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(54) Title: METAL COATING COMPOSITION

(57) Abstract: The present invention provides for a metal coating composition that includes a resin system with at least one unsaturated polyester polyol and a curing agent such as an isocyanate or a melamine. The compositions are suitable as a primer and provide good adhesion and moisture resistance to metal substrates.

METAL COATING COMPOSITION

DETAILED DESCRIPTION OF THE INVENTION

[0001] This application claims priority from U.S. Provisional Application 61/020,424 filed January 11, 2008, the entirety of which is incorporated herein by reference.

[0002] The present invention relates to coating compositions and more particularly to primer compositions for metal substrates.

[0003] Processing and manufacturing efficiency can be improved if a primer coating is suitable for application to a wide variety of metal substrates, such as aluminum, steel, stainless steel, and galvaneal, under a variety of curing conditions. The present invention describes a coating composition that uses an unsaturated polyester resin in combination with a suitable curing agent and, optionally, other conventional coating additives, to provide a primer composition that demonstrates excellent adhesion to a broad range of metal substrates and is useful in air dry, low bake, and high bake temperature curing environments.

[0004] Primer compositions as disclosed herein may be used with either air dry, low bake, or high bake topcoats or sealer coats. Though the compositions of the present invention are described as being useful for primer coats, other embodiments of the compositions may be useful as tinted or clear topcoats or sealer coats. As indicated, the composition provides good adhesion to a broad array of metal substrates, including aluminum, steel, stainless steel, galvaneal, and subsequent paint layers, and offers excellent moisture and corrosion protection.

[0005] In accordance herewith there is provided a coating composition that comprises: (a) an unsaturated polyester polyol resin, and (b) a suitable curing agent. The coating composition may comprise a resin system that includes at least one unsaturated polyester resin with one or more saturated polyester resins. In one embodiment, the coating composition may be substantially free of acrylic resins. Suitable curing agents may include isocyanates, which may be particularly useful in low temperature cure environments or melamine, which may be particularly useful in higher temperature cure environments.

[0006] One embodiment of the coating composition disclosed herein comprises (i) a resin system comprising at least one unsaturated polyester polyol, and (ii) a curing agent, which may comprise an isocyanate or a blend of isocyanates. Where isocyanate is used in the curing agent, the relative amounts of polyester resin and isocyanate may be expressed by the mole ratio of the reactive isocyanate groups to reactive hydroxyl groups, which may be from about 0.75:1 to about 2.5:1 NCO:OH molar ratio.

[0007] The resin system may comprise unsaturated polyester or a blend of saturated and unsaturated polyesters. The resin system may comprise non-polyester resins, but is preferably substantially free of acrylic resins.

[0008] The coating compositions of the present invention may comprise at least one unsaturated polyester resin. Suitable polyester resins may be obtained by the esterification of at least one ethylenically unsaturated di- or higher polycarboxylic acid, or anhydride, such as maleic anhydride, tetrahydrophthalic anhydride, phthalic anhydride, fumaric acid, glutaconic acid, itaconic acid, itaconic anhydride, mesaconic acid, citraconic acid, allylmalonic acid, tetrahydrophthalic acid, and others with saturated or unsaturated di- or higher polyols, such as ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, polyethylene glycol, 1,4-butylene glycol, triethylene glycol, 1,2- and 1,3-propanediols, 1,2-, 1,3- and 1,4-butanediols, 2-methylpropanediol, 2,2-dimethyl-1,3-propanediol, 3-hydroxy-2,2-dimethylpropyl-3-hydroxy-2,2-dimethylpropanoate, 2-butyl-2-ethyl-l,3-propanediol, 2-buten-1,4-diol, 2-butyn-1,4-diol, 2,4,4-trimethyl-1,3-pentanediol, 1,6-hexane diol, glycerol, pentaerythritol, mannitol, trimethylolethane, trimethylolpropane, 1,4-cyclohexanedimethanol, hydroxypivalylhydroxypivalate, dimethylolpropionic acid, hydrogenated bisphenol A, and others. Mixtures of saturated and unsaturated polyols may be used.

[0009] It will be appreciated that saturated di- or higher polycarboxylic acids or anhydrides may be incorporated into the monomer blend used to make the polyester resin in order to effect resin characteristics. Suitable saturated anhydrides and di- or polycarboxylic acids may include hexahydrophthalic anhydride, succinic anhydride, adipic acid, succinic acid, sebacic acid, azelaic acid, 1,4-cyclohexanedicarboxylic acid, and other, and/or by aromatic di- or higher polycarboxylic acids, such as phthalic acid, trimellitic acid, 2-(sodiosulfo) isophthalic acid, pyromellitic acid, isophthalic acid and

terephthalic acid. Fatty acid dimers may also be used. Mixtures of saturated and unsaturated di- or higher polyacids and/or mixtures of di- or higher polyols may be used.

[0010] When using an unsaturated polyester polyol in the resin composition, it is desirable to maintain unsaturation of the polyester in the coating, which is believed to enhance adhesion to metal substrates. Conventional uses of unsaturated polyesters in coating compositions promote the curing of the unsaturation of the polyester with monomers such as styrene and vinyl esters. However, the present invention maintains the unsaturation of the polyester on the backbone and does not involve free-radical reaction of the double bonds. The unsaturated polyester does not undergo further crosslinking in the coating through its double bonds, but rather the polyester undergoes crosslinking through hydroxyl functionality.

[0011] The monomer blend giving rise to the unsaturated polyester polyol resin may comprise from between about 0.1% to about 40% with respect to total monomer weight of ethylenically unsaturated di- or higher polycarboxylic acids, anhydrides or blends thereof. In other embodiments, the ethylenically unsaturated monomer portion may be about 0.1% to about 20% of the monomer blend. In some embodiments, the monomer blend for functional polyester resin may comprise maleic anhydride in amounts up to about 10% by weight with respect to total monomer weight.

[0012] In one embodiment, the unsaturated polyester polyol may be prepared from a group of monomers including neopentyl glycol, adipic acid, isophthalic acid, maleic anhydride, trimethylolpropane, cyclohexyl diacid, and hexahydrophthalic anhydride. In one useful embodiment, the polyester may comprise a combination of neopentyl glycol, adipic acid, isophthalic acid, and maleic anhydride. In another embodiment, the polyester may additionally comprise trimethylolpropane.

