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(54) **Flexible multilayer coating**

(57) The present invention pertains novel composite coating formulation for forming a multilayered film coating on a surface of an article, wherein the coating formulation includes a fluid rubber based coating formulation which, when applied to the article, forms a pliable primary coat-

ing, and a polyurethane based coating formulation which, when applied to the article having a cured/dried primary coating on its surface, forms a top coating providing a glossy finish.

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Description

[0001] The present invention relates to a composite coating formulation suitable for coating of a variety of articles to provide a long term surface protection against adverse environmental impacts and for design purposes. The invention further relates to a multilayered film coating comprising a flexible rubber based primary coating layer showing an excellent adherence behavior to the surface to be coated, and a polyurethane based top coating layer having an excellent adherence behavior to the primary coating. On the one hand, the multilayer film coating of the invention does not crack or flake and remains securely bonded to an article, but on the other hand can be easily removed without leaving any residue and without damaging the underlying surface. Further, the present invention relates to methods for coating articles with the multilayer film coating.

[0002] According to the field of application, a wide variety of surface protecting film coatings is formulated and designed having a certain spectrum of desired physicochemical characteristics. For example, rubber based coatings, e.g. used for designing body components of vehicles, exhibit good flexibility properties and can be removed without using tools or solvent containing means, but are less resistant to adverse environmental conditions like road salt or fuels. Multilayered varnish coatings on vehicles provide good toughness and protection properties, however due to their hardness they can be scratched easily. Further, varnish coatings such as metallic paints cannot be removed without using tools or caustic means and therefore cannot be easily replaced by a new coating. Instead, damages like scratches have to be repaired in an expensive manner. Generally, coatings are desired both having a good flexibility, toughness, adhesion, cohesion and providing chemical resistance to the coated article, and last but not least an aesthetic/desired appearance.

[0003] In the car styling industry, an increasing number of end customers desire removable coatings which can be formed on the original varnish/paint coating of a car, e.g. for design purposes and/or value conservation. In particular at authorities, like police authorities, there is a demand to temporarily mark their vehicles with special coatings until they are sorted out. Such coatings must have a sufficient bond strength to the surface to be coated to withstand various environmental conditions a car is subjected to, and at the same time need to be easily removable, e.g. by peeling with hand, without damaging the subjacent surface.

[0004] For car styling and labelling purposes, currently adhesive foils are widely used. Such foils protect the painted surface of vehicle components against stonechips and are available with a mat or glossy finish. Adhesive foils are useful for coating smaller areas of a car surface. However, coating with foils is difficult in handling if larger surfaces or even the entire outer surface of a car is to be coated. Inaccurate application of large sheets mostly results in the formation of blowholes and detachments on edges and joins of body components. Therefore, after some years of bonding to a varnished/painted surface, removing of the foil is often accompanied with chipping or flaking of the subjacent varnish/paint.

[0005] Rubber based coatings have been shown to possess good adhesion properties when applied to painted body components of vehicles and can be easily removed without impacting the integrity of the subjacent coating. Further, such coatings have a durable and good flexibility which makes them suitable for coating deformable parts of a car such as bumpers or interior panels.

[0006] Various compositions (fluid rubber formulations) for car dipping are known in the art and for example disclosed in US4536454. Herein, a composite film coating is described consisting of a primary coating and a top coating. The top coating contains a thermoplastic rubber. According to the authors of US4536454, the composite film coating provides good bond strength and forms an air-tight seal over the surface being coated.

[0007] A drawback of the most rubber based coatings is their sensitivity against various hydrocarbon compounds which can be found fuels such as in benzine, diesel or kerosene, e.g. aromatic substances such as benzene and its derivatives. A further disadvantageous of many rubber based coatings is their mat finish. Various approaches to overcoat the mat rubber coating with a clear coat failed, as the clear coat either did not adhere and/or the resulting composite coating could not be removed anymore without destroying the subjacent coating, as the rubber coating has lost its flexibility properties due to the top clear coat.

[0008] There is a need for new coating compositions to overcome the above mentioned drawbacks of the conventional coatings and to provide coatings both with good adhesion, protection and design properties. Further, there is a need for coating formulations which are suitable for providing such coatings and which can be processed easily and with high safety.

[0009] Therefore it was an object of the present invention to provide a coating composition which can be easily handled and after being applied, e.g. dipped, onto a surface of an article, e.g. exposed surfaces of a vehicle, forms a coating which combines excellent adhesion, long term flexibility over a large temperature range, easy peelability by hand and insensitivity against organic solvents together with a glossy finish.

[0010] Said object was solved by providing a composite coating formulation which, when applied to a surface of an article to be coated, forms a multilayered film coating on the surface, wherein the composite coating formulation comprises, essentially comprises or consists of

- a) a base coat formulation (P) for forming a primary coating, and

b) a top coat formulation (S) for forming a secondary coating.

[0011] The coat formulations described herein, are defined, if not otherwise indicated, on the basis of the respective working formulation, i.e. in a state ready for application. The term "working formulation" further means that the formulation is in the uncured state, preferably in the liquid state.

[0012] The term essentially comprising means that others than the indicated components can be present in the respective formulation. Said other components are present to a minor extent compared to the indicated components, and represent ingredients which are not mandatory to achieve the desired coating characteristics mentioned above.

[0013] The working base coat formulation (P) of the composite coating formulation of the present invention is a rubber based formulation and is preferably a fluid rubber formulation. The rubber based formulation comprises:

ai) a monomer component selected from an acrylate, (hydroxy-)C₁₋₃alkylacrylate, methacrylate, (hydroxy-)C₁₋₃alkylmethacrylate, acrylonitrile, styrene, butadiene, ethylene, butylene, vinylacetate, vinylhalogenid or a polymerisable mixture thereof, and/or

aii) a copolymer component comprising or consisting of 2-8 monomeric building blocks selected from an acrylate, (hydroxy-)C₁₋₃alkylacrylate, methacrylate, (hydroxy-)C₁₋₃alkylmethacrylate, acrylonitrile, styrene, butadiene, ethylene, butylene, vinylacetate and/or a vinylhalogenid component,

aiii) at least one organic solvent, and optionally

aiv) at least one additive selected from surfactants, wetting agents, thickeners, plasticizers, dispersing agents, coalescing agents, fillers and/or defoamers, and optionally

av) at least one pigment, in particular a color pigment,

wherein halogenid means fluoride, chloride, bromide or iodide, preferably chloride.

