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- (71) Applicant: **LUBRIZOL ADVANCED MATERIALS, INC.** [US/US]; 9911 Brecksville Road, Cleveland, Ohio 44141-3247 (US).
- (72) Inventors: **WEBER, Patrick**; Lubrizol Deutschland Gmbh, Postfach 11 55, 27717 Ritterhude (DE). **TIEDE, Bjoern A.**; Lubrizol Deutschland Gmbh, Postfach 11 55, 27717 Ritterhude (DE). **KUECK, Alexandra**; Lubrizol Deutschland Gmbh, Postfach 11 55, 27717 Ritterhude (DE).
- (74) Agents: **LAFERTY, Samuel B.** et al.; The Lubrizol Corporation, Legal Division, MD 022B, 29400 Lakeland Blvd., Wickliffe, Ohio 44092-2298 (US).

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(54) Title: MATTING OR TEXTURING EFFECTS THROUGH TUNG OIL IN UV COATINGS

(57) Abstract: The invention provides a composition including conjugated, unsaturated oils, e.g., tung oil, and a polymerization initiator for the polymerization of unsaturated compounds that provides a desirable matt or textured finish on the cured coating. A method for providing a matt finish on a radiation cured coating is also described.



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TITLEMATTING OR TEXTURING EFFECTS THROUGH TUNG OIL IN UV
COATINGSFIELD OF INVENTION

[0001] The invention provides surface matting or texturing to free radically polymerized radiation curable coatings and inks derived from polymerizing ethylenically unsaturated compounds. The matting function is achieved through the use of conjugated, unsaturated oils, e.g. tung oil, and polymerization initiators that can be activated by UV radiation.

BACKGROUND OF THE INVENTION

[0002] In UV coatings one typically uses a dispersed silica or dispersed wax type matting agent, if matting is desired. These agents function by scattering light incident to the surface of the UV cured film. During curing of the UV film the silica or wax may form elevated areas on the coating that help scatter incident light. The use of a large amount of silica or wax matting agent (to get a significant amount of matting) can affect the viscosity of the UV coating or ink and film physical properties.

[0003] US 1,893,611 (1933) discloses the use of a reaction product tung oil with linseed oil fatty acids, glycerol, and phthalic anhydride to make an additive that gave a wrinkle effect to air drying varnishes using chemical dryers. US 1,976,191 describes the use of rugo resin to form a wrinkle finish. US 2,344,189 (1944) describes wrinkle finish enamels using blown oils as a constituent. US 612,325 (1945) describes varnish wrinkle finish coatings and alkyd wrinkle finish coatings. US 669,736 describes improved protective coatings for ferrous and non-ferrous metals.

[0004] US 2,455,541 (1948) describes wrinkle finish from using an oil dryer in specific amounts relative to the resin. US 2,671,063 describes various vinyl resins that can be modified to have wrinkle finish coatings. US 2,600,818 describes a wrinkle finish coating requiring hardly any heating. US 2,676,918 describes the formation of wrinkling oils by polymerizing non-wrinkling bases. US 2,725,363 describes corrosion resistant wrinkle coating compositions containing finely divided titanium metal or alloy.

SUMMARY OF THE INVENTION

[0005] It has been found that tung oil, in a UV cured coating composition, (coating or ink) in the presence of relatively reactive UV activated initiators, can provide a surface wrinkling effect in the UV cured film that provides significant amount of matting or gloss reduction. The matting or gloss reduction is the result of a wrinkled coating surface on the coating or ink. A particularly preferred UV activated initiator is an alpha-amino ketone UV initiator.

[0006] This method of matting is desirable as it can be added in various amounts near the end of the coating or ink formulation process to adjust the level of matting of the final coating or ink during a coating or printing process. This method is also desirable as this particular type of wrinkle matting is less sensitive to concentration of the additive than existing technologies such as wax or silica additives so reproducibility of matting results are less sensitive to the small changes or variations in the amount of additive.

DETAILED DESCRIPTION OF THE INVENTION

[0007] Matting typically refers to the reduction of gloss of a coating. Gloss varies by the angle of the incident light and is often reported from measurement of reflected light at the same angle of 20, 60 and 85°. Matting (or gloss reduction) can also be thought of as causing variation in the angle of the reflected light relative to the incident light angle. If 100% of the incident light at 85° angle is reflected back off the surface at 85°, this would be 100% gloss. If only 20% of the incident light is reflected back at an angle of 85° (resulting in a gloss reading of 20 at the angle 85°), then the other 80% of the light is reflected back at other angles or is adsorbed by the film or coating.

[0008] Texturing of a coating or ink surface is a way to produce matting by scattering light reflected at non-anticipated angles from the coating surface. Texturing is disrupting the flat nature of a film by bumps, holes, indentations, ridges, wrinkles, crevices, etc. Texturing is normally described by the physical appearance of the modified surface by the observer. Texturing has been described as orange peel, dimpled, pebble finished, rippled, wrinkled, etc. As gloss measurements assume a perfectly flat reflective surface, any texturing variations

from a flat surface causes variations in the angle of incident light on the actual surface to vary from the intended angle (the equipment assumes the surface is perfectly flat). The variation in the actual incident light angle causes the angle of the reflected light from the actual surface to vary from the anticipated reflected angle.

[0009] Matting or texturing of radiation or UV cured films has typically been provided by dispersions of silica or wax in UV curable monomers. Typical particle sizes of the dispersed solid phase silica or wax has been a number average particle size of from a 1 or 2 μm to 50 μm and has tended to be in the range from about 5 to about 15 μm . If it is desired to change or adjust the level matting during a printing or coating process with silica or wax dispersions, it requires increasing or decreasing the amount of the dispersion in the formulation. This can change other properties of the ink or coating because the chemical composition of the matting agent is different than the rest of the coating. If the amount of the matting additive is increased in a coating or ink this can increase the viscosity of the coating or ink which can affect the film thickness and other processing parameters.

[0010] Dispersions of silica or wax can cause matting by a variety of mechanisms. The dispersions can cause bumps or indentations in the surface of a coating or film and these surface texturing effects can reduce the measured gloss. If the incident light penetrates the coating or film, differences between the refractive index of the coating and the refractive index of the silica or wax particles can cause significant variation in the amount and angle of reflected light. The extent of matting achievable with commercially available wax and silica dispersions can be limited and the wax and silica matting agent performance varies from coating or ink to coating or ink. This variation is due to the resin type, presence of solvent, dispersability of the silica or wax in the coating, etc. Thus, it is desirable to have a separate matting agent that functions by a separate mechanism to give an alternative or supplemental method of providing matting.