[0013] In one embodiment, the unsaturated polyester polyol may have a hydroxyl number from about 50 to about 400 mg KOH/g. However, the polyester may have a hydroxyl number from about 100 to about 300 mg KOH/g. In one useful embodiment, the polyester has a hydroxyl number of about 200 mg KOH/g.

[0014] The unsaturated polyester polyol has a weight average molecular weight of about 400 to about 4000. In one useful embodiment, the weight average molecular weight of the unsaturated polyester is from about 700 to about 2000. In yet another

useful embodiment, the weight average molecular weight of the unsaturated polyester is about 900.

[0015] The glass transition temperature (Tg) of the polyester can generally range between -40°C to about 20°C. In one useful embodiment, the Tg is about -15°C.

[0016] It will be appreciated that the coating composition of the present invention may include a combination of unsaturated polyesters and saturated polyesters. To alter the desired properties of the coating, the resin system may be modified through the addition of other types of thermoplastic and thermoset resin additions. These additions may include but are not limited to polyesters, epoxies, phenoxies, imines, aspartic esters, oxazolidines, low molecular weight polyols, urethane diols, castor oil derivatives, cellulose acetate butyrate resins, vinyl resins, and nitrocellulose resins. The use of the various polyols, isocyanates, and modifying resins are generally known in the art, and their use to achieve desired properties can be accomplished by those skilled in the polyurethane art. It is desirable that the resin system be substantially free of acrylic resins. The term "substantially free" means that the resin system comprises no more than 15% weight percent of acrylic resin on resin solids with respect to the total resin solids in the resin system. In one embodiment, the resin system may free of acrylic resin.

[0017] It is desirable that the resin system comprises at least 10% weight of the unsaturated polyester polyol resin. In one embodiment the unsaturated polyester resin may comprise about 25 to 100% of the resin solids in the resin system. In another embodiment the unsaturated polyester resin may comprise about 35 to 100% of the resin solids in the resin system. In another embodiment the unsaturated polyester may comprise about 50 to 100% of the resin solids in the resin system. In yet another embodiment the unsaturated polyester may comprise about 75 to 100% of the resin solids in the resin system.

[0018] A suitable crosslinking material that may be utilized in combination with the resin system may be an isocyanate that is selected from isocyanate-functional materials that are well known in the art and include mono-, di-, tri- and multi- functional isocyanates as well as polyisocyanates that utilize di-, tri-, and multi- functional isocyanate material.

[0019] Suitable isocyanate functional materials include but are not limited to aromatic, cycloaliphatic and aliphatic isocyanates such as cyclohexyl isocyanate, phenyl

isocyanate, toluene isocyanate, 1,3 and 1,4 phenylene diisocyanate, 4-chloro-1,3-phenylene diisocyanate, toluene-2,4- or 2,6-diisocyanate, 1,2,4-benzene triisocyanate, 1,5- and 1,4- naphthalene diisocyanate, 2,4' and 4,4' diphenylmethane diisocyanate, 3,3'-dimethyl-4,4'-diphenylene diisocyanate, triphenylmethane triisocyanate, polymethylene polyphenyl isocyanate, 1,6 hexamethylene diisocyanate, isophorone diisocyanate, 4,4-dicyclohexylmethane diisocyanate, 2,2,4(2,4,4)-trimethyl-1,6-hexamethylene diisocyanate, trimethylhexamethylene diisocyanate, 1,4-diisocyanato pentane, isocyanatomethylcyclohexyl isocyanate, 1,6,11-undecane triisocynate, p- and m-tetramethylxylene diisocynate, 1,4-tetramethylene diisocyanate, 1,10-decamethylene diisocyanate, m-xylene diisocyanate, 1,3-bis(isocyanatemethyl)cyclohexane, and mixtures thereof.

[0020] It has been found that aliphatic polyisocyanates are particularly useful in accordance with this invention. Blocked isocyanates may be employed as well. However, any known isocyanate may be used. The NCO group of the isocyanate reacts with the hydroxyl groups of the polyester to form crosslinks.

[0021] In one useful embodiment, the curing agent comprises a blend of isocyanates. For example, the curing agent may comprise a mixture of HDI isocyanate and an IPDI isocyanate resin. In this embodiment, the HDI isocyanate may comprise about 40 to about 100% by weight of the total isocyanate in the binder composition while the IPDI isocyanate resin may comprise about 0 to about 60% of the total isocyanate content in the binder composition. In another useful embodiment, the HDI isocyanate may comprise about 80% of the total isocyanate while the IPDI isocyanate resin comprises about 20% of the total isocyanate.

[0022] Generally, a crosslinking agent will be used in an amount sufficient to crosslink with the hydroxyl groups on the polyester(s) and other resins, where present, in the resin system. The relative amounts of polyester(s) and other resins and isocyanate may be expressed by the mole ratio of the reactive isocyanate groups to reactive hydroxyl groups. Generally, the isocyanate is present in a ratio of about 0.75:1 to about 2.5:1 based on the NCO:OH ratio. In one useful embodiment, the isocyanate is present in a ratio of about 0.8:1 to about 1.2:1 based on the NCO:OH ratio. In another useful embodiment, the isocyanate is present in a ratio of about 1:1 to about 1.1:1 based on the NCO:OH ratio.

[0023] In one embodiment, a catalyst may be used in the coating composition. A catalyst aids in completing or expediting the reaction. Catalysts that may be used in accordance with this invention for the isocyanate-hyroxyl reaction include nonmetal catalysts, such as amine catalysts like tertiary amines, including but not limited to triethyl diamine, 1-dimethylamino ethyl-4-methyl piperazine, 1,1,3,5,5-pentamethyl–diethylene triamine, N,N-dimethyl cyclohexylamine, N,N-diethyl piperazine, bis (2-dimethylaminoethyl) ether. Other catalysts that may be used are metal catalysts, including but not limited to dibutyl tin diluarate, dibutyl tin diacetate, dibutyl tin dioctoate, stannous octoate, zinc octoate, potassium octoate, and zirconium octoate. Chelating agents such as 2,4-pentanedione or volatile carboxylic acids may also be employed.

[0024] In one embodiment, the coating composition includes from about 0% to about 1% catalyst, such as the urethane catalysts described above, by weight based on the total resin solids. In another useful embodiment, the coating composition includes from about 0.005% to about 0.60% catalyst by weight based on the weight of the total resin solids. In yet another useful embodiment, the coating composition includes about 0.03 to 0.19% catalyst by weight based on the total resin solids.

