

Polyurethane Resin Composition for Printing Ink Binder

Technical Field

[0001]

This invention relates to a polyurethane resin composition and to a printing ink composition.

Background Art

[0002]

Conventionally, aromatic solvents having relatively a strong dissolving capability such as toluene and xylene, and ketones such as methyl ethyl ketone and methyl isobutyl ketone are used for a printing ink. In recent years, from global environmental conservation and regulatory viewpoints, consideration of environmental issues is required even in the printing ink industry. For this reason, a printing ink using ester/alcohol solvent system instead of those aromatic and ketone solvents is desired. For that end, researches on printing inks containing ester/alcohol solvent system have been carried out. However, compared with aromatic or ketone solvents, ester/alcohol solvent system has lower dissolving capability, resulting in inferior printability. Reinforcing the dissolving capability of ester/alcohol solvent system, however, degrades other properties such as resistance to alcohol bleeding or blocking resistance, so that many problems still remain.

[0003]

For example, Japanese Patent Laid-open No. H9-316156 discloses a polyurethane composition and printing ink composition comprising diphenylmethane diisocyanate, and that the compositions have an excellent adhesion to a various plastic films. However, the composition comprises, in order to ensure printability, methyl ethyl ketone of which elimination is required. Further, because a ratio, $[NCO]/[OH]$, is low, blocking resistance is not satisfactory.

[0004]

Japanese Patent Laid-open No. 2003-221539 discloses an ester/alcohol solvent system having an improved dissolving property used for an ink. However, the ink contains a hydroxycarboxylic acid, which causes problems of residual solvent, and low resistance to water and alcohol bleeding.

Prior art literature

Patent documents

[0005]

Patent Document 1: Japanese Patent Laid-open No. H 9-316156

Patent Document 2: Japanese Patent Laid-open No. 2003-221539

Summary of the invention

Problems to Be Solved by the Invention

[0006]

The present invention intends to provide a printing ink composition which neither contains aromatic organic solvents such as toluene and xylene nor ketone organic solvents such as methyl ethyl ketone or methyl isobutyl ketone. The present invention also intends to provide a printing ink composition comprising an ester/alcohol solvent system, which has excellent printability such as non-fogging of plate property, and printing properties such as adhesion to various plastic films, blocking resistance and resistance to alcohol breeding, and lamination property.

Means to Solve the Problems

[0007]

As a result of extensive studies in view of the aforesaid matters, the present inventors have found to make the invention that the use of a polyurethane resin obtained by using polyisocyanates including tolylene diisocyanate and alkanolamine as a reaction terminator, and by controlling synthesis parameters allows to design a printing ink composition that achieves both good printability and printing property though it contains an ester/alcohol solvent system having a relatively low dissolving capability.

[0008]

The first embodiment of the present invention is a polyurethane resin composition comprising a polyurethane resin and a mixed solvent, wherein the polyurethane resin is prepared by reacting a urethane prepolymer having terminal isocyanate groups with an organic diamine and an alkanol amine, said urethane prepolymer being prepared by reacting polyisocyanates comprising a tolylene diisocyanate with a polymeric polyol, wherein

(A) a molar ratio of total isocyanate groups of the polyisocyanates to hydroxyl groups of the polymeric polyol, $[NCO(\text{total})]/[OH]$, ranges from 1.8 to 2.3;

(B) a molar ratio of isocyanate groups of tolylene diisocyanate to hydroxyl groups of the polymeric polyol, $[NCO(TDI)]/[OH]$, ranges from 1.0 to 2.1;

(C) a hydroxyl value of the polyurethane resin ranges from 1.0 to 10.0 mgKOH/g;

(D) a molar ratio, $d1/d2$, where $d1$ represents a molar amount of the organic diamine, and $d2$ represents a molar amount of the alkanolamine, ranges from 3 to 25;

(E) the mixed solvent comprises an ester solvent and an alcohol solvent; and

(F) the polymeric polyol consists of a polyester diol and a polyether diol.

[0009]

The second embodiment of the present invention is the polyurethane resin composition, wherein the polymeric polyol contains 20 to 80 wt% of the polyester diol, and 80 to 20 wt% of the polyether diol.

[0010]

The third embodiment of the present invention is a printing ink composition comprising the polyurethane resin composition of the first or second embodiment of the present invention.

Effects of the Invention

[0011]

The embodiments of the present invention provide a printing ink composition which shows excellent printability and printing properties, although the solvent thereof is an ester/alcohol solvent system.

Embodiments for Carrying Out the Invention

[0012]

The polyurethane resin composition for a printing ink binder will be described below. The polyurethane resin is obtained by reacting a urethane prepolymer having terminal isocyanate groups with an organic diamine as a chain extender and an alkanolamine as a reaction terminator, which urethane prepolymer is obtained by reacting a polymeric polyol with polyisocyanates comprising tolylene diisocyanate.

[0013]

In the polyurethane resin used for printing ink binder, polyisocyanate to form urethane and urea bonds functioning as hard segments is an important factor for solubility thereof in ester/alcohol solvents, and for printing properties on various plastic films.

[0014]

In the present invention, polyisocyanates used for the polyurethane resin include tolylene diisocyanate, hereinafter it may be referred to as TDI. Tolylene diisocyanate is preferably 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, or a mixture thereof.

