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(54) **COATINGS AND INKS BASED ON
SOLVENTS HAVING NEGLIGIBLE
PHOTOCHEMICAL REACTIVITY**

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(57) **ABSTRACT**

Coating and ink compositions based on organic solvents that have negligible photochemical reactivity and methods for making them are disclosed. The organic solvents have calculated oxidation rate constants of less than about 1×10^{10} cm³/g·sec, and evaporation rates of not more than about 5 times that of n-butyl acetate. Coatings made by the method of the invention are used for wood, furniture, automotive, container, architectural, coil, aerosol, marine, transportation, industrial, ink, overprint varnish, and road-coating applications.

COATINGS AND INKS BASED ON SOLVENTS HAVING NEGLIGIBLE PHOTOCHEMICAL REACTIVITY

FIELD OF THE INVENTION

[0001] The invention relates to coating compositions and methods of preparing them. In particular, the invention relates to coatings and inks that contain solvents having negligible photochemical reactivity and favorable evaporation rates.

BACKGROUND OF THE INVENTION

[0002] Organic solvents, many of which are classified as VOCs, are widely used in traditional coating formulations (including inks). Generally, an organic compound is classified as a VOC unless it has been proven to not participate in atmospheric photochemical reactions. Ordinarily, these are compounds that undergo hydrogen atom abstraction by atmospheric hydroxyl radicals much faster than ethane. VOCs are hazardous to human health because they react with free radicals in the air and generate tropospheric ozone.

[0003] Pursuant to the Clean Air Act of 1990, the U.S. Environmental Protection Agency (EPA) recently mandated significant reductions in the amount of VOCs that may be used in coatings. Because of the mandate, the industry has an acute need for good coating solvents that have negligible photochemical reactivity and can therefore be exempt from regulation. Unfortunately, most organic solvents that have the desired low photochemical reactivity are either poor coating solvents or are subject to other regulations. For example, some solvents are classified as "ozone depleters" under the Montreal Protocol; others are regulated by the EPA as "hazardous air pollutants" (HAP solvents). Few organic solvents are valuable for coatings and have low photochemical reactivity, yet are not ozone depleters or HAP solvents.

[0004] The EPA has exempted some solvents from VOC status based on their negligible photochemical reactivity. Examples include acetone, methylene chloride, volatile methyl siloxanes, perchloroethylene, and p-chlorobenzyltrifluoride (PCBTF). Unfortunately, these solvents have drawbacks. Acetone and methylene chloride evaporate too fast. In addition, acetone is water-miscible, so coatings made with it absorb moisture too rapidly from the air. Acetone also has appreciable atmospheric photochemistry aside from its reaction with hydroxyl radicals because it strongly absorbs visible and near-UV light. Methylene chloride and perchloroethylene have toxicity concerns. The more exotic solvents, such as methyl siloxanes and PCBTF, are too expensive and are relatively poor coating solvents, as is evidenced by their relatively low Hansen solubility parameters (less than 8.0 (cal/cm³)^{1/2}).

[0005] Traditional approaches to reducing the VOC content of coatings and inks have focused in developing new resins, crosslinkers, and reactive diluents that do not require as much solvent to formulate. These approaches have succeeded only marginally in spite of their considerable expense. For example, water-borne coatings, which developed as an alternative to solvent-borne systems, sometimes contain even more VOCs than comparable high-solids formulations, and often give inferior performance. As another example, powder coatings may use little or no VOCs, but they require expensive equipment to apply and cure.

[0006] In sum, the coating and ink industry needs solvents that have low toxicity, are inexpensive, are not regulated as HAP solvents or ozone depleters, do not evaporate too rapidly, are good coating solvents, and most important, have negligible photochemical reactivity and could be exempt from VOC regulations.

SUMMARY OF THE INVENTION

[0007] The invention is a method of preparing a coating composition. The method comprises using as a coating component an organic solvent having negligible photochemical reactivity. Such solvents have an oxidation rate constant of less than about 1×10^{10} cm³/g-sec. This is a calculated or measured rate of hydrogen-atom abstraction from a compound by atmospheric hydroxyl radicals. In addition, the organic solvent has an evaporation rate of not more than about 5 times that of n-butyl acetate.