[0011] Radiation or UV cured films and inks are generally characterized by ethylenically unsaturated compounds (reactants) with relatively low evaporation rates under the coating conditions that polymerize by addition of successive monomer and oligomer units to a growing free radical polymer chain end. These

polymerization reactions are enabled by the presence of photoinitiators and exposure to UV light and can occur over a few seconds or fractions of a second making polymers of molecular weights from a few thousand g/mole to several million or infinite g/mole of polymer. These polymerizations typically exclude oxygen (such as the oxygen in typical air) or try to minimize the effect of oxygen on the growing chain ends. Oxygen can act as a chain transfer or chain termination reactant during these polymerizations (limiting molecular weight development) and results in the formation of undesirable low molecular weight polymer fractions that are tacky or detract from film hardness and physical properties (such as tensile strength, modulus, solvent resistance, abrasion resistance, etc.).

[0012] An older technology called alkyd resin or air drying resins utilizes the conjugated unsaturation in fatty acids portion of fatty acid triglycerides to react with metal driers and oxygen in the air to create peroxy compounds that degrade over time into free radicals that result in chemical bonds between a carbon atom of one fatty acid to a carbon atom of an adjacent fatty acid. Metal driers are metal compounds that speed the breakdown of peroxy compounds into free radicals that can create bonds between conjugated unsaturated species (like tung oil, linseed oil, etc.). Tung oil and linseed oil (both have three double bonds in at least one of the fatty acids of the triglyceride) were popular air drying resins (or alkyd resins) and were a source of the highly unsaturated and oxidatively reactive oil. Tung oil is sourced from the tung tree nuts. Linseed oil and tung oil made some of the earliest polymeric coatings on wood products to give them a shine and resistance to water penetration. Compounds having two adjacent double bonds are referred to as having conjugated unsaturation. The more conjugated unsaturation in an oil the more reactive the oil is in air drying processes. Tung oil has three adjacent double bonds in the 9, 11, and 13 positions of eleostearic acid. In air drying, a free radical termination or transfer step happens after nearly each free radical generation. Each termination is a potential crosslinking reaction between two highly unsaturated oligomers or polymers. Air drying is a continuous generation and consumption of free radical (through hydroperoxy processes) from various fatty acid unsaturation sites rather than a chain process.

[0013] In contrast, a chain polymerization involves the generation of a single radical chain end and the sequential addition of numerous monomer units (100s or 1000s) over a fraction of a second or maybe several seconds with the free radical chain end being re-generated sequentially on the terminal monomer or oligomer unit until a chain transfer or termination happens.

[0014] Two necessary components for achieving the desired wrinkle matting effect are the polyol ester of a polyol and a conjugated fatty acid (e.g. tung oil) wherein at least 40, 60, 70, or 80 wt.% of the conjugated fatty acid of said polyester is a eleostearic acid and a UV activated initiator that can generate enough free radicals under the operating conditions of the UV source to cause the rapid polymerization of a portion of said polyester forming a skin that becomes wrinkled as polymerization of the coating or ink proceeds. The UV activated free radical initiators are desirably present at concentrations from 0.5 to 5 or 10 parts by weight in a UV cured coating comprising the polyester from eleostearic acid, ethylenically unsaturated monomers, and the UV initiator at a total of 100 parts by weight.

[0015] The third component in the matting additive is free-radically polymerizable compound(s) characterized by having one or more ethylenically unsaturated group(s) per compound that can polymerize to form a polymeric ink or coating after initiation with a UV activated free radical initiator. The free-radically polymerizable compound(s) characterized by having one or more ethylenically unsaturated group(s) per compound also can help dissolve the UV activated initiator if the UV activated initiator is a solid at room temperature so the entire matting additive can be added as a homogenous liquid.

[0016] The polyol ester from a polyol and at least one conjugated fatty acid is desirably present in the matting additive in an amount from about 10 to about 80 parts by weight, more desirably from about 25 to about 70 parts by weight, and preferably from about 45 to 65 parts by weight. Desirably, the conjugated fatty acid of said polyester is at least 40, 60, 70, or 80 wt. % eleostearic acid. The polyol desirably has 2 or more hydroxyl groups, and more desirably from about 2 or 3 to about 5 hydroxyl groups. In one embodiment, the polyol is glycerol. In one embodiment, the polyester is a triglyceride available from the nuts of the tung tree called tung oil wherein about 40, 60, 70 or 80 wt.% of the fatty acid component is

identified as eleostearic acid. In another embodiment, a synthetic polyester from a polyol and eleostearic acid rich fatty acid source is used. Eleostearic acid is a tri-unsaturated fatty acid that has higher activity in oxidative crosslinking reactions than most other tri-unsaturated fatty acids.

[0017] The amount of free-radically polymerizable compound(s) characterized by having one or more ethylenically unsaturated group(s) per compound in the matting additive is desirably from about 10 or 20 to about 85 parts by wt., more desirably from about 20 or 30 to about 77 parts by weight and more preferably from about 40 to 70 parts by weight per 100 parts by weight of the combined three main ingredients of the matting additive. The free-radically polymerizable compound(s) characterized by having one or more ethylenically unsaturated group(s) per compound can be a mono-ethylenically unsaturated monomer or a poly-ethylenically unsaturated monomer such as tri-acrylated or tetra-acrylated polyol. The ethylenically unsaturated monomer may also be a linear or branched oligomer that has been functionalized to include two or more ethylenically unsaturated terminal groups.

[0018] The formulations of the present invention can include a mono-acrylate component. Suitable mono-acrylates or their mono(meth) acrylates components include monofunctional ethylenically unsaturated monomers such as, for example, monofunctional acrylate ester (CD277), monofunctional acrylate ester (CD278), acrylic ester (CD587), acrylic ester (CD585), acrylic monomer (CD420), 2-phenoxy ethyl acrylate (SR 339), cyclic trimethylolpropane formal acrylate (SR 531), isodecyl acrylate (SR 395), lauryl acrylate (SR 335), tridecyl acrylate (SR 489), stearyl acrylate (SR 257), 2(2-ethoxyethoxy) ethyl acrylate (SR 256), isooctyl acrylate (SR 440), tetrahydrofurfuryl acrylate (SR 285) (available from Sartomer, Exton, Pennsylvania), methyl acrylate, ethyl acrylate, isopropyl acrylate, n-hexyl acrylate, allyl acrylate, 2-(2'-vinylloxy ethoxy)ethyl acrylate (VEEA) (available from Nippon Shokubai Co., Inc, Tokyo, Japan), and acrylates or their (meth)acrylates of straight chain, branched chain, or cyclic alkyl alcohols of from 1 to 30 carbon atoms, including polyether alcohols.

