

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
22 May 2008 (22.05.2008)

PCT

(10) International Publication Number
WO 2008/058703 A1

(51) International Patent Classification:

C08G 18/42 (2006.01) **C09J 175/06** (2006.01)
C08G 18/12 (2006.01) **B32B 37/12** (2006.01)
C08G 18/66 (2006.01)

(21) International Application Number:

PCT/EP2007/009803

(22) International Filing Date:

13 November 2007 (13.11.2007)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

60/859,753 17 November 2006 (17.11.2006) US

(71) Applicant (for all designated States except US): **BOSTIK S.A.** [FR/FR]; 12, Place de l'Iris, F-92400 Courbevoie (FR).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **SCHREIBER, Peter** [DE/DE]; Am Westen 37, 45549 Sprockhoevel (DE). **HUERTER, Hans-Ulrich** [DE/DE]; Am Steinbruch 12, 58332 Schwelm (DE). **PUL, Omar** [DE/DE]; Elisenstrasse 9, 42107 Wuppertal (DE). **FIMMEL, Elke** [DE/DE]; Poststrasse 185, 44809 Bochum (DE).

(74) Agent: **GRANET, Pierre**; Bostik S.A., Département Propriété Intellectuelle, 12, place de l'Iris - La Défense 2, F-92062 Paris La Defense (FR).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))

Published:

- with international search report

(54) Title: SOLVENT-FREE LAMINATING ADHESIVE

(57) Abstract: The present invention provides a solvent-free adhesive composition for producing coloured foil and/or film laminates comprising (A) 5 to 95 wt% of at least one pigment-based colour concentrate comprising 1 to 60 wt% of at least one azo-free pigment and 99 to 40 wt% of at least one hydroxyl functional resin, based on the total weight of component (A), (B) 0 to 25 wt% of at least one hydroxyl functional resin, and (C) 5 to 95 wt% of at least one isocyanate functional ised crosslinker, the wt% based on the total weight of the adhesive composition, providing an increased heat resistance and a uniform application in thin layers and a uniform adhesive surface and a high mechanical stability without separation of the laminated film or foil strips and without discolouring (fading effect) of the laminates.



WO 2008/058703 A1

Solvent-free Laminating Adhesive

FIELD OF THE INVENTION

The invention is directed to a pigment based solvent-free laminating
5 adhesive with high temperature resistance, for producing coloured foil or
film laminates.

DESCRIPTION OF RELATED ART

Laminating adhesives are used for large-area bonding of individual
foils and films to form laminates like PET/PE (polyethylene terephthalate/
10 polyethylene), or PET/Al/PP (polyethylene terephthalate/aluminium foil
polyethylene). The properties of the individual foils and films are
combined in such a way that the laminate is suitable for subsequent use
as a packaging material for the packaging of goods, such as, for example,
foodstuffs, health care, medical or pharmaceutical articles or items which
15 need protection from damage prior to first usage.

Laminating adhesives most often consist as a rule of isocyanate
group-containing polyurethane binders, usually manufactured from
hydroxyl-group-containing polyesters, polyether or simultaneously ester-
and ether-group-containing hydroxyl-functional condensation products and
20 polyfunctional isocyanates, described, for example, in WO 99/24486, U.S.
6,503,981 and U.S. 6,914,102. Well-known are, for example, two-
component (2K) NCO/OH types or moisture curing one component (1K)
systems which are available as solvent-borne or solvent-free formulations.

Most of the available laminating adhesives give, after cross-linking,
25 a colour-less or transparent appearance of the resulted laminate. But
there exists a requirement to provide coloured laminates, e.g., golden
coloured laminates as packaging material for coffee and salmon or, e.g.,
pink, green or blue coloured laminates for medical purposes or electric
cable wrappings. These coloured laminates are based on solvent-borne
30 adhesives tinted with solvent-based dye or solvent-based concentrates of

mixtures of dyes and pigments, as commercially available as, e.g., Color Stick ® (Comp. Hartmann, now Sun Chemical).

Due to legal regulations a very limited number of raw materials are permitted or suitable for the use in flexible packaging adhesives, including solvent-based dye or dye/pigment concentrate compositions. Besides their damage to the environment because of the high content of volatile organic solvents, the necessity of high energy consuming drying tunnels to flash-off those solvents to achieve the demanding properties, even the necessary adhesive lay down needed for the production of the laminates is about two times higher than the lay down regarding solvent-free adhesives. Additionally the dye/pigment concentrate compositions are composed of azo dyes and pigments based on azo pigments which are not heat resistant with regard to sealing processes and/or which could be decomposed under forming primary aromatic amines which are suspected of causing cancer to human beings or animals.

