



(51) International Patent Classification:

C09D 175/06 (2006.01) **C09D 7/06** (2006.01)
C08G 18/06 (2006.01)

(21) International Application Number:

PCT/US2017/027935

(22) International Filing Date:

17 April 2017 (17.04.2017)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

201610243963.3 19 April 2016 (19.04.2016) CN

(71) Applicant: **VALSPAR SOURCING, INC.** [US/US]; 1101
South Third Street, P.O. Box 1461, Minneapolis, Minnesota
55440-1461 (US).

(72) Inventors: **YANG, Fan**; NO828 Jiaxin Rd., Jiading Dis-
trict, Shanghai 201818 (CN). **ZHOU, Zhai**; NO828 Jiaxin
Rd., Jiading District, Shanghai 201818 (CN). **XU, Wanjun**;
NO828 Jiaxin Rd., Jiading District, Shanghai 201818 (CN).

(74) Agent: **GWIN, JR., H. Sanders**; 1625 Radio Drive, Suite
100, Woodbury, Minnesota 55125 (US).

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

(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ,
UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ,
TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK,
EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV,
MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,
TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW,
KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

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

Published:

- with international search report (Art. 21(3))

(54) Title: TWO-COMPONENT POLYURETHANE TOPCOAT

(57) Abstract: The present disclosure is directed to a two-component polyurethane topcoat, comprising: a) a film-forming resin composition comprising i) an active hydrogen-containing polymer, having a hydroxyl value of 70 mg KOH/g polymer or more; ii) a polyester resin, having a hydroxyl value of less than 50 mg KOH/g resin and a viscosity of less than 6000 mPa.s at 25 °C; and iii) a package of flattening agents comprising a polysiloxane containing an effective silicon content of 30 wt% or more and an acrylics polymer having a weight average molecular weight in the range of 6,000 to 20,000 g/mol, wherein the weight ratio of the polysiloxane to the acrylics polymer is in the range of 1:5 to 1:15; and b) a polyisocyanate curing agent, wherein the ratio by weight of the component a) to the component b) is in the range of 100:10 to 100:25.



TWO-COMPONENT POLYURETHANE TOPCOAT

BACKGROUND

[0001] Polyurethane (PU) topcoats are widely used in the coating industry. A cured PU topcoat can provide a coating having good adhesion to an underlying coating such as, for example, an epoxy primer coating, and has good weatherability, corrosion resistance and high gloss. Therefore, PU topcoats are suitable for a wide variety of industrial paint applications, and the market may require up to one or more million tons per year.

[0002] A cured PU topcoat typically produces a coating exhibiting a gloss of at most 70% at 20 °C, and as such is not well suited for use in advanced paints such as vehicle finish paints. In practice, PU topcoats should have a gloss of at least 80% at 20 °C for application to a metal substrate.

[0003] Flatting performance of PU topcoats plays an important role in achieving its decorative effect, especially gloss. A PU topcoat with good flatting performance may produce a coating having high gloss, high distinctness of image (DOI) and fullness. In contrast, a PU topcoat with poor flatting performance after film-forming can form a coating with defects such as, for example, orange peel and ripples.

[0004] There is still a need for PU topcoat having excellent flatting performance and producing a coating exhibiting high gloss and high DOI.

SUMMARY

[0005] The present disclosure provides a two-component polyurethane topcoat, including: a) a film-forming resin composition including: i) an active hydrogen-containing polymer, having a hydroxyl value of 70 mg KOH/g polymer or more; ii) a polyester resin, having a hydroxyl value of less than 50 mg KOH/g resin and a viscosity of less than 6000 mPa.s at 25 °C; and iii) a package of flatting agents including a polysiloxane containing an effective silicon content of 30 wt% or more and an acrylic polymer having a weight average molecular weight in the range of 6,000 to 20,000 g/mol, wherein the weight ratio of the polysiloxane to the acrylic polymer is in the range of 1:5 to 1: 15; and b) a polyisocyanate curing agent, wherein the ratio by weight of component a) to component b) is 100 : 10 to 100 : 25.

[0006] In some embodiments, the film-forming resin composition further includes an optional mixture of solvents, each of which has a relative volatile rate in the range of 0.4 to 1.0, relative to butyl acetate.

[0007] In some embodiments, incorporation into the film-forming resin composition of a combined resin system including: i) a polyester resin having a low hydroxyl value and a low viscosity, and ii) an active hydrogen-containing polymer having a high hydroxyl value, as well as iii) a package of flattening agents including a particular weight ratio of a polysiloxane and an acrylic polymer, will produce a polyurethane topcoat having good flattening performance. The coating derived from the PU topcoat has excellent gloss and distinctness of image (DOI).

[0008] Gloss and DOI are both parameters reflecting the surface smoothness of coating, which mainly is affected by the flattening performance of the coating composition. A flattening agent can be added to a coating composition to improve its flattening performance.

[0009] It has been surprisingly found by the inventors that incorporation of polyester having a low hydroxyl value and a low viscosity into the film-forming resin composition may significantly improve its flattening performance without impairing adhesion of the topcoat to its underlying coating. It has been also surprisingly found by the inventors that incorporation of a particular weight ratio of a polysiloxane and an acrylic polymer into the film-forming resin composition may result in improved flattening performance. The thus formed coating has a gloss of at least 85%, even 88% or more at 20 °C and a DOI of at least 0.85, even up to 0.89, which is superior to conventional industrial paints, and even close to paints suitable for use as a vehicle topcoat.