In order to form the multilayered film coating of the invention, the working base coat formulation (P) is applied at first to form the first/primary coating layer of the multilayered film coating on the surface to be coated. Due to the excellent adhesion properties of the rubber based primary coating on a number of surfaces, it is generally not necessary to pretreat the surface to be coated with a primer. The working base coat formulation (P) can be in the form of a one component composition, i.e. film formation by drying or curing after being applied is performed without adding a hardener/curing agent. Alternatively, the working base coat formulation (P) is formulated as a two-component composition, i.e. to the formulation at least one curing agent is added shortly before its application in order to initiate polymerization and crosslinking of the monomers and/or copolymers.

[0014] The working top coat formulation (S) of the composite coating formulation of the invention comprises or consists of

b1) a binder containing composition (S1), comprising or consisting of

b1i) a binder component selected from a polyester polyol, a hydroxy-functionalized polyacrylate or mixtures thereof,

b1ii) at least one organic solvent, and optionally

b1iii) at least one light-stabilizing/light-protecting/light-absorbing agent, and optionally

b1iv) at least one additive selected from surfactants, wetting agents, thickeners and/or defoamers, and optionally

b1v) at least one agent capable of catalyzing a polymerisation reaction of the binder component with an isocyanate group containing compound, and optionally

b1vi) at least one pigment, in particular a color pigment.

[0015] In order to form the multilayered film coating of the invention, the working top coat formulation (S) is applied to the cured surface of the primary coating to form the secondary/top coating layer of the multilayered film coating on the surface to be coated. Due to the excellent adhesion and flexibility properties over a broad temperature range, the top coating does not peel from the base coating layer. Instead, the resulting layers provide a synergistic effect with respect

to peel behavior and chemical resistance, particularly when applied to painted surfaces.

[0016] In the following, the formulations of the composite coating composition of the invention will be described in detail.

a) Base coat formulation (P)

[0017] The monomer component of ai) of the rubber based base coat formulation (P) can be any monomer, suitable for forming rubber and is preferably derived from alkenes such as styrene (ethenylbenzene), ethylene, butylene, butadiene, in particular 1,3-butadiene; a C₁₋₆(hydroxy)alkyl methacrylate, C₁₋₆(hydroxy)alkyl acrylate, e.g. hydroxyethyl acrylate, hydroxypropyl acrylate, acrylonitrile, vinylchlorid and/or vinylacetate.

[0018] The copolymer component of aii) of the rubber based base coat formulation (P) can be any (block-)copolymer, suitable for forming rubber and is preferably selected from copolymers formed by the monomers indicated for ai), such as a styrene/1,3-butadiene copolymer, a styrene/ethylene/butylene/styrene block copolymer and/or a vinylchloride copolymer. A preferred copolymer is a styrene/1,3-butadiene polymer.

[0019] The amount of the monomer component of ai) and/or the copolymer component of aii) in the formulation (P) may vary over a broad range and is usually in the range of 10-80% (w/w), preferably 20-60% (w/w), more preferably 20-40% (w/w), referred to the amount of the formulation (P) being 100% (w/w).

[0020] The at least one organic solvent of aiii) can be selected from a number of organic solvents, preferably non-polar aprotic solvents. The selection of a suitable solvent/solvent mixture largely depends on the required processing conditions such as curing time, curing temperature, properties of the surface to be coated and the like. Preferably, the at least one organic solvent of aiii) is a non-polar aprotic solvent selected from alkanes, cycloalkanes, aromatic hydrocarbons, carboxylic acid esters, or any combination or mixture thereof. More preferably, the at least one organic solvent of aiii) is C₆₋₁₂alkane, alkylketone, naphtha, benzene, benzene mono- or di-substituted with a C₁₋₆alkyl, C₁₋₆oxoalkyl and/or aryl, C₁₋₆alkyl(glykol)-formiate, C₁₋₆alkyl(glykol)-acetate, C₁₋₆alkyl(glykol)-propionate, C₁₋₆alkyl(glykol)-butyrate, C₁₋₆alkoxy-C₁₋₆alkyl(glykol)-formiate, C₁₋₆alkoxy-C₁₋₆alkyl(glykol)-acetate, C₁₋₆alkoxy-C₁₋₆alkyl(glykol)-propionate, C₁₋₆alkoxy-C₁₋₆alkyl(glykol)-butyrate or any mixture thereof.

[0021] Most preferably, the at least one organic solvent of aiii) is heptane, xylene, toluene, methyl ethyl ketone, C₁₋₃alkylbenzene, naphtha or any combination or mixture thereof.

[0022] The solvent content, preferably the content of the solvent mixture as described above, referred to 100% (w/w) binder containing composition (S1), is between 20-90% (w/w), preferably 30-80% (w/w), more preferably 30-60% (w/w).

[0023] In a preferred embodiment, the solvent of aiii) essentially comprises or consists of xylene. In another preferred embodiment, the solvent of aiii) is a mixture essentially comprising of heptane, xylene, toluene, methyl ethyl ketone, ethyl benzene and naphtha.

[0024] The at least one additive of aiv) can be selected from a wide variety of available substances, depending on the desired application. A suitable agent for av) is Titanium oxide, in particular Titanium (IV) oxid (TiO₂).

[0025] The at least one pigment of av) can be selected from a wide variety of available substances, depending on the desired application. A suitable agent for av) is carbon black.