Therefore, there is a need to minimize the content of solvents and the risk of migration of primary aromatic amines into food in the tinted adhesives, to increase the heat resistance of the coloured adhesive and to reduce the necessary lay down of the tinted adhesive for the production of the coloured laminates while maintaining desired properties, such as, uniform application in thin layers and high mechanical stability without separation of the laminated film/foil separation of the laminated film/film or film/foil strips.

SUMMARY OF THE INVENTION

The present invention provides a solvent-free adhesive composition for producing coloured foil and/or film laminates comprising

- (A) 5 to 95 wt% of at least one pigment-based colour concentrate comprising 1 to 60 wt% of at least one azo-free pigment and 99 to 40 wt% of at least one hydroxyl functional resin, based on the total weight of component (A),
- (B) 0 to 25 wt% of at least one hydroxyl functional resin, and

(C) 5 to 95 wt% of at least one isocyanate functionalised cross-linker,

the wt% based on the total weight of the adhesive composition.

The adhesive composition according to the invention is a solvent-free laminating adhesive composition which is usable to produce coloured laminates. With the tinted adhesive according to the invention it is possible to increase the heat resistance of the adhesive and to reduce the necessary coating weight of the tinted adhesive for the production of the coloured laminates while providing a uniform application in thin layers and a uniform adhesive surface and a high mechanical stability without separation of the laminated film or foil strips and without discolouring (fading effect) of the laminates.

DETAILED DESCRIPTION OF THE INVENTION

The features and advantages of the present invention will be more readily understood, by those of ordinary skill in the art, from reading the following detailed description. It is to be appreciated those certain features of the invention, which are, for clarity, described above and below in the context of separate embodiments, may also be provided in combination in a single embodiment. Conversely, various features of the invention that are, for brevity, described in the context of a single embodiment, may also be provided separately or in any sub-combination. In addition, references in the singular may also include the plural (for example, "a" and "an" may refer to one, or one or more) unless the context specifically states otherwise.

The use of numerical values in the various ranges specified in this application, unless expressly indicated otherwise, is stated as the minimum and maximum values within the stated ranges. In this manner, slight variations above and below the stated ranges can be used to achieve substantially the same results as values within the ranges. Also, the disclosure of these ranges is intended as a continuous range including every value between the minimum and maximum values.

All patents, patent applications and publications referred to herein are incorporated by reference in their entirety.

The solvent-free adhesive composition according to the invention comprises the colour concentrate (A) based on azo-free pigments, the OH-
5 resin of component (B) and (C) to crosslink the resin of component (A) and of component (B).

Furthermore additives conventional in polyurethane chemistry can be used in the composition according to the invention.

The adhesive composition according to the invention is applicable
10 as two-component (2K) or as three-component (3K) composition.

The two-component (2K) composition comprises the colour concentrate of component (A) and the isocyanate cross-linker of component (C). The three-component (3K) composition comprises the colour concentrate of component (A), the additional resin of component (B)
15 and the isocyanate cross-linker of component (C).

The polyisocyanate cross-linker of component (C) can be diisocyanates and polyisocyanates, for example, aliphatic diisocyanates, trimerization products thereof, aromatic diisocyanates and/or pre-
20 polymers thereof as known by a person skilled in the art. Examples of diisocyanates are isophorone diisocyanate (IPDI), hexamethylene diisocyanate (HDI), meta-xylene-diisocyanate (m-XDI) or dicyclohexylmethane diisocyanate or the trimerization products, for example, aliphatic diisocyanate-based isocyanurates or mixtures thereof. Aromatic diisocyanate compounds may also be present, such as, for
25 example, toluene diisocyanate (TDI), diphenylalkyl diisocyanates or mixtures thereof.

To result in solvent-less polyisocyanate cross-linkers (C) with at least two terminal isocyanate (NCO) groups, suitable to be cross-linked with the colour concentrates (A) according to the invention, usually
30 polyalcohols are reacted with excess of di- and/or polyisocyanates, as described for example in EP-A 0 118 065 or DE-A 34 01 129.

Preferred is the use of TDI and MDI based solvent-borne or solvent-free pre-polymers in a range of 5 to 95 wt%, based on the total weight of the adhesive composition. The NCO content of these pre-polymers is in the range of, for example, 5 to 25%, based on the pre-polymer.