[0015]

Since tolylene diisocyanate has one aromatic ring in the molecule, it is more resistant to alcohol, compared with alicyclic isocyanates and aliphatic isocyanates. On the other hand, compared with the diphenylmethane diisocyanate having two aromatic rings, tolylene diisocyanate having one aromatic ring is more compatible with the ester/alcohol solvent system. Therefore, tolylene diisocyanate facilitates balancing printability such as non-fogging of plate property with resistance to alcohol bleeding of a printing ink containing an ester/alcohol solvent system.

[0016]

In a preparation of urethane prepolymer, a molar ratio of total isocyanate groups of the polyisocyanates to hydroxyl groups of polymeric polyol, $[NCO(\text{total})]/[OH]$, ranges from 1.8 to 2.3. When $[NCO(\text{total})]/[OH]$ is 1.8 or greater, excellent blocking resistance and resistance to alcohol breeding are achieved because of sufficient amount of hard segments. When $[NCO(\text{total})]/[OH]$ is 2.3 or smaller, excellent non-fogging of

plate property is achieved. Further, excellent adhesion and EL laminate strength are achieved because of adequate number of hard segments.

[0017]

In an embodiment of the invention, a molar ratio of isocyanate groups of tolylene diisocyanate to hydroxyl groups of polymeric polyol, $[\text{NCO}(\text{TDI})]/[\text{OH}]$, ranges from 1.0 to 2.1. In general, aromatic isocyanates react with hydroxyl groups or amino groups faster than aliphatic isocyanates or alicyclic isocyanates. For this reason, with $[\text{NCO}(\text{TDI})]/[\text{OH}]$ being 2.1 or smaller, a uniform polyurethane resin can be synthesized due to an appropriate reaction rate. In addition, excellent non-fogging of plate property is achieved because of an appropriate concentration of aromatic ring in a molecule. Further, a good resistance to alcohol bleeding is achieved when $[\text{NCO}(\text{TDI})]/[\text{OH}]$ is 1.0 or greater.

[0018]

Other polyisocyanate than tolylene diisocyanate can be used as long as the ranges of $[\text{NCO}(\text{total})]/[\text{OH}]$ and $[\text{NCO}(\text{TDI})]/[\text{OH}]$ are satisfied. The examples of other polyisocyanate include various known aliphatic isocyanates and alicyclic isocyanates commonly used in the production of polyurethane resin, for example, butane-1, 4 - diisocyanate, hexamethylene diisocyanate, isopropylidene diisocyanate, methylene diisocyanate, 2,2,4-trimethyl hexamethylene diisocyanate, lysine diisocyanate, cyclohexane-1,4 - diisocyanate, isophorone diisocyanate, dimethyl diisocyanate, dicyclohexyl methane-4, 4' - diisocyanate, 1,3 - bis (isocyanate methyl) cyclohexane, methyl cyclohexane diisocyanate, norbornane diisocyanate, and dimer diisocyanate having isocyanate groups converted from carboxyl groups of a dimer acid. Among these polyisocyanates, isophorone diisocyanate is preferable from the viewpoints of reaction rate of isocyanate group and other properties.

[0019]

A particularly excellent resistance to alcohol-bleeding is observed when 90 to 100 mole% of the total isocyanate groups are isocyanate groups of tolylene diisocyanate, and 10 to 0 mole% are those of isophorone diisocyanate. An excellent non-fogging of plate property is observed when 50 to 75 mole% of the total isocyanate groups are isocyanate groups of tolylene diisocyanate, 50 to 25 mole% are those of isophorone diisocyanate, and more than 35 wt% of the solvent in the printing ink composition are alcoholic solvents. The mixed solvent in the printing ink composition will be detailed later in the specification.

[0020]

A hydroxyl value of the polyurethane resin is an important factor to balance the printability such as non-fogging of plate property with the resistance to alcohol-bleeding in the ester/alcohol solvent system. In an embodiment of the present invention, the hydroxyl value of the polyurethane resin ranges from 1.0 to 10.0mgKOH/g. With the hydroxyl value of 1.0 mgKOH/g or higher, excellent adhesion, EL laminate strength,

solubility and thus non-fogging of plate property are achieved. With the hydroxyl value of 10.0 mgKOH/g or lower, excellent resistance to alcohol-breeding is achieved.

[0021]

Examples of the organic diamine as chain extender in the present embodiment includes ethylene diamine, propylene diamine, hexamethylene diamine, isophorone diamine, dicyclohexylmethane-4, 4'-diamine, and amines having a hydroxyl group such as 2-hydroxyethyl ethylene diamine, 2-hydroxyethyl propyl diamine, 2-hydroxyethyl propylene diamine, di-2-hydroxyethyl ethylene diamine, di-2-hydroxy ethylene diamine, di-2-hydroxyethyl propylene diamine, 2-hydroxypropyl ethylene diamine, di-2-hydroxypropyl ethylene diamine. These chain extenders can be used alone or a mixture of two or more of them. Among them, isophorone diamine is particularly preferred.

[0022]

In an embodiment of the present invention, a molar ratio, $d1/d2$, where $d1$ represents a molar amount of an organic diamine in the polyurethane resin, and $d2$ represents a molar amount of alkanolamine, ranges from 3 to 25. With $d1/d2$ being 3 or larger, excellent resistance to alcohol-breeding is achieved, and significantly good blocking resistance is also achieved because of a larger weight average molecular weight of the polyurethane resin. With $d1/d2$ being 25 or smaller, excellent adhesion, EL laminate strength, solubility and thus non-fogging of plate property are achieved.

