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(54) PROCESS FOR APPLYING A MULTILAYER COATING

(57) The invention pertains to a process for coating of a substrate comprising the steps of:
(a) Applying a first coating composition to a substrate, the first coating comprising a solvent and a first resin selected from the group consisting of polyol resin, alkyd resin and/or polyacrylate resin, the resin comprises a reactive group;
(b) Applying a second coating composition onto the first coating composition, the second coating composition comprising an epoxy resin, a second resin having OH and/or carboxylic acid functional groups, and a curing catalyst; and
(c) Curing the coating compositions to obtain a coated substrate.

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Description

[0001] The present invention relates to processes for applying a multilayer coating and to coated substrates.

[0002] Processes for applying a multilayer coating onto substrates, and in particular for coating onto substrates suitable for use in food and beverage containers, are known in the art. Such coating composition have to comply to many requirements: these composition need to be storage stable and easily and readily applicable to the substrate. The cured coating composition should further prevent corrosion, exhibit a good balance between hardness and elasticity, must adhere well to the substrate surface and may expose a low amount of volatile organic compounds (VOC). An additional challenge is to apply a multilayer coating that is compatible with ach other and exhibit good wettablility and surface coverage.

[0003] WO 2007/021780 and WO 2008/137562 disclose a two-layer coating system. The coating compositions in both layers comprise polyvinyl chloride, and furthermore contain cross-linkers in both layers to enable some hardening. The first coating layer (the undercoat) is at least partially cured before the second coating is applied, which is then subsequently cured.

[0004] It was now found that a multilayer coating suitable for application on food and beverage containers can be provided that is obtained by wet-on-wet application of two coating compositions.

[0005] The objective of the present invention is to provide an improved coating process and to providing improved coated substrates.

[0006] The present invention pertains to a process for coating of a substrate comprising the steps of:

(a) Applying a first coating composition to a substrate, the first coating composition comprising a solvent and a first resin selected from the group consisting of polyol resin, alkyd resin and/or polyacrylate resin, the resin comprises a reactive group;

(b) Applying a second coating composition onto the first coating composition, the second coating composition comprising an epoxy resin, a second resin having OH and/or carboxylic acid functional groups, and a curing catalyst; and

(c) Curing the coating compositions to obtain a coated substrate.

[0007] The process of the invention is a wet-on-wet application of two coating compositions (a) and (b). In the context of the present application the term "wet-on-wet application" refers to the sequential application of at least two coating compositions that will only be exposed to curing conditions after application of the second or top layer. An advantage of this process is that both coating layers can be applied relatively fast without an additional curing step in between the application. This combined with the fast curing of the top layer, renders the speed of the overall process to be acceptable for commercial production. In addition, the reactive groups of the epoxy resin, the second resin in the second layer and the first resin in the first layer allows for the first resin to be at least partially cross-linked by the epoxy resin and/or second resin, rendering a good adhesion between the second and the first coating layer. The coating compositions used in the process of the invention are furthermore relatively simple compared to known compositions, and is therefore commercially and economically attractive. As a consequence, these coating compositions used in the process of the invention can be readily applied to substrate surfaces even at high speeds using conventional coating devices. The inventive process leads to the formation of a cured coating that exhibits good retort-sterilisable properties, enhanced resistance towards chemicals, good adhesion to a wide variety of substrates, good abrasion resistance, and high compatibility to a wide variety of inks. Consequently, the color intensity of the inks may be improved allowing the use of a lower amount of ink.

[0008] In the context of this application the term "functional group(s)" or "reactive groups" refer to the (reactive) group(s) taking part in the curing process. Examples of such functional groups include epoxy, hydroxyl (-OH), carboxylic acid (-COOH), carboxylic ester (-COOR), linear carbonates ($R-CO_3$), cyclic carbonates, oxirane, oxetane, anhydrides (R-CO-O-CO-R'), thiol (-SH), amine ($-NH_2$), amide (-NHR), ether (-N-R-O-R') and alcohol (N-R-OH). Also other components of the coating composition of the invention may comprise functional groups capable of reacting with the functional groups comprised in the above coating compositions. Examples of such components include solvents and other resins.

