wachse eines Tropfpunkts von 45 bis 90 °C (im Folgenden "Weichwachskomponente") in einer bevorzugten Ausführungsform umfasst die Weichwachskomponente ihrerseits ein Gemisch von zwei oder mehreren Wachsen unterschiedlichen Tropfpunkts. In einer bevorzugten Ausführungsform enthält das erfindungsgemäße Lederpflegemittel daher 0,1 bis 30 Gew.-% vorzugsweise 5 bis 15 Gew.-%, eines oder mehrerer Wachse eines Tropfpunkts von 45 bis 70 °C und 0,1 bis 30 Gew.-%, vorzugsweise 5 bis 15 Gew.-%, eines oder mehrerer Wachse eines Tropfpunkts von 75 bis 90 °C.

[0019] Der Begriff "Wachs" soll für die Zwecke der vorliegenden Erfindung eine weitestgehende Bedeutung haben. So sind alle üblicherweise als Wachs oder wachsähnliche Substanzen bezeichnete Verbindungen geeignet, die die oben genannten Tropfpunktkriterien erfüllen. Es sind insbesondere die natürlichen Wachse, wie die pflanzlichen Wachse, tierischen Wachse, Mineralwachse und petrochemischen Wachse, die chemisch modifizierten Wachse und die synthetischen Wachse geeignet.

[0020] Als Hartwachskomponente ist ein Polyolefinwachs, insbesondere ein Polyethylenwachs, eines Tropfpunkts von 95 bis 120 °C insbesondere eines Tropfpunkts von 102 bis 107 °C, bevorzugt. Bei den Polyolefinwachsen handelt es sich um Polyolefine mit wachsartigem Charakter. Sie können durch direkte Polymerisation der Basemonomere, meistens Propylen bzw. Ethylen, unter Einsatz voniegeln oder durch Depolymerisation von Produkten mit höheren Molmassen hergestellt werden. Die Polyolefinwachse können geeignete Comonomere, insbesondere Vinylacetat und Acrylsäure, enthalten. Am meisten bevorzugt ist eine eng geschnittene Fraktion eines Polyolefinwachses, d. h. der Erweichungspunkt und der Tropfpunkt liegen nicht mehr als 15 °C, vorzugsweise nicht mehr als 10 °C auseinander. Besonders geeignete Polyolefinwachse weisen eine Säurezahl im Bereich von 22 bis 28 und eine Verseifungszahl von 45 bis 65 auf. Diese haben im Allgemeinen eine Dichte bei 20 °C von 0,95 bis 0,97 g/cm³.

[0021] Als Wachs eines Tropfpunkts von 45 bis 70 °C ist ein Paraffinwachs bevorzugt. Bei Paraffin handelt es sich um ein Gemisch überwiegend gesättigter, aliphatischer Kohlenwasserstoffe. Sie werden zu einem geringeren Anteil aus Braunkohleschmelze und zu einem größeren Anteil aus Rückständen der Erdöldestillation hergestellt. Von den Erdölparaffinen sind die sogenannten grobkristallinen Paraffinwachse und die Intermediate-Wachse bevorzugt. Ein besonders geeignetes Paraffinwachs weist einen Erstarrungspunkt von 58 bis 60 °C, eine Dichte bei 80 °C von 0,774 g/cm³ (bestimmt nach DIN 51757) und eine Nadelpenetration

bei 25 °C und 1/10 mm von 18 (bestimmt nach DIN 51579) auf.