[0026] In a first embodiment, the rubber base coat formulation (P) comprises:

a) aii) a styrene-1,3-butadiene copolymer,

a) aiii) an organic solvent, selected from heptane, xylene, toluene, methyl ethyl ketone, C₁₋₃alkylbenzene, naphtha or any combination or mixture thereof, and optionally

a) aiv) TiO₂, and optionally

a) av) at least one pigment such as carbon black.

[0027] Preferably, the rubber base coat formulation (P) of said first embodiment comprises:

a) aii) 10-60% (w/w), preferably 20-50% (w/w), more preferably 30-40% (w/w) of the styrene-1,3-butadiene copolymer,

a) aiii) 10-90% (w/w), preferably 20-80% (w/w), more preferably 30-70% (w/w) of the organic solvent selected from xylene, toluene, methyl ethyl ketone, C₁₋₃alkylbenzene, naphtha or any combination or mixture thereof, wherein the solvent is preferably xylene, and optionally

a) aiv) up to 50% (w/w), preferably 20-50% (w/w), more preferably 30-40% (w/w) TiO₂, and optionally

a) av) up to 5% (w/w), up to 3% (w/w), more preferably about 1 % (w/w) carbon black,

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wherein the indicated amounts of aii)-av) refer to the amount of the base coat formulation (P) and wherein the sum of said indicated amounts does not exceed 100%.

[0028] Suitable examples for formulations (P) are indicated in tables 1-3:

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Table 1:

Component	Content in% (w/w) referred to the base coat formulation (P)
Styrene-1,3-butadiene copolymer	68
Xylene	32

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Table 2:

Component	Content in% (w/w) referred to the base coat formulation (P)
Styrene-1,3-butadiene copolymer	30
Xylene	35
TiO ₂	35

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Table 3:

Component	Content in% (w/w) referred to the base coat formulation (P)
Styrene-1,3-butadiene copolymer	23.8-29
Naphtha	33.5-35.6
Xylene	12.5-13.0
Heptane	14.5-15.1
Methyl ethyl ketone	7.5-8.3
Ethyl benzene	3.0-3.2
Carbon black	0-1

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[0029] In a second embodiment, the rubber base coat formulation (P) comprises:

a) a methylmethacrylate copolymer,

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aii) an organic solvent, selected from xylene, toluene, 2-methoxyethanol, 1,1,1-trichloroethane or a mixture thereof,

aiv) fillers such as SiO₂, and optionally

av) at least one pigment, in particular a color pigment.

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[0030] Preferably, the rubber base coat formulation (P) of said second embodiment comprises:

20-50% (w/w) of a thermoplastic resin consisting of 45% (w/w) methylmethacrylate copolymer in a solvent mixture selected from toluene and 2-methoxyethanol,

50

0.2-0.4% (w/w) of a thermoplastic rubber consisting of styrene/ethylene/butylene/styrene block copolymer,

50-70% (w/w) of a solvent selected from xylene, toluene, 2-methoxyethanol, 1,1,1-trichloroethane or a mixture thereof,

55

1-5% (w/w) of SiO₂, and optionally

at least one pigment, in particular a color pigment,

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wherein the indicated amounts of the thermoplastic resin, the thermoplastic rubber, the solvent and SiO₂ refer to the amount of the base coat formulation (P) and wherein the sum of said indicated amounts does not exceed 100%.

[0031] Preferably, the solvent in said second embodiment is a mixture of xylene and 2-methoxyethanol, wherein the ratio of xylene:2-methoxyethanol is greater than 40:1, preferably greater than 50:1, more preferably 54:1.

[0032] Further suitable base coat formulations (P) of the present invention are those which are disclosed as base coat formulations in EP0135998A2. Said base coat formulations are incorporated herein by reference.

[0033] In a third embodiment, the rubber base coat formulation (P) comprises:

65-75% (w/w) of a mixture of monomers including 2-hydroxyethyl acrylate, hydroxypropoyl acrylate, methacrylate and acetonitrile monomers,

1-3% (w/w) of a plasticizer selected from a dialkylphthalate such as dibutylphthalate, preferably a substitute of said phthalate,

5-6.5% (w/w) of a coalescing agent selected from dipropylene glycol methylether, ethylene glycol butylether and mixtures thereof,

2.5-3.5% (w/w) of a polyacrylate thickener selected from an anionic acrylic emulsion copolymer, the emulsion containing about 28% solids and having a specific gravity (25°C) of 1.106 and a pH of between 2.1 and 4;

0.5% (w/w) of an anionic polymer type dispersing agent

0.5-0.75% (w/w) of a petroleum-based defoamer such as 2-octanol

5-10% (w/w) of an anionic wax emulsion containing Carnauba/Microwax blend

2-10% (w/w) pigments, in particular color pigments,

0.4-0.75% (w/w) ammonium hydroxide,

wherein the indicated amounts refer to the amount of the base coat formulation (P) and wherein the sum of said indicated amounts does not exceed 100%.

[0034] Further suitable base coat formulations (P) of the present invention are those which are disclosed in US5256716. Said formulations are incorporated herein by reference.

[0035] In a fourth embodiment, the rubber based base coat formulation (P) comprises:

60-94% (w/w) of a mixture containing a plasticized vinyl chloride copolymer wherein the plasticizer is a dialkylalkyl phthalate such as diethylhexyl phthalate, preferably a substitute of said phthalate and a synthetic latex containing 57% solids, balanced with water,

4-12% (w/w) of a solvent selected from C₁₋₆alkylacetate, preferably butylacetate,

0-4% (w/w) of a coalescing agent selected from an N-C₁₋₆alkylpyrrolidone, preferably N-methylpyrrolidone,

1-5% (w/w) of a plasticizer selected from an C₁₋₆alkylbenzyl phthalate such as butylbenzyl phthalate, preferably a substitute of said phthalate, an optionally

in balance defoamers, solvents, surfactants and thickeners,

wherein the indicated amounts refer to the amount of the base coat formulation (P) and wherein the sum of said indicated amounts does not exceed 100%.