[0009] The first coating composition comprises a solvent and a first resin selected from the group consisting of polyol resin, alkyd resin and/or polyacrylate resin, the resin comprises a reactive group. In one embodiment, the first resin generally does not cure by itself; the first resin does comprise reactive groups. These reactive groups may be able to react with the reactive groups in the first resin and/or the epoxy resin, preferably with the reactive groups in the epoxy resin. Such reactive groups enable a good compatibility between the first resins and the resins in the second coating composition.

[0010] The first resin of the invention generally comprises first functional groups or first reactive groups selected from the group consisting of hydroxyl (-OH), carboxylic ester (-COOR with R being C_1-C_6 alkyl), carboxylic acid (-COOH) and thiol (-SH). Preferably, the first functional group is at least one selected from the group of hydroxyl (-OH), carboxylic ester (-COOR with R being C_1-C_6 alkyl), and carboxylic acid (-COOH), more preferably selected from the group consisting of hydroxyl (-OH) and carboxylic acid (-COOH). The first resin may have more than one functional group, e.g. the first resin may contain both hydroxyl and carboxylic acids groups.

[0011] The first resin may have an average functionality between 1 and 6. Preferably the average functionality is at most 5, more preferably at most 4 and even more preferably at most 3. In an embodiment of the invention, the first resin comprises a first functional group being hydroxyl, and an average hydroxyl functionality between 1 and 6, preferably at most 5, more preferably at most 4 and even more preferably at most 3.

[0012] In the context of this application, the term "average functionality" or "average hydroxyl functionality" refers to the average number of functional groups or hydroxyl groups per monomer or monomeric unit in a resin.

[0013] The first resin of the invention may preferably have a weight average molecular weight (Mw) of at most 100,000, more preferably at most 50,000, even more preferably at most 20,000 and most preferably at most 10,000, and preferably at least 200, more preferably at least 250 and most preferably at least 300. When the first resin is a monomer, the first resin may preferably have a weight average molecular weight (Mw) of at most 10,000, more preferably at most 5,000, even more preferably at most 2,000 and most preferably at most 1,000, and preferably at least 200, more preferably at least 250 and most preferably at least 300.

[0014] The first resin, preferably the polyol, of the invention may be a monomer, an oligomer or polymer. Oligomers of the first resin refer to dimers, trimers and tetramers of the monomers of the first resin. Oligomeric polyols include dimers, trimers and tetramers of monomeric diols and/or triols.

[0015] The first resin is generally selected from the group consisting of polyol resin, alkyd resin and polyacrylate resin. Of these first resins polyol, and in particular polyester, is preferred. Examples of suitable monomeric polyols comprising hydroxyl functional groups include 1,4-butanediol, 1,3-butanediol, 1,5-pentanediol, 1,6-hexanediol, 2,5-hexanediol, 2-methyl-1,3-pentanediol, 2-ethyl-1,3-hexanediol, 2,2-dimethyl-1,3-pentanediol, 1,4-cyclohexanediol, trimethylolethane, trimethylolpropane, pentaerythritol, dipentaerythritol, 1,4-cyclohexanedimethanol, 1,2-bis(hydroxymethyl)cyclohexane, 1,2-bis(hydroxyethyl)cyclohexane, trimethylolpropane, 2,2-dimethyl-3-hydroxypropyl-2,2-dimethyl-hydroxyproprionate, diethylene glycol, triethylene glycol, dipropylene glycol, tetraethylene glycol, trimethylolethane, glycerol, and sorbitol; and polyols comprising oxirane functional groups bisphenol A, bisphenol F, bisphenol S, alkoxylated bisphenol A such as ethoxylated bisphenol A and propoxylated bisphenol A and alkoxylated bisphenol F such as ethoxylated bisphenol F and propoxylated bisphenol F; polyols comprising oxirane functional groups bisphenol A diglycidyl ether, 2,2'-bis(4-hydroxyphenyl)propane bis(2,3-epoxypropylether, bisphenol F diglycidyl ether, novolac glycidyl ether, ethoxylated bisphenol A and propoxylated bisphenol A.