[0019] Specific examples include acrylates of alcohols having more than four carbon atoms with acrylic or methacrylic acid, for example lauryl acrylate and

stearyl acrylate; (meth)acrylates of polyether alcohols, such as 2-(2-ethoxyethoxy)ethyl acrylate; (meth)acrylates, of cyclic alcohols, optionally containing an aliphatic linking group between the (meth)acrylate and the cyclic group, such as tetrahydrofuran acrylate (SR 285), oxetane acrylate, isobornyl acrylate (SR 506), cyclopentadiene acrylate, and the like and any sub-set thereof. Preferred mono-acrylate components include 2-(2'-vinylloxy ethoxy)ethyl acrylate, 2(2-ethoxyethoxy) ethyl acrylate, and tetrahydrofurfuryl acrylate. Preferred mono-acrylate components can also include isobornyl acrylate. Any combinations or subset of the foregoing may be utilized.

[0020] Other mono-ethylenically unsaturated monomers include C₆-C₁₅ styrene and substituted styrene, vinyl esters of vinyl alcohol with C₂ to C₁₈ carboxylic acids, acrylonitrile (optionally methyl, ethyl or propyl substituted), acrylamide monomers of 3 to 30 carbon atoms, vinyl chloride, vinyl pyridine, vinyl pyrrolidone, maleic anhydride, mono C₁-C₁₅ alkyl substituted fumarate monomers, di C₁-C₁₅ dialkyl substituted fumarate monomers, and C₈-C₂₀ alpha-beta unsaturated olefins.

[0021] Preferred diacrylates include, but are not limited to: ethylene glycol diacrylate, propylene glycol diacrylate, diethylene glycol diacrylate, dipropylene glycol diacrylate, triethylene glycol diacrylate, tripropylene glycol diacrylate, tetraethylene glycol diacrylate, tetrapropylene glycol diacrylate, polyethylene glycol diacrylate, polypropylene glycol diacrylate, ethoxylated bisphenol A diacrylate, bisphenol A diglycidyl ether diacrylate, resorcinol diglycidyl ether diacrylate, 1,3-propanediol diacrylate, 1,4-butanediol diacrylate, 1,5-pentanediol diacrylate, 1,6-hexanediol diacrylate, neopentyl glycol diacrylate, cyclohexane dimethanol diacrylate, ethoxylated neopentyl glycol diacrylate, propoxylated neopentyl glycol diacrylate, ethoxylated cyclohexanedimethanol diacrylate, propoxylated cyclohexanedimethanol diacrylate, epoxy diacrylate, aryl urethane diacrylate, aliphatic urethane diacrylate, polyester diacrylate, vinyl ester diacrylate and mixtures thereof.

[0022] Preferred triacrylates include, but are not limited to: trimethylol propane triacrylate, glycerol triacrylate, ethoxylated trimethylolpropane triacrylate, propoxylated trimethylolpropane triacrylate, tris (2-hydroxyethyl) isocyanurate

triacrylate, ethoxylated glycerol triacrylate, propoxylated glycerol triacrylate, pentaerythritol triacrylate, aryl urethane triacrylates, aliphatic urethane triacrylates, melamine triacrylates, epoxy novolac triacrylates, aliphatic epoxy triacrylate, polyester triacrylate, and mixtures thereof.

[0023] Preferred tetraacrylates include, but are not limited to: di-trimethylolpropane tetraacrylate, pentaerythritol tetraacrylate, ethoxylated pentaerythritol tetraacrylate, propoxylated pentaerythritol tetraacrylate, dipentaerythritol tetraacrylate, ethoxylated dipentaerythritol tetraacrylate, propoxylated dipentaerythritol tetraacrylate, aryl urethane tetraacrylates, aliphatic urethane tetraacrylates, polyester tetraacrylates, melamine tetraacrylates, epoxy novolac tetraacrylates, and mixtures thereof.

[0024] The low viscosity ink formulations of the present invention can include a vinyl ether component as a free radically polymerizable compound(s). Suitable vinyl ether components include vinyl ethers such as, for example, ethylene glycol divinyl ether, triethylene glycol divinyl ether, trimethylolpropane trivinyl ether, triethylene glycol monobutyl vinyl ether, cyclohexanedimethanol divinyl ether, hydroxybutyl vinyl ether, dodecyl vinyl ether, propenyl ether propylene carbonate, methyl vinyl ether, ethyl vinyl ether, isobutyl vinyl ether, diethylene glycol divinyl ether, butanediol divinyl ether, hexanediol divinyl ether, cyclohexanedimethanol monovinyl ether, cyclohexyl vinyl ether, 2-chloroethyl vinyl ether, 2-hydroxyethyl vinyl ether, 2,2-bis(4-vinyloxyethoxyphenyl)propane, and 1,4-bis(2-vinyloxyethoxy)benzene, specifically triethyleneglycol divinylether (Rapi-Cure(R) DVE-3), cyclohexane dimethyl divinyl ether (Rapi-Cure® CHVE), 4-hydroxybutylvinylether (Rapi-Cure® 4-HBVE), polyether cyclic polyols (Rapi-Cure® PECP), and dodecyl vinyl ether (Rapi-Cure® DDVE) (available from ISP Performance Chemicals, Wayne, New Jersey), ethyleneglycol monovinyl ether (EGM-VE), ethyl vinyl ether (E-VE), propyl vinyl ether (P-VE), isobutyl vinyl ether (iB-VE), 1,6-hexanediol divinyl ether (HD-DVE), aminopropyl vinyl ether (APVE), tert-amyl vinyl ether (TAVE), butanediol divinyl ether (BDDVE), n-butyl vinyl ether (NBVE), tert-butyl vinyl ether (TBVE), cyclohexanedimethanol divinyl ether (CHDVE), cyclohexanedimethanol monovinyl ether (CHMVE), cyclohexyl vinyl ether (CVE), diethylaminoethyl vinyl ether (DEAVE), diethyleneglycol

divinyl ether (DVE-2), diethyleneglycol monovinyl ether (MVE-2), dodecyl vinyl ether (DDVE), ethyleneglycol butyl vinyl ether (EGBVE), ethyleneglycol divinyl ether (EGDVE), ethylhexyl vinyl ether (EHVE), hexanediol divinyl ether (HDMVE), 4-hydroxybutyl vinyl ether (4-HBVE), isopropyl vinyl ether (IPVE), octadecyl vinyl ether (ODVE), polyethyleneglycol-520 methyl vinyl ether (MPEG500-VE), polytetrahydrofuran divinyl ether (PTHF290-DVE), plurio-E200 divinyl ether (PEG200-DVE), n-propyl vinyl ether (NPVE), tetraethyleneglycol divinyl ether (DVE-4), triethyleneglycol divinyl ether (DVE-3), triethyleneglycol methyl vinyl ether (MTGVE), and trimethylolpropane trivinyl ether (TMPTVE) (available from BASF Aktiengesellschaft, Ludwigshafen, Germany), and hydroxyl ethyl vinyl ether (HEVE), diethylene glycol divinyl ether (DEG-DVE), (available from Nisso Maruzen Chemical, Tokyo, Japan) and any combination or sub-set thereof.