[0025] In some embodiments or curing conditions, it may be useful to employ an amino curing agent. Amino curing agents include urea formaldehyde, melamine formaldehyde, benzoguanamine formaldehyde, glycoluril formaldehyde resins and mixtures there of. These amino curing agents may contain varying levels of methylation, alkylation, degree of polymerization, and functionality. The alkoxy groups may include but is not limited to methoxy, ethoxy, n-butoxy, or iso-butoxy groups or combinations thereof. The amino curing agents may also include carboxylic acid and other forms of modification. The amino curing agents react with hydroxyl groups and homopolymerize to form crosslinks. The amino curing agent may be 5-50% by weight based on the total resin solids.

[0026] Suitable catalysts for use with amino curing agents include but are not limited to blocked and unblocked p-toluene sulfonic acid, dodecylbenzene sulfonic acid, dinonylnaphthalene sulfonic acid, dinonylnaphthalene disulfonic acid, alkyl acid phosphate, phenyl acid phosphate, phosphoric acid, carboxylic acids, and metal salts such

as magnesium bromide, aluminum nitrate, and zinc nitrate. Catalyst level can range from 0.2-7% by weight based on the total resin solids.

[0027] The coating composition may, also, contain fillers or extenders that may be organic or inorganic, as well as mixtures thereof. Suitable fillers or extenders which may be added to the composition for various properties include the commonly used fillers or extenders, such as carbonates, silicates, sulfates, silicas, sulfites, clays, carbides, oxides, polyfluorinated ethylenes, ferrites, aluminas, nitrides, polymeric fillers, fibers, cellulosics, ceramics, and the associated precipitates, derivatives, and hydrates and the like, as well as mixtures thereof. These extenders may be in a treated or non-treated form, and may be natural occurring products or synthetically manufactured, and may be reclaimed or recycled, as well as combinations thereof.

[0028] The coating composition may include inorganic and organic corrosion inhibitors to minimize the potential for corrosion of metallic substrates. One or more corrosion inhibitors may used to achieve adequate corrosion protection. Many inorganic corrosion inhibiting pigments are available in different variations of borates, chromates, leads, molybdates, nitrates, phosphates, phosphites, and silicates. Some of these variations include barium metaborate, zinc borate, zinc potassium chromate, zinc tetroxy chromate, strontium chromate, red lead, basic lead silicochromate, zinc molybdate, calcium molybdate, calcium zinc molybdate, zinc phosphate, strontium phosphate, calcium phosphate, aluminum triphosphate, aluminum zinc. phosphate, zinc calcium phosphate, zinc aluminum calcium phosphate, zinc calcium strontium phosphate, zinc calcium aluminum strontium phosphate, strontium aluminum phosphate, calcium aluminum phosphate, zinc borate phosphate hydrate, zinc hydroxy phosphate, calcium borosilicate, calcium barium phosphosilicate, calcium strontium phosphosilicate, calcium strontium zinc phosphosilicate, calcium ion exchange silica, zinc oxide, and zinc dust. Organic corrosion inhibitors include but are not limited to 2-benzothiazolylthio-succinic acid, amine salt of 2-benzothiazolylthio-succinic acid, and amine, barium, calcium, magnesium, and zinc salts of dinonylnaphthalene mono sulfonic acid.

[0029] The coating composition may contain one or more pigments to introduce color to the composition. Common pigments used may include, titanium dioxide, phthalos, iron oxides, lamp black, carbon black, various organic and inorganic pigments, and mixtures thereof.

[0030] In one embodiment of the present invention, the primer composition contains pigments such that the composition is about 100% to 250% by weight pigments based on the weight of the resins solids. In one useful embodiment the pigments comprise about 180% by weight based on the weight of the resin solids.

[0031] Minor amounts of dispersing aids (such as, for example, polymeric dispersants) may be added to disperse and stabilize pigments. Any type of conventional dispersant may be used in accordance with this invention, such as anionic, cationic, amphoteric, or nonionic dispersants. Such dispersing agents include polymeric dispersants. In addition, particle dispersants may also be used.

[0032] Particle dispersants are particles that are very similar to the pigment to be dispersed promoting absorption on to that pigment particle. These particle dispersants, such as the Solsperse technology sold by Lubrizol Corp., are modified and contain anchoring sites to accept pigment dispersants. Particularly useful dispersants include those described in U.S. Patent Application Serial Number 11/756,084.

[0033] In one embodiment, the coating composition may include from about 0.1% to about 30%, by weight, dispersant based on the total pigment weight in the composition. In another useful embodiment the dispersant is present in an amount from about 0.5% to about 20%, by weight, based upon the total pigment weight of the composition. In yet another useful embodiment, dispersant is present in an amount of about 1% by weight, based on the total pigment of the composition.

[0034] Flow additives, defoamers, deaerators, suspension aids, scavengers, stabilizers, antioxidants, plasticizers, nonfunctional or nonreactive diluents, hydrocarbon oils, conductive additives, and the like, as well as mixtures thereof may be incorporated into the composition to tailor the properties of the primer/sealer. These and other additives generally comprise from about 0 to 2.5% by weight based on the total resin solids.

[0035] Additional adhesion promotion may be obtained through the use of adhesion promoting additives or coupling agents. These additives include but are not limited to organosilanes, titanates, zirconates, aluminates, and alkyl phosphate esters. These additives generally comprise from about 0 to 4% of the total paint weight.

[0036] In one embodiment, a solvent, or mixture of solvents, may be used in accordance with this invention. Although most conventional solvents that are used in the coatings industry may be used in accordance with this invention, in one embodiment, examples of useful solvents include oxygenated and hydrocarbon solvents. Oxygenated solvents typically consist of ketones and esters, and include but are not limited to acetone, methyl ethyl ketone, methyl propyl ketone, methyl isobutyl ketone, methyl n-amyl ketone, C-11 ketone, cyclohexanone, diisobutyl ketone, and methyl isoamyl ketone, as well as methyl acetate, ethyl acetate, n-propyl acetate, isopropyl acetate, n-butyl acetate, isobutyl acetate, 2-ethylhexyl acetate, n-butyl propionate, n-pentyl propionate, ethyl 3-ethoxypropoinate, propylene glycol methyl ether acetate, dipropylene glycol methyl ether acetate, ethylene glycol butyl ether acetate, and diethylene glycol butyl ether acetate. Hydrocarbon solvents that may be used in accordance with this invention include but are not limited to aromatic and halogenated solvents, such as for example toluene, xylene, aromatic 100, aromatic 150, aromatic 200, and parachlorobenzotrifluoride.