[0023]

It should be noted that the use of a larger amount of alkanolamine, which is a reaction terminator, leads to a polyurethane resin having a smaller weight average molecular weight. In addition, it also leads to a larger hydroxy value due to hydroxyl group contained in alkanolamine. Examples of alkanolamine include monoethanolamine, diethanolamine and so on. They can be used alone or as a mixture thereof. Especially preferred is monoethanolamine.

[0024]

As the polymeric polyol, any known polyester polyol and polyether polyol can be used alone or combination of two or more of them. Examples of polyester polyol include those prepared by dehydration condensing or polymerizing saturated or unsaturated low molecular weight polyols with polycarboxylic acids or anhydrides thereof. Examples of the low molecular weight polyols include ethylene glycol, 1,2 - propanediol, 1,3 - propanediol, 2-methyl-1,3-propanediol, 2-ethyl-2-butyl-1,3-propanediol, 1,3 - butanediol, 1,4 - butanediol, neopentyl glycol, pentanediol, 3 - methyl-1,5-pentanediol, hexanediol, octanediol, 1,4 - butynediol, 1,4 - butylene diol, diethylene glycol, triethylene glycol, dipropylene glycol, glycerol, trimethylol propane, trimethylol ethane, 1,2,6 - hexane triol, 1,2,4-butane triol, sorbitol and pentaerythritol; Examples of the polycarboxylic acid include adipic acid, phthalic acid, isophthalic acid, terephthalic acid, maleic acid, fumaric acid, succinic acid, oxalic

acid, malonic acid, glutaric acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, trimellitic acid, and pyromellitic acid.

Other examples of polyester polyol include those prepared by ring-opening polymerization of cyclic esters such as polycaprolactone, polyvalerolactone, poly(β -methyl- γ -valerolactone). Examples of polyether polyols include polymers or copolymers of methylene oxide, ethylene oxide, propylene oxide, and tetrahydrofuran. Polyester polyols and polyether polyols having a branched structure are particularly preferred.

[0025]

Preferred polymeric polyol contains 20 to 80 wt% of a polyester diol, and 80 to 20 wt% of polyether diol. With 80 wt% or lower amount of polyester diol, excellent non-fogging of plate property can be achieved. With 80 wt% or lower amount of polyether diol, blocking resistance is excellent.

[0026]

The polyurethane resin preferably has an amine value of from 2.0 to 7.0mgKOH/g, more preferably from 3.0 to 6.0mgKOH/g. When the amine value is 2.0mgKOH/g or larger, excellent non-fogging of plate property, adhesion and EL laminate strength are attained. When the amino value is 7.0mgKOH/g or less, excellent blocking resistance is attained.

[0027]

The polyurethane resin preferably has a weight average molecular weight of from 10000 to 70000, more preferably from 15000 to 60000. When the weight average molecular weight is 10000 or larger, excellent blocking resistance and good heat resistance, and hence EL laminate strength are achieved. When the weight average molecular weight is 70000 or lower, excellent non-fogging of plate property, adhesion and EL laminate strength are achieved.

[0028]

The polyurethane resin in the present embodiment may be produced by a prepolymer method as shown below:

1) A prepolymer having terminal isocyanate groups is produced by reacting polymeric polyol with polyisocyanates containing tolylene diisocyanate at a temperature of 10 to 100°C. In the reaction, a solvent inert to isocyanate groups may be used as needed. In addition, an urethane-forming catalyst may be used, if necessary.

2) The prepolymer is then reacted with an organic diamine as chain extender and an alkanolamine as reaction terminator at a temperature of from 10 to 80 °C to produce the polyurethane resin.

[0029]

The solvents used in the polyurethane resin composition of the present embodiment include a mixed solvent of ester solvent and alcohol solvent. Preferably, the following known solvents are used. Examples of ester solvents include ethyl acetate, n-propyl

acetate, isopropyl acetate, isobutyl acetate, propylene glycol monoethyl ether acetate, and propylene glycol monomethyl ether acetate. Examples of the alcohol solvents include methanol, ethanol, n-propanol, isopropanol, n-butanol, propylene glycol monoethyl ether and propylene glycol monomethyl ether.

[0030]

It is also possible to use a catalyst for forming urethane. Examples of the catalyst that can be used include catalytic tertiary amines such as triethylamine and dimethylaniline; and metallic catalyst such as tin, and zinc. These catalysts are normally used in an amount of from 0.001 to 1 mol% relative to a polyol.

[0031]

In the chain extension reaction, the alkanolamine as reaction terminator can be used together with the organic diamine as chain extender. Alternatively, the reaction terminator alone can be added to terminate reaction after the chain extension reaction has run for a while.

[0032]

For the printing ink composition of this embodiment, both inorganic and organic colorants can be used as a colorant. As a white colorant, it is possible to use inorganic titanium oxide colorant, and the one having basic pigment surface is preferred. Examples of non-white inorganic colorants include pigments such as carbon black, aluminum, and mica. Aluminum may be in the form of paste or powder, of which the paste is preferred in handling and safety viewpoints, and leafing one or non-leafing one may be chosen according to brightness and concentration viewpoints. Examples of organic colorants include organic pigments and organic dyes used for general use inks, paints, and recording agent, for example, azo-, phthalocyanine-, anthraquinone-, perylene-, perinone-, quinacridone-, thioindigo-, dioxazine-, isoindolinone-, quinophthalone-, azomethineazo-, diketopyrrolopyrrole-, and isoindoline-based colorants.