- 5 Particularly preferred are those polyisocyanate cross-linkers with a number average molecular weight M_n of 500 to 5000, with a 25°C viscosity of 1500 to 25000 mPas and a 70°C viscosity of 1000 to 4000 mPas.

- 10 The number-average molecular weight data stated in the present description are number-average molar masses determined or to be determined by gel permeation chromatography (GPC) using divinylbenzene-crosslinked polystyrene as the immobile phase, tetrahydrofuran as the liquid phase based on polystyrene standards.

- 15 The hydroxy functional resin of component A) and component (B) can be one or more diols and/or polyols having a number average molecular weight M_n of 1000 to 3500, and a hydroxyl number of 15 to 200, preferably in a range of 100 to 150.

The hydroxy functional resin can be polymers based on hydroxyl groups containing polyesters, hydroxyl groups containing polyethers and hydroxyl groups containing polyurethanes.

- 20 The hydroxyl groups containing polyesters can be linear aliphatic polyesters based on linear dicarboxylic acids having a carbon number in the range of C3 to C12, preferred in a range of C4 to C8, and diols.

Suitable linear dicarboxylic acids are e.g. adipic acid, sebacic acid, acelaic acid, succinic acid, derivatives thereof and mixtures thereof.

- 25 Diols which may be used are, for example, ethylene glycol, diethylene glycol, triethylene glycol, hexanediol, butanediol, propylene glycol, methylpropanediol-1.3, neopentylglycol, and mixtures thereof.

- 30 The polyesters may be produced in conventional manner as known to a person skilled in the art by performing an esterification reaction of an acid component with an alcohol component, for example, in a nitrogen

atmosphere, for example, at temperatures of between 140 and 260°C, with or without use of conventional esterification catalysts.

Hydroxyl groups containing polyurethanes are, for example, commercially available Desmocoll ® Types (Bayer AG).

- 5 Useable polyester polyols are, for example, commercially available Desmophen® Types such as Desmophen® 1800 or Desmophen® 1200 (Bayer AG).

The hydroxyl functional resin is used in component (A) in a preferred range of 40 to 98 wt% based on the weight of component (A).

- 10 The hydroxyl functional resin is used in component (B) in a range of 0 to 25 wt% and preferably in a range of 1 to 25 wt%, based on the total weight of the adhesive composition.

The pigment based colour concentrate (A) comprises one or more pigments which can be black, white and coloured types.

- 15 Pigments are those which are not based on or could be traced back to primary aromatic amines, and they include black, white and coloured type pigments, such as, for example, titanium dioxide, carbon black, iron oxide, aluminium bronze, phthalocyanine blue, phthalocyanine green, perylene, diketo-pyrrolo-pyrrol, thioindigo, pyranthrone, anthranthone and
20 mixtures thereof.

Preferred pigments are iron oxide, phthalocyanine blue, phthalocyanine green, isoindolin, perylene, diketo-pyrrolo-pyrrol, titanium dioxide

- 25 The pigments can be contained in component (A) of the adhesive composition according to the invention in the above mentioned quantity range, preferred in a range of 5 to 60 wt%, based on the component (A).

- 30 The pigment based colour concentrate (A) may comprise, for example, one ore more hydroxy functional resins, 0.5 to 25 wt% of black and coloured type pigments and/or up to 60 wt% of white pigments, based on the total weight of component (A), and may additionally comprise grinding aids and stabilizers usually used in the adhesive industry.

The pigment based colour concentrate is added to the components of the composition of the invention in a quantity to meet the wt% based on the total weight of the adhesive composition according to the invention.

For example, it is possible to provide a 2K composition comprising
5 the polyisocyanate crosslinker as one component and the pigment based colour concentrate as the other component.

Components A), B) and C) can be mixed in the described manner directly prior to application onto the substrates to be bonded. Mixing may be performed, for example, in a static two or three component mixing head
10 or a mixing tube.

The viscosity of the finished adhesive composition is the range of being applicable between 35 to 95°C on state of the art production laminators.

The adhesive composition according to the invention may contain
15 the additives conventional in polyurethane chemistry, such as, for example, catalysts, accelerators, light stabilizers, extenders in the amounts conventional in coating chemistry, e.g., from 0.5 to 5 wt.%, relative to the adhesive composition. Preferably, such additives are used.