[0022] Das Wachs eines Tropfpunkts von 75 bis 90 °C ist vorzugsweise ein Esterwachs, vorzugsweise mit einer Säurezahl von 4-80 insbesondere 20-40 und einer Verseifungszahl von 100 bis 180 insbesondere 115 bis 165. Esterwachse eines Tropfpunkts von etwa 80 bis 85 °C sind bevorzugt. Mitglieder dieser Gruppe sind vor allem alle pflanzlichen, tierischen sowie chemisch veränderte Wachse. Sie bestehen aus Estern, die aus linearen Carbonsäuren mit 18 bis 34 oder mehr C-Atomen und etwa gleichlangen linearen Alkoholen gebildet sind und können kleinere Anteile freier Säuren und Alkoholen aufweisen. Geeignete Esterwachse werden z. B. durch Veresterung von Oxidationsprodukten des Montanwachses mit ein- oder mehrwertigen aliphatischen Alkoholen erhalten. Es können auch Naturwachse, wie Carnaubawachs, Candelillawachs, Chinawachs, Montanwachs, harzhaltiges Montanwachs, Bienenwachs und Fruchtwachse eingesetzt werden. Ein besonders geeignetes Esterwachs weist z. B. einen Tropfpunkt von 80 bis 85 °C eine Säurezahl von 25 bis 35 und eine Verseifungszahl von 135 bis 155 sowie eine Dichte bei 20 °C von 1,00 bis 1,02 auf.

[0023] Der Tropfpunkt des Wachses ist die Temperatur bei der eine auf die Quecksilberkugel eines Thermometers aufgetragene Probe des Wachses unter ihrem Eigengewicht abtropft. Er wird für die Zwecke der vorliegenden Erfindung nach der Vorschrift DIN 51801 bestimmt.

[0024] Das erfindungsgemäße Lederpflegemittel enthält vorteilhafterweise 1 bis 15 Gew.-%, vorzugsweise 5 bis 10 Gew.-% eines oder mehrerer Emulgatoren. Die Verwendung von nichtionischen Emulgatoren, gegebenenfalls in Kombination mit anderen z. B. anionischen oder kationischen Emulgatoren ist bevorzugt. Insbesondere bevorzugt wird jedoch ausschließlich ein nichtionischer Emulgator bzw. ein Gemisch nichtionischer Emulgatoren eingesetzt.

[0025] Vorzugsweise umfasst der nichtionische Emulgator einen mit 2 bis 30 mol C₂-C₄-Alkanoxid, vorzugsweise Ethylenoxid oder Propylenoxid alkylierten C₆-C₂₂-Alkohol. Bei dem Alkohol kann es sich um Fettalkohole, d. h. langkettige lineare aliphatische Alkohole, Oxalkohole, d. h. teilweise verzweigte höhere Alkohole, die z. B. durch Oxo-Synthese gewonnen werden können, oder Alkylphenole handeln. Die Oxalkohole zeigen gegenüber den linearen Fettalkoholen ein vorteilhaftes Emulgiervermögen und sind daher bevorzugt. Im Einzelnen lassen sich als geeignete Emulgatoren solche anführen, die folgende allgemeine Strukturformel aufweisen.



worin R für teilweise verzweigtes C₁₃H₂₇ steht und x für 2 bis 20, insbesondere für 3, 5, 6, 5, 7, 8, 10, 12, 15, 20, vorzugsweise für 5, steht,

R für Alkylphenyl und x für 2 bis 20 insbesondere für 6, 7, 8, 9, 10, 14 oder 20 steht.

[0031] Alternativ oder zusätzlich enthält das erfindungsgemäße Lederpflegemittel 0,1 bis 10 Gew.-%, vorzugsweise 0,5 bis 5 Gew.-%, Mineralöl vorzugsweise mit einer kinematischen Viskosität von 10 bis 90

[0036] Die nachfolgenden Beispiele erläutern die Erfindung ohne sie zu beschränken.