[0010] It has been further surprisingly found by the inventors that incorporation of a solvent mixture having a gradient volatile rate into the film-forming resin composition can increase its flattening performance.

[0011] The details of one or more embodiments of the invention will be set forth in description below. The other features, objectives, and advantages of the invention will become apparent.

SELECTED DEFINITIONS

[0012] As used herein, "a", "an", "the", "at least one", and "one or more" are used interchangeably, unless indicated otherwise. Thus, for example, a coating composition that

comprises "an" additive can be interpreted to mean that the coating composition includes "one or more" additives.

[0013] Throughout the present disclosure, where compositions are described as having, including, or comprising specific components or fractions, or where processes are described as having, including, or comprising specific process steps, it is contemplated that the compositions or processes as disclosed herein may further comprise other components or fractions or steps, whether or not specifically mentioned in this disclosure, as long as such components or steps do not affect the basic and novel characteristics of the invention, but it is also contemplated that the compositions or processes may consist essentially of, or consist of, the recited components or steps.

[0014] For the sake of brevity, only certain ranges are explicitly disclosed herein. However, ranges from any lower limit may be combined with any upper limit to recite a range not explicitly recited, ranges from any lower limit may be combined with any other lower limit to recite a range not explicitly recited, and in the same way, ranges from any upper limit may be combined with any other upper limit to recite a range not explicitly recited. Additionally, within a range includes every point or individual value between its end points even though not explicitly recited. Thus, every point or individual value may serve as its own lower or upper limit combined with any other point or individual value or any other lower or upper limit, to recite a range not explicitly recited.

[0015] The term “distinctness of image (DOI)” as used herein refers to a parameter for characterizing surface smoothness of a coating. In the field of industrial paint, a coating usually has a DOI of at most 0.80.

[0016] The term “solubility parameter” as used herein refers to a parameter for characterizing compatibility among polymers. The closer the solubility parameters among polymers are, these polymers have better compatibility. The “solubility parameter” may be measured by technical experiments such as viscometry, or calculated by the Small equation. In various embodiments of the present disclosure, the solubility parameter of a polymer can be estimated by using the Small equation:

$$\delta = \rho \Sigma F_i / M,$$

in which

δ is solubility parameter of the polymer in $(\text{J}/\text{cm}^3)^{1/2}$

ρ is density of the polymer in g/cm^3 ,

F_i is molar gravitational constant of groups or atoms present in the repetitive structural unit of the polymer in $(\text{J} \cdot \text{cm}^3)^{1/2}/\text{mol}$; and

M is the molecular weight of the repetitive structure unit in g/mol.

[0017] As used in the context of “polysiloxane” as a flatting agent, the term “effective silicon content” refers to the amount of polydimethylsiloxane moiety contained in the polysiloxane flatting agent.

[0018] The term “hydroxyl value” as used herein refers to the amount in mg of KOH that is equivalent to the content of hydroxyl group in one gram of a sample. In an embodiment of the present disclosure, the hydroxyl value is determined according to GB12009.3-2009 by titrimetry.

[0019] The phrase “substantially free” of styrene means that a film-forming resin composition of the present disclosure contains less than 1,000 parts per million (ppm) of styrene. The phrase “essentially free” of styrene means that the film-forming resin composition contains less than 100 parts per million (ppm) of styrene. The phrase “essentially completely free” of styrene means that the film-forming resin composition contains less than 5 parts per million (ppm) of styrene. The phrase “completely free” of phrase means that the film-forming resin composition contains less than 20 parts per billion (ppb) of styrene.

[0020] The term “comprises” and variations thereof do not have a limiting meaning where these terms appear in the description and claims.

[0021] The terms “preferred” and “preferably” refer to embodiments of the invention that may afford certain benefits, under certain circumstances. However, other embodiments may also be preferred, under the same or other circumstances. Furthermore, the recitation of one or more preferred embodiments does not imply that other embodiments are not useful, and is not intended to exclude other embodiments from the scope of the invention.

DETAILED DESCRIPTION

[0022] The present disclosure provides a two-component polyurethane topcoat, including: a) a film-forming resin composition including: i) an active hydrogen-containing polymer having a hydroxyl value of 70 mg KOH/g polymer or more; ii) a polyester resin having a hydroxyl value of less than 50 mg KOH/g resin and a viscosity of less than 6000

mPa.s at 25 °C; and iii) a package of flatting agents including a polysiloxane containing an effective silicon content of 30 wt% or more and an acrylic polymer having a weight average molecular weight in the range of 6,000 to 20,000 g/mol, wherein the weight ratio of the polysiloxane to the acrylic polymer is 1:5 to 1: 15; and b) a polyisocyanate curing agent, wherein the ratio by weight of component a) to component b) is 100 : 10 to 100 : 25.

Film-forming resin composition

[0023] As used herein, the term, “film-formation resin composition”, refers to a resin composition which constructs the bulk of a coating to be formed from the two-component polyurethane topcoat of the present disclosure. In various embodiments, the PU topcoat may include an active hydrogen-containing polymer, a polyester resin, a flatting package, solvents, and optionally additional additives. In some embodiments, the film-forming resin composition includes, based on the total weight of the film-forming resin composition, 10 to 85 wt% of the active hydrogen-containing polymer, 5 to 85 wt% of the polyester resin; and 0.1 to 5 wt% of the package of flatting agents.