[0008] We surprisingly found that, among thousands of possible organic compounds potentially useful as coating and ink solvents, very few meet the needs of the industry, particularly when current VOC restrictions and relative evaporation rates are taken into account. By including a solvent having an oxidation rate constant of less than about 1×10^{10} cm³/g-sec, and also having an evaporation rate of not more than about 5 times that of n-butyl acetate, formulators can significantly reduce the proportion of photochemically reactive solvent used and still make good coatings.

[0009] The invention includes thermoplastic and thermoset coating compositions which comprise an organic solvent having negligible photochemical reactivity. These compositions include a resin or a crosslinker or both. The invention benefits coatings used for wood, furniture, automotive OEM, automotive refinish, container, architectural, coil, aerosol, marine, transportation, industrial maintenance, general industrial, inks, overprint varnishes, and road-coating applications.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

[0010] The invention is a method of preparing coating compositions, including inks. The method comprises using as a coating component an organic solvent having negligible photochemical reactivity, and also having an evaporation rate of not more than about 5 times that of n-butyl acetate.

[0011] By solvents having "negligible photochemical reactivity," we mean solvents that will undergo free-radical abstraction of a hydrogen atom of the solvent by atmospheric hydroxyl radicals at a measured or calculated rate less than or about equal to the corresponding rate of abstraction of hydrogen atoms from ethane. On a weight basis, this corresponds to an oxidation rate constant of less than about 1×10^{10} cm³/g-sec. Solvents having such low photochemical reactivities are potentially excludable as VOCs under EPA regulations. Solvents preferably used in the method of the invention have oxidation rate constants less than about 5×10^9 cm³/g-sec; most preferred are solvents having oxidation rate constants less than about 3×10^9 cm³/g-sec.

[0012] Oxidation rate constants of various coating solvents appear in Table 1 (below). As shown in the table, many traditional coating solvents such as toluene, xylenes, methyl isobutyl ketone, and n-butyl acetate have relatively high

oxidation rate constants and are classified by the EPA as VOCs. In contrast, the method of the invention uses solvents having negligible photochemical reactivity such as those listed in the top half of the table (e.g., tert-butyl acetate, dimethyl carbonate).

[0013] In addition to negligible photochemical reactivity, organic solvents useful in the method of the invention are limited to those having useful evaporation rates. Some otherwise useful (and currently VOC-exempt) organic solvents have limited value in coatings because they evaporate too rapidly. Examples are acetone and methylene chloride, which evaporate (respectively) roughly 6 and 14 times faster than n-butyl acetate. Organic solvents useful in the invention have evaporation rates of not more than about 5 times that of n-butyl acetate, which is the industry standard for comparison. More preferred organic solvents have evaporation rates of not more than about 3 times that of n-butyl acetate.

[0014] Traditional coating solvents classified as VOCs can be included in the method of the invention. These solvents may be critical for maintaining satisfactory coating processability or performance. Preferably, however, at least about 5 wt. % of the total solvent content of coatings made by the method of the invention comprises one or more organic solvents that have negligible photochemical reactivity and also have an evaporation rate of not more than about 5 times that of n-butyl acetate. More preferably, the organic solvent(s) having negligible photochemical reactivity is the major solvent component, i.e., at least about 50 wt. % of the solvent used is one or more solvents that have negligible photochemical reactivity. The solvent having negligible photochemical reactivity may be the only solvent component.

[0015] Organic solvents useful in the method of the invention should have good solvent properties for coatings. Preferably, the solvent will have a total Hansen solubility parameter (δ) of at least about $8.0 \text{ (cal/cm}^3)^{1/2}$. If the solvent has a δ value less than $8.0 \text{ (cal/cm}^3)^{1/2}$, it may not adequately solubilize coating components, may give poor film-forming properties, or may contribute to incompletely cured coatings. As noted above, some commercially available organic solvents (e.g., volatile methyl siloxanes and PCBTF) are VOC-exempt, but have δ values less than $8.0 \text{ (cal/cm}^3)^{1/2}$. Hansen solubility parameters and methods for calculating them appear, for example, in *Polymer Handbook*, 3rd ed., Brandrup and Immergut, eds. (1989), VII 519-544.

