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(54) Title: POLYURETHANE RESINS FOR LAMINATING INKS

(57) Abstract: A polyurethane resin which is particularly suitable for use in printing inks for laminating packaging applications is described. The polyurethane resin maintains its lamination bond strength before and after the laminate printed with the ink containing the polyurethane resin is subjected to sterilization conditions. Laminates which maintain a printed image and their structural integrity after sterilization are also described.

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Polyurethane Resins For Laminating Inks

Field of the invention

The invention relates to a special polyurethane resin maintaining the bond strength of printed and laminated packaging films before and after sterilization ("retort"), when used alone - preferred - or in combination with other suitable binder resins as film-forming backbone for corresponding solvent-based flexo or gravure inks employed for printing the laminate structures."

State of the Art

Recent diversification in package bags or containers has required a high degree of performance for printing inks or coating agents used for the ornamentation or surface protection thereof. Such inks or coating agents should exhibit excellent adhesiveness for various kinds of plastic films, blocking resistance, and resistance to pasteurization and sterilization conditions.

For instance, printing inks for plastic films are needed to provide better printability, adhesion to a wider range of films, and better blocking resistance and gloss than conventional ones.

Especially, in the field of food packaging, bags or containers made of laminated film materials are used for the reasons that they are sanitary and their contents do not come in direct contact with the ink, and to provide a satisfactory appearance as a high grade of printed products.

Generally there are two methods for producing such laminated film materials. One is an extrusion laminating method, wherein a plastic film substrate is printed with an ink, and if necessary, a primer is applied onto the inked surface; then a molten resin such as polyolefin is extruded onto the inked surface. Another method is an adhesive laminating method, wherein an adhesive is applied onto the inked surface of the plastic film substrate, and a plastic film is then laminated onto the same surface. Accordingly, the laminating inks must possess excellent adhesion to the printing substrate as well as to the film to be laminated.

To preserve the integrity of filling goods - particularly foodstuff - for an extended period time against microbial attack and therefore against premature decomposition when stored on supermarket shelves for example the packaged filling goods are often sterilized directly after packaging to destroy all traces of microorganisms of any kind, that are potential sources for significant shelf life reduction. The term sterilization in the following comprises state-of-the-art techniques like dry heat sterilization, steam sterilization and immersion in boiling water. Since only one printed packaging film is usually not sufficient to ensure a proper sealability and to provide the required barrier properties for water vapour or oxygen for example, laminates are commonly used, where two or more films are glued together by suitable adhesives combining the required performance properties. The ink film necessary for decoration and information purposes is printed onto the inner side of one of the films of the laminate structure, so that it has no direct contact with the filling goods. After printing this printed film is laminated with an adhesive against another non-printed film or against a non-printed laminate structure consisting of more than one film.

When the laminated film materials further undergo sterilization treatment such film laminates should not undergo delamination through the sterilization treatment. Most of these performance requirements for the printing ink or coating mainly depend upon the performance of the binder resin used. Accordingly, in the case of printing inks for plastic films, one or more of various binder resins are selected so as to meet the performance required for individual printing inks. Various polymers have been utilized in printing ink formulations, e.g., polyamides, cellulosics, acrylic and methacrylic esters, ketones, polyvinyl chloride (PVC), polyesters and polyvinyl butyral (PVB). However because of inconsistencies in adhesion properties to different substrates, selective solubility (either in alcohol or ester), incompatibility with coresins and poor lamination bond strengths have limited the use of these polymers.

Existing commercial polyurethane resins are useful in liquid inks lamination packaging applications. These polyurethane resins show good adhesion to numerous substrates, especially plastic films such as polyethylene terephthalate (PET) or polypropylene (PP). Existing polyurethane resins are also soluble in typical ink solvents, such as alcohol, ester and alcohol/ester blends, for use in flexo and gravure printing applications.

However, such resins possess poor sterilization properties.

Existing commercial polyurethanes exhibit a strong decrease of lamination bond strength after the sterilization process of more than 50%, that is not acceptable for packaging converters posing considerable risks like leakage, that is in contradiction to the required barrier properties for gases and microorganisms, or even mechanical failure with separation of the individual films of the laminate structure during transport or handling.

It is was an object of the present invention to provide a polyurethane resin that maintains a high lamination bond strength before as well as after sterilization processing, which resin still maintains solubility in alcohol, ester and alcohol/ester blends, adhesion to high barrier (typically silicon dioxide/aluminum oxide coated) substrates, good pigment grinding, and stable rheology.

Description of the invention

By way of the invention, a polyurethane resin for use in an ink composition for laminate packaging applications is provided, which polyurethane resin advantageously maintains its high lamination bond strength before and after being subjected to sterilization conditions.

An aspect of the invention then is a polyurethane resin which comprises the reaction product of a polyisocyanate and a polyalcohol to form an isocyanate-terminated prepolymer, which prepolymer is extended with a diamine to form the polyurethane resin of the invention. The resin of the invention substantially maintains its high lamination bond strength before and after sterilization.

The polyurethane resin of the invention possesses at least the same high lamination bond strength before and after sterilization processing, while also maintaining solubility in alcohol, ester and alcohol/ester blends, adhesion to high barrier (typically silicon dioxide/aluminum oxide coated) substrates, good pigment grinding, and stable rheology.

Another aspect of the invention is a printing ink composition suitable for laminating applications containing the polyurethane resin, a colorant, and an organic solvent, which ink composition is suitable for flexo or gravure packaging applications, particularly those packaging applications which are subjected to sterilization conditions.

Accordingly, another aspect of the present invention is a laminate having one surface printed with the ink composition of the invention, wherein the printed image remains substantially unchanged and the laminate remains free of delamination-related defects, after the laminate is subjected to sterilization conditions, due to the presence of the polyurethane resin of the invention in the ink composition.

In a first aspect the present invention relates to the use of a polyurethane resin as binder for a laminating ink for laminated packaging applications, which resin comprises the reaction product of a diisocyanate and a polyalcohol to form an isocyanate-terminated prepolymer, which prepolymer is extended with a diamine to form the polyurethane resin, said polyurethane resin having at least the same high lamination bond strength before and after sterilization with the proviso that if sterilization is done under the conditions 121°C/30 minutes/1.03 bar saturated water steam pressure then the lamination bond strength of the polyurethane before and after sterilization is at least 0,5 N/15 mm peeled at 300 mm/min wherein the lamination bond strength is measured with a dry ink film thickness in the range of 1 to 5 micrometers.