[0037] The typical method for applying primer coatings is by spraying. Various types of spray applications may be used. For example, the primer composition may be spray applied using air atomizing spray, airless spray, and air assisted airless application Air spray equipment includes conventional air spray (using 20-80 psi air pressure to atomize the liquid paint) which provides a low level of transfer efficiency, and high volume low pressure (HVLP) (uses less than 10 psi air pressure and 12-16 cubic feet of air per minute to atomize the liquid paint) which provides a higher level of transfer efficiency than conventional methods of application. Airless spray application (using 1500-3000 psi fluid pressure to force the coating through a small orifice to atomize the liquid paint) provides atomization for high viscosity coatings, and improved transfer efficiencies. Air assisted airless (using 700-1200 psi fluid pressure to force the coating though a small orifice and up to 35psi atomization air to atomize the liquid paint) provides atomization for higher viscosity coating, and improved film smoothness and appearance over airless application.

[0038] Additional application methods consist of electrostatic application using air atomizing spray equipment, air assisted airless, and high-speed rotary application equipment such as a bell or disc. Electrostatic application provides a higher level of transfer efficiency as compared to other non-electrostatic application.

[0039] As noted hereinabove the present coating composition may be useful both as primer and sealer. After being deposited onto a surface, other coatings may be applied via known methods. Other coatings may be applied to the primer or sealer before the curing process has begun (wet on wet application), after cure has begun, or after cure is complete.

[0040] The primer as disclosed herein contains good adhesion characteristics to metal substrates including but not limited to aluminum, anodized aluminum, cold rolled steel, hot rolled steel, stainless steel, hot dipped galvaneal, electrogalvaneal, hot dipped galvanized, electrogalvanized, and iron, manganese, or zinc phosphated steel.

[0041] Preparation of an uncoated metallic substrate may include cleaning the surface. Cleaning may involve mechanical cleaning, chemical cleaning, or both. Mechanical cleaning involves abrading the surface of the substrate by brushing, grinding, blasting, or wet and dry tumbling. Mechanical cleaning may be done by powered equipment or by hand.

[0042] Chemical cleaning may involve the use of one or more types of cleaning agents such as solvent cleaners, water-based cleaners, water based emulsion cleaners, alkaline cleaners (mild to strong), and acidic cleaners (mild to strong). Methods of cleaning with chemical cleaning agents include hand wiping and scrubbing, immersion cleaning, spray cleaning, steam cleaning, vapor degreasing, ultrasonic cleaning, and anodic and cathodic electrocleaning. Solvent cleaners may include various solvents including, but not limited to, alilphatic hydrocarbon solvents, naphtha, mineral spirits, toluene, xylene, dipentene, methanol, propanol, butoxyethanol, acetone, methyl isobutyl ketone, dimethoxypropane and mixtures thereof. Water based cleaners may comprise various detergent ingredients and water. The detergent and cleaning ingredients may include surfactants (anionic, cationic, and non-ionic), 2-methoxymethylethoxypropanol, 2-butoxyethanol, 2-(2-Butoxyethoxy)-ethanol, tripropylene glycol ether, phosphoric acid, potassium fluoride, and nickel dihydrogen phosphate.

[0043] The coating may be cured under air dry conditions, but a low temperature bake may be used as well. A low temperature bake may comprise of exposing the surface to temperatures of 70°F to 180°F for about 15-30 minutes. Higher bake temperatures such as 180°F to 300°F may be used as well. Moreover, the cure time, may range from about 10 minutes to about 60 minutes, as dependent on the oven temperature. Conventional

ovens can be employed to cure the composition once it is applied onto a surface. The primer alternatively has the capacity to be cured with IR radiation or other devices. Upon curing, the material polymerizes on the substrate, providing adhesion thereto.

[0044] In one useful embodiment, the polymer of the present invention may be cured by air dry conditions. In another useful embodiment, the polymer of the present invention may be cured by thermal exposure, such as by exposure in a conventional oven or through an IR cure, or combinations thereof.

For a more complete understanding of the present invention reference is made to the following illustrative examples.

[0045] PREPARATION OF POLYESTER

[0046] Resin Example 1

[0047] A 5-liter reactor was equipped with stirrer, thermocouple, nitrogen inlet, packed column, condenser and receiver. The reactor was charged with 1487.4 g of neopentyl glycol, 453.3 g of adipic acid, 618.4 g of isophthalic acid, 285.0 g of maleic anhydride and 1.9 g of butyl stanoic acid. The reaction mixture was gradually heated to 210°C under agitation and nitrogen blanket, while maintaining maximum packed column head temperature of 100°C. The temperature was hold at 210°C until the acid value reached 5 mg KOH/g maximum. The mixture was then cooled to 130°C before 679.3 g of n-butyl acetate was added. The reaction solution was mixed well, cooled, filtered and discharged. The product had a solid content of 74.9% by weight, Gardner color of 0.1, density of 8.93 lb/gal, acid value of 1.5 mg KOH/g, Gardner viscosity of O.

[0048] Resin Example 2

[0049] To the reactor described above, 333.1 g of trimethylolpropane, 1216.6 g of neopentyl glycol, 426.4 g of adipic acid, 581.7 g of isophthalic acid, 286.4 g of maleic anhydride and 1.9 g of butyl stanoic acid were charged. The reaction mixture was gradually heated to 210°C under agitation and nitrogen blanket, while maintaining maximum head temperature of 100°C. The temperature was hold at 210°C until the acid value reached 5 mg KOH/g maximum. The mixture was then cooled to 130°C before 738.9 g of n-butyl acetate was added. The reaction solution was mixed well, cooled, filtered and discharged. The product had a solid content of 72.8% by weight, Gardner color of 0.1, density of 8.98 lb/gal, acid value of 1.9 mg KOH/g, Gardner viscosity of T-.