[0016] Organic solvents useful in the method of the invention preferably contain no reactive halogen atoms, i.e., they contain no chlorine or bromine atoms, but may contain fluorine. In addition, preferred organic solvents are not regulated by the Montreal Protocol as stratospheric ozone depleters (e.g., CFCs), and are not classified by the EPA as hazardous air pollutants (HAP solvents; e.g., methylene chloride, perchloroethylene). Preferred organic solvents have relatively low toxicity.

[0017] Most or all of the hydrogen atoms in preferred solvents are part of methyl or tert-butyl groups, i.e., they are "primary" hydrogen atoms. For example, in tert-butyl acetate, all of the hydrogen atoms are part of a methyl group or a tert-butyl group, and are all primary hydrogens. Solvents useful in the invention can have secondary or tertiary hydrogens, but preferably such compounds will have an electron-withdrawing group attached to the carbon having the secondary or tertiary hydrogen atom. For example, 2-nitropropane, a solvent useful in the invention, has a tertiary hydrogen, but it is attached to a carbon having a

strong electron-withdrawing group (a nitro group) attached to it. Electron-withdrawing groups are well-known to those skilled in the art, and include, for example, nitro, halogen, carboxyl, carbonate, trifluoromethyl, cyano, acetyl, and the like.

[0018] Suitable solvents for use in the invention include, for example, nitroalkanes (e.g., 2-nitropropane, nitroethane, nitro-tert-butane), tert-butyl acetate, methyl benzoate, methyl trifluoroacetate, dimethyl carbonate, methyl pivalate, tert-butyl alcohol, propylene carbonate, tert-butyl benzoate, di-tert-butyl carbonate, methyl tert-butyl carbonate, and the like, and mixtures thereof. Most preferred is tert-butyl acetate.

[0019] Coating compositions made by the method of the invention are water-borne or solvent-borne, but are preferably solvent-borne. They contain acrylic, vinyl, amino, urethane, epoxy, alkyd, uralkyd, nitrocellulose, melamine, polyols, polyesters, or other resins that are soluble in the organic solvents used. The resins are thermoplastic or thermoset. The thermoset resins have carboxy, hydroxy, epoxy, isocyanate, amino, silane, anhydride, olefin, or allylic functionalities that are cured by reaction with a crosslinker or by self-crosslinking between polymer chains. Suitable crosslinkers include epoxy resins, isocyanates, melamines, and the like. The coatings can be clear or may contain pigments, fillers, or other additives. The coatings can be cured at ambient temperature or at elevated temperature by baking. The coatings cure by radiation, oxidation, or chemical crosslinking.

[0020] The invention includes a method of preparing a coating resin. The method comprises polymerizing one or more ethylenic monomers in the presence of an organic solvent having negligible photochemical reactivity and also having an evaporation rate of not more than about 5 times that of n-butyl acetate. Optionally, the polymerization is performed in the presence of a free-radical initiator. The mixture is heated under conditions effective to polymerize the monomers according to well-known techniques. Suitable ethylenic monomers and free-radical initiators are those well known in the art. The ethylenic monomers include, for example, vinyl aromatic monomers, acrylates, allylic alcohols, allylic esters, allylic ethers, cyclic unsaturated anhydrides, vinyl halides, and the like, and mixtures thereof. Peroxides are preferably used as free-radical initiators. If desired, other types of resins can be prepared in the presence of the organic solvent, such as those made by condensation polymerization (e.g., polyethers and polyesters).

[0021] The invention includes thermoplastic and thermoset coating compositions. The compositions comprise a resin or a crosslinker or both. In addition, the compositions comprise an organic solvent having negligible photochemical reactivity as measured by an oxidation rate constant of less than about $1 \times 10^{-13} \text{ cm}^3/\text{g} \cdot \text{sec}$, and also having an evaporation rate of not more than about 5 times that of n-butyl acetate.