[0016] Examples of suitable polyesters include Uradil SZ255 (TMP-based polyester), polyglycolide (PGA), polycaprolactone (PCL), polyhydroxyalkanoate (PHA), polyhydroxybutyrate (PHB), polyethylene adipate (PEA), polybutylene succinate (PBS), poly(3-hydroxybutyrate-co-3-hydroxyvalerate (PHBV), polyethylene terephthalate (PET), polybutylene terephthalate (PBT), polytrimethylene terephthalate (PTT), polyethylene naphthalate (PEN) and Vectran.

[0017] Examples of alkyd resins include polyesters which are modified by fatty acids or corresponding triglycerides like for example the commercially available under tradenames URULAC AN621 S-2 60 and URULAC AN637 S-2 60 (both ex DSM Resins). The alkyd resins may further be modified using phenolic resin, styrene, vinyl toluene, acrylic monomers and/or polyurethanes. More details of suitable alkyd resins and possible modifications can be found in US 2014/0360408.

[0018] Examples of polyacrylate resins include polymers derived from one or more of acrylate, methacrylate, ethyl acrylate, 2-chloroethyl vinyl ether, 2-ethylhexyl acrylate, 2-hydroxyethyl methacrylate, butyl acrylate, butyl methacrylate, 2-hydroxypropyl methacrylate, 3-hydroxypropyl methacrylate, 2-hydroxypropyl methacrylate, 3-hydroxypropyl methacrylate, hydroxystearyl acrylate and hydroxystearyl methacrylate. Copolymers of two or more of the aforementioned resins are also contemplated as long as the resulting resin contains reactive groups as is required by the invention.

[0019] In one embodiment of the invention, the coating composition comprises the first resin in an amount of at least 50 % by weight (wt%), based on the total weight of the first coating composition. Preferably, the first resin is present in an amount of at least 55 wt%, more preferably at least 60 wt%, even more preferably at least 65 wt% and most preferably at least 70 wt%, and preferably at most 99 wt%, more preferably at most 95 wt%, even more preferably at most 90 wt% and most preferably at most 85 wt%, based on the total weight of the first coating composition.

[0020] The first coating composition further comprises a solvent. The solvent may be any solvent known in the art. The solvent generally serves to improve the application, flowability and wetting properties of the coating composition. Examples of suitable solvents include Solvent Naphtha®, heavy benzene, various Solvesso® grades, various Shellsol® grades and Deasol®, various white spirits, mineral turpentine oil, tetralin, decalin, butyl glycol, 2-methoxypropanol, methanol, ethanol, diethanol, amino ethanol, glycol, n-propanol, iso-propanol, ethanethiol. N-butanol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monoethyl ether, diethylene glycol diethyl ether, diethylene monobutyl ether, ethyl 2-hydroxypropionate, 3-methyl-3-methoxybutanol, ethyl ethoxy propionate, methoxypropyl acetate, water, methyl ethyl ketone, methyl n-propyl ketone, acetone, ethyl acetate, and tertiary butyl acetate. Preferred solvents are reactive solvents that comprise third functional groups capable of reacting with the first resin, epoxy resin and/or second resin. The third functional groups may be hydroxyl or thiol.

Preferably, the third functional group is a hydroxyl. Examples of reactive solvents include alcohols such as methanol, ethanol, diethanol, amino ethanol, glycol, n-propanol, iso-propanol and ethanethiol, ethylene glycol, propylene glycol and neopentyl glycol; and amines such as methyl amine, ethanol amine, dimethyl amine, methyl ethanol amine, diphenyl amine, trimethyl amine, triphenyl amine and piperidine; and acrylates such as acrylate, methacrylate, ethyl acrylate, 2-chloroethyl vinyl ether, 2-ethylhexyl acrylate, 2-hydroxyethyl methacrylate, butyl acrylate, butyl methacrylate, 2-hydroxypropyl methacrylate, 3-hydroxypropyl methacrylate, 2-hydroxypropyl methacrylate, and 3-hydroxypropyl methacrylate; and water. The coating composition of the invention may comprise a reactive solvent and a non-reactive solvent, a combination of two or more solvents, or a combination of two or more reactive solvents. Coating compositions comprising a reactive solvent are preferred.