[0050] Resin Example 3

[0051] To the reactor described above, 433.6 g of trimethylolpropane, 1009.7 g of neopentyl glygol, 471.8 g of adipic acid, 643.7 g of isophthalic acid, 285.2 g of maleic anhydride and 1.8 g of butyl stanoic acid were charged. The reaction mixture was gradually heated to 210°C under agitation and nitrogen blanket, while maintaining maximum packed column head temperature of 100°C. The temperature was hold at 210°C until the acid value reached 5 mg KOH/g maximum. The mixture was then cooled to 130°C before 729.1 g of n-butyl acetate was added. The reaction solution was mixed well, cooled, filtered and discharged. The product had a solid content of 75.3% by weight, Gardner color of 0.1, density of 9.11 lb/gal, acid value of 3.9 mg KOH/g, Gardner viscosity of X~Y.

[0052] Resin Example 4

[0053] To the reactor described above, 149.3g of trimethylolpropane, 1207.9 g of neopentyl glycol, 507.7 g of adipic acid, 692.7 g of isophthalic acid, 286.4 g of maleic anhydride and 1.9 g of butyl stanoic acid were charged. The reaction mixture was gradually heated to 210°C under agitation and nitrogen blanket, while maintaining maximum packed column head temperature of 100°C. The temperature was hold at 210°C until the acid value reached 5 mg KOH/g maximum. The mixture was then cooled to 130°C before 783.0 g of n-butyl acetate was added. The reaction solution was mixed well, cooled, filtered and discharged. The product had a solid content of 75.4% by weight, Gardner color of 0.2, density of 9.04 lb/gal, acid value of 3.1 mg KOH/g, Gardner viscosity of X+.

[0054] Resin Example 5

[0055] To the reactor described above, 663.0 g of trimethylolpropane, 922.5 g of neopentyl glycol, 438.7 g of cyclohexyl diacid, 675.8 g of maleic anhydride and 1.8 g of butyl stanoic acid were charged. The reaction mixture was gradually heated to 210°C under agitation and nitrogen blanket, while maintaining maximum packed column head temperature of 100°C. The temperature was hold at 210°C until the acid value reached 5 mg KOH/g maximum. The mixture was then cooled to 130°C before 684.6 g of n-butyl acetate was added. The reaction solution was mixed well, cooled, filtered and discharged. The product had a solid content of 74.5% by weight, Gardner color of 0.1, density of 9.14 lb/gal, acid value of 4.8 mg KOH/g, Gardner viscosity of Y+.

[0056] Resin Example 6

[0057] To the reactor described above, 1090.0 g of neopentyl glycol, 397.2 g of isophthalic acid, 185.2 g of maleic anhydride, 307.4 g of hexahydrophthalic anhydride and 1.9 g of butyl stanoic acid were charged. The reaction mixture was gradually heated to 190°C under agitation and nitrogen blanket, while maintaining maximum head temperature of 100°C. The temperature was hold at 190°C until the acid value reached 10 mg KOH/g maximum. The mixture was then cooled to 130°C before 277.0 g of n-butyl acetate was added. The reaction solution was mixed well, filtered and discharged. The product had a solid content of 73.9% by weight, Gardner color of 0.0, density of 8.96 lb/gal, acid value of 9.2 mg KOH/g, Gardner viscosity of V~W.

[0058] PREPARATION OF PRIMER

[0059] Primer Example 1

[0060] 129.3 grams of polyester described in Resin Example 1, 16.7 grams of Shersperse S (a proprietary dispersant of The Sherwin-Williams Company), 17.6 grams of ethyl 3-ethyloxypropionate, and 4.5 grams of methyl n-amyl ketone were placed in a container. The contents were mixed with a cowles blade for 5 minutes. 213.9 grams of barium sulfate, 174.6 grams of titanium dioxide (Ti-Pure R706 from DuPont), 66.7 grams of ceramic microspheres (Zeeospheres W210 from 3M Chemicals), 58.9 grams of calcium carbonate, 2.1 grams of rheological modifier (Bentone SD-2 from Elementis), and 18.1 grams of methyl n-amyl ketone were slowly added under medium agitation. The batch was mixed at high speed for 30 minutes to achieve a grind/clean of 6H/5H. Then 86.2 grams of polyester described in Resin Example 1, 5.5 grams of a 2% dibutyl tin diluarte/n-butyl acetate solution (Air Products and Chemicals), and 10 grams of methyl n-propyl ketone was added to the batch and mixed for 5 minutes.

[0061] The primer was catalyzed with 89.0 grams of HDI (Tolonate HDT-LV from Rhodia Inc.) and 34.6 grams of IPDI (Desmodur Z4470 SN/BA from Bayer Corporation), and reduced with 161.6 grams of n-butyl acetate, 16.2 grams of 1-methyloxy-2-propanol acetate, and 3.1 grams of 2-butoxyethyl acetate.

[0062] The primer and topcoat were applied to 5052 aluminum, 6111 aluminum, 3003 aluminum, cold rolled steel, hot dipped galvaneal, and electrogalvaneal substrates as described in the application procedures. This example provided a gravelometer rating of

6B over 5052 aluminum, 6B over 6111 aluminum, 6C over 3003 aluminum, 6B over cold rolled steel, 6B over hot dipped galvaneal, and 6B over electrogalvaneal. Dry adhesion was 5B over 5052 aluminum, 1B over 6111 aluminum, 0B over 3003 aluminum, 5B over cold rolled steel, 5B over hot dipped galvaneal, and 5B over electrogalvaneal. Wet adhesion in 96 hour humidity was 5B over 5052 aluminum, 5B over 6111 aluminum, 5B over 3003 aluminum, 5B over cold rolled steel, 5B over hot dipped galvaneal, and 0B over electrogalvaneal. In 96 hour humidity, 9D blisters were seen over 5052 aluminum, 6111 aluminum, 3003 aluminum, cold rolled steel, hot dipped galvaneal, and electrogalvaneal. Wet adhesion in 240 hour water immersion was 5B over 5052 aluminum, 5B over 6111 aluminum, 5B over 3003 aluminum, 5B over cold rolled steel, 5B over hot dipped galvaneal, and 0B over electrogalvaneal. In 240 hour water immersion, 9D blisters were seen 5052 aluminum, 6111 aluminum, 3003 aluminum, cold rolled steel, and hot dipped galvaneal, and 6D blisters were seen over electrogalvaneal.