[0033]

The colorant is preferably contained in such an amount sufficient to ensure coloring capability of the printing ink, namely from 1 to 50 wt% based on the total weight of the printing ink. The colorants can be used alone or a mixture of two or more of them.

[0034]

The printing ink composition of the present invention can be prepared by dissolving and/or dispersing in an organic solvent the resin, colorant and so on. Specifically, a pigment dispersion is prepared by dispersing pigment, polyurethane resin composition and other compounds as necessary in an organic solvent, to which polyurethane resin composition, and an organic solvent, and other compounds as necessary are further incorporated, whereby the ink is prepared.

[0035]

Pigments are dispersed stably in an organic solvent by the polyurethane resin, but a dispersant may also be used to disperse more stably. As the dispersant, an anionic, nonionic, cationic, or zwitterionic surfactant may be used. The dispersant is contained in the ink preferably in an amount of at least 0.05wt% from the viewpoint of storage stability of the ink, and of at most 5 wt % from the viewpoint of lamination property, based on the total weight of the ink. More preferably, it is contained in an amount of from 0.1 to 2 wt%.

[0036]

A particle size distribution of the pigment in the pigment dispersion can be adjusted by properly adjusting size of a grinding media of a disperser, filling ratio of the grinding medium, dispersion time, discharge rate of the pigment dispersion, and viscosity of the pigment dispersion. As a disperser, roller mill, ball mill, pebble mill, attritor, or sand mill can be used.

[0037]

Solvents used for the printing ink composition of the present invention comprise a mixed solvent of alcohol solvent and an ester solvent. As the ester solvent and alcohol solvents, known solvents are preferably used and examples thereof are as described above.

[0038]

When bubbles and coarse particles are included unexpectedly in the ink, they are preferably removed by filtration because they degrade printing quality. Any known filter can be used.

[0039]

A viscosity of the ink thus produced is preferably at least 10mPa.s to prevent sedimentation of the pigment and to disperse the pigment appropriately, and at most 1000mPa.s in view of working efficiency in ink manufacturing or printing process. Note that the above viscosity is measured at 25 °C by using a B-type viscometer, ex Tokimec Inc.

[0040]

The printing ink composition may be used in known printing methods such as gravure printing, and flexographic printing. When used in gravure printing, for example, it is diluted to a viscosity and concentration suitable for gravure printing, and is supplied to a printing unit alone or in combination with other ink. Gravure printing is preferred.

[0041]

Substrate to which the printing ink composition can be applied include polyolefins such as polyethylene and polypropylene, polyesters such as polyethylene terephthalate, polycarbonate, and polylactic acid, polystyrene resins such as polystyrene, AS resin and ABS resin, polyamide, polyvinyl chloride, polyvinylidene chloride, cellophane, paper, and aluminum, and a sheet-like or film-like composite of these materials. A printed matter can be obtained by applying the printing ink composition on a substrate by

aforesaid printing method, and by drying it in an oven to fix it. The substrate may be surface treated by vacuum depositing metal oxide or the like, and/or by coating polyvinyl alcohol or the like. The surface may also be corona-treated.

[0042]

A laminated body is obtained by subjecting a printed material to a laminate processing and aging. Methods of laminating include

1) Extrusion laminate method comprising the steps of applying an anchor coating agent to a printed surface of the printed material as needed, and extruding a molten resin;

2) Dry laminate method comprising the steps of applying an adhesive, drying as needed, and laminating a plastic film.

As the molten resin, low density polyethylene, polypropylene, ethylene - vinyl acetate copolymer or the like can be used. Examples of the adhesive include imine-, isocyanate-, polybutadiene-, and titanate-based adhesives.

Examples

[0043]

The embodiments of the present invention are described below in detail with reference to examples. However, the present invention is not limited to those examples. In the description below, "parts" and "%" represent "parts by weight" and "% by weight", respectively, unless otherwise specified.

[0044]

A hydroxyl value was determined according to JIS K0070 where an amount of hydroxyl groups in 1g of a resin is determined by acetylating the hydroxyl groups of the resin with an acetylating reagent and then by back titrating an excess amount of the acetylating reagent with an alkali, and the amount of hydroxyl groups determined is converted to an amount of potassium hydroxide in mg. An amine value is an amount of potassium hydroxide in mg equivalent to an amount of hydrochloric acid required to neutralize the amino groups contained in 1g of the resin. An acid value is an amount of potassium hydroxide in mg required to neutralize acid groups in 1g of the resin, which can be determined by any known method, generally according to JIS K0070 (1996). A molecular weight was determined by measuring molecular weight distribution with GPC (gel permeation chromatography) and by converting to a polystyrene molecular weight. Method for measuring amine value is as follows.

[0045]

[Method for Measuring Amine Value]

Weigh precisely 0.5 to 2 g of a sample (amount of sample: S g). Add 30mL of neutral ethanol (BDG neutral) to the sample. To thus obtained solution, add bromophenol blue as an indicator, and titrate with 0.2mol/L ethanolic hydrochloric acid solution (titer: f). Determine an amount of the titrant (A mL) required to change the

color of the solution to a color between yellow and green and calculate the amine value according to the following equation 1.