[0021] Preferably, the first coating composition is substantially free from water and/or non-reactive solvents. The term "substantially free" means that less than 100 parts per million of water and/or non-reactive solvent is present in the first coating composition. Preferably, the first coating composition is completely free from water and/or non-reactive solvent, which means that the cured coating contains less than 20 parts per billion (ppb) of water and/or non-reactive solvent. Generally, water-based coating compositions are not suitable for the process of the invention as the presence of water and/or non-reactive solvent tends to reduce the quality of the coating, e.g. blistering of the multilayer coating, insufficient wetting of the substrate and/or the second coating composition.

[0022] In one embodiment of the invention, the first coating composition comprises the solvent, preferably reactive solvent, in an amount of at most 50 % by weight (wt%), based on the total weight of the first coating composition. Preferably, the first resin is present in an amount of at most 45 wt%, more preferably at most 40 wt%, even more preferably at most 35 wt% and most preferably at most 30 wt%, and preferably at least 1 wt%, more preferably at least 5 wt%, even more preferably at least 10 wt% and most preferably at least 15 wt%, based on the total weight of the first coating composition.

[0023] The first coating composition may further comprise additives commonly used in coating compositions including pigments and dyes, surfactants, flow controlling agents, thixotropic agents, anti-gassing agents, ultraviolet light stabilizers and adhesion enhancing resins. Examples of pigments and dyes include metal oxides like titanium dioxide, iron oxide, zinc oxide and chromium oxide; metal hydroxides; metal sulfides, metal sulfates, metal carbonates such as calcium carbonate; carbon black, china clay, phthalo blues and greens, organo reds and other organic dyes. It was found that the coating compositions of the invention may increase the color intensity of the pigments and dyes. This may lead to a reduction in the total amount of pigment and/or dye used.

[0024] The remaining part of the first coating composition may be comprised of other components commonly used in coating compositions such as the additives. With the first resin and the solvent the other components add up to 100 wt% of the total weight of the coating composition.

[0025] The second coating composition comprises an epoxy resin, a second resin having hydroxyl (-OH) and carboxylic acid (-COOH) functional groups, and a curing catalyst.

[0026] The epoxy resin may be any epoxy resin known in the art. Suitable epoxy resins include cycloaliphatic epoxy resins such as 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate; glycidyl epoxy resins such as trimethylolpropane triglycidyl ether, diglycidyl ester of hexahydrophthalic acid and dodecanol glycidyl ether; phenolic epoxy resins such as bisphenol A diglycidyl ether epoxy resin (BADGE) and bisphenol F diglycidyl ether epoxy resin; Novolac epoxy resin such as epoxy phenol novolacs (EPN) and epoxy cresol novolacs (ECN); glycidylamine epoxy resins such as triglycidyl-p-aminophenol and N,N,N,N-tetraglycidyl-4,4.methylene bisbenzylamine; end-capped epoxy resin such as poly(bisphenol A-co-epichlorohydrin) glycidyl end-capped; substituted oxetane and mixtures thereof. Preferred epoxy resins are cycloaliphatic epoxy resins. Most preferred is 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate.

[0027] In a preferred embodiment of the invention, the molar ratio of functional groups of the epoxide resin to the functional groups of the first and second resins is above 1. This has the advantage that any reactive solvent can be readily built in. Preferably, the ratio is at least 2, more preferably at least 5, even more preferably at least 8, even more preferably at least 10, and most preferably at least 15, and preferably at most 100, more preferably at most 75, even more preferably at most 50, and most preferably at most 40.