[0063] Primer Example 2

[0064] 125.5 grams of polyester described in Resin Example 2, 17.8 grams of Shersperse S, 16.4 grams of ethyl 3-ethyloxypropionate, and 4.2 grams of methyl n-amyl ketone were placed in a container. The contents were mixed with a cowles blade for 5 minutes. 228.4 grams of barium sulfate, 186.5 grams of titanium dioxide , 71.4 grams of ceramic microspheres, 62.9 grams of calcium carbonate, 2.1 grams of rheological additive, and 16.9 grams of methyl n-amyl ketone were slowly added under medium agitation. The batch was mixed at high speed for 30 minutes to achieve a grind/clean of 6H/5H. Then 83.6 grams of polyester described in Resin Example 2, 5.5 grams of a 2% dibutyl tin diluarte/n-butyl acetate solution, and 9.4 grams of methyl n-propyl ketone was added to the batch and mixed for 5 minutes.

[0065] The primer was catalyzed with 112.1 grams of HDI and 43.6 grams of IPDI, and reduced with 179.8 grams of n-butyl acetate, 17.4 grams of 1-methyloxy-2-propanol acetate, and 3.4 grams of 2-butoxyethyl acetate.

[0066] The primer and topcoat were applied to 5052 aluminum, 6111 aluminum, 3003 aluminum, cold rolled steel, hot dipped galvaneal, and electrogalvaneal substrates as described in the application procedures. This example provided a gravelometer rating of 6B over 5052 aluminum, 6B over 6111 aluminum, 8B over 3003 aluminum, 5B over cold rolled steel, 6B over hot dipped galvaneal, and 5B over electrogalvaneal. Dry adhesion

was 5B over 5052 aluminum, 5B over 6111 aluminum, 5B over 3003 aluminum, 5B over cold rolled steel, 5B over hot dipped galvaneal, and 5B over electrogalvaneal. Wet adhesion in 96 hour humidity was 5B over 5052 aluminum, 5B over 6111 aluminum, 5B over 3003 aluminum, 5B over cold rolled steel, 5B over hot dipped galvaneal, and 0B over electrogalvaneal. In 96 hour humidity, 9D blisters were seen over electrogalvaneal. Wet adhesion in 240 hour water immersion was 5B over 5052 aluminum, 5B over 6111 aluminum, 5B over 3003 aluminum, 5B over cold rolled steel, 5B over hot dipped galvaneal, and 0B over electrogalvaneal. In 240 hour water immersion, 7D blisters were seen over electrogalvaneal.

[0067] Primer Example 3

[0068] 131.7 grams of polyester described in Resin Example 3, 16.7 grams of Shersperse S, 17.6 grams of ethyl 3-ethyloxypropionate, and 4.5 grams of methyl n-amyl ketone were placed in a container. The contents were mixed with a cowles blade for 5 minutes. 214.6 grams of barium sulfate, 175.2 grams of titanium dioxide, 66.9 grams of ceramic microspheres, 59.1 grams of calcium carbonate, 2.1 grams of rheological modifier, and 18.1 grams of methyl n-amyl ketone were slowly added under medium agitation. The batch was mixed at high speed for 30 minutes to achieve a grind/clean of 6H/5H. Then 87.8 grams of polyester described in Resin Example 3, 5.5 grams of a 2% dibutyl tin diluarte/n-butyl acetate solution, and 10 grams of methyl n-propyl ketone was added to the batch and mixed for 5 minutes.

[0069] The primer was catalyzed with 90.2 grams of HDI and 35.1 grams of IPDI, and reduced with 162.6 grams of n-butyl acetate, 16.3 grams of 1-methyloxy-2-propanol acetate, and 3.1 grams of 2-butoxyethyl acetate.

[0070] The primer and topcoat were applied to 5052 aluminum, 6111 aluminum, 3003 aluminum, cold rolled steel, hot dipped galvaneal, and electrogalvaneal substrates as described in the application procedures. This example provided a gravelometer rating of 8B over 5052 aluminum, 6B over 6111 aluminum, 8B over 3003 aluminum, 5B over cold rolled steel, 5B over hot dipped galvaneal, and 5B over electrogalvaneal. Dry adhesion was 5B over 5052 aluminum, 5B over 6111 aluminum, 5B over 3003 aluminum, 5B over cold rolled steel, 5B over hot dipped galvaneal, and 5B over electrogalvaneal. Wet adhesion in 96 hour humidity was 5B over 5052 aluminum, 5B over 6111 aluminum, 5B over 3003 aluminum, 5B over cold rolled steel, 5B over hot dipped galvaneal, and 0B

over electrogalvaneal. In 96 hour humidity, 9D blisters were seen over electrogalvaneal. Wet adhesion in 240 hour water immersion was 5B over 5052 aluminum, 5B over 6111 aluminum, 5B over 3003 aluminum, 5B over cold rolled steel, 5B over hot dipped galvaneal, and 0B over electrogalvaneal. In 240 hour water immersion, 7D blisters were seen over electrogalvaneal.

[0071] Primer Example 4

143.4 grams of polyester described in Resin Example 4, 15.1 grams of Shersperse S, 16.3 grams of ethyl 3-ethyloxypropionate, and 4.2 grams of methyl n-amyl ketone were placed in a container. The contents were mixed with a cowles blade for 5 minutes. 194.2 grams of barium sulfate, 158.5 grams of titanium dioxide, 60.3 grams of ceramic microspheres, 53.5 grams of calcium carbonate, 2.0 grams of rheological modifier, and 16.8 grams of methyl n-amyl ketone were slowly added under medium agitation. The batch was mixed at high speed for 30 minutes to achieve a grind/clean of 6H/5H. Then 95.6 grams of polyester described in Resin Example 4, 5.5 grams of a 2% dibutyl tin diluarte/n-butyl acetate solution, and 9.3 grams of methyl n-propyl ketone was added to the batch and mixed for 5 minutes.

[0072] The primer was catalyzed with 57.9 grams of HDI and 22.5 grams of IPDI, and reduced with 137.1 grams of n-butyl acetate, 14.5 grams of 1-methyloxy-2-propanol acetate, and 2.8 grams of 2-butoxyethyl acetate.