[0025] Other high viscosity vinyl ether monomers may also be utilized, examples of which are bis-(4- vinyl oxy butyl) isophthalate (VEctomer® 4010), bis-(4- vinyl oxy butyl) adipate (VEctomer® 4060), Tris(4-vinyloxybutyl)trimellitate (VEctomer® 5015), bis-(4-vinyl oxy butyl)hexamethylenediurethane (VEctomer® 4230), and bis[[4-(ethenyloxy)methyl]cyclohexyl]methyl]terephthalate (VEctomer® 4051) (available from Morflex Inc., Greensboro, North Carolina,).

[0026] Alternately, vinyl ether based oligomers may be utilized in the formulations of the invention. An example of a vinyl ether based oligomer is VEctomer® 1312, a mixture of vinyl ether terminated aromatic ester oligomers (available from Morflex Inc., Greensboro, North Carolina). Any combinations or subset of the foregoing may be utilized.

[0027] The formulations of the present invention may also include a hybrid component containing both vinyl ether and acrylate functionality. These difunctional monomers are especially useful for decreasing the viscosity of curable compositions. Exemplary difunctional monomers include but are not limited to 2-(2-vinylethoxy)ethyl (meth)acrylate, 2-(2-vinylethoxy)-2-propyl (meth)acrylate, 2-(2-vinylethoxy)-3-propyl (meth)acrylate, 2-(2-vinylethoxy)-2-butyl(meth)acrylate, 2-(2-vinylethoxy)-4-butyl (meth)acrylate, 2-(2-allylethoxy) ethyl (meth)acrylate, 2-(2-allylethoxy)-2-propyl (meth)acrylate, 2-(2-allylethoxy)-3-propyl (meth)acrylate,

2-(2-allylethoxy)-2-butyl (meth)acrylate, 2-(2-allylethoxy)-4-butyl (meth)acrylate, 2-(2-vinylpropoxy)ethyl (meth)acrylate, 2-(2-vinylpropoxy)2-propyl (meth)acrylate, 2-(2-vinylpropoxy)-3-propyl (meth)acrylate, 2-(3-vinylpropoxy)ethyl (meth)acrylate, 2-(3-vinylpropoxy)-2-propyl (meth)acrylate, 2-(3-vinylpropoxy)-3-propyl (meth)acrylate, and sub-sets and combinations comprising at least one of the foregoing. The compound 2-(2-vinylethoxy)ethyl acrylate (VEEA) is commercially available from Nippon Shokubai Co., Inc, Tokyo, Japan. Any combinations or subset of the foregoing may be utilized.

[0028] The free-radically polymerizable compound(s) characterized by having one or more ethylenically unsaturated group(s) per compound may be commercially available epoxide based oligomers (made from ring opening epoxide functionalized compounds with carboxylic acids, amine functional reactants, or polyols) and reacting on one or more ethylenically unsaturated group per compound. These are well known commercially to formulators of UV curable coatings. They can have a variety of glass transition temperatures and good resistance to thermal degradation, hydrolysis, solvent swelling, fracture, etc. The epoxide based oligomers can be derived from aromatic epoxides like the diglycidyl ethers of bisphenol A or they can be derived from aliphatic epoxides. Epoxides can be formed from the olefin peroxidation and thus can have a variety of structures.

[0029] The free-radically polymerizable compound(s) characterized by having one or more ethylenically unsaturated group(s) per compound may be commercially available polyesters, polyethers or urethanes functionalized with ethylenically unsaturated groups. These could be any aliphatic or aromatic polyester, polyether or urethane. Aromatic polyesters and urethanes tend to have higher potential use temperatures than aliphatic urethane and polyesters (but that can be varied by the choice of the other components in the polyester or polyurethane such as the polyol used in the polyester and the macromolecular diol or diamine reactant). It is desirable that both the polyester, polyether and polyurethane be functionalized with one or more ethylenically unsaturated group so they can be co-polymerized during the UV activated free radical reaction.

[0030] When the free-radically polymerizable compound(s) characterized by having one or more ethylenically unsaturated group(s) per compound are oligomeric

polyepoxide, oligomeric polyester, oligomeric polyether or oligomeric polyurethane, desirably they have a number average molecular weight from about 200, 300, or 500 to about 5000 or 10,000 g/mole and said one or more ethylenically unsaturated groups (more desirably two or more ethylenically unsaturated groups and preferably 2 to 5 ethylenically unsaturated groups. More desirably the number average molecular weight is from about 300, 500, 800, or 1000 to about 2000 or 3000 g/mole.

[0031] The amount of the UV activated free radical initiator in the matting additive/agent is desirably from about 5 to about 30 parts by weight, more desirably from about 8 to 15 parts by weight, and preferably from about 10 to about 20 parts by weight per 100 parts total of the polyester, ethylenically unsaturated monomer(s) and the UV activated initiator. In one embodiment, the UV activated initiator belongs to the group of alpha-amino ketone based UV activated initiators. In one embodiment, the UV activated initiator comprises 2-methyl-1-[4-(methylthio)phenyl]-2-(4-morpholinyl)-1-propanone (IrgacureTM 907) or 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1 (IrgacureTM 369) or mixtures thereof. In one embodiment, the UV activated initiator comprises an acylphosphine oxide, benzophenone, benzoates, and/or thioxanthone (preferably said UV activated initiator comprises (IrgacureTM 819) phenyl bis(2,4,6-trimethylbenzoyl)-phosphine oxide; (GenocureTM PBZ) 4-phenylbenzophenone; (GenocureTM BDMM) 2-benzyl-2-dimethylamino-4-morpholinobutyrophenone; (GenocureTM MBF) methylbenzoylformate; (GenocureTM ITX) thioxanthone; or (GenocureTM EPD) ethyl-4-(dimethylamino)benzoate; or mixtures thereof). GenocureTM EPD and ITX are often considered synergists to be used with other UV initiators that benefit from synergists. In one embodiment, said UV activated initiator comprises an alpha-hydroxyketone (preferably said UV activated initiator comprises (IrgacureTM 184) (hydroxycyclohexyl)(phenyl)ketone; (IrgacureTM 1173) 2-hydroxy-2-methylpropiophenone; (IrgacureTM 2959) 1-[4-(2-hydroxyethoxy)-phenyl]-2-hydroxy-2-methyl-1-propane-1-one) or mixtures thereof. GenocureTM is a trademark of Rahn AG in Zurich Switzerland while IrgacureTM is a trademark of BASF in Germany.