[0024] According to the present disclosure, as used herein, the term, “active hydrogen-containing polymer”, unless specified otherwise, is intended to refer to any polymer originally containing functional groups capable of offering active hydrogen. The active hydrogen is well known for its reactivity with an isocyanate group, and may be donated by many functional groups such as –COOH, –OH, –SH, secondary amino, and primary amino. In an embodiment of the present disclosure, the active hydrogen is donated by a hydroxyl group.

[0025] The active hydrogen-containing polymer has a hydroxyl value of 80 mg KOH/g polymer or more, or 90 mg KOH/g polymer or more, or 100 mg KOH/g polymer or more. In typical applications, the hydroxyl value of the active hydrogen-containing polymer should not be greater than 150 mg KOH/g polymer, or no greater than 120 mg KOH/g polymer. It has been observed that incorporation of an active hydrogen-containing polymer having too high hydroxyl value may in some cases negatively affect the mechanical performance of the coating to be formed.

[0026] In various embodiments, the active hydrogen-containing polymer is used to provide a resin component for the film-formation resin composition and hence the two-component polyurethane topcoat. On the one hand, this resin component functions as a binder which provides adhesion to a substrate or its underlying coating for the

polyurethane topcoat and holds together other components, such as pigment, in the film-formation resin composition to impart basic cohesive strength to the coating. On the other hand, this resin component has good reactivity with the polyisocyanate curing agent to achieve crosslinking of the polymeric chains, thereby forming a coating having suitable mechanical strength.

[0027] In various embodiments, the active hydrogen-containing polymer has a viscosity of at least 4,000 mPa.s, or at least 6,000 mPa.s, or at least 6,500 mPa.s, or at least 8,000 mPa.s at 25 °C. There is no particular limitation on the upper limit of the viscosity of the active hydrogen-containing polymer, but in typical applications, the viscosity of the active hydrogen-containing polymer is no greater than 20,000 mPa.s at 25 °C, or no greater than 10,000 mPa.s at 25 °C. The viscosity may be determined with Brookfield viscosimeter using No. 3 spindle at about 10 rpm. It has been observed that above viscosity range results in two-component polyurethane topcoat having suitable applicability.

[0028] In various embodiments, the active hydrogen-containing polymer has a weight average molecular weight of 10,000 g/mol or more, a weight average molecular weight of 15,000 g/mol or more, a weight average molecular weight of 20,000 g/mol or more, a weight average molecular weight of 30,000 g/mol or more, or 35,000 g/mol or more, or 40,000 g/mol or more, or 50,000 g/mol or more. There is no particular limitation on the upper limit to the weight average molecular weight of the active hydrogen-containing polymer, but for most applications the weight average molecular weight of the active hydrogen containing polymer is no greater than 100,000 g/mol. The weight average molecular weight may be determined by GPC. It has been observed that the active hydrogen containing polymer having higher weight average molecular weight can in some cases provide a two-component polyurethane topcoat with greater mechanical strength.

[0029] In some embodiments, the active hydrogen containing polymer has a solid content in the range of about 60% to about 90%, or in the range of about 65% to about 85%, wherein the solid content is understood as the weight ratio of non-volatile components in the active hydrogen containing polymer. In particular, the active hydrogen containing polymer has a solid content of about 67.5%, about 70.0%, about 72.5%, about 75.0%, about 77.5%, about 80.0% or about 82.5%.

[0030] In an embodiment of the present disclosure, the active hydrogen containing polymer includes an acrylic polymer having a hydroxyl group.

[0031] The active hydrogen containing polymer may be prepared by polymerization processes such as, for example, emulsion polymerization. Alternatively, suitable commercially available active hydrogen containing polymers may be used such as, for example, those available under the trade designation AP-541 from Jiadian Resin Company, Suzhou, China.

[0032] In various embodiments, the film-forming resin composition, relative to the total weight of the film-forming resin composition, includes about 10 wt% to about 85 wt%, or about 20 wt% to about 75 wt% of the active hydrogen containing polymer. In some examples, the film-forming resin composition relative to the total weight of the film-forming resin composition includes about 25 wt%, about 30 wt%, about 35wt%, about 40 wt%, about 45 wt%, about 50 wt%, about 55 wt%, about 60 wt% or about 65 wt% of the active hydrogen containing polymer.

[0033] In some embodiments, a polyester polymer is used together with above active hydrogen containing polymer to constitute the resin component of the film-forming resin composition. The term “polyester polymer” as used herein is understood as an oligomer or polymer containing at least one $-C(O)O-$ ester group in its molecular backbone, which oligomer or polymer may be prepared, for example, by condensing polyacid or polyanhydride with polyols or bisphenol under suitable esterification conditions.

[0034] In various embodiments, the polyester resin has a hydroxyl value of less than 50 mg KOH/g resin and a viscosity of less than 3500 mPa.s at 25 °C. Preferably, the polyester resin has a lower hydroxyl value and preferably has a hydroxyl value less than 45 mg KOH/g resin, or less than 40 mg KOH/g resin, or less than 30 mg KOH/g resin, or less than 20 mg KOH/g resin. In some embodiments, a polyester resin having a hydroxyl value of about 10 mg KOH/g resin or less may be used. In some cases, introduction of a polyester resin with a low hydroxyl value does not bring about a substantial effect on the curing performance of the polyurethane topcoat. The polyester resin preferably has a lower viscosity, preferably less than 5500 mPa.s, or less than 5000 mPa.s, or less than 4500 mPa.s, or less than 4000 mPa.s, or in the range of 2500 to 3000 mPa.s at 25 °C. The viscosity may be determined with Brookfield viscosimeter using No. 3 spindle at about 10 rpm.