[0028] In one embodiment of the invention, the second coating composition comprises the epoxy resin, preferably the cycloaliphatic epoxy resin, in an amount of at least 25 % by weight (wt%), based on the total weight of the second coating composition. Preferably, the epoxy resin is present in an amount of at least 35 wt%, more preferably at least 40 wt%, even more preferably at least 50 wt% and most preferably at least 70 wt%, and preferably at most 99 wt%, more preferably at most 95 wt%, even more preferably at most 90 wt% and most preferably at most 85 wt%, based on the total weight of the second coating composition.

[0029] The second resin may be any suitable resin having hydroxyl and/or carboxylic acid functional groups known in the art. The second resin may be a polyol resin, an alkyd resin or a polyacrylate resin. Preferably, the second resin is a polyol, in particular a polyester, or an alkyd resin, and most preferably the second resin is a polyol resin, in particular a polyester resin. The second resin can be a polyol resin, alkyd resin or polyacrylate resin as described above for the first resin. The second resin can be the same as or different from the first resin. Preferably, the second resin has a higher average functionality than the first resin.

[0030] In one embodiment of the invention, the second coating composition comprises the second resin, preferably the polyester resin, in an amount of at most 60 % by weight (wt%), based on the total weight of the second coating composition. Preferably, the second resin is present in an amount of at most 45 wt%, more preferably at most 40 wt%, even more preferably at most 25 wt% and most preferably at most 20 wt%, and preferably at least 1 wt%, more preferably at least 2 wt%, even more preferably at least 5 wt% and most preferably at least 10 wt%, based on the total weight of the second coating composition.

[0031] The curing catalyst is any catalyst known in the art capable of initiating the curing of the epoxy resin and/or second resin. The curing catalyst is preferably a latent cationic catalyst. In Particular, the latent cationic catalyst is a thermally induced catalyst. Upon activation, the catalyst preferably forms a strong acid, preferably the strong acid has a pKa of below 1. The latent cationic catalyst may comprise a cation and an anion. The cation may be selected from the group comprising ammonium, quaternary ammonium salts, bi- or poly quaternary ammonium compounds, Gemini surfactants, quaternary phosphonium, tertiary sulphonium, onium cations with monovalent substitutions, onium cations with polyvalent substitutions, double onium dications, metal cations, aluminum halides, aluminum alkyls, metallocenes (of Group III metals, Group IV metals, lanthanides and actinides), post-metallocenes (of Group VIII metals, Group IX metals and Group X metals), skipped diene metal compounds, carbocations and carbenium ions. The anion may be selected from hexafluoroanitimonates, hexachloroantimonates, hexaiodoantimonates, hexabromoantimonates, symmetrical and asymmetrical mixtures of halideantimonates, hexafluorophosphates, hexachlorophosphates, hexaiodophosphates, hexabromophosphates, symmetrical and asymmetrical mixtures of halidearsenates, triflic acid salts and tetra-substituted boranes and mixtures thereof. An example of a suitable curing catalyst is quaternary ammonium hexafluoroantimonate.

[0032] In one embodiment of the invention, the second coating composition comprises the curing catalyst in an amount of at most 25 % by weight (wt%), based on the total weight of the second coating composition. Preferably, the curing catalyst is present in an amount of at most 20 wt%, more preferably at most 15 wt%, even more preferably at most 10 wt% and most preferably at most 5 wt%, and preferably at least 0.1 wt%, more preferably at least 0.5 wt%, even more preferably at least 1 wt% and most preferably at least 1.5 wt%, based on the total weight of the second coating composition.

[0033] The curing catalyst may be diluted by a solvent, preferably a reactive solvent as described above, or a mono-epoxide or di-epoxide. In a further embodiment, the curing catalyst may further be combined with a Lewis base. Examples of Lewis bases include amines such as dimethylaminoethanol, triethyl amine, quinuclidine, pyridine and acetonitrile; ethers such as diethyl ether and tetrahydrofuran (THF); ketones such as acetone; acetates such as ethyl acetate, acetamides like dimethyl acetamide; sulfoxides such as dimethyl sulfoxide (DMSO); and tetrahydrothiophene. Preferred Lewis bases are the amines.