In a prefered embodiment the present invention relates to the use of a polyurethane resin as binder for a laminating ink for laminated packaging applications, which resin comprises the reaction product of a diisocyanate and a polyalcohol to form an isocyanate-terminated prepolymer, which prepolymer is extended with a diamine to form the polyurethane resin, said polyurethane resin having at least the same high lamination bond strength before and after sterilization with the proviso that if sterilization is done under the conditions 121°C/30 minutes/1,03 bar saturated water steam pressure then the lamination bond strength of the polyurethane before and after sterilization is at least 1,2 N/15 mm (which corresponds to 200 g/inch) peeled at 300 mm/min wherein the lamination bond strength is measured with a dry ink film thickness in the range of 1 to 5 micrometers.

Polyurethane resins are described herein which are useful as binders in formulating printing inks for packaging applications, in preparing laminates, which laminates maintain their printed ink images and structural integrity after being subjected to sterilization conditions.

The polyurethane resin of the invention is soluble in an organic solvent, such as alcohol, ester and alcohol/ester blends, and is particularly useful in formulating packaging laminating inks. The resins solubility in alcohol, ester and alcohol/ester blends allows for the formulation of ink or coating compositions for flexo and gravure applications.

Laminating ink and coating compositions formed with the polyurethane resin of the invention exhibit excellent extrusion bond strengths, block resistance, printability, resolubility, sterilization resistance, and superior adhesion on a wide variety of films, as compared to laminating inks and coatings made with conventional and commercially available polyurethane resin binder systems. Particularly, the ink compositions containing the polyurethane resin of the invention are especially suitable for packaging applications wherein laminates printed with the ink compositions undergo sterilization treatment.

The polyurethane resin is prepared by reacting an aliphatic, cycloaliphatic, aromatic or alkylaromatic diisocyanate with a polyalcohol to provide an isocyanate-terminated polyurethane prepolymer. The prepolymer is then chain extended using a diamine to form urea linkages. Typically, the resulting polyurethane resin has a number average molecular weight of from 10000 to 100000 Daltons, preferably from 20000 to 60000.

Any diisocyanate of the formula:

OCN-Z-NCO

wherein Z is an aliphatic, cycloaliphatic, aromatic, or alkylaromatic group can be reacted with a polyalcohol such as a polyether diol, a polyester diol, or combinations thereof to prepare the isocyanate-terminated polyurethane prepolymer. Examples of diisocyanates include, but are not limited to, 1,4-diisocyanatobutane, 1,6-diisocyanatohexane, 1,5-diisocyanato-2,2-dimethylpentane, 2,2,4- or 2,4,4-trimethyl-1,6-diisocyanatohexane, 1,10-diisocyanatodecane, 1,3- and 1,4-diiso-cyanatocyclo-hexane, 1-isocyanato-5-isocyanatomethyl-3,3,5-trimethylcyclohexane (isophorone diisocyanate), 2,3-, 2,4- and 2,6-

diisocyanato-1-methylcyclohexane, 4,4'- and 2,4'-diisocyanatodicyclohexylmethane, 1-isocyanato-3(4)-isocyanatomethyl-1-methyl-cyclohexane, 2,4-, and 2,5- and 2,6-tolylene diisocyanate, 1,3- and 1,4-phenylene diisocyanate, 4,4'- and 2,4'-diisocyanatodiphenylmethane, 1,3-bis(1-isocyanato-1-methylethyl)benzene, dimer diisocyanate and mixtures thereof. Preferred is dicyclohexylmethane diisocyanate.

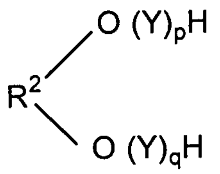
Suitable polyalcohols include one or more polyether diols, one or more polyester diols, and mixtures thereof.

Suitable polyether diols include those represented by the formula:

$$HO - (RO)_n - H$$

wherein R is an alkylene group with 2 to 8 carbon atoms which may be linear or branched. Preferably, R is a C_2 to C_4 alkylene group. Examples of particularly useful polyether diols include, but are not limited to, poly (ethylene ether) glycols, poly (propylene) ether glycols and poly (tetramethylene ether) glycols, with poly (tetramethylene ether) glycols being preferred. Particularly preferred is a mixture of polytetramethylene glycol and polypropylene glycol in a ratio of 50:50. The number average molecular weight of the polyether diol typically ranges from 250 to 10000, preferably from 1000 to 2500, and more preferably from 1250 to 2000. The polyether diols can also contain a minor percentage by weight, e.g., up to 40 weight percent, of ester units. These diols can be obtained, e.g., by reacting one or more of the aforesaid polyether diols with a lactone such as e-caprolactone.

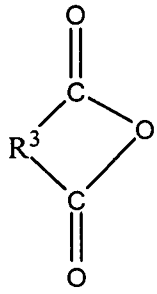
Useful polyester diols include those represented by the formula:

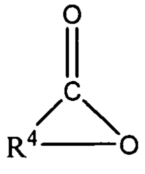


wherein

- R^2 the residue of a diol HOR^2OH, wherein R^2 is an alkylene group with 2 to 8 carbon atoms which may be linear or branched
- Y is $-OCR^3COOR^2O$ in which R^2 has the aforestated meaning and R^3 is the residue of a dicarboxylic acid $HOOCR^3COOH$ or anhydride (I) thereof, wherein R^3 is an alkylene group with 2 to 8 carbon atoms which may be linear or branched and p and q

independently is from 0 to 600 and preferably from 1 to 100, the sum of p + q being from 1 to 1200 and preferably from 1 to 250, or Y is $-OCR^4O-$ in which R^4 is the residue of a lactone (II) or an α, ω – hydroxycarboxylic acid HOR^4COOH and p, q and the sum of p + q have the aforestated values. Diols HOR^2OH, carboxylic acids $HOOCR^3COOH$, anhydrides (I), lactones (II) and α, ω – hydroxycarboxylic acids HOR^4COOH that can be used herein include any of those known for preparing polyester diols. Suitable diols include ethylene glycol, propylene glycol, 1, 4-butane diol, neopentyl diol, hexanediol, diethylene glycol, dipropylene glycol, and the like. Suitable dicarboxylic acids and anhydrides include adipic acid, phthalic acid, phthalic anhydride, and the like. Suitable lactones and α, ω – hydroxycarboxylic acids include butyrolactone, caprolactone, α, ω – hydroxycaproic acid and the like. Examples of particularly useful polyester diols include, but are not limited to, poly(caprolactone) diols, poly(diethylene glycol-co-ortho-phthalic acid), poly(1,6 hexanediol-co-ortho-phthalic acid), poly(neopentyl glycol-co-adipatic acid), and poly(ethylene glycol-co-adipic acid). The number average molecular weight of the polyester diol typically ranges from 250 to 10000, preferably from 500 to 2500, and more preferably from 1000 to 2000. The polyester diols can also contain ether units. In a prefered embodiment the polyester diols contain ether units in an amount of up to 40% (percentage by weight). These diols can be obtained, e.g., by reacting one or more of the aforesaid polyester diols with one or more 1,2-alkylene oxides such as ethylene oxide, propylene oxide, etc.