[0036] Further suitable base coat formulations (P) of the present invention are those which are disclosed as base coat formulations in US5192608. Said formulations are incorporated herein by reference.

b) Top coat formulation (S)

b1) The binder containing composition (S1)

5 **[0037]** As mentioned above, the binder component of b1i) is selected from a polyester polyol, hydroxy-functionalized polyacrylate or mixtures thereof, preferably a polyester polyol. A suitable polyester polyol or hydroxy-functionalized polyacrylate has a hydroxyl content of about 2-10%, preferably about 3-8%, more preferably about 3-6% and most preferably about 4-6%. A suitable binder component is a polyester polyol with a hydroxyl content of about 5% as manufactured by Synthopol Chemie Dr. Koch GmbH & Co. KG under the trade designation "Synthoester HD-165". A further
10 suitable binder component is a polyester polyol with a hydroxyl content of about 3.5% as manufactured by Bayer MaterialScience AG under the trade designation "Desmophen® 670 BA".

[0038] The use of a polyester polyol or a hydroxy-functionalized polyacrylate having the indicated hydroxyl content provides a top coating layer having both a durable low-temperature flexibility and weather resistance. According to the area of application, flexibility characteristics can be further adapted by altering the amount of the polyol as well as the
15 amount and/or kind of the curing agent as described below.

[0039] The content of the binder component b1i) in the composition (S1) is between 20-80% (w/w), 30-70% (w/w), preferably 30-60% (w/w), more preferably 40-60% (w/w) and most preferably between 43-53% (w/w), referred to 100% (w/w) binder containing composition (S1). In a preferred embodiment an amount of 40-80% (w/w), more preferably 50-70% (w/w), most preferably 55-65% of a polyester polyol containing composition as manufactured by Synthopol
20 Chemie Dr. Koch GmbH & Co. KG under the trade designation "Synthoester HD-165" is used, having a solid content of 80% (w/w).

[0040] The at least one organic solvent of b1ii) can be selected from a number of organic solvents, preferably non-polar aprotic solvents. The selection of a suitable solvent/solvent mixture largely depends on the required processing conditions such as curing time, curing temperature, properties of the surface to be coated and the like. Preferably, the
25 at least one organic solvent of b1ii) is a non-polar aprotic solvent selected from alkanes, cycloalkanes, aromatic hydrocarbons, carboxylic acid esters, or any combination or mixture thereof. More preferably, the at least one organic solvent of b1ii) is benzene, benzene mono- or di-substituted with a C₁₋₆alkyl, C₁₋₆oxoalkyl and/or aryl, C₁₋₆alkyl(glykol)-formiate, C₁₋₆alkyl(glykol)-acetate, C₁₋₆alkyl(glykol)-propionate, C₁₋₆alkyl(glykol)-butyrate, C₁₋₆alkoxy-C₁₋₆alkyl(glykol)-formiate, C₁₋₆alkoxy-C₁₋₆alkyl(glykol)-acetate, C₁₋₆alkoxy-C₁₋₆alkyl(glykol)-propionate, C₁₋₆alkoxy-C₁₋₆alkyl(glykol)-butyrate or
30 any mixture thereof.

[0041] Most preferably, the at least one organic solvent of b1ii) is xylene, toluene, butyl acetate, propyl acetate, methoxypropyl acetate, butylglykol acetate or any combination or mixture thereof.

[0042] The solvent content, preferably the content of the solvent mixture as described above, referred to 100% (w/w) binder containing composition (S1), is between 20-80% (w/w), 30-70% (w/w), preferably 30-60% (w/w), more preferably
35 40-60% (w/w) and most preferably between 46-56% (w/w).

[0043] In a preferred embodiment, the solvent of b1ii) is a mixture essentially comprising of xylene, toluene, butyl acetate, propyl acetate, methoxypropyl acetate and butylglykol acetate, wherein the content of the solvents, referred to 100% (w/w) binder containing composition (S1), is as follows:

40 5-20% (w/w) xylene,

0-2% (w/w) toluene,

45 20-40% (w/w) butyl acetate,

2-10% (w/w) propyl acetate,

0-2% (w/w) methoxypropyl acetate,

50 0-10% (w/w) butylglykol acetate.

[0044] In a preferred aspect of this embodiment, the solvent content, referred to 100% (w/w) binder containing composition (S1), is 40-60% (w/w), preferably 46-56% (w/w).

[0045] The at least one light-stabilizing/light-protecting/light-absorbing agent of b1iii) of the binder containing composition (S1) can be selected from a wide variety of compounds according to the desired purpose. For coatings of weather exposed surfaces of vehicles usually UV-light absorbers are used to prevent the UV sensitive substances such as color pigments from degeneration. A preferred UV-light absorber is a compound selected from the hydroxyphenylbenzotriazole class such as 2-(2H-benzotriazol-2-yl)-4,6-diterpentyphenol as for example manufactured by BASF SE under the trade

designation "TINUVIN®".

[0046] The amount of at least one light-stabilizing/light-protecting/light-absorbing agent of b1 iii) in the composition can vary according to the field of application. Coatings of the invention adapted for surfaces which are not exposed to sun light, e.g. electric cable or communication cable surfaces do not need to contain a light protection.

[0047] For vehicle coatings, a useful amount of an UV absorbing agent, e.g. selected from a hydroxyphenyl benzotriazole, e.g. as described above, is between 0-2% (w/w), preferably 0.1-1% (w/w), referred to 100% (w/w) binder containing composition (S1). In a preferred embodiment, the UV absorbing agent is 2-(2H-benzotriazol-2-yl)-4,6-diterpentylphenol as for example manufactured by BASF SE under the trade designation "TINUVIN®" in an amount of 0.2-0.4% (w/w).

[0048] The at least one additive of b1 iv) of the binder containing composition (S1) facilitates the processing, i.e. the application of the working top coat formulation (S) e.g. by reducing air bubbles and foaming, and improving flowability of the formulation on the surface to be coated, in particular when applied to the dried/cured primary coating by spray application or brush application techniques.