[0037] In einem Rührbehälter wurden unter Erwärmen auf etwa 95 °C folgende Komponenten zusammengeschmolzen

Paraffin (Trp. 58-60 °C)	40 Gew.-Telle
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(fortgesetzt)

Esterwachs (Tfp. 80-85 °C)	8,5 Gew.-Teile
PE-Wachs (Tfp. von 102-107 °C)	2 4 Gew.-Teile
ethoxylierter langkettiger Alkohol	5,5 Gew. Teile
Sorbitantrioleat	2 0 Gew.-Teile
Sorbitantristearat	1,0 Gew.-Teile

[0038] Die Mischung wurde unter starkem Rühren in 68,1 Gew. Teile Wasser das auf eine Temperatur von 80 °C vorgewärmt war, eingetragen. Unter weiterem Rühren wurden 3 Gew.-Teile Silcondl (12 500 mm²/s), 5 Gew.-Teile Silcondlamulsion (38 Gew.-% Silcondl 100 000 mm²/s und Emulgator) 2 Gew. Teile Spindöl, 0,3 Gew. Teile Konservierungsmittel und 0 2 Gew.-Teile Parfüm dazugegeben. Die Emulsion wurde in flache Tiegel abgefüllt und erstarrte zu einer viskoelastischen Masse. Auf gleiche Weise können eingefärbte Lederpflegemittel hergestellt werden wobei 0 1 bis 3 Gew.-Teile Farbmittel verwendet werden und der Wasseranteil entsprechend vermindert wird.

[0039] Das Ergebnis einer Kriech-/Rückverformungsmessung an einem Haake Rheometer mit CS-Modus und Mess-Sensor PP 35 TI bei einer Schubspannung von 750 Pa und jeweils 5 Minuten Kriech- und Relaxationsphase ist in Fig. 1 dargestellt (dreieckige Symbole).

Vergleichsbeispiel

[0040] Es wurde eine Lederpflegeemulsion gemäß folgender Rezeptur hergestellt (die Rezeptur entspricht der in der Firmenschrift der Hoechst AG "Die Ökologie braucht das Know-How" angegebenen)

10,0 Gew. Teile	Hoechst-Wachs 8
10,0 Gew. Teile	Tafelparaffin (52-62 °C)
2,0 Gew.-Teile	Kolophonum
2,0 Gew.-Teile	Genapol T-110/Hoechst (nichtionischer Emulgator)
0,5 Gew.-Teile	KOH, 88%lg
75,4 Gew. Teile	Wasser
0,1 Gew.-Teile	Konservierungsmittel

[0041] Die etwa 110 °C heiße Schmelze aus Wachs, Kolophonum und Emulgator wurde in das etwa 90 °C heiße, KOH-haltige Wasser eingerührt und das Konservierungsmittel dazugegeben. Nach dem Abkühlen wurde eine pastenförmige Masse erhalten.

[0042] Das Ergebnis der Kriech-/Rückverformungsmessung (Bedingungen wie im vorstehenden Beispiel) ist in Fig. 2 dargestellt (quadratische Symbole). Die maximale Deformation in der Kriechphase beträgt 4, 75, die bleibende Deformation beträgt 100 % der maximalen Deformation.

Patentansprüche

1 Lederpflegemittel, das im Wesentlichen frei von flüchtigen organischen Lösungsmitteln ist und eine Emulsion von Wachs, Wasser und Emulgator umfasst, dadurch gekennzeichnet, dass es, jeweils bei einer Temperatur von 23 °C, bei 5-minütiger Einwirkung einer Schubspannung von 750 Pa eine maximale Deformation γ von 0,1 oder weniger und nach 5-minütiger Relaxation eine bleibende Deformation von 50 % der maximalen Deformation oder weniger aufweist.

2. Lederpflegemittel nach Anspruch 1 dadurch gekennzeichnet, dass das Gewichtsverhältnis von Emulgator zu Wachs 1:3 bis 1,5:1 beträgt.