[0035] It has been surprisingly found by the inventors that the resin component of the film-forming resin composition formed by combining the above polyester resin with the active hydrogen containing polymer can in some cases significantly improve the strength wettability performance of the composition to a substrate and thus significantly improve the flatting performance of the PU topcoat. Moreover, adhesion of the resin composition to a substrate or its underlying coating is further improved without degrading other beneficial properties of the coating.

[0036] Preferably, the polyester resin has a weight average molecular weight of 15000 to 20000 g/mol. The weight average molecular weight may be determined by GPC. It has been observed that the polyester resin with a weight average molecular weight in the above range results in two-component polyurethane topcoat having greater mechanical strength.

[0037] In various embodiments, the polyester resin has a solid content of about 70% to about 90%, wherein the solid content is understood as the weight ratio of non-volatile components in the polyester resin. In some examples, the polyester resin has a solid content of about 77.5%, about 80.0%, about 82.5%, about 85.0% or about 87.5%.

[0038] The polyester resin of the present disclosure may be prepared by known polymerization processes, or suitable commercial products may be used such as, for example, those available under the trade designation AK1188P polyester resin from Valspar, USA.

[0039] In various embodiments, the film-forming resin composition includes, relative to the total weight of the film-forming resin composition, includes about 10 wt% to about 85 wt%, or about 10 wt% to about 55 wt% of the polyester resin. In some examples, the film-forming resin composition includes, relative to the total weight of the film-forming resin composition, about 12.5 wt%, about 15 wt%, or about 20 wt% of the polyester resin.

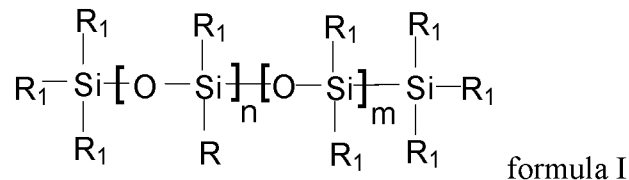
[0040] In some embodiments, a polyester resin should be selected that is more compatible with the active hydrogen containing polymer. In some embodiments, the difference between the solubility parameter of the active hydrogen-containing polymer and the solubility parameter of the polyester resin is less than $0.5 \text{ (J/cm}^3)^{1/2}$, or less than $0.1 \text{ (J/cm}^3)^{1/2}$. It has been surprisingly found by the inventors that incorporation of the polyester resin that has a good compatibility with the active hydrogen containing polymer into the film-forming resin composition may in some cases further improve wettability of

the resin composition to the substrate or primer, thereby enhancing the flattening properties of polyurethane topcoat.

[0041] In some embodiments, the film-forming resin composition further includes a package of flattening agents, which as used herein refers to an agent capable of promoting resin composition to form a flat coating without folding. Suitable flattening agents in the film-forming resin composition include, but are not limited to, a polysiloxane, an acrylic polymer, or combinations thereof.

[0042] In the context of the present disclosure, “polysiloxane” refers to an agent that is capable of decreasing the surface tension of the coating composition so that the coating composition may flow effectively along the substrate or its underlying coating and thus may smooth the surface defects contained in the substrate or underlying coating. The term “polysiloxane” as used herein refers to a polymer containing a –Si-O- structural unit in its molecular backbone.

[0043] In an embodiment of the present disclosure, the polysiloxane has the structure of formula I:



in which

R_1 is at each occurrence independently chosen from C_1 - C_6 alkyl, preferably methyl;

R represents a polyether residue or a polyester residue, preferably polyester residue;

the sum of m and n is an integer of 30 to 250; and

the ratio of m to n is 3: 7 to 9:1.

[0044] In one embodiment, the polysiloxane includes polyester modified polysiloxane. It has been observed that incorporation of above polysiloxane into the film-forming resin composition of the present disclosure as one of flattening agents would be particularly favorable.

[0045] Preferably, polysiloxane has an effective silicon content of 40 wt% or more, or 50 wt% or more, or 60 wt% or more, or 65 wt% or more, 70 wt% or more, or 75 wt% or more. Polysiloxanes with a higher effective silicon content have been found to be particularly

advantageous. However, the effective silicon content should be no greater than 99 wt%, or no greater than 95 wt%, or no greater than 90 wt%. In some embodiments, the inventors have found that if the effective silicon content is too low, the polysiloxane flattening agent will not be sufficient to decrease the surface tension of coating composition so that the coating composition may not flow effectively along the substrate and thus its underlying coating.

[0046] The polysiloxane flattening agent as disclosed in the present disclosure may be prepared well-known methods of modifying polysiloxane with polyester. Alternatively, commercially available polysiloxane flattening agents may be used, and suitable examples include, but are not limited to, DC56 or DC57 polysiloxane available from Dow Corning, Midland, MI, USA.

[0047] In the context of the present disclosure, “acrylic polymer” refers to an agent that has limited compatibility with other resin components and is capable of migrating to the coating surface to form a new film layer. The term “acrylic polymer” as used herein refers to poly(meth)acrylate homopolymer or copolymer.