[0022] Any desired technique can be used for applying coatings made by the method of the invention. Suitable techniques include, spraying, brushing, lay down, dipping, or other methods. The coatings can be applied to coated or uncoated metal, plastic, glass, concrete, asphalt, or other hard surfaces. Coatings made by the method of the invention are used in wood, furniture, automotive OEM, automotive refinish, container, architectural, coil, aerosol, marine, transportation, industrial maintenance, general industrial, inks, overprint varnishes, and road-coating applications. The

examples below show just a few possible formulations that contain reduced levels of photochemically reactive solvents. The performance characteristics of these coatings should rival those of the comparative examples with larger proportions of photochemically reactive solvents.

[0023] Example 23 and Comparative Example 24 show properties of a two-component polyurethane coating made from a hydroxy-acrylic resin. The examples show that excellent coating properties are maintained when tert-butyl acetate is used in place of n-butyl acetate to give a formulation with an 11 wt. % reduction in the content of photochemically reactive organic solvent.

[0024] The following examples merely illustrate the invention. Those skilled in the art will recognize many variations that are within the spirit of the invention and scope of the claims.

EXAMPLE A

Preparation of a Zero-VOC Acrylic Resin Solution

[0025] Tert-butyl acetate (150 g) is charged to a glass polymerization reactor equipped with reflux condensor, heating mantle, and addition funnel. A mixture of styrene (42 g), methyl methacrylate (42 g), butyl acrylate (35 g), butyl methacrylate (147 g), hydroxyethyl acrylate (84 g), and benzoyl peroxide (20 g) is cooled to 5° C. and is then charged to the addition funnel. The tert-butyl acetate is heated to reflux (98° C.), and the monomer mixture is added gradually over 4 h. The mixture is refluxed for an additional hour after monomer addition is complete. The reactor contents are cooled to room temperature, and the mixture is discharged. The resulting hydroxy-functional acrylic resin solution is expected to have a solids content of about 70 wt. %. The solid component of the resin solution has a hydroxyl number within the range of about 110 to 120 mg KOH/g.

TABLE 1

Oxidation Rate Constants ¹ of Coating Solvents (cm ³ /g.sec)	
tert-butyl acetate	2.3 × 10 ⁹
dimethyl carbonate	2.9 × 10 ⁹
methyl tert-butyl carbonate	3.3 × 10 ⁹
di-tert-butyl carbonate	3.5 × 10 ⁹
methyl benzoate	3.7 × 10 ⁹
propylene carbonate	4.1 × 10 ⁹
ethane (for comparison)	5.4 × 10 ⁹
tert-butyl benzoate	7.7 × 10 ⁹
tert-butyl alcohol	8.8 × 10 ⁹
n-butyl acetate	2.5 × 10 ¹⁰
toluene	3.9 × 10 ¹⁰
methyl isobutyl ketone	8.5 × 10 ¹⁰
xylene	1.3 × 10 ¹¹

¹Weight-based rate of abstraction of a hydrogen atom by atmospheric hydroxyl radicals. Measured or calculated rates in cm³/molecule . sec are reported by Atkinson. See, for example, R. Atkinson, *Int.J.Chem.Kinet.*, 19 (1987) 799, and R. Atkinson, *Environ.Tox.Chem.*, 7 (1988) 435. The rates here are reported in cm³/g . sec to correct for volatility and to normalize for differing numbers of hydrogen atoms. To convert a rate in cm³/molecule.sec to a rate in cm³/g . sec, multiply the former by 6.022 × 10²³ molecules per mole, and divide by the molecular weight (g/mole) of the solvent.

[0026]

Example 1 and Comparative Example 2 2K High-Solids Acrylic-Urethane Gloss Clearcoat for Air-Dry Applications		
Example	1	C2
Part A: Acrylic Polyol		
G-CURE 105P70 acrylic polyol ¹	800	800
methyl amyl ketone	0	80
tert-butyl acetate	80	0
dibutyltin dilaurate (2% in methyl ethyl ketone)	7.0	7.0
Part B: Isocyanate		
LUXATE FIT-2000 isocyanate adduct ²	200	200
propylene glycol methyl ether acetate	16.6	33.3
methyl ethyl ketone	0	33.3
tert-butyl acetate	49.9	0
Pounds (#) of photochemically reactive solvent		
reactive #s per gallon	2.4	3.3
reactive #s per # of solids applied	0.35	0.52

¹product of Henkel; ²of ARCO Chemical. The amounts listed are in parts by weight.