(I)


(II)

Polyether diols are desirable in terms of the product polyurethane resin having greater solubility in aliphatic alcohol solvents compared with polyester diols. However, polyester diols impart greater tensile strength to the resin. Therefore, depending on the choice of polymeric diol, the polyurethane resin obtained in accordance with the invention can vary from those resins possessing high solubility and relatively low tensile strength, i.e., those made entirely from polyether diol to those of relatively low solubility and relatively high tensile strength made entirely from polyester diol, and all of the combinations of solubility and tensile strength properties in between as would be the case where mixtures of polyether and polyester diols are employed. Optimum proportion of solubility and strength can be obtained through routine testing.

The polyalcohol and diisocyanate are reacted under conditions which are well known to those skilled in the art. Preferably, the reaction is carried out in the presence of a solvent, which is a solvent that is typically used in compositions formulated using the resin such as the solvent system of an ink formulation. Examples of suitable solvents in which the diisocyanate and polyalcohol can be reacted include, but are not limited to alkyl (1-5 carbon) acetates such as methyl acetate, ethyl acetate, propyl acetate, butyl acetate and pentyl acetate, with butyl acetate being particularly preferred.

The ratio of diisocyanate to polyalcohol is selected to obtain a desired molecular weight as well as a desired level of urethane and urea segments. An excess of diisocyanate is used to ensure that the prepolymer is isocyanate terminated. The equivalent ratio of diisocyanate to diol generally ranges from 1,2-5,0 to 1, preferred is a ratio of 2,0 to 1.

The total amount of solvent used for preparation of the isocyanate-terminated prepolymer typically ranges from 0 to 95 percent by weight of the total solution, preferably ranges from 10 to 80 percent by weight of the total solution, and more preferably ranges from 20 to 40 percent by weight of the total solution.

Formation of the isocyanate-terminated prepolymer is generally carried out at a temperature ranging from 0 to 130°C, preferably ranging from 50 to 90°C. The time of the reaction generally ranges from a period of from 1 to 12 hours, preferably from 2 to 4 hours.

The isocyanate-terminated prepolymer is then chain extended with a diamine to form a polyurethane resin. The diamine can be any aliphatic, cycloaliphatic, aromatic, or heterocyclic diamine in which each of the amine groups possesses at least one labile hydrogen atom. Among the many suitable diamines are ethylene diamine, 1,2-diaminopropane, 1,3-diaminopropane, hydrazine, diaminobutane, hexamethylene diamine, 1,4-diaminocyclohexane, 3-aminomethyl-3,5,5-trimethylcyclohexylamine (isophorone diamine), 1,3-bis(aminomethyl)cyclohexane, 1,3-bis(aminomethyl)benzene, 2-(aminomethyl)-3,3,5-trimethylcyclopentylamine, bis-(4-aminocyclo-hexyl)-methane, bis-(4-amino-3-methylcyclohexyl)-methane, 1-amino-1-methyl-3(4)-aminomethyl-cyclohexane, bis-(4-amino-3,5-diethylcyclohexyl)-methane, bis-amino-methyl-hexahydro-4,7-methanoindane, 2,3-, 2,4- and 2,6-diamino-1-methyl-cyclohexane, dimer diamine (diamine from dimerized fatty acids), norbornane diamine, 2,2,4- and 2,4,4-trimethyl-1,6-hexanediamine, DuPont brand Dytek™ A and Dytek™ EB, Huntsman's Jeffamine™ brand bis(propylamino) polypropylene oxide diamines, bis(aminomethyl)tricyclodecane, piperazine, 1,3-di-piperidylpropane, aminoethylpiperazine. Isophorone diamine is preferred.

The conditions under which the diamine is reacted with the prepolymer are not critical and are within the purview of one skilled in the art. Preferably, the reaction is carried out in the solvent or in a component of the solvent system ultimately used in the final composition formulated from the ink resin as described. The amount of solvent utilized in the chain extension reaction generally ranges from 0 to 90 percent by weight, and preferably from 35 to 60 percent by weight. The ratio of isocyanate end groups of the prepolymer to amines from the diamine determines the final polymer molecular weight of the resin as well as the level of urea groups. Generally the mole ratio of diisocyanate to diamine is from 6:1 to 1:5, preferably from 4:1 to 1:4. Typically, when the prepolymer is reacted with a stoichiometric excess of the diamine, no residual unreacted isocyanate groups remain in the prepolymer. Accordingly, reaction of the chain-extended prepolymer with an amine or alcohol terminating agent to endcap unreacted isocyanate groups on the chain-extended prepolymer is not required. Alternatively, if less than a stoichiometric excess of diamine is utilized, unreacted isocyanate groups may be present which can be endcapped as described below. The chain extension reaction with diamine is generally carried out at a temperature ranging from 0 to 90°C, and preferably ranging from 25 to 75°C.

Following the chain extension reaction with diamine, if unreacted isocyanate groups exist some or all of the remaining isocyanate groups are preferably endcapped with an amine or alcohol to terminate the foregoing poly(urethane-urea) resin. Examples of suitable amines are monoamines and diamines including, but not limited to butylamine, dibutylamine, aminopropylmorpholine, aminoethylpiperazine, dimethylaminopropylamine, di(isopropanol)amine, aminoethoxyethanol, aminoundecanoic acid, ethanolamine, dimethanolamine, 4-aminophenol, isophoronediamine, dimer diamine, oleyl amine, hydrazine, Jeffamine brand mono or bis (aminopropyl) polypropyleneoxides. Examples of suitable alcohols include, but are not limited to, 1-propanol, 2-propanol, 1-butanol, 2-butanol, neopentyl alcohol, ethanol, oleyl alcohol, 12-hydroxystearic acid, N-(hydroxyethyl)stearamide, ethoxylated nonylphenol, propoxylated nonylphenol, glycolic acid, or 6-hydroxycaproic acid.

The endcapping reaction of any remaining free isocyanate groups is carried out under conditions which are well known to those skilled in the art. Preferably, this reaction is carried out in the presence of a solvent or in a component of the solvent system ultimately used in the final composition formulated from the ink resin as described above. The total amount of solvent utilized to endcap the free isocyanate groups generally ranges from 0 to 90 percent by weight, preferably ranges from 25 to 75 percent by weight.