[0048] The molecular weight of the acrylic polymer is known to affect its compatibility with other resin components of film-forming resin composition. In various embodiments, the acrylic polymer as flattening agent may have a weight average molecular weight of 6000 to 20000 g/mol, or 8000 to 12000 g/mol. The weight average molecular weight may be determined by GPC. If the weight average molecular weight of the acrylic polymer is too high, its compatibility with other components will be poor so that it cannot disperse the coating surface homogeneously. If the weight average molecular weight of the acrylic polymer is too low, the film from the coating composition containing the acrylic polymer will have poor durability. In some embodiments, acrylic polymers in the above molecular weight range have shown good flattening performance.

[0049] The acrylic polymer flattening agent as disclosed in the present disclosure may be prepared by well known techniques, or any suitable commercial product may be used such as, for example EFKA 3777, EFKA 3772, EFKA 3600 or EFKA 3500 from BASF, Wyandotte, MI, USA.

[0050] In various embodiments, the weight ratio of polysiloxane flattening agent to acrylic polymer flattening agent may be 1:5 to 1:15, or 1:5 to 1:10, or 1:5 to 1:8. In some embodiments, a film-forming resin composition of the present disclosure with the

combination of polysiloxane and acrylic polymer in such weight ratio as flattening agent will result in the two-component polyurethane topcoat having even superior flattening properties. The thus formed coating may have a gloss of at least 85%, even 88% or more at 20 °C, and DOI of at least 0.85 and even up to 0.89, which is much superior to conventional industrial paint and even close to paints used in a vehicle finish. It has been surprisingly found by the inventors that the weight ratio of polysiloxane flattening agent to acrylic polymer flattening agent would also affect the flattening performance of the PU topcoat. Relative to the weight of polysiloxane flattening agent, too high or low amount of acrylic flattening agent will result in the PU topcoat having poor flattening performance.

[0051] Optionally, the film-forming resin composition further includes a mixture of solvents, each of which has a relative volatile rate in the range of 0.4 to 1.0, relative to butyl acetate. Solvent as used herein may include any known solvents suitable for coating compositions including, but not limited to, aliphatic hydrocarbons, aromatic hydrocarbons, terpenes, alcohols, ketones, esters, alcohol ethers, ester ethers, substituted hydrocarbons or any combination thereof. In some embodiments, the solvent includes esters, aromatic hydrocarbons, ester ethers, substituted hydrocarbons, or combinations thereof.

[0052] In one embodiment of the present disclosure, the solvent mixture includes, relative to the total weight of the solvent mixture, 0-55 wt% of butyl acetate; 0-30 wt% of xylene, 0-20 wt% of propylene glycol methyl ether acetate; and 0-15 wt% of 150# solvent oil, preferably 0.1-55 wt% of butyl acetate; 0.1-30 wt% of xylene, 0.1-20 wt% of propylene glycol methyl ether acetate; and 0.1-15 wt% of 150# solvent oil.

[0053] In some embodiments, the film-forming resin composition may further include one or more conventional additives for a polyurethane topcoat that do not adversely affect the coating composition or coating obtained therefrom. Suitable additives include, for example, those that can be used to improve the processability or manufacturability of the composition, enhance composition aesthetics, or improve a particular functional property or characteristic of the coating composition or the cured composition resulting therefrom, such as adhesion to a substrate. Suitable examples of such additives include, but are not limited to, pigments, anti-migration aids, anti-microbials, chain-extendors, lubricants, biocides, plasticizers, defoamers, colorants, waxes, anti-oxidants, adhesion promoters, UV stabilizers, or combinations thereof. Each optional ingredient can be included in a sufficient amount to serve its intended purpose, but preferably not in such an amount to

adversely affect the coating composition or cured coating obtained therefrom. In one example embodiment, the film-forming resin composition according to the present disclosure includes a pigment, a defoamer, a bactericide, a fungicide, or any combination thereof. According to the present disclosure, the total amount of the conventional additives is about 0.1 to about 15 % by weight relative to the total weight of the film-forming resin composition.

[0054] In some embodiments, the film-forming resin includes, relative to the total weight of the film-forming resin composition, 10 to 85 wt% of the active hydrogen-containing polymer; 10 to 85 wt% of the polyester resin; 0.1 to 0.5 wt% of the polysiloxane; 0.1 to 4.9 wt% of the acrylic polymer; 0.1 to 20 wt% of the mixture of solvents; and 0-15 wt% of the additional additives.

[0055] In various embodiments, the preparation of the film-forming resin composition may be achieved by any suitable mixing process that is known to those skilled in the art. For example, the film-forming resin composition can be prepared by adding to a vessel an active hydrogen containing polymer, a polyester resin, polysiloxane, an acrylic polymer, a solvent mixture, and additional additives, if any, and mixing the mixture until homogenous.

[0056] In some embodiments, the film-forming resin composition is substantially free of styrene, preferably essentially free of styrene, more preferably essentially completely free of styrene and even more preferably completely free of styrene.

Curing agent

[0057] As used herein, the term, “polyisocyanate curing agent”, is intended to refer to a poly-isocyanate compound, an isocyanate prepolymer, or a combination thereof. The poly-isocyanate curing agent has two or more isocyanate functionalities, and is capable of reacting with the active hydrogen-containing polymer to achieve chain extension and crosslinking, thereby allowing the three-dimensional network structure to be formed in the coating.