[0034] In one embodiment of the invention, the curing catalyst comprises the solvent, preferably the reactive solvent, in an amount of at most 60 % by weight (wt%), based on the total weight of the curing catalyst, solvent and Lewis base. Preferably, the solvent is present in an amount of at most 40 wt%, more preferably at most 30 wt%, even more preferably at most 20 wt% and most preferably at most 10 wt%, and preferably at least 0.1 wt%, more preferably at least 2 wt%, even more preferably at least 3 wt% and most preferably at least 5 wt%, based on the total weight of curing catalyst, solvent and Lewis base.

[0035] In one embodiment of the invention, the curing catalyst comprises the Lewis base in an amount of at most 30 % by weight (wt%), based on the total weight of the curing catalyst, solvent and Lewis base. Preferably, the solvent is present in an amount of at most 25 wt%, more preferably at most 20 wt%, even more preferably at most 15 wt% and most preferably at most 10 wt%, and preferably at least 0.5 wt%, more preferably at least 1 wt%, even more preferably at least 2 wt% and most preferably at least 5 wt%, based on the total weight of curing catalyst, solvent and Lewis base.

[0036] The remaining part of the second coating composition may be comprised of other components commonly used in coating compositions. With the epoxy resin, second resin and curing catalyst, the other components add up to 100 wt% of the total weight of the coating composition.

[0037] The second coating composition may further comprise additives commonly used in coating compositions including pigments and dyes, surfactants, flow controlling agents, thixotropic agents, anti-gassing agents, ultraviolet light stabilizers, adhesion enhancing promoters, waxes, filling agents, matting agents, and defoamers. The additives can be any additive known in the art. Examples of pigments and dyes include metal oxides like titanium dioxide, iron oxide, zinc oxide and chromium oxide; metal hydroxides; metal sulfides, metal sulfates, metal carbonates such as calcium carbonate; carbon black, china clay, phthalo blues and greens, organo reds and other organic dyes. The coating compositions of the invention may increase the color intensity of the pigments and dyes. This may lead to a reduction in the total amount of pigment and/or dye used. Examples of ultraviolet light stabilizers include benzophenone such as hydroxydodecyl benzophenone, 2,4-dihydroxy-3',5'-di-t-butylbenzophenone, 2-hydroxy-4-acryloxyethoxybenzophenone and 2-hydroxy-4-methoxy-2'-carboxybenzophenone. It was found that the coating compositions of the invention may increase the color intensity of the pigments and dyes. This may lead to a reduction in the total amount of pigment and/or dye used.

[0038] The coating composition of the invention may comprise the additives in an amount of at most 30 % by weight (wt%), based on the total weight of the coating composition. Preferably, the additive is present in an amount of at most

25 wt%, more preferably at most 20 wt%, even more preferably at most 15 wt% and most preferably at most 30 wt%, and preferably at least 1 wt%, more preferably at least 2 wt%, even more preferably at least 5 wt% and most preferably at least 10 wt%, based on the total weight of the coating composition.

[0039] The invention also pertains to a coated substrate comprising a substrate and a cured multilayer coating composition applied to at least part of the substrate, the multilayer coating composition being applied in accordance with the process of the invention. In an embodiment of the invention the coated substrate is a food or beverage container. The cured coating composition has all the advantages as described above for the cured coating composition. A further advantage of the cured coating composition is that the volatile organic compounds level is generally very low.

[0040] The substrate of the invention can be any substrate known in the art. The substrate may be porous or non porous. Examples of suitable substrates include metals such as aluminum, aluminum alloys, steel, steel alloys, tin, tin allows, zinc, zinc alloys, chrome and chrome alloys; glass such as fused silica glass, aluminosilicate glass, soda-lime-silica glass, borosilicate glass and lead-oxide glass; ceramics such as porcelain, bone china, alumina, ceria, zirconia, carbides, borides, nitrides and silicides; plastic such as functionalized polyethylene (PE), functionalized polypropylene (PP), polyethylene terephthalate (PET), polyvinyl chloride (PVC) and nylons; and wood. Preferably, the substrate is metal, in particular aluminum.