The temperature of the endcapping reaction generally ranges from 0 to 100°C, and preferably ranges from 25 to 75°C. The time of the endcapping reaction generally ranges from a period of from 0.1 to 6 hours, and preferably from 0.25 to 1 hours. The NCO-equivalent ratio of the chain-extended resin to amine or alcohol generally ranges from 5:1 to 1:5, and preferably ranges from 1:2 to 2:1.

The polyurethane resins of the present invention advantageously maintain at least the high laminate bond strengths before and after laminates, printed with the ink compositions containing the polyurethane resins, are subjected to sterilization.

By the polyurethane resins maintaining at least the high lamination bond strength before and after retort, a laminate printed with an ink composition containing the polyurethane resin as a binder advantageously maintains its printed image and structural integrity, i.e., the laminate remains substantially free of delamination-related defects.

The term "high lamination bond strength" shall be understood to encompass those polyurethane resins exhibiting lamination bond strength of greater than 0,5 N/15 mm peeled at 300 mm/min. In a preferred embodiment the lamination bond strength is at least 1,2 N/15 mm peeled at 300 mm/min

The laminating ink composition of the invention comprises the polyurethane resin of the invention; a colorant; and an organic solvent. The ink composition of the invention may be used in either flexo or gravure printing. In particular, the ink of the invention comprises, based on the weight of the ink: 10 wt. % to 50 wt. % of the polyurethane resin, 6 wt. % to 50 wt. % of the colorant and 10 wt. % to 80 wt. % of the organic solvent, where component concentrations may be adjusted for use in flexo or gravure printing. Preferably, the gravure ink comprises 8 wt. % to 60 wt. % of the polyurethane resin, 3 wt. % to 30 wt. % of the colorant and 10 wt. % to 80 wt. % of the organic solvent such as alkyl ester solvent; and the flexo ink comprises, 8 wt. % to 60 wt. % of the polyurethane resin, 3 wt. % to 50 wt. % of the colorant and 10 wt. % to 80 wt. % of the organic solvent such as an alcohol solvent. The ink suitably has a viscosity between 15 seconds to 30 seconds, as measured in a Zahn 2 efflux cup. Efflux cup measurements are conventional methods for measuring ink viscosities, and involve timing the flow of a calibrated quantity of ink through a calibrated orifice. The lower viscosity inks typically are used in gravure printing and the higher viscosity inks typically are used in flexo printing. Thus, when the ink has a viscosity of 28 seconds as measured in a Zahn 2 efflux cup, it is suitable for flexo printing; and when the ink has a viscosity of 18 seconds as measured in a Zahn 2 efflux cup, it is suitable for gravure printing applications.

Another aspect of the invention relates to the printing of the laminating ink image wise onto a surface of a polymeric substrate and forming a dried ink image on a surface of the substrate, which image is tack-free, firmly adherent to the surface of the substrate, and unblocked when contacted under pressure at ambient temperatures to a second surface of the same or another substrate. Although any polymeric substrate may be printed with this method, preferred polymeric substrates include polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), cellulose acetate, cellulose acetate butyrate, polycarbonate (PC), polyamide (PA), PVDC coated polyethylene terephthalate, PVDC coated polypropylene, metallized polyethylene terephthalate, or metallized polypropylene. Particularly preferred film substrates used for lamination are PET, PP, PA, silicon dioxide coated PET, PA and PP and aluminum oxide coated PET, PA and PP films.

A second substrate or even more may be laminated to the dried ink image on the first substrate by any conventional method to form a printed laminate. Thus, the second substrate may be applied as an extruded melt onto the dried image to form the second substrate; alternatively, a preformed second substrate or a combination of films may be laminated to the dried ink image through an adhesive surface. The second substrate or a combination of films may be composed of the same material as the first substrate or it may be different depending on the nature of the end use of the printed laminate.

In general, at least one of the substrates will be translucent to visible light and, more typically, transparent. Such transparency or translucency will allow colorant to present a hue and/or resolvable image through the substrate.

An additional embodiment of the present invention further comprises subjecting the printed laminate to sterilization conditions to form a sterilized laminate, wherein the ink image remains substantially unchanged and wherein the sterilized laminate is free of delamination defects. In this embodiment, the printed laminate can be a packaging material for contents (e.g., such as foods, medicines and the like) which are processed in situ at elevated temperatures by sterilization. A typical sterilization operation commonly used in the food packaging industry involves water steam at 121°C/30 minutes/1,03 bar saturated water steam pressure.

The sterilized laminate advantageously maintains the properties described above after being subjected to sterilization due to the presence of the polyurethane resin of the invention in the printing ink composition used to form the printed image.

The following Examples are illustrative of the present invention and should not be construed in any manner whatsoever as limiting of the scope of the invention.

EXAMPLES

1. Test methods

US units and SI

US units and SI units can be interconverted as follows:

250°F = 121.1°C
175°F = 79.4C
1 g/inch = 0.005791 N/15 mm
1 psi = 0.0689475728 bar
1 lb/ream = 1.631g/m^2

Printing

A 165P hand proofer from Pamarco was used in printing inks onto the films.

Tape adhesion

The tape Scotch® 610 from 3M was stuck immediately after the prints were dried:

0% = poor ink adhesion with 100% ink coming off from the substrate
100% = excellent ink adhesion with 0% ink coming off from the substrate

Block resistance

Prints were folded to have ink/back and ink/ink contact.
Folded prints were subjected to 52°C/2.8 bar/24 h (which corresponds to125 F/40 psi /24 h) in an oven.

1 = poor block resistance with 100% ink transfer from the print side
10 = excellent block resistance with 0% ink transfer from the print side

Adhesive lamination

Laminate structure (example): film/ink/adhesive/film

Dry adhesive film thickness: 3.3 - 4.9 g/m^2 (corresponds to 2-3 lb/ream)

Lamination condition: 79°C/1.438 bar/1 sec (corresponds to 175 F/20 psi/1 sec) using a CARD/GUARD® laminator from Jackson-Hirsh Laminating.

Adhesives were applied on the printed film. The coating weight and cure conditions were followed according to the adhesive manufacturer's recommendations. For the solvent-based adhesive Adcote® 812/Adcote® 811B, a coating weight of at 3.3 - 4.9 g/m^2 dry (corresponds to 2-3 lb/ream) was applied and the laminates were cured at 52° C for 3 days. For the solvent-based adhesive Liofol® UR 3644/Hardener UR 6055, a coating weight of 3.3 - 4.9 g/m^2 dry (corresponds to 2-3 lb/ream) was applied and the laminates were cured at room temperature for 3 days.

Sterilization conditions

After the laminates were cured they were subjected to water steam sterilization at 121°C/30 minutes/1.03 bar saturated water steam pressure (corresponds to 250 F/15 psi/30 min) in an All American Electric Pressure Steam Sterilizer. Bond strengths of the laminates were measured before and immediately after sterilization.