[0046]

<Equation 1>

Amine value = $(A \times f \times 0.2 \times 56.108)/S$ [mgKOH/g]

[0047]

[Synthesis Example 1]

In a four-necked flask equipped with a stirrer, a thermometer, a reflux condenser, and nitrogen gas inlet, 111.99 parts of PPA2000 having a molecular weight of 2000 (hydroxyl value 56.1 mgKOH/g), 111.99 parts of PPG1000 having a molecular weight of 1000 (hydroxyl value 112.2mgKOH/g), 52.65 parts of tolylene diisocyanate, 0.03 part of tin (II) 2-ethylhexanoate, and 82.5 parts of ethyl acetate were fed, which were reacted under nitrogen gas flow at 90 °C for 3 hours to produce 359.16 parts of a solution of a isocyanate-terminated prepolymer. Then, to a mixture of 21.74 parts of isophorone diamine, 1.64 parts of monoethanolamine, 290 parts of isopropyl alcohol, and 327.47 parts of ethyl acetate, 359.16 parts of the solution of isocyanate-terminated prepolymer obtained was added slowly, which were reacted at 50 °C for 1 hour to produce a polyurethane resin composition (PU01) having a solid content of 30.0%, a weight average molecular weight of 30,000, and an amine value of 4.0mgKOH/g.

[0048]

[Synthesis Examples 2-26]

According to the formulation shown in Tables 1-3, polyurethane resin compositions (PU02 - PU26) were produced In the same manner as in Synthesis Example 1.

[0049]

[Example 1]

30.00 parts of titanium oxide (TITONE R45M manufactured by Sakai Chemical Industry Co., Ltd.), 10.00 parts of the polyurethane resin composition (PU01), 10.00 parts of ethyl acetate/isopropyl alcohol (70/30 in weight ratio) mixed solvent were mixed and kneaded with a sand mill. To the mixture obtained, 40.00 parts of the polyurethane resin composition (PU01), and 10.00 parts of ethyl acetate/isopropyl alcohol (70/30 in weight ratio) mixed solvent were added and mixed to produce a white printing ink composition (W01). Further, to 100.00 parts of the white printing ink composition, 40 pars of a dilution solvent 1, ethyl acetate/isopropyl alcohol = 85/15 by weight, and a dilution solvent 2, ethyl acetate/isopropyl alcohol = 50/50 by weight were mixed, respectively, to produce the diluted white printing ink 1 and the diluted white printing ink 2 for evaluation.

[0050]

[Examples 2-18], [Comparative Examples 1-8]

White printing ink compositions (W02 - 26) were obtained in the same manner as in Example 1 with the exception of replacing the polyurethane resin composition

(PU01) with the polyurethane resin composition (PU02) - (PU26), as shown in Tables 4 - 6. To 100.00 parts of each white printing ink composition, 40.00 parts of a dilution solvent 1, ethyl acetate/isopropyl alcohol = 85/15 by weight, and a dilution solvent 2, ethyl acetate/isopropyl alcohol = 50/50 by weight, respectively, were mixed to produce respective diluted white printing ink 1 and white printing ink 2 for evaluation.

[0051]

The following materials were used in the examples and synthetic example.

PPA2000: poly (1,2 - propylene adipate) diol (number average molecular weight 2000)

NPG2000: poly (neopentyl adipate) diol (number average molecular weight 2000)

PMPA2000: poly (3 - methyl-1, 5 - pentane adipate) diol (number average molecular weight 2000)

PPG1000: poly (1,2 - propylene glycol) (number average molecular weight 1000)

TDI: tolylene diisocyanate

IPDI: isophorone diisocyanate

MDI: diphenylmethane diisocyanate

IPDA: isophorone diamine

MEA: monoethanolamine

DEA: diethanolamine

DBA: Di -n-butylamine

IPA: isopropyl alcohol

HDA: hexamethylene diamine

AEA: 2 - hydroxyethyl ethylene diamine

[0052]

[Non-Fogging of Plate Property]

Each of the diluted white printing ink 1 and the diluted white printing ink 2 was set on a gravure printing machine manufactured by Fuji Machinery Co., Ltd. equipped with an impression cylinder made of NBR (nitrile butadiene rubber) having a rubber hardness of 80Hs, a ceramic-plated doctor blade having a 60 μ m-thick cutting edge (40 μ m-thick base material, 10 μ m-thick ceramic layer on each side), and an electronic engraving with a chromium plate hardness of 1050Hv (stylus angle 120 degrees, 200 lines/inch), manufactured by TOYO Prepress Co., Ltd. Subsequently, after a 60-minute idling at a doctor blade pressure of 2 kg/cm², and at a rotational speed of 100m/min, the ink was printed on a corona-treated surface of an one side corona-treated OPP film "Pylen P-2161 (manufactured by Toyobo Co., Ltd.)" at a printing rate of 100m/min and at a printing pressure of 2 kg/cm², and then dried by hot air at 60 °C. The printed matter thus obtained was attached onto a black paper, and an amount of the ink adhered to a margin (non-image portion) was rated according to the following criteria.

A++: Ink transfer was not observed at all in the non-image area.

A+ : Ink transfer was slightly observed in the non-image area.

A : Ink transfer was observed in a small portion of the non-image area.

Ratings from A to A++ are practically acceptable.

B : Ink transfer was observed in a large portion of the non-image area.

C : Ink transfer was observed in almost the entire surface of the non-image area.
(An amount of the transfer was between those of B and D.)

D : Ink transfer was observed in the entire surface of the non-image area.