[0032] The matting agent and/or the UV curable ink or coating can optionally include tertiary amines and their derivatives. Whilst many compounds can react with photoinitiators to generate radicals, the process is often relatively inefficient. A particular family of compounds capable of reacting efficiently with the excited photoinitiator is the tertiary amines and their derivatives, including amino alcohols and amino acids. Tertiary amines are commonly used and, in the context of radiation curing, are often referred to as amine synergists. The α -aminoalkyl radicals generated as a result of hydrogen abstraction from the tertiary amines are very reactive towards (meth)acrylate double bond. Tertiary amines perform yet another useful function in radiation curable systems based on (meth)acrylates, and this is directly related to their mechanism of photo-oxidation [R F Bartholomew and R S Davidson, Journal of the Chemical Society Chemical Communications, (1970), 1174-1175, Journal of the Chemical Society (C) (1971), 2347-2351]. It was found that the α -aminoalkyl radicals produced from tertiary amines react rapidly with oxygen to produce peroxy radicals. These peroxy radicals can then attack tertiary amines that have yet to form radicals, thus generating further α -aminoalkyl radicals, i.e. a chain reaction is initiated in which oxygen is sequestered as a peroxidic species.

[0033] The UV-curing of formulations based on (meth)acrylates is usually performed in air, which allows the ready ingress of oxygen into the UV-curable formulation. During the photopolymerisation process, the radical intermediates may react with molecular oxygen and be diverted from the polymerisation process, thereby decreasing the efficiency of the cure process. This is known to those skilled in the art as oxygen inhibition. If a suitable tertiary amine, in an appropriate amount, is added to the matting agent or UV-curable formulation, radicals generated from the amine rapidly scavenge oxygen present in the formulation, thereby allowing the desired polymerisation process to proceed. For this strategy to be successful, the consumption of oxygen within the coating has to proceed, or have the potential to proceed, at a rate that is substantially greater than the rate of ingress of oxygen from the air into the coating.

[0034] The matting additive can further comprise a conventional matting or texturing aid such as a fine particle size silica or wax. The silica can function as a

surface texturing aid if the particles float upward in the ink or coating as it polymerizes and cures. The silica can also have sufficiently different refractive index from the coating or ink that it can cause scattering of the light as it enters the coating, which can contribute to matting. The wax is usually a micronized or small particle wax dispersed in a free-radically polymerizable compound. The wax or wax type additives can be any of a variety of oligomeric or polymeric species that have wax type feel and wax type melting behavior. The wax type molecules typically have a melting temperature (often broad melting temperature) of from about 35 °C to about 200 °C.

[0035] The matting additive can further comprise a variety of additives to help stabilize the matting additive to environmental factors prior to use or to help compatibilize or blend the matting additive into the final coating, adhesive, or ink. These can include free radical scavengers (in small amounts as polymerization inhibitors during storage), biocides, wetting agents, dispersants, etc.

[0036] The matting additive can be added to any UV cured coating or ink composition at any stage during the formulation of the coating or ink. A particular benefit of the matting additive of this disclosure is that the matting additive amount can be increased during use of the coating or ink to increase the extent of matting. Thus, if after a few minutes or hours of operation, it is desired to increase the extent of matting, some additional matting additive can be metered into the coating or ink and incorporated homogeneously. Then the printing or coating process can be continued. If the extent of matting is too significant, the coating or ink can be diluted with a coating or ink of similar composition but without matting additive. In this way, the concentration of matting additive can be decreased during a coating or printing process to provide less matting.

[0037] The matting additive is usually used at a dosage of 3 to 20 wt.% of the weight of the coating or ink, and more desirably from about 4 or 5 to about 10 or 15 wt.% of the UV curable coating or ink.

[0038] The amount of the polyol ester from a polyol and at least one conjugated unsaturated fatty acid, such as eleostearic acid, present in the UV curable or cured coating or ink is from about 2 to about 25 parts by weight, more desirably from about 2 to about 10 parts by weight, and preferably from about 2, 3, or 4 to about 5,

6, 7, or 8 parts by weight based on 100 parts by weight of combined weight of polyol ester, free-radically polymerizable compound(s), UV activated initiator(s), and optional finely divided particulate pigment or filler.

[0039] The amount of free-radically polymerizable compound(s) characterized by having one or more ethylenically unsaturated group(s) per compound in the UV cured or curable coating or ink will generally be higher than the amount of free-radically polymerizable compound(s) in the matting additive. The UV curable coating has ethylenically unsaturated monomers and oligomers specifically selected from the earlier provided group that give the desired physical properties of the coating or ink after curing (e.g. film hardness or softness).

[0040] The amount of the free-radically polymerizable compound(s) characterized by having one or more ethylenically unsaturated group(s) per compound present in the UV cured coating or ink is from about 44.5 to about 97.5 parts by weight, more desirably from about 66 to about 99.5 parts by weight, and preferably from about 70, 71, 72, or 73 to about 97, 98, or 99 parts by weight based on 100 parts by weight of combined weight of polyester, free-radically polymerizable compound(s), UV activated initiator(s), and optional finely divided particulate pigment or filler.

[0041] The UV activated initiator in the UV curable coating may be from the formulation of the coating or ink or from the matting additive formulation. Of course, if the formulation has sufficient UV activated initiator present initially in the formulation, any UV activated initiator in the matting additive will be surplus.

[0042] The amount of the UV activated initiator present in the UV curable coating or ink is from about 0.5 to about 5 or 10 parts by weight, more desirably from about 0.5 to about 4 parts by weight, and preferably from about 0.5 to about 1, 2, 3, or 4 parts by weight based on 100 parts by weight of combined weight of polyester, free-radically polymerizable compound(s), UV activated initiator(s), and optional finely divided particulate pigment or filler.