Bond strength test

Thwing Albert Friction/Peel tester Model 225-1, prints were supported with tape, peeled at 180°C with 300 mm/min speed, values are average of 3 readings in N/15 mm.

Destruct: complete film tear during peel

FT: partial film tear during peel

Decal: 100% = all ink coming off from the printed film during peel

0% = no ink coming off from the printed film during peel

2. Raw materials

Desmodur W® from Bayer
Pluriol P 2000® from BASF
Poly THF 2000® from BASF
BiCat 8® from Shepherd Chemical
Pluracol 2010® from BASF
BiCat-8® from Shepherd Chemical
Versamid PUR 1120® from Cognis
Mondur ML® from Bayer

Blue 15:4 = Lionol Blue FG 7400 G pigment from Toyo
TR 52 = Titanium dioxide pigment from Huntsman
RDE 2 = Titanium dioxide pigment from Kemira

T523-3 = 15 µm corona pre-treated boPP film from AET Films
Mylar® 813 = 12 µm corona pre-treated PET from DuPont
Techbarrier® NR = 15 µm SiO_X coated oPA film (not corona treated) from Mitsubishi Plastics
Techbarrier® TZ = 12 µm SiO_X coated PET film (not corona treated) from Mitsubishi Plastics
Emblem® 1500 = 15 µm corona pre-treated boPA film from Honeywell
Tredegar® CPP = 76 µm corona pre-treated white, opaque cPP film from Tredegar
50 µm corona pre-treated white, opaque PE film from Southern Converter
26 µm aluminium foil from Reynolds

Adcote® 812/Adcote® 811B = 2-component polyurethane adhesive from Rohm & Haas
Liofol® UR 3644/Hardener UR 6055 = 2-component polyurethane adhesive from Henkel

PVB blue ink = SFP Blue from Siegwerk
PVB white ink = HP 930 White from Siegwerk

Polyurethane Examples

Example Resin 1:

6.65% Desmodur™ W, 12.64% Pluriol™ P 2000 and 12.64% Poly THF™ 2000 were reacted using 0.02% BiCAT™ 8 as catalyst and 8.75% butylacetate as solvent at 80-85° C for 2 hrs under nitrogen flow until NCO% of 2.60 was achieved. This resulted in an isocyanate terminated prepolymer with 78.50% solids and a viscosity of 2220 cps at 25° C.

The final polyurethane resin solution was prepared by adding the above prepolymer solution at a controlled rate to 2.72% of isophorone diamine in 45.51% 1-propanol and 11.06% butylacetate.

The final polyurethane solution had a viscosity of 580 cps at 25° C, solids of 36.5% and Gardner color of less than 2.

Example Resin 2:

6.76% Desmodur™ W, 25.90% PolyTHF™ 2000 were reacted using 0.02% BiCAT™ 8 as catalyst and 8.95% butylacetate as solvent at 80-85° C for 2 hrs under nitrogen flow until NCO% of 2.60 was achieved. This resulted in an isocyanate terminated prepolymer with 81.8% solids and a viscosity of 14,000 cps at 25° C.

The final polyurethane resin solution was prepared by adding the above prepolymer solution at a controlled rate to 2.75% of isophorone diamine in 45.91% 1-propanol and 9.72% butylacetate.

The final polyurethane solution had a viscosity of 6060 cps at 25° C, solids of 35.80% and Gardner color of less than 2.

Example Resin 3:

6.47% Mondur™ ML, 13.10% Plurocol™ 2010 and 13.10% Poly THF™ 2000 were reacted using 0.02% BiCAT™ 8 as catalyst and 8.95% butylacetate as solvent at 80-85° C for 2 hrs under nitrogen flow until NCO% of 2.60 was achieved. This resulted in an isocyanate terminated prepolymer with 80.50% solids and a viscosity of 3670 cps at 25° C.

The final polyurethane resin solution was prepared by adding the above prepolymer solution at a controlled rate to 2.71% of isophorone diamine in 45.93% 1-propanol and 9.73% butylacetate.

The final polyurethane solution had a viscosity of 3990 cps at 25° C, solids of 35.3% and Gardner color of less than 2.

Example Resin 4:

6.48% Mondur™ ML, 26.20% Plurocol™ 2010 reacted using 0.02% BiCAT™ 8 as catalyst and 8.95% butylacetate as solvent at 80-85° C for 2 hrs under nitrogen flow until NCO% of 2.60 was achieved. This resulted in an isocyanate terminated prepolymer with 79.70% solids and a viscosity of 926 cps at 25° C.

The final polyurethane resin solution was prepared by adding the above prepolymer solution at a controlled rate to 2.67% of isophorone diamine in 45.94% 1-propanol and 9.73% butylacetate.

The final polyurethane solution had a viscosity of 696 cps at 25° C, solids of 32.7% and the solution was turbid.

Example Resin 5:

6.76% Desmodur™ W, 25.88% Plurocol™ 2010 reacted using 0.02% BiCAT™ 8 as catalyst and 8.94% butylacetate as solvent at 80-85° C for 2 hrs under nitrogen flow until NCO% of 2.60 was achieved. This resulted in an isocyanate terminated prepolymer with 81.70% solids and a viscosity of 828 cps at 25° C.

The final polyurethane resin solution was prepared by adding the above prepolymer solution at a controlled rate to 2.78% of isophorone diamine in 45.89% 1-propanol and 9.72% butylacetate.

The final polyurethane solution had a viscosity of 367 cps at 25° C, solids of 40.0% and Gardner color of less than 2.

Ink formula	Example ink 1	Example ink 2	Example ink 3	Example ink 4	Example ink 5
Example resin 1 (g)	35,8				
Example resin 2 (g)		36,3			
Example resin 3 (g)			36,8		
Example resin 4 (g)				39,8	
Example resin 5 (g)					32,5
Blue 15:4 (g)	17,0	17,0	17,0	17,0	17,0
1-propanol/butyl acetate 8:2 (g)	47,2	46,7	46,2	43,2	50,5
Total (g)	100,0	100,0	100,0	100,0	100,0
Glass beads (g)	30	30	30	30	30
Total solids (%)	30	30	30	30	30
Grinding time (min)	30	30	30	30	30
Pigment : binder ratio	1.3 : 1.0	1.3 : 1.0	1.3 : 1.0	1.3 : 1.0	1.3 : 1.0
Initial viscosity (Zahn 2 cup, sec)	33	92	80	37	21
% dilution with 1-propanol to 25 se	10	20	20	12	0

Performance Examples

Performance Example 1:

Laminate structure: boPP or PET/ink/Adcote® 812/Adcote® 811B/Emblem® 1500/Adcote® 812/Adcote® 811

T523-3 boPP film	Example Ink 1	Example Ink 2	Example Ink 3	Example Ink 4	Example Ink 5
Lamination bond strength (with tape) before sterilization	destruct	destruct	destruct	destruct	2.9 (FT)
Decal					50%
Lamination bond strength (with tape) after sterilization	destruct	destruct	3.0 (FT)	3.2 (FT)	1.9
Decal			10%	10%	100%
Mylar® 813 PET	Example Ink 1	Example Ink 2	Example Ink 3	Example Ink 4	Example Ink 5
Lamination bond strength (with tape) before sterilization	destruct	destruct	2.9	2.1	1.7
Decal			70%	70%	90%
Lamination bond strength (with tape) after sterilization	destruct	destruct	2.5	destruct	0.04
Decal			50%		70%

Example resin 1 comparison with a commercial PVB ink.