Adhesion promoters may be used in quantities under 3 wt% based
20 on the adhesive composition. Preferably, no adhesive promoters are used.

The adhesive composition according to the invention may be used to stick the most varied materials together. These materials may be, for example, web-form materials of plastics, such as, polyethylene,
25 polypropylene, polyamide, PET (polyethylene terephthalate), paper or metal, e.g., metal foils, such as, aluminium foils, or plastics films, such as, metal oxide vapour-deposited films, e.g. Toppan® or Ceramis®, or metal vapour-deposited plastics films, e.g. Camclear®.

The invention also provides use of the adhesive composition of the
30 invention for bonding substrates, in particular, for producing laminates for packaging.

The application speed employed in the course of the method according to the invention should be in the range as usually used, for example, of about 50 to 250 m/min. Basically, however one can also use faster speeds if the machines are designed accordingly.

- 5 A thin application of, for example, about 0.5 to 5 g/m², preferably about 1.0 to 2.5 g/m², is sufficient.

- The composition according to the invention can be used on all solvent-less laminators suitable for flexible multi-ply constructions being equipped with a heatable application mechanism suitable for thin
10 application at the required machine operating speed. The adhesive application can be accomplished with all state of the art solvent-less application heads with smooth rollers. This is known to a person skilled in the art. To get the best and most uniform application possible, the lamination may be accomplished immediately after the application
15 mechanism.

 The processing temperature is selected between 30 and 95°C, depending on viscosity of the adhesive composition according to the invention and on the desired processing web speed.

- The application is possible in continuous or discontinuous (reel-to-reel) application manner as known to a person skilled in the art.
20

 After application of the adhesive composition according to the invention, the resulted laminates may be sealed with usual used sealing machines, for example, under pressure and sealing temperatures in a range of, for example, 140 to 280°C.

- 25 The present invention is further defined in the following Examples. It should be understood that these Examples are given by way of illustration only. From the above discussion and these Examples, one skilled in the art can ascertain the essential characteristics of this invention, and without departing from the spirit and scope thereof, can
30 make various changes and modifications of the invention to adapt it to various uses and conditions. As a result, the present invention is not

limited by the illustrative examples set forth herein below, but rather is defined by the claims contained herein below.

The following Examples illustrate the invention. All parts and percentages are on a weight basis unless otherwise indicated.

5

EXAMPLES

Example 1:

Production of the Adhesive Composition According to the Invention

1.1 Preparation of a Hydroxyl Functional Polyester Resin:

758 g Ethylenglycol, 147 g Diethylenglycol and 1095 g Adipic acid
10 are heated in a 2l reactor with interior thermometer, stirrer and distilling device. The temperature is increased up to 250°C until an acid value of 10 mg KOH/g is attained.

Then the batch is cooled down to 180°C and fitted to a vacuum
pump. The temperature is increased again to 230°C and batch is
15 condensed to a viscosity of 2500 mPas and a hydroxyl value of 90 to 100. The hydroxyl value has priority.

After reaching the above specifications, the batch is cooled below
60°C and discharged.

Results:	Acid value:	4mgKOH/g
20	Viscosity:	2500 – 3000 mPas
	Colour(Gardner):	0 – 4
	Hydroxyl value :	80 – 90
	Water content:	below 0.05%

1.2 Preparation of an Isocyanate Functionalised Polyurethane Resin as

25 Cross-linker (C):

375 g of 2.4'-Diphenylmethanediisocyanate and 375g of 4,4'
diphenyl methane diisocyanate are filled into a 4l reactor with interior
thermometer and stirrer and homogenized by heating to 50°C. 912 g of
the polyester of Example 1.1 is added and heated until the exothermic
30 reaction starts. The batch is kept at 80°C for 1 hour and cooled to 60°C to

charge 1508 g of polypropylene glycol 1100. The batch is heated to 80°C again and stirred for 2 hours at this temperature. 72 g of dipropylene glycol is added and one hour later viscosity (100°C) and the isocyanate content is measured.

5 Results: Isocyanate content: 6.7%
 Viscosity (100°C): 564 mPas

1.3 Preparation of the Adhesive Composition:

50 parts per weight of a hydroxyl functional polyester based on ethylene glycol, diethylene glycol and adipic acid are mixed together under
10 stirring with 3 parts per weight of an azo-free yellow pigment (commercial available) and 14 parts per weight of an azo-free red pigment (commercial available). After 20 minutes further 33 parts per weight of the hydroxyl functional polyester based on ethylene glycol, diethylene glycol and adipic acid are added. After homogenizing, the resulted pigment concentrate is
15 allowed to stand for 12 hours, and is then dispersed to a particle size of 10 µm or lower.