[0043] UV curable coatings and inks are used in industry are desirable and used in industry because of their ability to be formulated and applied without organic solvents and/or water. This eliminates an evaporation step in the coating or printing process and eliminates drying lines and ovens. UV curable coatings and

inks are also fast curing allowing them to be used on production lines and to produce articles and printed materials that can be immediately packaged and shipped without concern about damage to the coating or printed images. Conventional polymeric coatings often are limited with respect to hardness of the polymer or extent of crosslinking as those polymers need to coalesce into films during the film formation process. UV curable coatings and inks can also be formulated in a wide varieties of viscosities allowing them to be applied by spraying, rolling, brushing, doctor blades, various printing processes (such as gravure, transfer, lithographic, ink jet, etc.). Since UV curable coatings go on as low molecular weight species (with low viscosities) rather than as polymers, they tend to have good wetting onto various substrates, some penetration into porous substrates and enhanced adhesion. As UV curable coatings can be accurately cross-linked to a controlled extent, they can have enhance resistance to swelling relative to coatings that are applied as polymer dispersions or solutions and are then cross-linked.

[0044] UV curable coatings and inks can be used for wood coatings including floor coatings, furniture coating, trim coating; metal coatings including appliances, lawn and garden equipment, vehicles, sports equipment, etc.; plastic coatings including a variety of household and industrial goods, vehicles, sports equipment, etc.; and media printing including paper, plastic, rolled goods, etc.

[0045] UV sources including mercury vapor lamps and UV LED (light emitting diode) technologies and other conventional UV sources are known to the art.

[0046] The following examples provide illustrations of the invention. These examples are non-exhaustive and are not intended to limit the scope of the invention.

EXAMPLES

Ingredients:

Benzophenone is a UV activated free radical initiator available from Sigma Aldrich.

BYKTM A-530 is a defoamer available from Altana AG.

CarbocureTM 7000, a commercially available wax matting agent available from The Lubrizol Corp..

DPGDA is dipropylene glycol diacrylate available from Allnex or BASF SE.

External EM2380 TF (EOTMPTA) is ethoxylated tetramethylol propane triacrylate available from Eternal Chemical Co., Ltd.

EbecrylTM 3700/30TP is bisphenol A epoxy acrylate oligomer diluted with 30% of tripropyleneglycol diacrylate available from Allnex.

EbecrylTM 210 is a polyurethane acrylate available from Allnex.

EbecrylTM 600 is an epoxy acrylate available from Allnex.

EbecrylTM 6040 is an epoxy acrylate available from Allnex.

EbecrylTM P116 is a low viscosity reactive amine additive available from Allnex to increase the cure speed of UV activated initiators.

IrgacureTM 907 is a UV activated free radical initiator available from BASF SE.

IrgacureTM 500 is a UV activated free radical initiator available from BASF SE.

LaromerTM LR 9004 is a polyester acrylate available from BASF SE.

LaromerTM LR 8986 is an epoxyacrylate available from BASF SE.

SartomerTM SR 306 (TPGDA) is tripropylene diacrylate available from Sartomer Arkema Group.

Acematt 3300 is a silica matting agent available from Evonic.

Prints were done Lenata paper with the Prüfbau printing press. We used 0.5gfff varnish on the roll $\approx$ ca. 4.5 μ m film thickness, compacting pressure: 600N, 0,5m/sec tape speed, UV Lamps: stage1 and 1

TABLE 1: Formulation of Test varnish TL-04-11 (UV curing Flexo ink):

Starting Point Formulation		Content (%)
1	Etermer TM EM2380 TF (EOTMPTA)	40.0
2	Sartomer SR 306 (TPGDA)	10.0
3	Benzophenone	10.0
4	Ebecryl P 116 (amine co-initiator)	7.0
5	Ebecryl 3700/30TP (Bis epoxy acrylated)	33.0
	Total	100.0

All components were added under stirring. The formulation is finished when benzophenone is totally dissolved.

TABLE 2: Gloss Readings on TL-04-11 with different additives in different amounts

TL-04-11 +	Example #	Gloss(Byk gardner micro TRI gloss)		
		20°	60°	85°
Control	Control A	60.8	93.4	92.4
5% Lanco 1362SF	Control B	15.3	49.5	61.1
5% Lanco 1362D	Control C	12.3	42.1	50.5
5% Acematt 3300	Control D	2.0	14.2	22.9
10% Lanco 1362D	Control E	4.6	23.5	36.2
10% Lanco 1362SF	Control F	2.2	13.2	15.8
15% Carbocure 7000	Control G	7.5	39.9	73.3
30% Carbocure 7000	Control H	0.8	8.5	58.0

TABLE 3 : Formulation of TL-04-12 (UV curable wood finish for indoor (based on epoxy acrylics))

Starting Point Formulation		Content (wt.%)
1	Ebecryl 6040	40.00
2	Ebecryl 600	20.00
3	DPGDA	32.50
4	Ebecryl 210	3.50
5	BYK A-530	0.25
6	Irgacure 500	3.75
	Total	100.

Components 1 and 2 were combined in a suitable vessel. Separately components 3 and 4 were combined to make a premix and the premix of 3 and 4 was heated with stirring to approximately 55-60 °C to fully dissolve the Ebecryl 210. Then the premix of 3 and 4 was combined with the components 1 and 2 in the other vessel and mixed further. Components 5 and 6 were then added with stirring and mixed for 10 minutes, while protecting the ingredients from all light (as the UV initiator was present and may start an uncontrolled in-container curing process). The mixture had a density of 1.23 g/m³. A lamp intensity of 80W/cm and a conveyor speed of 10-20 m/min were used for curing.

TABLE 4: Formulation of TL-04-13 (UV curable general wood finish (based on polyester / epoxy acrylics))

Starting Point Formulation		Content (wt.%)
1	Laromer LR 9004	40.00
2	Laromer LR 8986	31.00
3	Laromer DPGDA	24.70
4	BYK A-530	0.30
5	Irgacure 500	4.00
	Total	100.

Components 1 and 2 were combined in a suitable vessel. Component 3 and was added to the mix of 1 and 2 with for approximately 5 minutes. Components 4 and 5 were then added with stirring and mixed for 10 minutes, while protecting the ingredients from all light (as the UV initiator was present and may start an uncontrolled in-container curing process). The mixture had a density of 1.23 g/m³. A lamp intensity of 80W/cm and a conveyor speed of 10-20 m/min were used for curing.