	White ink formula	**Blue ink formula**
	Example ink 1	**Example ink 1**
Example resin 1 (g)	30,00	39,56
TR 52/RDE 2 1:1 (g)	42,00	
Blue 15:4 (g)		18,00
1-propanol/1-propyl acetate 8:2 (g)	28,00	42,44
Total (g)	100,00	100,00
Glass beads (g)	30,00	30,00
Grinding time (min)	60	60
Initial viscosity (Zahn 2 cup, sec)	53	30
Solids (%)	52,50	31,85
Pigment : binder ratio	4,00	1,30

	White ink formulas		Blue ink formulas	
Flow behavior	**PVB ink**	**Example Ink 1**	**PVB ink**	**Example Ink 1**
% dilution with ethanol/ethyl acetate 80:20 to 25 sec (Zahn 2 cup)		15		7
% dilution with ethanol/propyl acetate 80:20 to 25 sec (Zahn 2 cup)	13		4	
Ink solids (%)	40	45,9	27	28,1

Performance Example 2:

Laminate structure: Mylar® 813/ink/adhesive /Techbarrier® NR/adhesive/Tredegar® CPP

	White inks with Adcote 812-811B			White inks with Liofol UK 3644-UK 6055		
	PVB ink	Example ink 1		PVB ink	Example ink 1	
Tape adhesion	95%	100%		95%	100%	
Block resistance	8	10		8	10	
Lamination bond strength (with tape) before sterilization	destruct	1.2		2.4 (FT)	1.0	
Decal		90%		0%	85%	
Lamination bond strength (with tape) after sterilization	5.0	1.1		Destruct	0.8	
Decal	50%	90%			90%	

	Blue ink with Adcote® 812/Adcote® 811B			Blue ink with Liofol® UR 3644/Hardener UR 6055		
	PVB ink	Example ink 1		PVB ink	Example ink 1	
Tape adhesion	100%	100%		100%	100%	
Block resistance	10	9		10	9	
Lamination bond strength (with tape) before sterilization	2.6	destruct		0.8	destruct	
Decal	5%			0%		
Lamination bond strength (with tape) after sterilization	2.0	destruct		destruct	2.6	
Decal	0%				40%	

	White over blue inks with Adcote® 812/Adcote® 811B			White over blue inks with Liofol® UR 3644/Hardener UR 6055		
	PVB ink	Example ink 1		PVB ink	Example ink 1	
Tape adhesion	100%	100%		100%	100%	
Block resistance	8	9		8	9	
Lamination bond strength (with tape) before sterilization	1.9	destruct		0.8	destruct	
Decal	85%			0%		
Lamination bond strength (with tape) after sterilization	1.3	3.3 (FT)		destruct	2.3	
Decal	80%	70%			90%	

Performance Example 3:

Laminate structure: Mylar® 813/ink/adhesive /aluminum foil/adhesive/Tredegar® CPP

	White inks with Adcote® 812/Adcote® 811B			White inks with Liofol® UR 3644/Hardener UR 6055		
	PVB ink	Example ink 1		PVB ink	Example ink 1	
Tape adhesion	95%	100%		95%	100%	
Block resistance	8	10		8	10	
Lamination bond strength (with tape) before sterilization	3.7 (FT)	1.3		destruct	1.7	
Decal	95%	90%			90%	
Lamination bond strength (with tape) after sterilization	destruct	1.0		destruct	1.4	
Decal		95%			95%	

	Blue inks with Adcote® 812/Adcote® 811B			Blue inks with Liofol® UR 3644/Hardener UR 6055		
	PVB ink	Example ink 1		PVB ink	Example ink 1	
Tape adhesion	100%	100%		100%	100%	
Block resistance	10	9		10	9	
Lamination bond strength (with tape) before sterilization	3.9 (FT)	destruct		3.7	destruct	
Decal	5%			5%		
Lamination bond strength (with tape) after sterilization	destruct	destruct		destruct	destruct	
Decal						

	White over blue inks with Adcote® 812/Adcote® 811B			White over blue inks with Liofol® UR 3644/Hardener UR 6055		
	PVB ink	Example ink 1		PVB ink	Example ink 1	
Tape adhesion	100%	100%		100%	100%	
Block resistance	8	9		8	9	
Lamination bond strength (with tape) before sterilization	destruct	destruct		4.1 (FT)	destruct	
Decal				60%		
Lamination bond strength (with tape) after sterilization	2.1	destruct		destruct	destruct	
Decal	70%					

Performance Example 4:

Laminate structure: Techbarrier® TZ/ink/adhesive/Tredegar® CPP

	White inks with Adcote® 812/Adcote® 811B			White inks with Liofol® UR 3644/Hardener UR 6055		
	PVB ink	Example ink 1		PVB ink	Example ink 1	
Tape adhesion	100%	100%		100%	100%	
Block resistance	10	10		10	10	
Lamination bond strength (with tape) before sterilization	2.1	destruct		1.7	0.5	
Decal	95%			95%	90%	
Lamination bond strength (with tape) after sterilization	destruct	destruct		destruct	destruct	
Decal						

	Blue inks with Adcote® 812/Adcote® 811B			Blue inks with Liofol® UR 3644/Hardener UR 6055		
	PVB ink	Example ink 1		PVB ink	Example ink 1	
Tape adhesion	100%	95%		100%	95%	
Block resistance	10	8		10	8	
Lamination bond strength (with tape) before sterilization	destruct	destruct		1.4	2.2	
Decal				5%	95%	
Lamination bond strength (with tape) after sterilization	destruct	destruct		destruct	destruct	
Decal	5%					