Prior to application 40 parts per weight of the pigment concentrate are mixed with 100 parts per weight of the isocyanate functionalised polyurethane resin of Example 1.2 to form the adhesive composition.

20 Example 2

Production of an Adhesive Composition According to Prior Art

25.7 g of a solution comprising 20 g ®Orasol Orange-G (cobalt complex dye, Ciba) and 180 g ethylacetate are mixed together with 11.7 g of a solution comprising 10 g hydroxyl functional polyester (based on
25 ethylene glycol, diethylene glycol, 1,1,1-trimethylol propane, adipic acid and phthalic acid anhydride) and 1.7 g isocyanate cross-linker (based on tripropylene glycol and MDI) until homogenizing is complete (about 2 minutes).

Example 3**Application of the Adhesive Compositions and Results**

2 g/m² of the adhesive composition of Example 1 is applied with a laminating machine (firma Nordmeccanica, Labo Combi) under an application speed of 50 m/min on a PET foil (12 µm thickness) and is then laminated with an aluminium foil (12µm thickness). A gold-coloured laminate results which is cured in an oven under a temperature of 60°C in a time period of 16 hours.

The adhesive composition of Example 2 is applied on an aluminium foil (30 µm thickness) and is dried for 1 minute under a temperature of 60°C (adhesive application: about 3.0 g/m²). Then the aluminium foil is laminated with a PET foil (12µm thickness), and the laminate is cured in an oven in a time period of 16 hours under a temperature of 60°C. An orange-coloured laminate results.

The laminates are sealed with a sealing machine (firma ETK Brugger München) under the following conditions: pressure 3 bar, time period 1 second, different sealing temperatures (see Table 1). Both metal sealing parts of the machine are heated.

Table 1: Results

Sealing Temperature[°C]	Example 1 (visual evaluation)	Example 2 (visual evaluation)
160°	ok	not ok
180°	ok	not ok
200°	ok	not ok
220°	ok	not ok
240°	ok	not ok

After sealing the applied adhesive compositions under high temperature as mentioned in Table 1, the adhesive according to the prior art (Example 2) show fading (discolouring) effects and layer defects in form of blistering while the adhesive of the invention (Example 1) is free of such defects, and, therefore show a high heat resistance and high mechanical stability and a uniform surface.

Claims

1. A solvent-free adhesive composition for producing coloured foil and/or film laminates comprising
 - (A) 5 to 95 wt% of at least one pigment-based colour concentrate comprising 1 to 60 wt% of at least one azo-free pigment and 99 to 40 wt% of at least one hydroxyl functional resin, based on the total weight of component (A),
 - (B) 0 to 25 wt% of at least one hydroxyl functional resin, and
 - (C) 5 to 95 wt% of at least one isocyanate functionalised crosslinker,the wt% based on the total weight of the adhesive composition.
2. The composition according to claim 1 comprising
 - (A) 5 to 95 wt% of at least one pigment-based colour concentrate comprising 1 to 60 wt% of at least one azo-free pigment and 99 to 40 wt% of at least one hydroxyl functional resin, based on the total weight of component (A), and
 - (C) 5 to 95 wt% of at least one isocyanate functionalised crosslinker,the wt% based on the total weight of the adhesive composition.
3. The composition according to claim 1 wherein the pigment-based colour concentrate (A) comprising 0.5 to 25 wt% of black and coloured type pigments and up to 60 w% of white pigments.
4. The composition according to claim 1 wherein the hydroxy functional resin of component A) and component (B) are one or more diols and/or polyols having a number average molecular weight M_n of 1000 to 3500, and a hydroxyl number of 15 to 200 wherein the number-average molecular weight M_n is the number-average molar mass determined or to be determined by gel

permeation chromatography (GPC) using divinylbenzene-crosslinked polystyrene as the immobile phase, tetrahydrofuran as the liquid phase based on polystyrene standards.