[0041] In the context of the present application the term "cure" or "cured" refers to the process of hardening of the coating composition by polymerization and/or crosslinking. This curing process can be initiated by exposure to ultraviolet radiation, heat, electron beams and chemical additives. The coating compositions of the invention preferably cure through exposure to heat.

[0042] The invention further pertains to a kit of parts comprising a first coating composition and a second coating composition,

the first coating composition comprising a solvent and a first resin selected from the group consisting of polyol resin, alkyd resin and/or polyacrylate resin, the resin comprises a reactive group, and

the second coating composition comprising an epoxy resin, a second resin having OH and/or carboxylic acid functional groups, and a curing catalyst.

[0043] A further advantage of the cured coating composition is that the volatile organic compounds (VOC) level is generally very low. The VOC level is typically determined using standard method ASTM D3960-05(2013). The amount of VOC in the coating composition of the invention is generally at most 100 g/l, preferably at most 75 g/l, more preferably at most 60 g/l, and most preferably at most 50 g/l.

[0044] Preferably, the first and second coating compositions after curing are substantially free from any one component from the group consisting of bisphenol A, bisphenol F, novoac glycidyl ether, (free) formaldehyde, styrene, neopentyl glycol and silicon oil. More preferably, the first and second coating compositions are completely free from any one component from the group consisting of bisphenol A, bisphenol F, novoac glycidyl ether, (free) formaldehyde, styrene, neopentyl glycol and silicon oil. The terms "substantially free" and "completely free" are as defined above and applied to the indicated substances.

[0045] The invention is exemplified in the following Examples.

Examples

Examples 1 to 5

[0046] Bright 33 cl aluminium cans were provided with 40 to 60 mg of ink by using a roll coater system. The inks are typically used in 2-piece beer and beverage can production. The colours studied, supplied by INX International Ink Co, are black, green, red, blue and yellow. The white ink is purchased produced by DIC.

[0047] The wet inked cans were provided with 40 to 60 mg of top coating using a roll coater. In each case no ink pick up or bleeding was observed (and *vice versa*). Wetting of layer 2 over layer 1 was found to be excellent. The coated cans were heated up in a box oven for 30 seconds at 210 °C. The cans were checked physically on tackiness and cure response. Next the cans were allowed to cure for 3 minutes at 210 °C. As reference, wet inked cans were also coated with the current water-based (pasteurisation-resistant) coating NovoShield 4718E (Comparative Example A). The dry film weight was approximately 50 mg.

[0048] The top coatings were prepared as follows: a 250 ml glass vessel is charged with the compounds described in Table 1 and thoroughly homogenized under stirring. The compositions and their ingredients are shown in Table 1 below.

Table 1: Coating compositions

	Comparative Example A: NovoShield 4718E	Exemple 1	Exemple 2	Exemple 3	Exemple 4	Exemple 5
Compound		**% (m/m)**	**% (m/m)**	**% (m/m)**	**% (m/m)**	**% (m/m)**
(3,4-Epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate		50	50	40	60	49.8
Hydroxyl-containing saturated polyester		30	30	30	30	30
C12-C14 glycidyl ether		10	10	10	8	10
BPA-glycidyl ether: Epikote 828				10		
Butylglycol		8	8	8		8
Quaternary ammonium hexafluoroantimonate (25% in MEK)		1.5		1.5	1.5	1.5
Amine salt of triflic acid			1.5			
Flow additive		0.5	0.5	0.5	0.5	0.5
Adhesion promoter: vinylphosphate dimethylester						0.2

[0049] After cooling down, the coatings were tested on the following properties:

- Adhesion (on substrate and intercoat via tape test with cross cuts)
- Water and water vapour pasteurisation resistance
- Sterilisation resistance
- Scratch/mar resistance (Taber test)
- Curing/cross linking (MEK rubs)
- Color and gloss (Optical)
- Appearance of cured film (Microscope)
- Deformability (stretch and compression)
- Loss-on-drying (150 °C)

[0050] The properties as described above were assessed and the results are shown in the Table below.