[0058] Suitable polyisocyanate curing agents include, but are not limited to, aliphatic polyisocyanates, aromatic polyisocyanates, or any combination thereof. As used herein, the term, “aliphatic polyisocyanates”, is intended to refer to any polyisocyanate compound having isocyanate groups directly attached to an aliphatic chain or ring. As used herein,

the term, “aromatic polyisocyanates”, is intended to refer to any polyisocyanate compound having isocyanate groups directly attached to an aromatic ring.

[0059] Suitable polyisocyanate compounds include, but are not limited to, hexamethylene diisocyanate, dodecamethylene diisocyanate, cyclohexene-1,4-diisocyanate, 4,4'-dicyclohexene methane diisocyanate, cyclopentene-1,3-diisocyanate, p-phenylene diisocyanate, toluene-2,4-diisocyanate, naphthalene-1,4-diisocyanate, diphenyl-4,4'-diisocyanate, benzene-1,2,4-triisocyanate, xylylene-1,4-diisocyanate, xylylene-1,3-diisocyanate, diphenylene methane diisocyanate, butane-1,2,3-triisocyanate, or polymethylene polyphenyl isocyanate. Suitable polyisocyanate compound include, but are not limited to, N-3390 from Covestro, Germany.

[0060] Suitable isocyanate prepolymers include, but are not limited to, polyurethane based prepolymers of any of the polyisocyanate compounds listed above, polyester based prepolymers of any of the polyisocyanate compounds listed above, and polyether based prepolymers of any of the polyisocyanate compounds listed above. The polyurethane based prepolymer, the polyester based prepolymer or the polyether based prepolymer may be prepared by any suitable method well known to a person skilled in the art. For example, the polyurethane based prepolymer may be prepared by reacting a monomeric polyol with one or more of polyisocyanate compounds under suitable conditions; the polyester based prepolymer or the polyether based prepolymer may be prepared by reacting polyester polyol or polyether polyol with one or more of the polyisocyanate compounds under suitable conditions. Alternatively, commercially available polyurethane based prepolymers, the polyester based prepolymers, or polyether based prepolymers may be used such as, for example, N-75 from BASF, Germany, or TPA-90 from ASAHIKASEI, Japan.

[0061] In some embodiments, the polyisocyanate curing agent may be diphenyl methane diisocyanate monomer, polymethylene polyphenyl isocyanate, polyether based diphenyl methane diisocyanate prepolymer, polyester based diphenyl methane diisocyanate prepolymer, or any combination thereof. In some embodiments, polymethylene polyphenyl isocyanate, polyether based diphenyl methane diisocyanate prepolymer or polyester based diphenyl methane diisocyanate prepolymer is used.

[0062] In various embodiments, the weight ratio of the film-forming resin composition to the multi-isocyanate hardener is 100: 10 to 100: 25. In general, when the weight ratio

of the polyisocyanate curing agent to the film-formation resin composition is less than 10:100, then the curing performance of the resulting coating is insufficient. In general, when the weight ratio of the polyisocyanate curing agent to the film-formation resin composition is greater than 25:100, then the processability of the two-component polyurethane topcoat and/or the mechanical properties of the resulting coating may be degraded. In various embodiments, during the preparation process of the film-forming resin composition and/or the polyisocyanate curing agent, additional inert diluents may be added which will not affect the reactivity of the above film-forming resin composition and polyisocyanate curing agent, such as, for example, to reduce the viscosity of the components. Therefore, the weight ratio of the film-forming resin composition and the polyisocyanate curing agent is not limited to the above range, and can be adjusted according to actual demand.

[0063] In various embodiments, a two-component polyurethane topcoat can be prepared by simply mixing the film-forming resin composition with the polyisocyanate curing agent in a mixing device at a predetermined weight ratio before application. The resulting polyisocyanate topcoat can be applied in a variety of ways that are familiar to those skilled in the art, including spraying (e.g., air assisted, airless or electrostatic spraying), brushing, rolling, flooding and dipping. In an embodiment of the present disclosure, the resulting polyurethane topcoat is coated by spraying.

[0064] The polyurethane topcoat can be applied in various wet film thicknesses, and in some embodiments is applied in a wet film thickness to provide a coating with a dry thickness from about 13 μm to about 260 μm (about 0.5 to about 10 mils) and more preferably from about 25 μm to about 75 μm (about 1 to about 3 mils). The applied paint may be cured by air drying or by accelerating drying with various drying devices (e.g., ovens) that are familiar to those skilled in the art.

EXAMPLES

[0065] The present disclosure is more particularly described in the following examples that are intended as illustrations only, since numerous modifications and variations within the scope of the present disclosure will be apparent to those skilled in the art. Unless otherwise noted, all parts, percentages, and ratios reported in the following examples are on a weight basis, and all reagents used in the examples are commercially available and used directly without further treatment.

Test Methods

[0066] Adhesion was measured according to GB/T 9779-2005.

[0067] Hardness was measured by pencil hardness measuring apparatus according to GB/T 6739.

[0068] Gloss was measured according to GB/T 1743-1989.

[0069] Distinctness of image (DOI) was measured by Dorigon DOI measuring apparatus according to ASTM D5767.