5. The composition according to claim 1 wherein the hydroxy functional resin of component A) and component (B) are polymers selected from the group consisting of hydroxyl groups containing polyesters, hydroxyl groups containing polyethers and hydroxyl groups containing polyurethanes.
6. The composition according to claim 5 wherein the hydroxyl groups containing polyesters are linear aliphatic polyesters based on linear dicarboxylic acids having a carbon number in the range of C3 to C12, and diols.
7. The composition according to claim 1 wherein the isocyanate functionalised cross-linker (C) having a number average molecular weight M_n of 500 to 5000 with a 25°C viscosity of 1500 to 25000 mPas and a 70°C viscosity of 1000 to 4000 mPas.
8. The composition according to claim 1 wherein the isocyanate functionalised cross-linker (C) is TDI and/or MDI based solvent-borne or solvent-free pre-polymers.
9. The composition according to claim 7 wherein the NCO content of the pre-polymer is in the range of 5 to 25%, based on the prepolymer.
10. A process of preparation of the composition according to claim 1 wherein the components A), B) and C) are mixed together directly prior to application onto the substrates to be bonded resulting in a viscosity of the finished adhesive composition of claim 1 in a range of being applicable between 35 to 95°C.
11. Use of the composition according to claim 1 to bond web-form materials of plastics selected from the group consisting of

polyethylene, polypropylene, polyamide, polyethylene terephthalate (PET), of paper, metals, metal foils, plastics films, metal oxide vapour-deposited films and metal vapour-deposited plastics films.

12. The use according to claim 11 for producing laminates for packaging.
13. Bonded substrate using the composition according to claim 1.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2007/009803

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08G18/42 C08G18/12 C08G18/66 C09J175/06 B32B37/12

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08G C09J B32B

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

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

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Week 200234 Derwent Publications Ltd., London, GB; AN 2002-298315 XP002468501 & JP 2002 003814 A (DAINIPPON INK & CHEM INC) 9 January 2002 (2002-01-09) abstract	1-13
A	----- US 2006/046067 A1 (KLEINEBERG OLAF [DE] ET AL) 2 March 2006 (2006-03-02) paragraphs [0001] - [0005], [0013] examples 1-3; table 1	1-13
A	----- US 2004/198900 A1 (MADAJ EDMUND J [US]) 7 October 2004 (2004-10-07) paragraphs [0012], [0064], [0065] example 1 ----- -/--	



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

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

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

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

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

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

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

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

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

& document member of the same patent family

Date of the actual completion of the international search

12 February 2008

Date of mailing of the international search report

25/02/2008

Name and mailing address of the ISA/

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

Authorized officer

Neugebauer, Ute

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2007/009803

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 1 531 414 A (HERBERTS & CO GMBH) 8 November 1978 (1978-11-08) page 1, line 45 - page 2, line 119 page 3, lines 60-95 -----	1-13
A	WO 99/24486 A (HENKEL KGAA [DE]; HUEBENER ACHIM [DE]; HENKE GUENTER [DE]; BAUER ANDRE) 20 May 1999 (1999-05-20) cited in the application page 3, lines 12-30 page 5, lines 14-30 page 32, lines 12-14 example 6; tables 2,3 -----	1-13

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2007/009803

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
JP 2002003814	A	09-01-2002	NONE	
US 2006046067	A1	02-03-2006	EP 1791880 A1 WO 2006026670 A1	06-06-2007 09-03-2006
US 2004198900	A1	07-10-2004	MX PA04003144 A	31-03-2005
GB 1531414	A	08-11-1978	AR 206361 A1 AT 347698 B AT 880774 A BE 835022 A1 BR 7507221 A CA 1059890 A1 DE 2549227 A1 DK 494475 A ES 442282 A1 FI 753067 A FR 2289589 A1 GB 1531413 A IT 1054359 B JP 1347286 C JP 51069579 A JP 58050165 B MX 142840 A NL 7512917 A SE 419870 B SE 7512342 A US 4092202 A	15-07-1976 10-01-1979 15-05-1978 30-04-1976 03-08-1976 07-08-1979 26-05-1976 05-05-1976 01-04-1977 05-05-1976 28-05-1976 08-11-1978 10-11-1981 13-11-1986 16-06-1976 09-11-1983 05-01-1981 06-05-1976 31-08-1981 05-05-1976 30-05-1978
WO 9924486	A	20-05-1999	BR 9814131 A CA 2309593 A1 CN 1278835 A DE 19851182 A1 EP 1030869 A1 HU 0100117 A2 JP 2001522908 T PL 340365 A1	03-10-2000 20-05-1999 03-01-2001 12-05-1999 30-08-2000 28-06-2001 20-11-2001 29-01-2001