[0049] Preferably, the at least one additive of b1iv) is a silicone glycol containing compound such as a silicone glycol having a carbinol functionality and/or a poly-diC₁₋₆alkylsiloxan compound optionally modified with a polyester and/or a polyether. More preferably, the at least one additive of b1iv) is a mixture of a silicone glycol having a carbinol functionality and a polyether modified poly-diC₁₋₆alkylsiloxan such as polyether modified poly-dimethylsiloxan.

[0050] The silicone based additives reduce the surface tension and prevents Bénard cell formation while increasing the surface smoothness, and improves the glossiness of the resulting top coating. It confers the working formulation good leveling properties and the resulting coating good slip and mar-resistance properties.

[0051] A suitable polyether modified poly-diC₁₋₆alkylsiloxan is a polyether modified poly-dimethylsiloxan containing composition as for example manufactured by BYK-Chemie GmbH under the trade designation "BYK-331".

[0052] A suitable silicone glycol having a carbinol functionality can be obtained by Dow Corning Corporation under the trade designation "Dow Corning® 11".

[0053] The amount of the at least one additive of b1iv) as described above, referred to 100% (w/w) binder containing composition (S1), is between 0-2% (w/w), 0.01-1% (w/w), 0.01-0.3% (w/w), 0.05-0.25% (w/w), preferably 0.05-0.2% (w/w), more preferably 0.1-0.15% (w/w).

[0054] In a preferred embodiment, the additive of b1 iv) is a mixture of a silicone glycol having a carbinol functionality, e.g. as obtained by Dow Corning Corporation under the trade designation "Dow Corning® 11", and a polyether modified poly-dimethylsiloxan, e.g. as obtained by BYK-Chemie GmbH under the trade designation "BYK-331",

wherein the amount of the polyether modified poly-dimethylsiloxan, referred to 100% (w/w) binder containing composition (S1), is between 0.01-0.2% (w/w), 0.05-0.2% (w/w), preferably 0.01-0.1% (w/w), more preferably 0.04-0.08% (w/w), and the amount of the silicone glycol having a carbinol functionality, referred to 100% (w/w) binder containing composition (S1), is between 0.01-0.2% (w/w), 0.05-0.2% (w/w), preferably 0.01-0.1% (w/w), more preferably 0.05-0.09% (w/w), and wherein

the amount of both additives together, referred to 100% (w/w) binder containing composition (S1), is between 0.02-0.3% (w/w), 0.05-0.25% (w/w), preferably 0.05-0.2% (w/w), more preferably 0.1-0.15% (w/w).

[0055] In a preferred aspect of this embodiment, the amount of the polyether modified poly-dimethylsiloxan, referred to 100% (w/w) binder containing composition (S1), is between 0.04-0.08% (w/w), and the amount of the silicone glycol having a carbinol functionality, referred to 100% (w/w) binder containing composition (S1), is between 0.05-0.09% (w/w),

wherein the amount of both additives together, referred to 100% (w/w) binder containing composition (S1), is between 0.1-0.15% (w/w).

[0056] The at least one agent of b1v) of the binder containing composition (S1), capable of catalyzing a polymerisation reaction of the binder component of b1 i) as described above, with an isocyanate group containing compound can be selected from an C₁₋₆alkyltin, diC₁₋₆alkyltin such as a dibutyltin, and/or a derivate thereof, or any mixture thereof. A suitable agent of b1v) is a mixture of butyltin derived compounds as can be obtained by Rohm and Haas under the trade designation "Metatin™ Katalysator 712 ES". The agent of b1v) can be further selected from tin-free metal carboxylate compounds as manufacture by OMG Borchers GmbH under the trade designation "Borchi® Kat".

[0057] The amount of the agent of b1v) can vary over a broad range, depending on the amount of binder and the field of application. For vehicle coating purposes, the amount of the agent of b1v), referred to 100% (w/w) binder containing composition (S1), is between 0-2% (w/w), 0.01-1% (w/w), preferably 0.01-0.1% (w/w), more preferably 0.02-0.06% (w/w).

[0058] In a first embodiment, the binder containing composition (S1) according to the present invention comprises, essentially comprises or consists of

b1i) 40-60% (w/w) of the binder component which is selected from a polyester polyol, hydroxy-functionalized polyacrylate or mixtures thereof, each as described above,

b1ii) 40-60% (w/w) of the at least one organic solvent as described above,

b1iii) 0-2% (w/w) of the at least one light-stabilizing/light-protecting/light-absorbing agent as described above,

b1iv) 0-2% (w/w) of the at least one additive selected from surfactants, wetting agents, thickeners and/or defoamers as described above,

b1v) 0-2% (w/w) of the at least one agent capable of catalyzing a polymerisation reaction of the binder component with an isocyanate group containing compound as described above, and optionally

b1vi) at least one pigment, in particular a color pigment,

each referred to the amount of the binder containing composition (S1) being 100% (w/w).

[0059] In a preferred aspect of said first embodiment, the amount of the binder component of b1i) is 43-53% (w/w) and/or the amount of the solvent is 46-56% (w/w), each referred to the amount of the binder containing composition (S1) being 100% (w/w).