[0073] The primer and topcoat were applied to 5052 aluminum, 6111 aluminum, 3003 aluminum, cold rolled steel, hot dipped galvaneal, and electrogalvaneal substrates as described in the application procedures. This example provided a gravelometer rating of 7B over 5052 aluminum, 6B over 6111 aluminum, 7B over 3003 aluminum, 6B over cold rolled steel, 6B over hot dipped galvaneal, and 6B over electrogalvaneal. Dry adhesion was 5B over 5052 aluminum, 5B over 6111 aluminum, 5B over 3003 aluminum, 5B over cold rolled steel, 6B over hot dipped galvaneal, and 6B over electrogalvaneal. Wet adhesion in 96 hour humidity was 5B over 5052 aluminum, 5B over 6111 aluminum, 5B over 3003 aluminum, 5B over cold rolled steel, 5B over hot dipped galvaneal, and 0B over electrogalvaneal. In 96 hour humidity, 9D blisters were seen over 5052 aluminum, 6111 aluminum, 3003 aluminum, cold rolled steel, hot dipped galvaneal, and electrogalvaneal. Wet adhesion in 240 hour water immersion was 5B over 5052

aluminum, 5B over 6111 aluminum, 5B over 3003 aluminum, 5B over cold rolled steel, 5B over hot dipped galvaneal, and 0B over electrogalvaneal. In 240 hour water immersion, 9D blisters were seen over were seen over 5052 aluminum, 6111 aluminum, 3003 aluminum, cold rolled steel, and hot dipped galvaneal, and 7D blisters were seen over electrogalvaneal.

[0074] Primer Example 5

[0075] 114.4 grams of polyester described in Resin Example 5, 17.8 grams of Shersperse S, 18.6 grams of ethyl 3-ethyloxypropionate, and 4.8 grams of methyl n-amyl ketone were placed in a container. The contents were mixed with a cowles blade for 5 minutes. 227.9 grams of barium sulfate, 186.1 grams of titanium dioxide, 71.1 grams of ceramic microspheres, 62.8 grams of calcium carbonate, 2.2 grams of a rheological modifier, and 19.2 grams of methyl n-amyl ketone were slowly added under medium agitation. The batch was mixed at high speed for 30 minutes to achieve a grind/clean of 6H/5H. Then 76.4 grams of polyester described in Resin Example 5, 5.6 grams of a 2% dibutyl tin diluarte/n-butyl acetate solution, and 10.6 grams of methyl n-propyl ketone was added to the batch and mixed for 5 minutes.

[0076] The primer was catalyzed with 120.2 grams of HDI and 46.7 grams of IPDI, and reduced with 192.4 grams of n-butyl acetate, 18.7 grams of 1-methyloxy-2-propanol acetate, and 3.6 grams of 2-butoxyethyl acetate.

[0077] The primer and topcoat were applied to 5052 aluminum, 6111 aluminum, 3003 aluminum, cold rolled steel, hot dipped galvaneal, and electrogalvaneal substrates as described in the application procedures. This example provided a gravelometer rating of 10A over 5052 aluminum, 9B over 6111 aluminum, 10A over 3003 aluminum, 8A over cold rolled steel, 7B over hot dipped galvaneal, and 8B over electrogalvaneal. Dry adhesion was 5B over 5052 aluminum, 5B over 6111 aluminum, 5B over 3003 aluminum, 5B over cold rolled steel, 5B over hot dipped galvaneal, and 5B over electrogalvaneal. Wet adhesion in 96 hour humidity was 5B over 5052 aluminum, 5B over 6111 aluminum, 1B over 3003 aluminum, 5B over cold rolled steel, 5B over hot dipped galvaneal, and 2B over electrogalvaneal. Wet adhesion in 240 hour water immersion was 5B over 5052 aluminum, 5B over 6111 aluminum, 5B over 3003 aluminum, 5B over cold rolled steel, 5B over hot dipped galvaneal, and 0B over electrogalvaneal. In 240 hour water immersion, 6D blisters were seen over electrogalvaneal.

[0078] Primer Example 6

[0079] 117.5 grams of polyester described in Resin Example 6, 17.2 grams of Shersperse S, 18.0 grams of ethyl 3-ethyloxypropionate, and 4.6 grams of methyl n-amyl ketone were placed in a container. The contents were mixed with a cowles blade for 5 minutes. 220.0 grams of barium sulfate, 179.7 grams of titanium dioxide, 68.6 grams of ceramic microspheres, 60.6 grams of calcium carbonate, 2.1 grams of a rheological modifier, and 18.5 grams of methyl n-amyl ketone were slowly added under medium agitation. The batch was mixed at high speed for 30 minutes to achieve a grind/clean of 6H/5H. Then 78.4 grams of polyester described in Resin Example 6, 5.6 grams of a 2% dibutyl tin diluarte/n-butyl acetate solution, and 10.3 grams of methyl n-propyl ketone was added to the batch and mixed for 5 minutes.

[0080] The primer was catalyzed with 110.2 grams of HDI and 42.8 grams of IPDI, and reduced with 184.1 grams of n-butyl acetate, 18.1 grams of 1-methyloxy-2-propanol acetate, and 3.5 grams of 2-butoxyethyl acetate.

[0081] The primer and topcoat were applied to 5052 aluminum, 6111 aluminum, 3003 aluminum, cold rolled steel, hot dipped galvaneal, and electrogalvaneal substrates as described in the application procedures. This example provided a gravelometer rating of 9A over 5052 aluminum, 9A over 6111 aluminum, 8A over 3003 aluminum, 7B over cold rolled steel, 7B over hot dipped galvaneal, and 7B over electrogalvaneal. Dry adhesion was 5B over 5052 aluminum, 5B over 6111 aluminum, 5B over 3003 aluminum, 5B over cold rolled steel, 5B over hot dipped galvaneal, and 5B over electrogalvaneal. Wet adhesion in 96 hour humidity was 5B over 5052 aluminum, 5B over 6111 aluminum, 5B over 3003 aluminum, 5B over cold rolled steel, 5B over hot dipped galvaneal, and 5B over electrogalvaneal. Wet adhesion in 240 hour water immersion was 5B over 5052 aluminum, 5B over 6111 aluminum, 5B over 3003 aluminum, 5B over cold rolled steel, 5B over hot dipped galvaneal, and 5B over electrogalvaneal.

[0082] SUBSTRATE PREPARATION

[0083] Aluminum (5052, 6111, 3003) and Cold rolled steel panels were abraded with 180 grit sand paper with a dual action sander. Hot dipped galvaneal, electrogalvaneal, and abraded aluminum and cold rolled steel substrates were cleaned with R7K158 SHER-WILL-CLEAN® solvent cleaner and dried.

[0084] PRIMER APPLICATION PROCEDURE

[0085] Primer components were mixed and reduced as described in each individual example. The primer was applied to already cleaned substrates. Primer was applied within 6 hours of substrate preparation. The primer was applied with conventional air spray application equipment to a dry film thickness of 1.5-2.5 mils. The primer received a 24 hour flash before topcoat application.