3. Lederpflegemittel nach Anspruch 1 oder 2, enthaltend:

- (a) 0, 1 bis 15 Gew.-% eines oder mehrerer Wachse eines Tropfpunkts von 95 bis 140 °C,
- (b) 0,2 bis 60 Gew.-% eines oder mehrerer Wachse eines Tropfpunkts von 45 bis 90 °C,
- (c) 1 bis 15 Gew.-% Emulgator,
- (d) 0 bis 20 Gew.-% fakultative Bestandteile und
- (e) Differenz auf 100 Gew.-% Wasser

4. Lederpflegemittel nach Anspruch 3, enthaltend als Komponente (b)

- (b1) 0 1 bis 30 Gew.-% eines oder mehrerer Wachse eines Tropfpunkts von 45 bis 70 °C und
- (b2) 0,1 bis 30 Gew.-% eines oder mehrerer Wachse eines Tropfpunkts von 75 bis 90 °C.

5. Lederpflegemittel nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, dass der Emulgator einen nichtionischen Emulgator umfasst.

6. Lederpflegemittel nach Anspruch 5, dadurch gekennzeichnet, dass der Emulgator einen mit 2 bis 30 mol C₁-C₄-Alkanold alkoxylierten C₈-C₂₅-Alkohol und/oder einen Sorbitanmono-, -di- oder -triest einer C₈-C₂₅-Carbonsäure umfasst.

7 Lederpflegemittel nach Anspruch 6, dadurch gekennzeichnet, dass der Alkohol ein verzweigter aliphatischer Alkohol ist.

8. Lederpflegemittel nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, dass es außerdem wenigstens einen weiteren, unter Silcondl und Mineralöl ausgewählten Bestandteil, jeweils in einer Menge von 0,1 bis 10 Gew.-%, enthält.

9. Lederpflegemittel nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, dass es außerdem wenigstens ein Farbmittel enthält.

10. Verfahren zur Herstellung eines Lederpflegemittels nach einem der vorhergehenden Ansprüche, bei dem die Wachse und der (die) Emulgator(en) bei erhöhter Temperatur geschmolzen werden, die Schmelze mit dem Wasser unter Eintrag von Scherenenergie vermischt wird und das Gemisch abgekühlt wird.