TABLE 5: Formulation of Test varnish TL-04-14 (UV curing Flexo ink, very reactive)

Starting Point Formulation		Content (wt.%)
1	Etermmer EM2380 TF (EOTMPTA)	40
2	Sartomer SR 306 (TPGDA)	10
3	Irgacure 907	10
4	Ebecryl P 116 (amine co-initiator)	7
5	Ebecryl 3700/30TP (Bis epoxy acrylated)	33
	Total	100

Same mixing procedure as Table 2 (replace benzophenone with Irgacure 907).

TABLE 6: Gloss Results for TL-04-14 with various matting agents

TL-04-14 +	Example #	Gloss		
		20°	60°	85°
Control	Control I	71.7	95.8	98.4
5% Lanco 1362SF	Control J	21.7	62.1	72.6
5% Lanco 1362D	Control K	22.9	63.2	75.4
5% Acematt 3300	Control M	4.6	26.9	40.3
10% Lanco 1362D	Control N	12.8	48.3	59.1
10% Lanco 1362SF	Control O	12.7	48.3	61.5
15% Carbocure TM (CBC)7000	Control P	54.1	84	92.8
30% Carbocure TM 7000	Control Q	18.3	55.6	85.1
5% Gasil HP 380	Control R	9.0	39.1	49.3

TABLE 7: Testing some oils in UV cured coatings for matting effect in TL-04-14:

TL-04-14 + 5% Oil	Example #	Gloss		
		20°	60°	85°
sesame oil	Control S	49.5	91	93.1
linseed oil	Control T	53.4	88.3	89.4
Tung oil	Example 1	5.4	16.4	16.7
castor oil	Control U	60.3	93.6	92
salmon oil	Control V	32.4	76.6	83.4

TABLE 8: Gloss results with various Oils in Test Formulation TL-04-11

TL-04-11 + 5% Oil		Gloss		
		20°	60°	85°
tung oil	Control X	no matting		
castor oil	Control Y	no matting		
salmon oil	Control Z	no matting		
sesame oil	Control A1	no matting		
linseed oil	Control B1	no matting		

TABLE 9: Comparison of Formulations TL-04-14 with matting and TL-04-11 without matting. Note the different free radical initiator. Tung oil plus Irgacure 907 shows matting/structure

TL-04-14	
Starting Point Formulation	
Etermer EM2380 TF (EOTMPTA)	40
Sartomer SR 306 (TPGDA)	10
Ebecryl P 116 (amine co-initiator)	7
Irgacure 907	10
Ebecryl 3700/30TP (Bis epoxy acrylated)	33
Total	100

TL-04-11	
Starting Point Formulation	
Etermer EM2380 TF (EOTMPTA)	40
Sartomer SR 306 (TPGDA)	10
Ebecryl P 116 (amine co-initiator)	7
Benzophenone	10
Ebecryl 3700/30TP (Bis epoxy acrylated)	33
Total	100

TABLE 10: Composition of Matting additives

Components		Matting additive 1	Matting additive 2	Matting additive 3	Carbocure™ 7000, Control
1	DPGDA g	65	50	45	-
2	Irgacure™ 907 g	15	30	15	-
3	Tung oil g	20	20	40	-

Tests matting additive/agent formulations 1-3 were heated to 60 C to help put the Irgacure 907 into solution

TABLE 11: TL-04-11 UV curing Flexo ink Gloss Reduction Values for 3 different formulations and control, Gloss Reduction Values for 3 different formulations and control. 10wt.% matting agent

Gloss value at Gloss angle	Example 2, Matting additive 1	Example 3, Matting additive 2	Example 4, Matting additive 3	Control C1, Carbocure™ 7000
20°	39.6	56.4	9.6	50.6
60°	89.1	92.4	25.6	84.6
85°	77.6	94	32.7	95.1

TABLE 12: TL-04-14 UV curing Flexo ink (very reactive), Gloss Reduction Values for 3 different formulations and control. 10wt.% matting agent

Gloss value at Gloss angle	Example 5, Matting additive 1	Example 6, Matting additive 2	Example 7, Matting additive 3	Control D1, Carbocure™ 7000
20°	59.7	65.9	2	46.8
60°	90.5	94.3	11.1	82.4
85°	85.2	87.4	18.5	74.6

TABLE 13: TL-04-12 UV Curable Wood Finish for Indoor (based on epoxy acrylics), Gloss Reduction Values for 3 different formulations and control. 10wt.% matting agent

Gloss value at Gloss angle	Example 8, Matting additive 1	Example 9, Matting additive 2	Example 10, Matting additive 3	Control E1, Carbocure™ 7000
20°	69.9	51.4	23.3	17.1
60°	95.4	92.6	56.4	57.5
85°	94.8	76.4	56.4	77.8

TABLE 14: TL-04-13 UV Curable General Wood Finish (based on polyester/epoxy/acrylics), Gloss Reduction Values for 3 different formulations and control. 10wt.% matting agent

Gloss value at Gloss angle	Example 11, Matting additive 1	Example 12, Matting additive 2	Example 13, Matting additive 3	Control F1, Carbocure™ 7000
20°	63.9	54.7	37.4	22.9
60°	93.9	92	69.6	61.3
85°	84.9	85.8	61.7	85

[0047] Each of the documents referred to above is incorporated herein by reference. Except in the Examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like, are to be understood as modified by the word "about." Unless otherwise indicated, each chemical or composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, by-products, derivatives, and other such materials which are normally understood to be present in the commercial grade. However, the amount of each chemical component is presented exclusive of any solvent or diluent oil, which may be customarily present in the commercial material, unless otherwise indicated. It is to be understood that the upper and lower amount, range, and ratio limits set forth herein may be independently combined. Similarly, the ranges and amounts for each element of the invention may be used together with ranges or amounts for any of the other elements.

[0048] While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.