[0086] TOPCOAT APPLICATION PROCEDURE

[0087] The topcoat system used was an acrylic polyurethane single stage topcoat (Genesis® from The Sherwin-Williams Company). The topcoat was applied with conventional air spray application equipment. The topcoat was applied to a dry film thickness of 2.0-2.5 mils. The topcoat was allowed to cure under ambient conditions.

[0088] PAINT EVALUATION PROCEDURE

[0089] Testing of the painted substrate began no sooner than 7 days after the primed substrate had been topcoated. Testing consisted of specific test methods and test equipment described in ASTM and SAE Test Methods.

[0090] ASTM References

[0091] ASTM D3359 Adhesion Method B

[0092] ASTM D2247 Humidity

[0093] ASTM D714 Degree of Blistering

[0094] ASTM D870 Water Immersion

[0095] SAE J400 gravelometer Method A

[0096] While the present invention has been illustrated by the description of embodiments thereof, and while the embodiments have been described in considerable detail, it is not the intention of the applicants to restrict or in any way limit the scope of the appended claims to such detail. Additional advantages and modifications will readily appear to those skilled in the art. Therefore, the invention, in its broader aspects, is not limited to the specific details, the representative apparatus, and illustrative examples shown and described. Accordingly, departures may be made from such details without departing from the spirit or scope of the applicant's general inventive concept.

We Claim:

1. A coating composition, comprising:

   (a) A resin system, wherein the resin system comprises at least one unsaturated polyester polyol and is substantially free of acrylic resin; and

   (b) a curing agent; and

   wherein the at least one unsaturated polyester polyol is unsaturated in the backbone of the polyester and does not undergo crosslinking in the coating composition through double bonds in the backbone of the polyester.

2. The composition of claim 1, wherein the unsaturated polyester polyol is the reaction product of a monomer blend comprising:

   (a) an ethylenically unsaturated monomer selected from the group consisting of ethylenically unsaturated polycarboxylic acids, ethylenically unsaturated polycarboxylic anhydrides and blends thereof; and

   (b) a di- or higher polyol.

3. The composition of claim 1, wherein the monomer blend further comprises a saturated monomer selected from the group consisting of di- or higher saturated polycarboxylic acids, anhydrides and blends thereof.

4. The composition of claim 2, wherein the monomer blend comprises about 10% by weight of maleic anhydride.

5. The composition of claim 1, wherein the polyester has a weight average molecular weight from about 700 to about 2000.

6. The composition of claim 1, wherein the polyester has an OH value from about 50 to about 400 mg KOH/g.

7. The composition of claim 1, wherein the polyester has an OH value from about 100 to about 300 mg KOH/g.

8. The composition of claim 1, therein the resin system contains no acrylic resin.

9. The composition of claim 1, wherein the curing agent is an isocyanate.

10. The composition of claim 9, wherein the isocyanate is an aliphatic isocyanate.

11. The composition of claim 1, wherein curing agent is present in a ratio of about 0.8 to about 1.2 based on the NCO:OH ratio of the polyester and curing agent.

12. The composition of claim 1, further comprising a pigment.

13. The composition of claim 12, wherein the pigment comprises barium sulfate, or titanium dioxide, or blends thereof.

14. The composition of claim 13, further comprising ceramic microspheres.

15. A method of priming a metal substrate, comprising the step of spraying onto the substrate a coating composition comprising:

(a) A resin system, wherein the resin system comprises at least one unsaturated polyester polyol and is substantially free of acrylic resin; and

(b) a curing agent;

wherein the at least one unsaturated polyester polyol is unsaturated in the backbone of the polyester and does not undergo crosslinking in the coating composition through double bonds in the backbone of the polyester.

16. The method of claim 15, wherein the substrate is selected from the group consisting of aluminum, anodized aluminum, cold rolled steel, hot rolled steel, stainless steel, hot dipped galvaneal, electrogalvaneal, hot dipped galvanized, electrogalvanized, and iron, manganese, and zinc phosphated steel.

17. A primer composition, comprising:

(a) a resin system, wherein the resin system is substantially free of acrylic resin and comprises at least one unsaturated polyester polyol, the unsaturated polyester polyol being the esterification reaction product of a monomer blend comprising (i) at least one ethylenically unsaturated di- or higher polycarboxylic acid or ethylenically unsaturated polycarboxylic anhydride, or blend thereof, (ii) at least one saturated di- or higher polycarboxcylic acid or saturated polycarboxylic anhydride, or blend thereof; and (iii) at least one di or higher polyol, and wherein the unsaturated polyester polyol is unsaturated in the backbone of the polyester and does not undergo crosslinking in the coating composition through double bonds in the backbone of the polyester;

(b) an isocyanate curing agent; and

(c) a pigment.

18. The primer composition of claim 17, wherein, the monomer blend comprises from about 0.1 to about 40% by weight of ethylenically unsaturated di- or higher polycarboxylic acid or ethylenically unsaturated polycarboxylic anhydride or blend thereof.

19. The primer composition of claim 18, wherein the monomer blend comprises maleic anhydride.

20. The primer composition of claim 17, wherein the pigment comprises barium sulfate, or titanium dioxide, or blends thereof.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2009/000191

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G18/68 C08K5/00 C08K5/29 C08K13/02
ADD. C08K3/00 C08K3/22 C08K3/30 C08K7/16

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08G C08K

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2007/049686 A1 (BAUCHET FREDERIC [US] ET AL) 1 March 2007 (2007-03-01) abstract; claims 1-6; examples 1-4 paragraphs [0004], [0011] - [0013], [0024]	1-13, 17-20
X	US 6 458 898 B1 (WAMPRECHT CHRISTIAN [DE] ET AL) 1 October 2002 (2002-10-01) abstract; claims 1-8; examples 1-6,9; table 1 column 4, paragraph 23 - column 5, paragraph 15 column 5, line 65 - column 6, line 18 column 6, lines 47-59 column 7, lines 3,42,43	1-13, 17-20
Y	column 10, line 66 - column 11, line 14	15,16

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[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

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"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	Date of mailing of the international search report
25 March 2009	07/04/2009

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Schütte, Maya

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2009/000191

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE CA [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; AKAMATSU, YOSHIHIRO: "Thick UV-curable coatings" XP002520918 retrieved from STN Database accession no. 1988:632869	1-13, 17-20
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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