[0027]

Example 3 and Comparative Example 4 White Polyester-Urethane 2K Air-Dry Coating ¹		
Example	3	C4
Part A		
5760 polyester resin solution ²	28.9	28.9
TTANOX 2090 titanium dioxide ³	37.3	37.3
n-butyl acetate	0	9.45
tert-butyl acetate	9.45	0
soya lecithin	0.32	0.32
BYK 300 additive ⁴	0.40	0.40
dibutyltin dilaurate	0.040	0.040
Part B		
DESMODUR N-75 isocyanate adduct ⁵	0	19.9
LUXATE HT2000 isocyanate adduct ⁶	14.9	0
ethylene glycol ethyl ether acetate	0	3.72
tert-butyl acetate	4.97	0
Pounds (#) of photochemically reactive solvent		
reactive #s per gallon	1.1	2.6
reactive #s per # of solids applied	0.087	0.27

¹See E.W. Flick, *Contemporary Industrial Coatings*, 1985, p. 101.

²product of Cargill; ³product of Kronos; ⁴product of Byk Chemie; ⁵ product of Bayer;

⁶product of ARCO Chemical. The amounts listed are in parts by weight.

[0028]

Example 5 and Comparative Example 6 White Alkyd Topcoat ¹		
Example	5	C6
5720 alkyd resin solution ²	48.7	48.7
TITANOX 2090 titanium dioxide ³	29.2	29.2
BYK 300 additive ⁴	0.20	0.20
n-butyl acetate	0	20.3
tert-butyl acetate	20.3	0
cobalt (18%) drier	0.13	0.13
zirconium (18%) drier	0.39	0.39
ACTIV-8 additive ⁵	0.20	0.20
EXKIN #2 anti-skinning agent ⁶	0.14	0.14
Pounds (#) of photochemically reactive solvent		
reactive #s per gallon	1.9	3.5
reactive #s per # of solids applied	0.20	0.50

¹See E.W. Flick, Contemporary Industrial Coatings, 1985, p. 113.²product of Cargill; ³of Kronos; ⁴product of Byk Chemie;⁵product of R.T. Vanderbilt; ⁶product of Nuodex.

The amounts listed are in parts by weight.

[0029]

Example 7 and Comparative Example 8 Polyester Urethane Furniture Coating ¹		
Example	7	C8
MULTRON R-12A polyester polyol ²	275	275
MODAFLOW resin modifier ³	1.0	1.0
DESMODUR HL isocyanate adduct ²	370	370
toluene	0	179
ethylene glycol ethyl ether acetate	65	175
tert-butyl acetate	289	0
Pounds (#) of photochemically reactive solvent		
reactive #s per gallon	2.8	4.4
reactive #s per # of solids applied	0.43	1.0

¹See M. Ash and I. Ash, A Formulary of Paints and Other Coatings, 1978, p. 203.²product of Bayer; ³product of Monsanto.

The amounts listed are in parts by weight.

[0030]

Example 9 and Comparative Example 10 Acrylic-Nitrocellulose Aircraft White Gloss Coating ¹		
Example	9	C10
RBH White titanium dioxide dispersion #6610 ²	23.8	23.8
½ sec RS nitrocellulose ³	5.90	5.90
ACRYLOID B-82 acrylic resin ⁴	28.6	28.6
dioctyl phthalate	5.40	5.40
toluene	0	7.16
methyl ethyl ketone	0	13.1
tert-butyl acetate	36.3	0
methyl isobutyl ketone	0	16.0
Pounds (#) of photochemically reactive solvent		

-continued

Example 9 and Comparative Example 10 Acrylic-Nitrocellulose Aircraft White Gloss Coating ¹		
Example	9	C10
reactive #s per gallon	3.8	5.2
reactive #s per # of solids applied	0.58	1.5

¹See M. Ash and I. Ash, A Formulary of Paints and Other Coatings, 1978, p. 140.²product of Inmont; ³product of Hercules; ⁴product of Rohm and Haas.