	White over blue inks with Adcote® 812/Adcote® 811B			White over blue inks with Liofol® UR 3644/Hardener UR 6055		
	PVB ink	Example ink 1		PVB ink	Example ink 1	
Tape adhesion	100%	100%		100%	100%	
Block resistance	8	10		8	10	
Lamination bond strength (with tape) before sterilization	destruct	destruct		destruct	1.9	
Decal					90%	
Lamination bond strength (with tape) after sterilization	2.7	destruct		destruct	destruct	
Decal	85%					

Performance Example 5:

Laminate structure: Emblem® 1500/ink/adhesive/Tredegar® CPP

	White inks with Adcote® 812/Adcote® 811B			White inks with Liofol® UR 3644/Hardener UR 6055		
	PVB ink	Example ink 1		PVB ink	Example ink 1	
Tape adhesion	100%	100%		100%	100%	
Block resistance	9	10		9	10	
Lamination bond strength (with tape) before sterilization	destruct	2.6 (FT)		1.8	1.8	
Decal		90%		90%	95%	
Lamination bond strength (with tape) after sterilization	3.3	1.4		3.4	1.5	
Decal	90%	95%		90%	95%	

	Blue inks with Adcote® 812/Adcote® 811B			Blue inks with Liofol® UR 3644/Hardener UR 6055		
	PVB ink	Example ink 1		PVB ink	Example ink 1	
Tape adhesion	100%	100%		100%	100%	
Block resistance	9	8		9	8	
Lamination bond strength (with tape) before sterilization	1.9	destruct		2.2	destruct	
Decal	80%			10%		
Lamination bond strength (with tape) after sterilization	2.8	destruct		2.4	destruct	
Decal	40%			65%		

	White over blue inks with Adcote® 812/Adcote® 811B			White over blue inks with Liofol® UR 3644/Hardener UR 6055		
	PVB ink	Example ink 1		PVB ink	Example ink 1	
Tape adhesion	100%	100%		100%	100%	
Block resistance	7	10		7	10	
Lamination bond strength (with tape) before sterilization	1.6	destruct		1.4	destruct	
Decal	85%	10%		90%		
Lamination bond strength (with tape) after sterilization	2.2	destruct		2.4	destruct	
Decal	85%			85%		

Performance Example 6:

Laminate structure: Techbarrier® NR/ink/adhesive/Tredegar® CPP

	White inks with Adcote® 812/Adcote® 811B			White inks with Liofol® UR 3644/Hardener UR 6055		
	PVB ink	Example ink 1		PVB ink	Example ink 1	
Tape adhesion	100%	100%		100%	100%	
Block resistance	8	10		8	10	
Lamintion bond strength (with tape) before sterilization	5.0	2.8		2.3	0.6	
Decal	85%	85%		95%	90%	
Lamination bond strength (with tape) after sterilization	1.8	destruct		3.4	5.8	
Decal	95%			90%	95%	
	Blue inks with Adcote® 812/Adcote® 811B			Blue inks with Liofol® UR 3644/Hardener UR 6055		
	PVB ink	Example ink 1		PVB ink	Example ink 1	
Tape adhesion	90%	95%		90%	95%	
Block resistance	7	8		7	8	
Lamination bond strength (with tape) before sterilization	3.7	8.3		2.3	2.8	
Decal	20%	50%		35%	95%	
Lam bond strength (with tape) after retort condition	4.1	7.7		1.9	8.9	
Decal	10%	35%		80%	5%	
	White over blue inks with Adcote® 812/Adcote® 811B			White over blue inks with Liofol® UR 3644/Hardener UR 6055		
	PVB ink	Example ink 1		PVB ink	Example ink 1	
Tape adhesion	100%	100%		100%	100%	
Block resistance	7	9		7	9	
Lamination bond strength (with tape) before sterilization	1.3	5.8		1.8	2.2	
Decal	85%	65%		90%	95%	
Lamination bond strength (with tape) after sterilization	2.2	6.4		2.7	7.1	
Decal	90%	60%		85%	70%	

As can be seen from the bond strength data above for six laminate structure Performance Examples of the invention, the lamination bond strength of the polyurethane, before and after sterilization, remained above at least 0,5 N/15 mm, thus providing a laminate substantially free of delamination defects while also maintaining the integrity of the printed image.

Patent Claims

1) The use of a polyurethane resin as binder for a laminating ink for laminated packaging applications, which resin comprises the reaction product of a diisocyanate and a polyalcohol to form an isocyanate-terminated prepolymer, which prepolymer is extended with a diamine to form the polyurethane resin, said polyurethane resin having at least the same lamination bond strength before and after sterilization with the proviso that if sterilization is done under the conditions 121°C/30 minutes/1.03 bar saturated water steam pressure then the lamination bond strength of the polyurethane before and after sterilization is at least 0,5 N/15 mm peeled at 300 mm/min wherein the lamination bond strength is measured with a dry ink film thickness in the range of 1 to 5 micrometers.
2) The use of clam 1 having a number average molecular weight of from 10,000 to 100,000 Daltons.
3) The use of claim 2 wherein the number average weight of the resin is from 20,000 to 60,000 Daltons.
4) The use of claim 1 wherein the diisocyanate is selected from the group consisting of 1,4-diisocyanatobutane, 1,6-diisocyanatohexane, 1,5-diisocyanato-2,2-dimethylpentane, 2,2,4- or 2,4,4-trimethyl-1, 6-diisocyanatohexane, 1,10-diisocyanatodecane, 1,3- and 1,4-diiso-cyanatocyclo-hexane, 1-isocyanato-5-isocyanatomethyl-3,3,5-trimethylcyclohexane, 2,3-, 2,4- and 2,6-diisocyanato-1-methylcyclohexane, 4,4'- and 2,4'-diisocyanatodicyclohexylmethane, 1-isocyanato-3(4)-isocyanatomethyl-1-methyl-cyclohexane, 2,4-, 2,5- and 2,6-tolylene diisocyanate, 1,3- and 1,4-phenylene diisocyanate, 4,4'- and 2,4'-diisocyanatodiphenylmethane, 1,3-bis(1-isocyanato-1-methylethyl)benzene, dimer diisocyanate and mixtures thereof.
5) The use of claim 4 wherein the diisocyanate is 2,4'-diisocyanatodicyclohexylmethane dicyclohexylmethane diisocyanate.
6) The use of claim 1 wherein the polyalcohol is selected from one or more polyether diols, one or more polyester diols, and mixtures thereof.
7) The use of claim 6 wherein the polyether diol is of the formula:

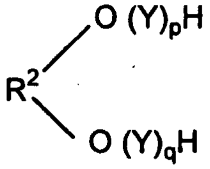
$$HO — (RO)_n — H$$

wherein R is a C_2 to C_8 straight chain or branched hydrocarbon group.

8) The use of claim 7 wherein R is a C_2-C_4 alkylene group.