Table 2: Performance tests

Performance tests	**Comparative Example A**	**Exemple 1**	**Exemple 2**	**Exemple 3**	**Exemple 4**	**Exemple 5**
Appearance after 30 s, 210 °C	Tack-free	Tack-free	Tack-free	Tack-free	Tack-free	Tack-free
Appearance after 210 s, 210 °C	Tack-free, colourless	Tack-free, colourless	Tack-free, yellowing	Tack-free, colourless	Tack-free, colourless	Tack-free, colourless
Appearance after pasteurization (85 °C, 2 hours)	No blushing or cracking No delamination	No blushing or cracking No delamination	No blushing or cracking, yellowing more pronounced,especially onwhite ink No delamination	No blushing or cracking No delamination	No blushing or cracking No delamination	No blushing or cracking No delamination
Adhesion	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent
Scratch resistance	High	High	High	High	High	High
Gloss	Fair	High	Medium	High	High	High
MEK double rubs	>50	>50	>50	>50	>50	>50
Appearance after sterilization (121 °C, 40 minutes)	Blushing and hydrolysis of coating	No blushing or cracking No delamination	No blushing or cracking, Yellowing. No delamination	No blushing or cracking No delamination	No blushing or cracking No delamination	No blushing or cracking No delamination
Loss-on-drying of formulation upon heating at 150 °C		<3% (m/m)	<3% (m/m)	<3% (m/m)	<3% (m/m)	<3% (m/m)

[0051] The coating compositions of Examples 1 to 5 (in accordance with the present invention) clearly show that wet-on-wet coatings based on cationic thermally cured processes of cyclic epoxy resin combined with hydroxyl- of carbonyl-functionalized polymers (second resin) give excellent results outperforming the conventional coating of Comparative Example A, in particular the multilayer coatings of Examples 1 to 5 show improved resistance under retort-sterilization conditions. It is further noted that the multilayer coatings of Examples 1 to 5 do not contain bisphenol A (BPA), formaldehyde, neopentyl glycol, silicon oils and/or passive solvents, therewith meeting the present environmental and regulatory criteria.

Claims

1. A process for coating of a substrate comprising the steps of:

(a) Applying a first coating composition to a substrate, the first coating comprising a solvent and a first resin selected from the group consisting of polyol resin, alkyd resin and/or polyacrylate resin, the resin comprises a reactive group;
(b) Applying a second coating composition onto the first coating composition, the second coating composition comprising an epoxy resin, a second resin having OH and/or carboxylic acid functional groups, and a curing catalyst; and
(c) Curing the coating compositions to obtain a coated substrate.

2. Process according to claim 1 wherein the first coating composition is substantially free of a crosslinking agent.

3. Process according to any one of claims 1 and 2 wherein the first resin is a polyester.

4. Process according to any one of the preceding claims wherein the reactive group is a hydroxyl or a carboxylic acid

5. Process according to any one of the preceding claims wherein the epoxy resin in the second coating composition is a cycloaliphatic epoxy resin.

6. Process according to any one of the preceding claims wherein the second resin is a polyester.

7. Coated substrate obtainable by the process according to any one of the preceding claims.

8. Coated substrate of claim 7 wherein the substrate is aluminum.

9. A kit of parts comprising a first coating composition and a second coating composition, the first coating composition comprising a solvent and a first resin selected from the group consisting of polyol resin, alkyd resin and/or polyacrylate resin, the resin comprises a reactive group, and
the second coating composition comprising an epoxy resin, a second resin having OH and/or carboxylic acid functional groups, and a curing catalyst.

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EUROPEAN SEARCH REPORT

Application Number
EP 15 24 8041

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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B05D

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
The Hague	7 October 2015	Slembrouck, Igor

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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