The amounts listed are in parts by weight.

[0031]

Example 11 and Comparative Example 12 Epoxy-Amine Clear Can Coating ¹		
Example	11	C12
EPON 1001 B-80 epoxy resin ²	246	246
UNJ-RLEZ 2100P75 curing agent ³	250	250
n-butyl alcohol	84.0	84.0
n-propyl alcohol	0	62.0
toluene	0	45.6
methyl butyl ketone	0	21.5
tert-butyl acetate	158	0
ethylene glycol ethyl ether	50.0	78.5
Pounds (#) of photochemically reactive solvent		
reactive #s per gallon	3.2	4.0
reactive #s per # of solids applied	0.64	1.1

¹See M. Ash and I. Ash, A Formulary of Paints and Other Coatings, 1978, p. 144.²of Shell; ³product of Union Camp.

The amounts listed are in parts by weight.

[0032]

Example 13 and Comparative Example 14 Black Acrylic Lacquer for Wood Coatings ¹		
Example	13	C14
ACRYLOID B-99 acrylic resin solution ²	7.67	7.67
ACRYLOID B-48N solid acrylic resin ²	117	117
carbon black	3.83	3.83
toluene	0	144
xylenes	38.0	368
ethylene glycol ethyl ether acetate	62.8	123
tert-butyl acetate	534	0
Pounds (#) of photochemically reactive solvent		
reactive #s per gallon	3.7	6.3
reactive #s per # of solids applied	0.85	5.2

¹See M. Ash and I. Ash, A Formulary of Paints and Other Coatings, 1978, p. 293.²product of Rohm and Haas.

The amounts listed are in parts by weight.

[0033]

Example 15 and Comparative Example 16 Blue Flexographic Ink ¹		
Example	15	C16
SUNFAST BLUE 249-2083 dye ²	6.32	6.32
ACRYLOID DM-55 acrylic resin ³	2.11	2.11
ACRYLOID B-72 acrylic resin ³	23.1	23.1
n-propyl acetate	0.72	21.2
ethyl alcohol (denatured)	23.6	38.6
tert-butyl acetate	42.2	0
ethyl acetate	0	8.70
Pounds (#) of photochemically reactive solvent		
reactive #s per gallon	3.7	5.3
reactive #s per # of solids applied	0.83	2.2

¹See E.W. Flick, PrintingInkandOverprintVarnishFormulations, 1991, p. 17.
²product of Sun Chemicals; ³product of Rohm and Haas.
The amounts listed are in parts by weight.

[0034]

Example 17 and Comparative Example 18 Beige Polyester-Melamine Baking Enamel for Coil Coatings ¹		
Example	17	C18
5781 polyester poiyo resin ²	27.9	27.9
CYMEL 350 melamine resin ³	11.7	11.7
titanium dioxide pigment	28.1	28.1
carbon black pigment	0.070	0.070
yellow iron oxide pigment	0.84	0.84
silica flattng agent	2.96	2.96
acid catalyst	1.27	1.27
propylene glycol methyl ether acetate	7.59	17.6
n-butyl acetate	0	9.50
methyl pivalate	19.5	0
Pounds (#) of photochemically reactive solvent		
reactive #s per gallon	1.4	3.2
reactive #s per # of solids applied	0.12	0.39

¹See E.W. Flick, ContemporaryIndustrialCoatings, 1985, p. 95.
²product of Cargill; ³product of Cytec.
The amounts listed are in parts by weight.

[0035]

Example 19 and Comparative Example 20 SAA Resinous Polyol—Urethane Clearcoat for Wood ¹		
Example	19	C20
Part A		
SAA 103 resinous polyol ²	150	150
n-butyl acetate	0	200
tert-butyl acetate	200	0
Part B		
LUXATE HT2000 isocyanate adduct ²	70.0	70.0
n-butyl acetate	0	20.0
tert-butyl acetate	20.0	0

-continued

Example 19 and Comparative Example 20 SAA Resinous Polyol—Urethane Clearcoat for Wood ¹		
Example	19	C20
Pounds (#) of photochemically reactive solvent		
reactive #s per gallon	0	4.0
reactive #s per # of solids applied	0	1.0

¹Note: Mix parts A and B at 1:1 by weight. Reduce with solvent to the desired application viscosity.
²product of ARCO Chemical.
The amounts listed are in parts by weight.