9) The use of claim 7 wherein the polyether diol is a mixture of polytetramethylene glycol and polypropylene glycol.

10) The use of claim 6 wherein the polyester diol is of the formula:



wherein R^2 is the residue of a diol having the formula HOR^2OH, Y is $-OC R^3COOR^2O$ in which R^2 is of the aforestated formula and R^3 is the residue of a dicarboxylic acid $HOOCR^3COOH$ or anhydride thereof, and p and q independently are from 0 to 600, the sum of p + q being from 1 to 1200, or Y is $-OCR^4 O-$ in which R^4 is the residue of a lactone or an α, ω – hydroxycarboxylic acid HOR^4COOH.

The use of claim 11 wherein the polyester diol is selected from the group consisting of a poly(caprolactone) diol, poly(diethylene glycol-co-ortho-phthalic acid), poly(1,6 hexane diol-co-ortho-phthalic acid), poly(neopentyl glycol-co-adipatic acid), poly(ethylene glycol-co-adipic acid) and mixtures thereof.

11) The use of claim 1 wherein the diisocyanate and polyalcohol are reacted in a ratio of 1,2-5 to 1.

12) The use of claim 1 wherein the diamine is selected from the group consisting of ethylene diamine, 1,2-diaminopropane, 1,3-diaminopropane, hydrazine, diaminobutane, hexamethylene diamine, 1,4-diaminocyclohexane, 3-aminomethyl-3, 5,5-trimethylcyclohexylamine (isophorone diamine), 1,3-bis(aminomethyl)cyclohexane, 1,3 bis(aminomethyl)benzene, 2-(aminomethyl)-3,3,5-trimethylcyclopentylamine, bis-(4-aminocyclo-hexyl)-methane, bis-(4-amino-3-methylcyclohexyl)-methane, 1-amino-1-methyl-3(4)-aminomethyl-cyclohexane, bis-(4-amino-3,5-diethylcyclohexyl)-methane, bis-amino-methyl-hexahydro-4,7-methanoindane, 2,3-, 2,4- and 2,6-diamino-1-methyl-cyclohexane, dimer diamine, norbornane diamine, 2,2,4- and 2,4,4-trimethyl-1,6-hexanediamine, bis(propylamino) polypropylene oxide diamine, bis(aminomethyl)tricyclodecane, piperazine, 1,3-di-piperidylpropane, aminoethylpiperazine and mixtures thereof.

13) The use of claim 12 wherein the diamine is isophorone diamine.

14) The use of claim 1 wherein the isocyanate-terminated prepolymer and the diamine are reacted in a molar ratio of from 6:1 to 1:5.

15) A laminating ink composition for laminated packaging applications, which ink comprises:
    (a) the polyurethane resin of claim 1;
    (b) a colorant; and
    (c) an organic solvent.

16) The ink composition of claim 15 wherein the polyurethane resin is present in an amount of from 10% to 50% by weight; the colorant is present in an amount of from 6% to 50% by weight; and the solvent is present in an amount of from 10% to 80% by weight, based on the weight of the composition.

17) A laminate for use in packaging applications, which laminate comprises a polymeric substrate printed with the ink composition of claim 15 to form a printed image on said substrate, said printed image remaining substantially intact and said laminate having substantially the same lamination bond strength before and after sterilization.

18) The laminate of claim 17 wherein the lamination bond strength before and after sterilization is at least 0,5 N/15 mm peeled at 300 mm/ min.

19) The laminate of claim 17 wherein the polymeric substrate is selected from the group consisting of polyethylene, polypropylene, polyester, cellulosic, polycarbonate, polyamide and polylactic acid.

20) The laminate of claim 19 wherein the substrate is corona pre-treated.

21) The laminate of claim 19 wherein the substrate is chemically pre-treated.

22) The laminate of claim 19 wherein the substrate is metallized.

23) The laminate of claim 19 wherein the substrate is silicon dioxide coated.

24) The laminate of claim 19 wherein the substrate is aluminum oxide coated.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2008/008672

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G18/10 C08G18/28 C08G18/40 C08G18/42 C08G18/48
C09D175/08 C09D11/02

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 C09D

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 496 071 A (SICPA HOLDING SA [CH]) 12 January 2005 (2005-01-12) column 1, line 20 - line 23 column 1, line 35 - line 44 example 1 example 2 claim 11	1-24
X	EP 1 743 911 A (DSM IP ASSETS BV [NL]) 17 January 2007 (2007-01-17) column 1, line 42 - line 47 column 3, line 8 - line 16 column 13, line 30 - line 38 example 1 claim 8	1-24

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☒ 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

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"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 5 February 2009	Date of mailing of the international search report 16/02/2009
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Müller, Marcus

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2008/008672

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 604 890 A (SAKATA INX CORP [JP]) 6 July 1994 (1994-07-06) page 13, line 40 - line 45 page 14, line 14 - line 21 example 1 example 2	1-24
X	WO 02/38643 A (SUN CHEMICAL CORP [US]) 16 May 2002 (2002-05-16) page 1, line 27 - line 33 example 3 examples 10-12 table 12 example 13	1-24
X	WO 01/14442 A (COGNIS CORP [US]) 1 March 2001 (2001-03-01) page 1, line 20 page 23, line 13 - line 20 page 23, line 23 - line 28 example 1	1-24

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2008/008672

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 1496071 A	12-01-2005	AT 304564 T	15-09-2005
		AU 2004255320 A1	20-01-2005
		CA 2532037 A1	20-01-2005
		DE 60301623 T2	16-03-2006
		DK 1496071 T3	19-12-2005
		WO 2005005505 A1	20-01-2005
		ES 2248687 T3	16-03-2006
		US 2006167205 A1	27-07-2006
EP 1743911 A	17-01-2007	CN 101223203 A	16-07-2008
		CN 101238159 A	06-08-2008
		WO 2007006583 A1	18-01-2007
		WO 2007006586 A1	18-01-2007
		US 2008226880 A1	18-09-2008
		US 2008226881 A1	18-09-2008
EP 0604890 A	06-07-1994	DE 69317996 D1	20-05-1998
		DE 69317996 T2	03-09-1998
		ES 2115002 T3	16-06-1998
		JP 3471055 B2	25-11-2003
		JP 6248051 A	06-09-1994
		US 5556925 A	17-09-1996
WO 0238643 A	16-05-2002	CA 2428687 A1	16-05-2002
		EP 1358239 A2	05-11-2003
		US 6723820 B1	20-04-2004
WO 0114442 A	01-03-2001	AU 6777400 A	19-03-2001
		BR 0013434 A	30-04-2002
		EP 1208127 A1	29-05-2002
		JP 2004513977 T	13-05-2004