Table1. Materials used for various examples

Item	Materials	Supplier	Description
1	AP-451	Jiadian resin Inc, Suzhou, China	Hydroxyl acrylate polymer
2	AK1188P	Valspar, USA	Polyester resin
3	DC56	Dow Corning, Japan	Polysiloxane flatting agent
4	EFKA 3777	BASF, Germany	Acrylic polymer flatting agent
5	N-3390	Bayer, Germany	polymethylene polyphenyl polyisocyanate curing agent
6	139# yellow	Glarent, Germany	Organic pigment
7	Butyl acetate	General chemicals	Solvent
8	Xylene	General chemicals	Solvent
9	Propylene glycol methyl ether acetate	General chemicals	Solvent
10	150# solvent oil	General chemicals	solvent
11	Two-component PU topcoat	PPG	PU Topcoat for control

Example 1**Preparation of film-forming resin composition****Preparation of epoxy resin component**

[0070] In a mixing vessel, 450 g of AP-451, 150 g of AK1188P, 250 g of pigment, 2 g of DC-56, 20 g of EFKA 3777 and 50 g of a solvent mixture including 50 wt% of butyl acetate, 25 wt% of xylene, 15 wt% of propylene glycol methyl ether acetate and 10 wt% of 150# solvent oil were added and mixed with stirring at 800-1000 rpm homogeneously, thereby obtaining a film-forming resin composition.

Preparation of two-component polyurethane topcoat

[0071] Before application, above prepared film-forming resin composition and N3390, i.e. polymethylene polyphenyl polyisocyanate curing agent from Bayer, Germany were mixed in a weight ratio of 100: 20.

Coating formulation

[0072] A suitable amount of the present two-component polyurethane topcoat was spray applied onto Duraspar 200 FC epoxy primer available from Valspar, USA so that a coating having a dry film thickness of about 50 micrometers was formed.

[0073] As described in the testing method, adhesion, hardness, gloss and DOI were measured and listed in the following table 2.

Comparative Example A

[0074] A suitable amount of the commercial available two-component polyurethane topcoat from PPG was spray applied onto Duraspar 200 FC epoxy primer available from Valspar, USA so that a coating having a dry film thickness of about 50 micrometers was formed.

[0075] As described in testing method, adhesion, hardness, gloss and DOI were measured and listed in the following table 2.

Table 2

Examples	Adhesion	Hardness	Gloss at 20°/60°	DOI
Example 1	4B	2H	88%/96%	0.88
Comp. Ex A	5B	H	78%/90%	0.7

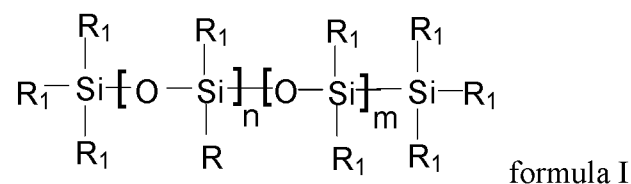
[0076] From above results, relative to a conventional polyurethane topcoat including an active hydrogen containing polymer as the only film-forming resin and including polysiloxane flatting agent alone, the present two-component polyurethane topcoat exhibited superior adhesion to a primer coating and hardness. The thus formed coating had especially excellent gloss and DOI, even close to those measured on vehicle paints.

[0077] While the invention has been described with respect to a number of embodiments and examples, those skilled in the art, having benefit of this disclosure, will appreciate that other embodiments can be devised which do not depart from the scope and spirit of the invention as disclosed herein.

WHAT IS CLAIMED:

1. A two-component polyurethane topcoat, comprising:
 - a) a film-forming resin composition comprising
 - i) an active hydrogen-containing polymer, having a hydroxyl value of 70 mg KOH/g polymer or more;
 - ii) a polyester resin, having a hydroxyl value of less than 50 mg KOH/g resin and a viscosity of less than 6000 mPa.s at 25 °C; and
 - iii) a package of flatting agents comprising a polysiloxane containing an effective silicon content of 30 wt% or more and an acrylic polymer having a weight average molecular weight in the range of 6,000 to 20,000 g/mol, wherein the weight ratio of the polysiloxane to the acrylic polymer is in the range of 1:5 to 1: 15; and
 - b) a polyisocyanate curing agent,wherein the ratio by weight of component a) to component b) is 100 : 10 to 100 : 25.
2. The two-component polyurethane topcoat according to claim 1, wherein the film-forming resin composition comprises, based on the total weight of the film-forming resin composition,
 - 10 to 85 wt% of the active hydrogen-containing polymer;
 - 5 to 85 wt% of the polyester resin; and
 - 0.1 to 5 wt% of the package of flatting agents.
3. The two-component polyurethane topcoat according to claim 1, wherein the active hydrogen-containing polymer has a viscosity of at least 4,000 mPa.s at 25 °C.
4. The two-component polyurethane topcoat according to claim 1, wherein the active hydrogen-containing polymer has a weight average molecular weight of 10,000 g/mol or more.
5. The two-component polyurethane topcoat according to claim 1, wherein the polyester resin has a viscosity of 2,500 to 3,000 mPa.s at 25 °C.

6. The two-component polyurethane topcoat according to claim 1, wherein the polyester resin has a weight average molecular weight of 15,000 to 20,000 g/mol.
7. The two-component polyurethane topcoat according to claim 1, wherein the difference between the solubility parameter of the active hydrogen-containing polymer and the solubility parameter of the polyester resin is less than $0.5(\text{J}/\text{cm}^3)^{1/2}$.
8. The two-component polyurethane topcoat according to claim 1, wherein the polysiloxane has an effective silicon content of 60 wt% or more.
9. The two-component polyurethane topcoat according to claim 1, wherein the polysiloxane has the structure of formula I:



in which

R_1 is at each occurrence independently selected from the group consisting of C_1 - C_6 alkyl, preferably methyl;

R represents a polyether residue or a polyester residue;

the sum of m and n is an integer of 30 to 250; and

the ratio of m to n is 3:7 to 9:1.