[0053]

[Blocking Resistance]

Each of the diluted white printing ink 1 was printed on a corona-treated OPP film (Taiko FOR, # 20, ex Futamura Chemical CO., LTD.) using a gravure proof press equipped with a 35 μ m-deep gravure plate, and dried at a temperature from 40 to 50 °C. From the printed matter thus obtained, a 4cm $\times$ 4cm test piece was sampled. At a temperature of 50 °C, the printed surface of the test piece was pressed against a non-treated and non-printed surface of the OPP film of the same size at a pressure of 10kgf. After 12 hours, the test piece was peeled off and observed for stripped ink (ink transfer) and for resistance to peeling.

A++: Ink transfer from the printed matter was not observed at all, and no resistance to peeling was sensed.

A+ : Ink transfer from the printed matter was not observed at all, but resistance to peeling was sensed.

A: Less than 10% in surface area of ink was transferred from the printed material.
Ratings from A to A++ are practically acceptable.

B: From 10 to less than 50 % in surface area of ink was transferred from the printed matter.

C: More than 50 % in surface area of ink was transferred from the printed matter.

[0054]

[Adhesion]

To the printed matter prepared in the test for blocking resistance, a cellophane tape (12 mm-wide, ex Nichiban Co., Ltd.) was attached. After having been rubbed strongly 5 times with a thumb, the cellophane tape was slowly peeled off to a predetermined position, and then rapidly peeled off. The printed matter was observed for ink exfoliation.

A+ : No exfoliation of ink was observed even by the rapid peeling.

A : No exfoliation of ink by the slow peeling, and an exfoliation of less than 20% in surface area of ink by the rapid peeling were observed.

Ratings of A and A+ are practically acceptable.

B : No exfoliation of ink by the slow peeling, and an exfoliation of 20% or more in surface area of ink by the rapid peeling were observed.

C : An exfoliation of up to about 50% in surface area of ink was observed even by the slow peeling.

D : Most of ink was exfoliated even by the slow peeling.

[0055]

[Resistance to Alcohol Breeding]

Each of the diluted white printing ink 1 was printed on a corona-treated OPP film (Taiko FOR, # 20, ex Futamura Chemical CO., LTD.) using a gravure proof press equipped with a 35 μ m-deep gravure plate, and dried at a temperature from 40 to 50 °C. The printed matter thus obtained was coated in-line with isopropyl alcohol and dried at a temperature from 40 to 50 °C. The coated printed matter was observed for traces of breeding.

A+ : No defect in appearance was observed in the printed matter.

A : A little bit of blurred part was observed in the printed matter.

Ratings of A and A+ are practically acceptable.

B : Traces of breeding were vaguely observed in the printed matter.

C : Traces of breeding were clearly observed in the printed matter.

[0056]

[EL Laminate Strength]

Under the printing conditions same as those in the test for non-fogging of plate property, each diluted white printing ink 1 was printed on a corona-treated surface of a substrate to prepare printed matter. The substrates used were a polypropylene film sold under the trade name of "Pylon P-2161" (manufactured by Toyobo Co., Ltd.) which is treated with corona on one side thereof and has a thickness of 20 μ m, hereinafter referred to as "OPP", and a polyethylene terephthalate film sold under the trade name of "E5100" (manufactured by Toyobo Co., Ltd.) which is treated with corona on one side thereof and has a thickness of 12 μ m, herein after referred to as "PET." Then, on the printed surface, a polyethyleneimine-based anchor coat agent sold under the trade name of "Oribain EL-420" (manufactured by Toyo Morton Co., Ltd.) was coated. Further, on the coated surface, a low density polyethylene as a sealant sold under the trade name of "Novatec LC600" (manufactured by Nippon Polychem Co., Ltd.) was extruded at a temperature of 315 °C to form a laminated product. Thus, the laminated product was prepared by extrusion laminate (EL). The extrusion temperature of the low density polyethylene was measured by a contact thermometer (HL-100 ex Anritsu Keiki Co.,

Ltd.) located immediately below a T-die of the extrusion laminating machine. A 15 mm-wide test piece was cut out from the laminated product. After peeling between the substrate and the extruded resin layer at the end of the test piece, a peeling strength was measured by an universal tensile tester, model 201, ex Intesco Ltd.

For the laminated products using OPP (OPP/ imine configuration), a peeling strength of 1.0N/15mm or more is practically acceptable, and for those using PET(PET/ imine configuration), a peeling strength of 1.5N/15mm or more is practically acceptable.

[0057]

Evaluation results are summarized in Tables 4-6. Compared with the printing ink compositions of Comparative Examples 1 to 8, the printing inks of Examples 1 to 18 provide printing ink compositions which show superior printability such as non-fogging of plate property, and superior printing properties such as blocking resistance, adhesion, resistance to alcohol breeding, and laminate strength.