[0036]

Example 21 and Comparative Example 22 One-Component Thermoplastic Acrylic Clearcoat		
Example	21	C22
ACRYLOID B-82 solid acrylic resin ¹	150	150
n-butyl acetate	0	225
tert-butyl acetate	225	0
Pounds (#) of photochemically reactive solvent		
reactive #s per gallon	0	4.9
reactive #s per # of solids applied	0	1.5

¹product of Rohm and Haas.
The amounts listed are in parts by weight.

[0037]

Example 23 and Comparative Example 24 Two-Component Hydroxy-Acrylic Polyurethane Coating		
Example	23	C24
G-CURE 105P70 acrylic polyol ¹	100	100
T-12 catalyst ² (1 wt. % in toluene)	1.9	1.9
silicone flow additive (10%)	0.34	0.34
LUXATE HT-2000 isocyanate adduct ³	25.5	25.5
ethylene glycol ethyl ether acetate	25.0	25.0
methyl amyl ketone	25.0	25.0
n-butyl acetate	0	25.0
tert-butyl acetate	28.0	0
Coating Properties		
Pot life (sec, Zahn #2 cup) T = 0;	21.1; 29.7	21.2; 29.9
T = 4 h		
Dry time (h, 21.5° C., 59% rel. hum).	0.25; 1.5; 2.0;	0.20; 1.4; 1.6;
evap time; gel time; dry time; total	3.0	3.2
Film thickness (mil)	2.8	2.7
Gloss (20°); (60°)	88; 95	88; 95
Pencil hardness; Pendulum hardness	4 H; 89	4 H; 91
Forward, reverse impact (in./lb.)	160+; 160+	160+; 160+
Adhesion	pass	pass
DOI	90	90
Photochemically reactive pounds per gallon	3.8	4.3

-continued

Example 23 and Comparative Example 24 Two-Component Hydroxy-Acrylic Polyurethane Coating		
Example	23	C24
Chemical & solvent resistance, 30 min.: 10% HCl, 10% HOAc, 10% NaOH, xylenes, MEK; MEK 100 double rubs	no change	no change

¹Product of Henkel, 70 wt. % in propylene glycol methyl ether acetate;²product of Air Products;³product of ARCO Chemical.

The amounts listed are in parts by weight. Samples tested on ACT cold roll steel 4 × 12 × 0.032 B1000 P60 DIW; polish.

[0038]

Example 25 and Comparative Example 26 Thermoset Overprint Varnish ¹		
Example	25	C26
CAP 482-0.5 cellulose acetate propionate ²	10.8	10.8
BECKAMINE 21-511 urea resin ³	18.0	18.0
acid catalyst	0.050	0.050
ethyl alcohol (denatured)	24.5	49.5
ethyl acetate	0	21.2
methyl pivalate	46.2	0
Pounds (#) of photochemically reactive solvent		
reactive #s per gallon	4.4	5.7
reactive #s per # of solids applied	1.4	3.5

¹See E. W. Flick, Printing Ink and Overprint Varnish Formulations, 1991, p. 122.²product of Eastman;³product of Reichhold.

The amounts listed are in parts by weight.

[0039] The preceding examples are meant as illustrations; the following claims define the scope of the invention.

We claim:

1. A method of preparing a coating composition, said method comprising using as a coating component an organic solvent having negligible photochemical reactivity as measured by an oxidation rate constant of less than about 1×10^{10} cm³/g·sec, and also having an evaporation rate of not more than about 5 times that of n-butyl acetate.

2. The method of claim 1 wherein the organic solvent has a total Hansen solubility parameter of at least about 8.0 (cal/cm³)^{1/2}.