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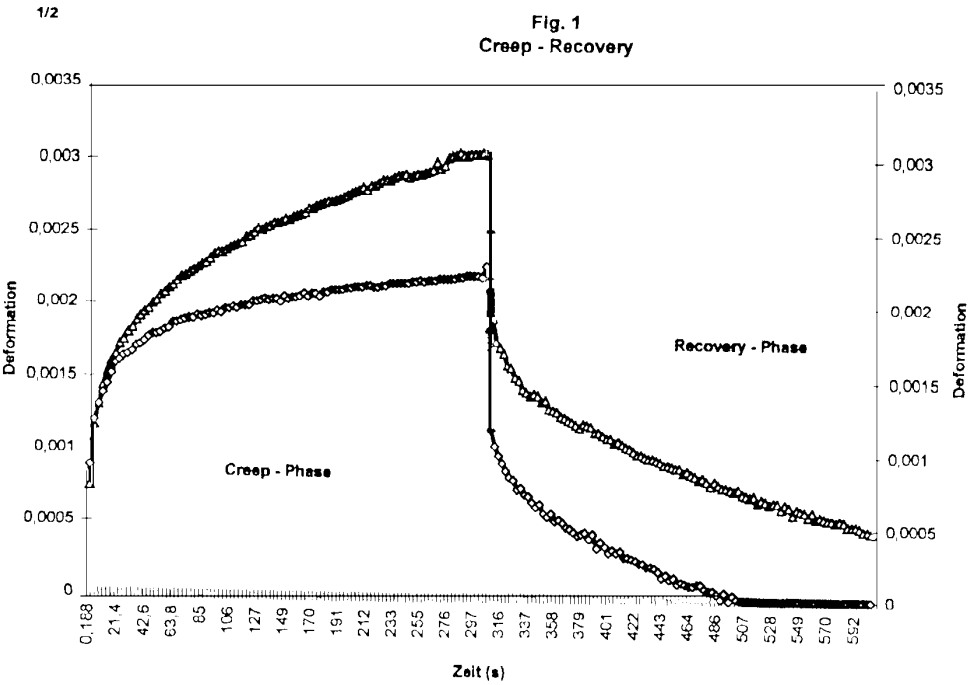
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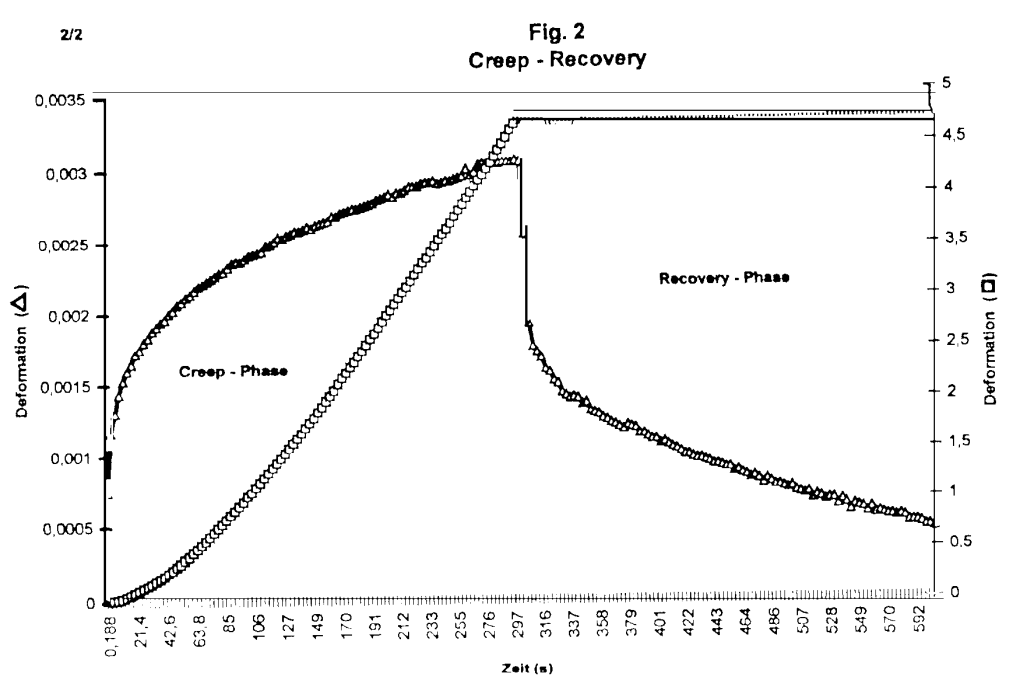
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EP 1 000 990 A2



146

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(54) Lederpflegemittel

(57) Beschrieben wird ein Lederpflegemittel, das im Wesentlichen frei von flüchtigen organischen Lösungsmitteln ist und eine Emulsion von Wachs, Wasser und Emulgator umfasst, dadurch gekennzeichnet, dass es bei einer Temperatur von 23 °C bei 5 minütiger Einwirkung einer Schubspannung von 750 Pa eine maximale Deformation von 0,1 oder weniger und nach 5-minütiger Relaxation eine bleibende Deformation von 50 % der maximalen Deformation oder weniger aufweist. Das Lederpflegemittel umfasst vorzugsweise

eines Tropfpunkts von 95 bis 140 °C,
(b) 0,2 bis 80 Gew.-% eines oder mehrerer Wachse
eines Tropfpunkts von 45 bis 80 °C,
(c) 1 bis 15 Gew.-% Emulgator,
(d) 0 bis 20 Gew.-% fakultative Bestandteile und
(e) Differenz auf 100 Gew.-% Wasser

Fakultative Bestandteile sind z. B. Silicone, Minerale und Farbstoffe

(a) 0,1 bis 15 Gew.-% eines oder mehrerer Wachse

EP 1 000 990 A3

145



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