Table 1

			Synthesis Example 1	Synthesis Example 2	Synthesis Example 3	Synthesis Example 4	Synthesis Example 5	Synthesis Example 6	Synthesis Example 7	Synthesis Example 8
Name of polyurethane resin composition			PU01	PU02	PU03	PU04	PU05	PU06	PU07	PU08
Reaction	Prepolymer	PPA2000	111.99	107.74	106.90	106.07	105.02			101.43
		NPG2000						107.74		
		PMPA2000							107.74	
		PPG1000	111.99	107.74	106.90	106.07	105.02	107.74	107.74	101.43
		TDI	52.65	56.28	47.38	38.62	27.43	56.28	56.28	55.58
		IPDI			10.80	21.43	35.01			6.83
		MDI								
		Tin(II) 2-ethylhexanoate	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
		Ethyl acetate	82.5	82.5	82.5	82.5	82.5	82.5	82.5	82.5
	Chain extension	IPDA	21.74	26.61	26.40	26.17	25.88	26.61	26.61	33.09
		MEA	1.64	1.64	1.63	1.63	1.64	1.64	1.64	1.63
		DEA								
		Ethyl acetate	327.47	327.47	327.47	327.47	327.47	327.47	327.47	327.47
		IPA	290	290	290	290	290	290	290	290
	Total		1000	1000	1000	1000	1000	1000	1000	1000
Urethane parameters	Solid content		30.0	30.0	30.0	30.0	30.0	30.0	30.0	30.0
	NCO(Total)/OH		1.8	2.0	2.0	2.0	2.0	2.0	2.0	2.3
	NCO(TDI)/OH		1.8	2.0	1.7	1.4	1.0	2.0	2.0	2.1
	NCO group mole % of TDI in total NCO groups		100	100	85	70	50	100	100	91
	Polyester diol wt % in polymertic polyol		50	50	50	50	50	50	50	50
	Molar ratio of diamine (d1)/monoamine (d2)		4.8	5.8	5.8	5.8	5.7	5.8	5.8	7.3
	Hydroxy value		5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
	Amine value		4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
	Weight average molecular weight		30000	28000	28000	28000	28000	28000	28000	25000

[0058]

Table 2

			Synthesis Example 9	Synthesis Example 10	Synthesis Example 11	Synthesis Example 12	Synthesis Example 13	Synthesis Example 14	Synthesis Example 15	Synthesis Example 16
Name of polyurethane resin composition			PU09	PU10	PU11	PU12	PU13	PU14	PU15	PU16
Reaction	Prepolymer	PPA2000	99.24	107.56	107.92	20.90	41.43	182.73	210.08	107.41
		NPG2000								
		PMPA2000								
		PPG1000	99.24	107.56	107.92	179.58	162.60	45.68	23.06	107.41
		TDI	30.82	56.19	56.38	66.18	63.84	47.73	44.61	56.11
		IPDI	36.76							
		MDI								
		Tin(II) 2-ethylhexanoate	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
		Ethyl acetate	82.5	82.5	82.5	82.5	82.5	82.5	82.5	82.5
	Chain extension	IPDA	32.32	28.27	24.81	31.71	30.50	22.23	20.61	27.67
		MEA	1.63	0.41	2.97	1.62	1.63	1.63	1.64	
		DEA								1.41
		Ethyl acetate	327.47	327.47	327.47	327.47	327.47	327.47	327.47	327.47
		IPA	290	290	290	290	290	290	290	290
		Total	1000	1000	1000	1000	1000	1000	1000	1000
Urethane parameters	Solid content		30.0	30.0	30.0	30.0	30.0	30.0	30.0	30.0
	NCO(Total)/OH		2.3	2.0	2.0	2.0	2.0	2.0	2.0	2.0
	NCO(TDI)/OH		1.2	2.0	2.0	2.0	2.0	2.0	2.0	2.0
	NCO group mole % of TDI in total NCO groups		52	100	100	100	100	100	100	100
	Polyester diol wt % in polymertic polyol		50	50	50	10	20	80	90	50
	Molar ratio of diamine (d1)/monoamine (d2)		7.1	24.5	3.0	7.0	6.7	4.9	4.5	12.2
	Hydroxy value		5.0	1.3	9.1	5.0	5.0	5.0	5.0	5.0
	Amine value		4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
	Weight average molecular weight		26000	50000	15000	30000	30000	30000	30000	40000

[0059]

Table 3

			Synthesis Example 17	Synthesis Example 18	Synthesis Example 19	Synthesis Example 20	Synthesis Example 21	Synthesis Example 22	Synthesis Example 23	Synthesis Example 24	Synthesis Example 25	Synthesis Example 26
Name of polyurethane resin composition			PU17	PU18	PU19	PU20	PU21	PU22	PU23	PU24	PU25	PU26
Reaction	Prepolymer	PPA2000	99.59	116.58	98.40	101.94	98.29	107.50	107.08	108.01	108.12	108.76
		NPG2000										
		PMPA2000										
		PPG1000	99.59	116.58	98.40	101.94	98.29	107.50	107.08	108.01	108.12	108.76
		TDI		48.72	64.25	61.24	20.15	56.16	55.94	56.42	56.48	56.81
		IPDI					49.65					
		MDI	74.76									
		Tin(II) 2-ethylhexanoate	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
		Ethyl acetate	82.5	82.5	82.5	82.5	82.5	82.5	82.5	82.5	82.5	82.5
	Chain extension	IPDA	24.42	16.47	37.32	33.25	32.00	28.83	26.45	24.00	23.94	17.92
		HDA										6.10
		AEA									1.69	
		MEA	1.64	1.64	1.62	1.64	1.63			3.56	1.64	1.65
		DBA							3.45			
		Ethyl acetate	327.47	327.47	327.47	327.47	327.47	327.47	327.47	327.47	327.47	327.47
		IPA	290	290	290	290	290	290	290	290	290	290
		Total	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000
Urethane parameters	Solid content		30.0	30.0	30.0	30.0	30.0	30.0	30.0	30.0	30.0	30.0
	NCO(Total)/OH		2.0	1.6	2.5	2.3	2.3	2.0	2.0	2.0	2.0	2.0
	NCO(TDI)/OH		0.0	1.6	2.5	2.3	0.8	2.0	2.0	2.0	2.0	2.0
	NCO group mole % of TDI in total NCO groups		0	100	100	100	34	100	100	100	100	100
	Polyester diol wt % in polymeric polyol		50	50	50	50	50	50	50	50	50	50
	Molar ratio of diamine (d1)/monoamine (d2)		5.3	3.6	8.3	7.3	7.1	-	5.8	2.4	5.8	5.8
	Hydroxy value		5.0	5.0	5.0	5.0	5.0	0	0	10.9	8.1	5.1
	Amine value		4.0	4.0	4.0	4.0	4.0	1.5	4.0	8.0	4.0	8.0
	Weight average molecular weight		30000	30000	24000	25000	26000	80000	30000	9000	28000	28000