3. The method of claim 1 wherein the organic solvent contains no chlorine or bromine atoms.

4. The method of claim 1 wherein the organic solvent is selected from the group consisting of nitroalkanes, tert-butyl acetate, methyl benzoate, methyl trifluoroacetate, dimethyl carbonate, methyl pivalate, tert-butyl alcohol, propylene carbonate, tert-butyl benzoate, di-tert-butyl carbonate, and methyl tert-butyl carbonate.

5. The method of claim 1 wherein the organic solvent is tert-butyl acetate.

6. The method of claim 1 wherein the oxidation rate constant is less than about 5×10^9 cm³/g·sec.

7. The method of claim 1 wherein the oxidation rate constant is less than about 3×10^9 cm³/g·sec.

8. The method of claim 1 wherein the organic solvent comprises at least about 5 wt. % of the total solvent component of the coating composition.

9. The method of claim 1 wherein the organic solvent having negligible photochemical reactivity comprises the major solvent component of the coating composition.

10. A method of preparing a coating composition, said method comprising using as a coating component an organic solvent having negligible photochemical reactivity as measured by an oxidation rate constant of less than about 1×10^{10} cm³/g·sec, and also having an evaporation rate of not more than about 5 times that of n-butyl acetate, a total Hansen solubility parameter of at least about 8.0 (cal/cm³)^{1/2}, and no chlorine or bromine atoms.

11. The method of claim 10 wherein the organic solvent is selected from the group consisting of nitroalkanes, tert-butyl acetate, methyl benzoate, methyl trifluoroacetate, dimethyl carbonate, methyl pivalate, tert-butyl alcohol, propylene carbonate, tert-butyl benzoate, di-tert-butyl carbonate, and methyl tert-butyl carbonate.

12. The method of claim 10 wherein the oxidation rate constant is less than about 5×10^9 cm³/g·sec.

13. The method of claim 10 wherein the organic solvent comprises at least about 5 wt. % of the total solvent component of the coating composition.

14. A method of preparing a coating resin, said method comprising polymerizing one or more ethylenic monomers in the presence of an organic solvent having negligible photochemical reactivity as measured by an oxidation rate constant of less than about 1×10^{10} cm³/g·sec, and also having an evaporation rate of not more than about 5 times that of n-butyl acetate.

15. The method of claim 14 wherein the polymerization is performed in the presence of a free-radical initiator.

16. The method of claim 14 wherein the oxidation rate constant is less than about 5×10^9 cm³/g·sec.

17. The method of claim 14 wherein the solvent is selected from the group consisting of nitroalkanes, tert-butyl acetate, methyl benzoate, methyl trifluoroacetate, dimethyl carbonate, methyl pivalate, tert-butyl alcohol, propylene carbonate, tert-butyl benzoate, di-tert-butyl carbonate, and methyl tert-butyl carbonate.

18. The method of claim 14 wherein the solvent is tert-butyl acetate.

19. A thermoplastic or thermoset coating composition which comprises:

(a) an organic solvent having negligible photochemical reactivity as measured by an oxidation rate constant of less than about 1×10^{10} cm³/g·sec, and also having an evaporation rate of not more than about 5 times that of n-butyl acetate; and

(b) one or more components selected from the group consisting of coating resins and crosslinkers.

20. The composition of claim 19 wherein the oxidation rate constant is less than about 5×10^9 cm³/g·sec.

21. The composition of claim 19 wherein the organic solvent is selected from the group consisting of nitroalkanes, tert-butyl acetate, methyl benzoate, methyl trifluoroacetate, dimethyl carbonate, methyl pivalate, tert-butyl alcohol, propylene carbonate, tert-butyl benzoate, di-tert-butyl carbonate, and methyl tert-butyl carbonate.

22. The composition of claim 19 wherein the organic solvent is tert-butyl acetate.

23. The composition of claim 19 comprising a crosslinker selected from the group consisting of polyisocyanates and isocyanate-terminated prepolymers.

24. A wood, furniture, automotive OEM, automotive refinish, container, architectural, coil, aerosol, marine, transportation, industrial maintenance, general industrial, ink, overprint varnish, or road coating made from the composition of claim 19.

25. A thermoplastic or thermoset coating composition which comprises tert-butyl acetate and one or more components selected from the group consisting of coating resins and crosslinkers.

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