[0060] In a second embodiment, the binder containing composition (S1) according to the present invention comprises, essentially comprises or consists of

b1i) 40-60% (w/w) of the binder component which is selected from a polyester polyol as described above, wherein the hydroxyl content of the binder component is 2-10%, 3-8%, 3-6% or 4-6%,

b1ii) 40-60% (w/w) of the at least one organic solvent which is selected from benzene, benzene mono- or di-substituted with a C₁₋₆alkyl, C₁₋₆oxoalkyl and/or aryl, C₁₋₆alkyl(glykol)-formiate, C₁₋₆alkyl(glykol)-acetate, C₁₋₆alkyl(glykol)-propionate, C₁₋₆alkyl(glykol)-butyrate, C₁₋₆alkoxy-C₁₋₆alkyl(glykol)-formiate, C₁₋₆alkoxy-C₁₋₆alkyl(glykol)-acetate, C₁₋₆alkoxy-C₁₋₆alkyl(glykol)-propionate, C₁₋₆alkoxy-C₁₋₆alkyl(glykol)-butyrate or any combination thereof. Preferably in this embodiment, the at least one organic solvent of b1ii) in this embodiment is xylene, toluene, butyl acetate, propyl acetate, methoxypropyl acetate, butylglykol acetate or any combination or mixture thereof as described above,

b1iii) 0-2% (w/w) of the at least one light-stabilizing/light-protecting/light-absorbing agent as described above,

b1iv) 0.01-1% (w/w) of the at least one additive which is selected from a silicone glycol optionally having a carbinol functionality, and/or a poly-diC₁₋₆alkylsiloxan optionally modified with a polyester and/or a polyether. Preferably in this embodiment, the at least one additive of b1iv) is a mixture of a silicone glycol having a carbinol functionality and/or a polyether modified poly-dimethylsiloxan as described above,

b1v) 0-2% (w/w) of the at least one agent capable of catalyzing a polymerisation reaction of the binder component with an isocyanate group containing compound, wherein said agent is a dibutyltin compound and/or a tin-free metal carboxylate compound each as described above, and optionally

b1vi) at least one pigment, in particular a color pigment,

each referred to the amount of the binder containing composition (S1), being 100% (w/w).

[0061] In a preferred aspect of said second embodiment, the amount of the binder component of b1 i) is 43-53% (w/w) and/or the amount of the solvent of b1 ii) is 46-56% (w/w), and/or the amount of the additive of b1iv) is 0.02-0.3% (w/w), each referred to the amount of the binder containing composition (S1) being 100% (w/w).

[0062] In a third embodiment, the binder containing composition (S1) according to the present invention comprises, essentially comprises or consists of

b1i) 40-60% (w/w) of the binder component which is selected from a polyester polyol having a hydroxyl content of between 3-6%, wherein the binder component is preferably a polyester polyol as manufactured by Synthopol Chemie Dr. Koch GmbH & Co. KG under the trade designation "Synthoester HD-165" or as manufactured by Bayer MaterialScience AG under the trade designation "Desmophen® 670 BA" each as described above.

b1ii) 40-60% (w/w) of the at least one organic solvent being a mixture essentially comprising or consisting of xylene, toluene, butyl acetate, propyl acetate, methoxypropyl acetate and butylglykol acetate, wherein the content of the solvents, referred to 100% (w/w) binder containing composition (S1), is as follows:

5-20% (w/w) xylene,

0-2% (w/w) toluene,

20-40% (w/w) butyl acetate,

5 2-10% (w/w) propyl acetate,

0-2% (w/w) methoxypropyl acetate,

10 0-10% (w/w) butylglykol acetate,

b1iii) 0-2% (w/w) of the at least one light-stabilizing/light-protecting/light-absorbing agent as described above,

b1iv) 0.02-0.3% (w/w) of the at least one additive which is selected from a mixture of a silicone glycol having a carbinol functionality, e.g. as obtained by Dow Corning Corporation under the trade designation "Dow Corning® 11", and a polyether modified poly-dimethylsiloxan, e.g. as obtained by BYK-Chemie GmbH under the trade designation "BYK-331",

b1v) optionally 0.01-1% (w/w) of the at least one agent capable of catalyzing a polymerisation reaction of the binder component with an isocyanate group containing compound, wherein said agent is a dibutyltin compound and/or a tin-free metal carboxylate compound each as described above, and optionally

b1vi) at least one pigment, in particular a color pigment,

each referred to the amount of the binder containing composition (S1), being 100% (w/w).

25 **[0063]** In a preferred aspect of said third embodiment, the amount of the binder component of b1i) is 43-53% (w/w) and/or the amount of the solvent of b1ii) is 46-56% (w/w), and/or the amount of the additive of b1iv) is 0.1-0.15% (w/w), each referred to the amount of the binder containing composition (S1) being 100% (w/w).

30 **[0064]** Additionally or alternatively to the previous aspect, in a further preferred aspect of said third embodiment, the amount of the polyether modified poly-dimethylsiloxan, referred to 100% (w/w) binder containing composition (S1), is between 0.04-0.08% (w/w), and the amount of the silicone glycol having a carbinol functionality, referred to 100% (w/w) binder containing composition (S1), is between 0.05-0.09% (w/w), wherein the amount of both additives together, referred to 100% (w/w) binder containing composition (S1), is between 0.1-0.15% (w/w).

[0065] In a fourth embodiment, the binder containing composition (S1) according to the present invention comprises or essentially comprises:

35 b1i) 20-80% (w/w), 30-70% (w/w), preferably 30-60% (w/w), more preferably 40-60% (w/w) and most preferably between 43-53% (w/w) of a polyester polyol a hydroxy-functionalized polyacrylate or a mixture thereof, each having a hydroxyl content of about 2-10%, preferably about 3-8%, more preferably about 3-6% and most preferably about 4-6% and

40 b1ii) 20-80% (w/w), 30-70% (w/w), preferably 30-60% (w/w), more preferably 40-60% (w/w) and most preferably between 46-56% (w/w) of an organic solvent mixture containing xylene, toluene, butyl acetate, propyl acetate, methoxypropyl acetate and butylglykol acetate,

45 each referred to 100% (w/w) binder containing composition (S1).