[0060]

Table 4

			Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9
Name of polyurethane resin composition			PU01	PU02	PU03	PU04	PU05	PU06	PU07	PU08	PU09
Name of white printing ink composition			W01	W02	W03	W04	W05	W06	W07	W08	W09
Evaluation	Non-fogging of plate	Diluted printing ink 1	A+	A+	A+	A+	A+	A+	A+	A	A++
		Diluted printing ink 2	A	A	A	A+	A+	A	A	A	A+
	Blocking resistance		A	A+	A+	A+	A+	A+	A+	A++	A++
	Adhesion		A+	A+	A+	A+	A+	A+	A+	A	A
	Resistance to alcohol breeding		A+	A+	A	A	A	A+	A+	A+	A
	EL laminate strength	OPP/Imine	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.0	1.0
		PET/Imine	3.0	2.0	2.0	2.0	2.0	2.0	2.0	1.5	1.5

[1900]

[0063]

Table 5

			Example 10	Example 11	Example 12	Example 13	Example 14	Example 15	Example 16	Example 17	Example 18
Name of polyurethane resin composition			PU10	PU11	PU12	PU13	PU14	PU15	PU16	PU25	PU26
Name of white printing ink composition			W10	W11	W12	W13	W14	W15	W16	W25	W26
Evaluation	Non-fogging of plate	Diluted printing ink 1	A	A++	A+	A+	A+	A	A	A+	A+
		Diluted printing ink 2	A	A+	A	A	A	A	A	A	A
	Blocking resistance		A++	A	A	A+	A++	A++	A+	A+	A+
	Adhesion		A	A+	A	A+	A+	A	A	A	A
	Resistance to alcohol breeding		A+	A	A+	A+	A+	A+	A+	A	A+
	EL laminate strength	OPP/Imine	1.0	2.0	1.5	2.0	2.0	1.5	1.5	1.5	1.5
		PET/Imine	1.5	3.0	1.5	2.0	2.0	1.5	2.0	2.0	2.0

[0062]

Table 6

			Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6	Comparative Example 7	Comparative Example 8
Name of polyurethane resin composition			PU17	PU18	PU19	PU20	PU21	PU22	PU23	PU24
Name of white printing ink composition			W17	W18	W19	W20	W21	W22	W23	W24
Evaluation	Non-fogging of plate	Diluted printing ink 1	D	A++	D	C	A++	D	C	A++
		Diluted printing ink 2	D	B	D	D	A+	D	D	A
	Blocking resistance		C	C	A++	A++	A++	A++	A+	C
	Adhesion		A	A+	C	A	A	D	B	A+
	Resistance to alcohol breeding		A+	C	A+	A+	B	A+	A+	B
	EL laminate strength	OPP/Imine	1.0	2.0	0.5	1.0	1.0	0.5	1.0	1.0
		PET/Imine	1.5	3.0	0.5	1.5	1.5	1.0	1.5	2.0

Claims

1. A polyurethane resin composition comprising a polyurethane resin and a mixed solvent, wherein the polyurethane resin is prepared by reacting a urethane prepolymer having terminal isocyanate groups with an organic diamine and an alkanol amine, said urethane prepolymer being prepared by reacting polyisocyanates comprising a tolylene diisocyanate with a polymeric polyol, characterized in that the composition meets the following (A) to (F).

(A) a molar ratio of total isocyanate groups of the polyisocyanates to hydroxyl groups of the polymeric polyol, $[NCO(\text{total})]/[OH]$, ranges from 1.8 to 2.3;

(B) a molar ratio of isocyanate groups of tolylene diisocyanate to hydroxyl groups of the polymeric polyol, $[NCO(TDI)]/[OH]$, ranges from 1.0 to 2.1;

(C) a hydroxyl value of the polyurethane resin ranges from 1.0 to 10.0 mgKOH/g;

(D) a molar ratio, $d1/d2$, where $d1$ represents a molar amount of the organic diamine, and $d2$ represents a molar amount of the alkanolamine, ranges from 3 to 25;

(E) the mixed solvent comprises an ester solvent and an alcohol solvent; and

(F) the polymeric polyol consists of a polyester diol and a polyether diol.

2. The polyurethane resin composition according to claim 1, wherein the polymeric polyol consists of a polyester diol and a polyether diol, and the polymeric polyol contains 20 to 80 wt% of the polyester diol, and 80 to 20 wt% of the polyether diol.

3. A printing ink composition comprising the polyurethane resin composition according to claim 1 or 2.