What is claimed is:

1. A matting additive for a coating or ink curable by radicals generated by UV radiation, said coating or ink comprising;
 - b) 10 to 70 parts by weight of a polyol ester of a polyol and at least one conjugated fatty acid, wherein at least 40 wt. % of said at least one conjugated fatty acid comprises eleostearic acid (in a more preferred embodiment at least 50, 60, 70 or 80 wt.% eleostearic acid),
 - c) 10-85 parts by weight of free-radically polymerizable compound(s) characterized by having one or more ethylenically unsaturated group(s) per compound, and
 - d) 5 to 30 parts by weight of a UV activated free radical initiator (preferably selected from alpha-amino ketone, benzophenone, thoxanthrone, aminobenzoate, acylphosphine oxide, and alpha-hydroxyketone), wherein said parts by weight are based on 100 parts by weight of said matting additive.
2. A matting additive for coating or ink according to claim 1, wherein said free-radically polymerizable compound(s) comprises b1) mono-ethylenically unsaturated monomer such as acrylate; b2) compound(s) having at least two ethylenically unsaturated groups per monomer, such as two ethylenically unsaturated acrylate groups connected into a single monomer or oligomeric compound via ester linkages between the carbonyl groups of said acrylate groups; and a linking group such as 1) hydrocarbon based polyol (such as TMP, dipropylene glycol, etc.) , 2) an epoxy functionalized hydrocarbon polyol (such as bisphenol A), 3) epoxy functionalized polyester, 4) urethane oligomer with terminal hydroxyl or epoxy groups, or mixtures thereof.
3. A matting additive for a coating or ink curable by radicals generated by UV radiation according to claim 1 or 2, wherein the amount of polyol ester of a polyol and a conjugated fatty acid is present from 15 to 45 parts by weight and said polyol ester of a polyol and a conjugated fatty acid comprises tung oil.
4. A matting additive for a coating or ink curable by radicals generated by UV radiation according to claim 1, 2 or 3, further comprising a silica or wax type dispersion type matting agent.

5. A matting additive for a coating or ink curable by radicals generated by UV radiation according to claim 4, wherein said silica or wax dispersion comprises a continuous phase that is a mono or poly-ethylenically unsaturated monomer and said silica or wax has a number average particle size between 1 μm and 50 μm .
6. A coating or ink curable by radicals generated by UV radiation, said coating or ink comprising
 - a) 2 to 25 parts by weight of a polyol ester of a polyol and at least one conjugated fatty acid, wherein at least 50 wt. % of said at least one conjugated fatty acid comprises eleostearic acid (in a more preferred embodiment at least 60, 70 or 80 wt.% eleostearic acid),
 - b) 44.5-97.5 parts by weight of free-radically polymerizable compound(s) characterized by having one or more ethylenically unsaturated group(s) per compound,
 - c) 0.5 to 10 parts by weight of an UV activated initiator (preferably selected from α -amino ketone, benzophenone, thioxanthrone, aminobenzoate, acylphosphine oxide, and α -hydroxyketone); wherein said parts by weight are based on 100 parts by weight of said radiation curable coating or ink, and optionally
 - d) up to 30 parts by weight of an inorganic or organic particulate pigment or filler of a number average particle diameter of less than 50 μm .
7. A coating or ink curable by radicals generated by UV radiation according to claim 6, further comprising an oxygen scavenger.
8. A coating or ink curable by radicals generated by UV radiation according to claim 6 or 7, optionally further comprising said particulate material of less than 50 μm in diameter, wherein the combined weight of said free-radically polymerizable compound(s) and said optional particulate species is at least 80 wt.% of the weight of said coating or ink (more desirably at least 90 wt.%).
9. A coating or ink curable by radicals generated by UV radiation according to any of claims 6-8, wherein said coating or ink is a coating.
10. A coating or ink curable by radicals generated by UV radiation according to any of claims 6-9, wherein said UV activated initiator comprises an α -amino ketone (preferably said α -amino ketone comprises 2-methyl-1-[4-

(methylthio)phenyl]-2-(4-morpholinyl)-1-propanone (Irgacure 907) or 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1 (Irgacure 369) or mixtures thereof).

11. A coating or ink curable by radicals generated by UV radiation according to any of claims 6-9, wherein said UV activated initiator is selected from the group comprising acylphosphine oxide, benzophenone, benzoates, and thioxanthone (preferably said UV activated initiator comprises (Irgacure 819) phenyl bis(2,4,6-trimethylbenzoyl)-phosphine oxide; (PBZ) 4-phenylbenzophenone; (BDMM) 2-benzyl-2-dimethylamino-4'morpholinobutyrophenone; (MBF) methylbenzoylformate; (ITX) thioxanthone; or (EPD) ethyl-4-(dimethylamino)benzoate; or mixtures thereof).

12. A coating or ink curable by radicals generated by UV radiation according to any of claims 6-9, wherein said UV activated initiator comprises an alpha-hydroxyketone (preferably said UV activated initiator comprises (Irgacure 184) (hydroxycyclohexyl)(phenyl)keton; (Irgacure 1173) 2-hydroxy-2-methylpropiophenone; (Irgacure 2959) 1-[4-(2-hydroxyethoxy)-phenyl]-2-hydroxy-2-methyl-1-propane-1-one).

13. A coating or ink curable by radicals generated by UV radiation according to any of claims 6-10, wherein at least 50 weight percent of said free-radically polymerizable compound(s) characterized by having one or more ethylenically unsaturated group(s) per compound are characterized by having at least one acrylate functional group as an ethylenically unsaturated group (more desirably at least 60 or 70 wt.% are characterized by having at least one acrylate functional group).

14. A coating or ink curable by radicals generated by UV radiation according to any of claims 6-11, wherein said coating or ink is a wood finish.

15. A coating or ink curable by radicals generated by UV radiation according to any of claims 6-11, wherein said film is a metal finish.

16. A coating or ink curable by radicals generated by UV radiation according to any of claims 6-11, wherein said coating or ink is an overcoat varnish on a printed item.

17. A coating or ink curable by radicals generated by UV radiation according to any of claims 6-11, wherein said coating or ink is a printing ink (such as offset, flexographic, lithographic, etc.).

18. A coating or ink curable by radicals generated by UV radiation according to any of claims 6-15, further comprising a matting agent comprising a dispersion of silica or wax type additive.

19. A coating or ink curable by radicals generated by UV radiation according to any of claims 6-15, wherein said free-radically polymerizable compound(s) comprises at least one oligomer with more than one acrylate functional groups, vinyl ester polymer with more than one ethylenically unsaturated group, or epoxy resin with more than one ethylenically unsaturated group.

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2015/040505

A. CLASSIFICATION OF SUBJECT MATTER

INV. C09D5/28 C09D11/101
ADD.

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)
C09D

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 047 422 A (SITES BENJAMIN L ET AL) 31 July 1962 (1962-07-31)	1-5
A	claims; examples	6-9
X	US 1 893 611 A (BRADLEY THEODORE F) 10 January 1933 (1933-01-10)	1-5
A	cited in the application claims; examples	6-19



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Zeslawski, Wojciech

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2015/040505

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 3047422	A	31-07-1962	NONE	

US 1893611	A	10-01-1933	NONE	