10. The two-component polyurethane topcoat according to claim 1, wherein the acrylic polymer has a weight average molecular weight of 8,000 to 12,000 g/mol.
11. The two-component polyurethane topcoat according to any one of claims 1-10, wherein the active hydrogen-containing polymer comprises a polymer containing one or more of $-\text{COOH}$, $-\text{OH}$, $-\text{SH}$, secondary amino, or primary amino.

12. The two-component polyurethane topcoat according to claim 11, wherein the active hydrogen-containing polymer is selected from an acrylic polymer containing a hydroxyl group.
13. The two-component polyurethane topcoat according to any one of claims 1-10, wherein the film-forming resin composition further comprises a mixture of solvents, each of which has a relative volatile rate of 0.4 to 1.0, relative to butyl acetate.
14. The two-component polyurethane topcoat according to claim 13, wherein the mixture of solvents comprises, relative to the total amount of the mixture of solvents,
0-55 wt% of butyl acetate;
0-30 wt% of xylene;
0-20 wt% of propylene glycol methyl acetate; and
0-15 wt% of 150 solvent oil.
15. The two-component polyurethane topcoat according to claim 13, wherein the film-forming resin composition comprises, based on the total weight of the film-forming resin composition,
10 to 85 wt% of the active hydrogen-containing polymer;
10 to 85 wt% of the polyester resin;
0.1 to 0.5 wt% of the polysiloxane;
0.1 to 4.9 wt% of the acrylic polymer; and
0.1 to 20 wt% of the mixture of solvents.
16. The two-component polyurethane topcoat according to any one of claims 1-10, wherein the polyisocyanate curing agent comprises one or more of aliphatic polyisocyanates, aromatic polyisocyanates, or any combination thereof.
17. The two-component polyurethane topcoat according to claim 16, wherein the polyisocyanate curing agent comprises one or more of hexamethylene diisocyanate, dodecamethylene diisocyanate, cyclohexene-1,4-diisocyanate, 4,4'-dicyclohexene methane diisocyanate, cyclopentene-1,3-diisocyanate, p-phenylene diisocyanate, toluene-2,4-

diisocyanate, naphthalene-1,4-diisocyanate, diphenyl-4,4'-diisocyanate, benzene-1,2,4-triisocyanate, xylylene-1,4-diisocyanate, xylylene-1,3-diisocyanate, diphenylene methane diisocyanate, butane-1,2,3-triisocyanate, polymethylene polyphenyl isocyanate, a polyurethane based prepolymer thereof, a polyester based prepolymer thereof, a or polyether based prepolymer thereof, or any combination thereof.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2017/027935

A. CLASSIFICATION OF SUBJECT MATTER IPC (2017.01) C09D 175/06, C08G 18/06, C09D 7/06 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC (2017.01) C09D, C08G 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 practicable, search terms used) Databases consulted: THOMSON INNOVATION, Esp@cenet, Google Patents, Google Scholar, FamPat database Search terms used: polyurethane, topcoat, resin, paint, active hydrogen, polyester, flattening agent, polyisocyanate, high gloss, leveling, sil*		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN 103497604 A DONGLAI COATING TECHNOLOGY SHANGHAI 08 Jan 2014 (2014/01/08) abstract, para. [0011], [0007], [0013], [0015], [0018], [0020], [0024], [0032], [0055]	1-17
A	US 8563648 B2 PPG INDUSTRIES OHIO INC 22 Oct 2013 (2013/10/22) The whole document	1-17
A	EP 2621982 B1 COATINGS FOREIGN IP CO LLC 30 Jul 2015 (2015/07/30) para. [0002], [0010], [0023], [0072]	1-17
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 24 Jul 2017		Date of mailing of the international search report 30 Jul 2017
Name and mailing address of the ISA: Israel Patent Office Technology Park, Bldg.5, Malcha, Jerusalem, 9695101, Israel Facsimile No. 972-2-5651616		Authorized officer GUTMAN Ariel Telephone No. 972-2-5657816

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2017/027935

Patent document cited search report			Publication date	Patent family member(s)			Publication Date
CN	103497604	A	08 Jan 2014	CN	103497604	A	08 Jan 2014
<hr/>							
US	8563648	B2	22 Oct 2013	US	2011098394	A1	28 Apr 2011
				US	8563648	B2	22 Oct 2013
				CA	2778011	A1	12 May 2011
				CA	2778011	C	08 Jul 2014
				CN	102597140	A	18 Jul 2012
				CN	102597140	B	25 Mar 2015
				EP	2493992	A1	05 Sep 2012
				HK	1172922	A1	22 Jan 2016
				KR	20120075488	A	06 Jul 2012
				KR	101397880	B1	20 May 2014
				MX	2012005061	A	13 Jun 2012
				MX	328627	B	17 Mar 2015
				RU	2012121880	A	10 Dec 2013
				RU	2515742	C2	20 May 2014
				WO	2011056555	A1	12 May 2011
<hr/>							
EP	2621982	B1	30 Jul 2015	EP	2621982	A1	07 Aug 2013
				EP	2621982	B1	30 Jul 2014
				WO	2012044509	A1	05 Apr 2012
<hr/>							