[0066] In one aspect of said fourth embodiment, the content of the solvents of the solvent mixture of b1ii), referred to 100% (w/w) binder containing composition (S1), is as follows:

50 5-20% (w/w) xylene,

0-2% (w/w) toluene,

20-40% (w/w) butyl acetate,

55 2-10% (w/w) propyl acetate,

0-2% (w/w) methoxypropyl acetate,

0-10% (w/w) butylglykol acetate,

[0067] Additionally or alternatively to the previous aspect, in another aspect of said fourth embodiment, the binder containing composition (S1) further comprises b1iv) 0.02-0.3% (w/w), preferably 0.05-0.25% (w/w), more preferably 0.05-0.2% (w/w), most preferably 0.1-0.15% (w/w) of a mixture of a silicone glycol having a carbinol functionality, e.g. as obtained by Dow Corning Corporation under the trade designation "Dow Corning® 11", and a polyether modified polydimethylsiloxan, e.g. as obtained by BYK-Chemie GmbH under the trade designation "BYK-331",

[0068] Additionally or alternatively to anyone of the previous aspects, in still another aspect of said fourth embodiment, the binder containing composition (S1) further comprises b1iv) 0.04-0.08% (w/w) of the polyether modified polydimethylsiloxan e.g. as obtained by BYK-Chemie GmbH under the trade designation "BYK-331", and 0.05-0.09% (w/w) of the silicone glycol having a carbinol functionality, e.g. as obtained by Dow Corning Corporation under the trade designation "Dow Corning® 11", each referred to 100% (w/w) binder containing composition (S1), wherein the amount of both additives together, referred to 100% (w/w) binder containing composition (S1), is between 0.1-0.15% (w/w).

b2) The curing agent containing composition (S2)

[0069] For an appropriate handling of the composite coating formulation of the invention it is preferred, that the top coat formulation (S) is a multi-component, preferably a two-component lacquer/coating formulation further comprising

b2) a curing agent containing composition (S2), comprising or consisting of

b2i) at least one curing agent having at least two isocyanate groups or at least two blocked isocyanate groups wherein the isocyanate groups are blocked by a thermolabile protection group,

b2ii) at least one organic solvent.

[0070] The curing agent of b2i) is preferably selected from a curing agent having at least two (blocked) isocyanate groups, wherein a suitable curing agent is selected from a di-, tri-, tetra-, penta-, hexa-, hepta-, octa-, nona- or decamethylene diisocyanate, toluene-2,4-diisocyanate, diphenylmethane diisocyanate, methylenediphenyl diisocyanate, polymerized diphenylmethane diisocyanate, isophorone diisocyanate, 4,4'-diisocyanato dicyclohexylmethane or a prepolymer derived from said diisocyanate compounds, or any mixture thereof, wherein the aliphatic diisocyanate compounds are especially preferred in formulations applied for the coating of weather exposed surfaces.

[0071] Most preferably, the curing agent contains an isocyanate group containing prepolymer, e.g. as obtainable by BASF AG under the trade designation Basonat® HB 275 B.

[0072] The at least one organic solvent of b2ii) can be selected from a wide number of non-polar aprotic solvents, e.g. solvents selected from aromatic hydrocarbons, carboxylic acid esters, or any mixture thereof. Preferably, the at least one organic solvent of b2ii) is benzene, benzene mono- or di-substituted with a C₁₋₆alkyl, C₁₋₆oxoalkyl and/or aryl, C₁₆alkyl(glykol)-formiate, C₁₋₆alkyl(glykol)-acetate, C₁₋₆alkyl(glykol)-propionate, C₁₆alkyl(glykol)-butyrate, C₁₋₆alkoxy-C₁₋₆alkyl(glykol)-formiate, C₁₋₆alkoxy-C₁₋₆alkyl(glykol)-acetate, C₁₋₆alkoxy-C₁₋₆alkyl(glykol)-propionate, C₁₋₆alkoxy-C₁₋₆alkyl(glykol)-butyrate or any mixture thereof. Xylene, toluene, Butyl acetate, butyl acetate, propyl acetate, methoxypropyl acetate, butylglykol acetate or any mixture thereof is preferred. More preferred is a mixture of Butyl acetate and methoxypropyl acetate.

[0073] The content of the curing agent component b2i) may vary depending on the intended application and is between 5-80% (w/w), 10-70% (w/w), preferably 20-60% (w/w), more preferably 40-60% (w/w), most preferably 48-52% (w/w), referred to 100% (w/w) of the curing agent containing composition (S2).

[0074] When formulated as a two-component formulation, the working top coat formulation (S) is obtained by mixing compositions (S1) and (S2) immediately before application. The mixing ratio is selected to achieve a degree of cross linking of the binder component b1 i) is between 60-200%, 80-200%, preferably 90-200%, more preferably 100%-200%, most preferably 100%-160%, especially 100%-120%. This can be achieved by mixing both compositions together, wherein the volume ratio of S1:S2 is up to 20:1, e.g. between 20:1 to 1:20, 20:1 to 1:2 or 1:1, 10:1 to 1:10, 10:1 to 1:2 or 1:1, 4:1 to 1:4, 4:1 to 1:2, preferably 4:1 to 1:1, more preferably 3:1 to 1:1, most preferably 2:1.

[0075] A preferred two-component top coat working formulation (S) ready for application contains or consists of

b1) a binder containing composition (S1) as described above as the first, second, third or fourth embodiment of the composition (S1) including their aspects, and

b2) a curing agent containing composition (S2) as defined above, containing, referred to 100% (w/w) composition (S2), 40-60% (w/w), preferably 48-52% (w/w) of an isocyanate group containing curing agent as defined above,

preferably an isocyanate group containing prepolymer such as obtainable by BASF AG under the trade designation Basonat® HB 275 B", the rest being the at least one organic solvent of b2ii) as described above, preferably a mixture of butyl acetate and methoxypropyl acetate,

5 wherein the mixing ratio of S1:S2 is selected to achieve a degree of cross linking of the binder component b1i) of between 90-200%.

[0076] A preferred composite coating formulation of the invention comprises or consists of the following formulations:

10 a) a base coat formulation (P) as described above as the first, second, or third embodiment, preferably the first embodiment of the coating formulation (P),

b) a two-component top coat formulation (S) containing or consisting of

15 b1) a binder containing composition (S1) as described above as the first, preferably the second, more preferably the third or fourth embodiment of the compositions S1 including their aspects, and

20 b2) a curing agent containing composition (S2) as defined above, containing 40-60% (w/w), preferably 48-52% (w/w) of an isocyanate group containing curing agent as defined above, preferably an isocyanate group containing prepolymer such as obtainable by BASF AG under the trade designation Basonat® HB 275 B", the rest being the at least one organic solvent of b2ii) as described above, preferably a mixture of butyl acetate and methoxypropyl acetate,

25 wherein the mixing ratio of S1:S2 is selected to achieve a degree of cross linking of the binder component b1 i) of between 90-200%.

[0077] In said preferred composite coating formulation, the combination of a base coat formulation (P) as described above as the first embodiment of the coating formulation (P), in particular as defined in Tables 1-3 herein, and a two-component top coat formulation (S) containing a binder containing composition (S1) as described above as the third or fourth embodiment of the compositions S1 including their aspects, is especially preferred.

30 **[0078]** A top coat formulation (S) as defined above can be used to form a top coating with a glossy finish. In a preferred embodiment, the top coat formulation (S) does not contain a coloring agent/pigment, allowing the formation of a transparent coat having only limited opacity.

[0079] A further aspect of the present invention is a composite coating formulation comprising, essentially comprising of consisting of

35 a) a base coat formulation (P) for forming a primary coating,
 b) a top coat formulation (S) for forming a secondary coating, and
 c) a color coat formulation (I) for forming an intermediate coating, the working color coat formulation (I) comprising at least one color pigment,

40 wherein the a base coat formulation (P) and the top coat formulation (S) are as described above.

[0080] The working color coat formulation (I) can be selected from a wide variety of pigmented lacquer/varnish formulations. A suitable color coat formulation (I) is a pigmented lacquer/varnish composition used for forming a base coat in car industry. Preferably, a suitable color coat formulation (I) is a pigmented alkyd resin containing or a nitro pyroxylin containing lacquer/varnish composition.

45 **[0081]** A composite coating formulation of the invention comprising or consisting of a base coat formulation (P), a top coat formulation (S) and a color coat formulation (I), is suitable for providing a tri-layered film coating, wherein, if the working formulations are applied in the sequence (P), (I), (S), the primary coating/layer directly adheres to the surface to be coated, the intermediate coating/layer directly adheres to the first coating/layer, and the secondary coating/layer directly adheres to the intermediate coating/layer.

50 **[0082]** In a composite coating formulation of the invention comprising or consisting of a base coat formulation (P), a top coat formulation (S) and a color coat formulation (I), only the color coat formulation (I) may contain color pigments, and the base coat formulation (P) and the top coat formulation (S) are preferably free of pigments. This has the advantage that the working formulations (P) and (S) respectively, can be formulated as standard formulations and any desired color/color effect is provided by the color coat formulation (I) only. This means that the working formulations (P) and (S) need not be adapted for each desired color; instead the working formulations (P) and (S) respectively each can be identical in applications in which different colors/color effects are provided.

55 **[0083]** Surprisingly it was found that the profile of desired characteristics of the resulting primary and secondary coating

in the multilayer film coating of the invention, such as long term flexibility over a large temperature range, peeling behavior when applied onto varnish coated surfaces and chemical resistance, is not adversely affected by the intermediate color coating layer.

[0084] A further aspect of the present invention is a coating formulation (S) for forming a coating, preferably a top coating on a surface of an article, the coating formulation (S) contains or consists of

b1) a binder containing composition (S1) as described above as the second, third or fourth, preferably third or fourth embodiment of the compositions S1 including their aspects, and optionally

b2) a curing agent containing composition (S2) as defined above, containing 40-60% (w/w), preferably 48-52% (w/w) of an isocyanate group containing curing agent as defined above, preferably an isocyanate group containing prepolymer such as obtainable by BASF AG under the trade designation Basonat® HB 275 B", the rest being the at least one organic solvent of b2ii) as described above, preferably a mixture of butyl acetate and methoxypropyl acetate,

wherein the mixing ratio of S1:S2 is selected to achieve a degree of cross linking of the binder component b1 i) of between 90-200%.

[0085] The formulation (S) optionally further contains rust-inhibiting agents.

[0086] The coating formulation (S) of the invention is suitable for providing a large number of different articles/surfaces with a flexible, glossy coating and an air-tight seal, including articles/surfaces which are plastically and/or elastically deformable. The working/uncured coating formulation (S) of the present invention is reasonably viscous and highly adherent to a surface upon which it is applied, properties which it retains while in the liquid state. In particular, the working/uncured coating formulation (S) of the present invention is highly adherent to the dried/cured base coating formulation (P) as herein described. Surprisingly, it was found out, the said coating formulation (S) cures uniformly on a variety of surfaces and in particular on a primary coating layer as obtained by or obtainable by applying the base coat formulation (P) as herein described. Further, a coating using the formulation (S) is created without premature surface curing or skinning which would otherwise impede the loss of excess solvent from an uncured core.

[0087] The coating formulation (S) has good filling characteristics. Therefore the coating formulation (S) can be used to repair smaller surface defects such as defects in paint work, e.g. on vehicle components.

Further, the coating formulation (S) can be used to provide surfaces with a glossy finish. Therefore, the invention further relates to a method of providing a glossy finish/clear coat on a surface of an article, preferably on a mat surface, e.g. a surface coated with a rubber coat such as a primary coating as described herein. The process comprises the step of applying the working formulation (S) to the surface to be coated and allowing the formation of the coating, e.g. by drying/curing under ambient conditions.

The coating formulation (S) provides a coating with high toughness and resistance against various chemical and mechanical impacts. Therefore, the invention further relates to a method to protect a surface of an article, preferably a metallic surface, a painted surface, a chromed surface or a surface coated with a rubber coat such as a primary coating as described herein against chemical destruction and/or mechanical destruction. The process comprises the step of applying the working formulation (S) as defined above to the surface to be coated and allowing the formation of the coating, e.g. by drying/curing under ambient conditions.

[0088] The present invention further relates to a method for preparing a multilayered, preferably an at least two-layered film coating on a surface of an article, wherein the composite coating formulation as described above is used, comprising the base coat formulation (P) for forming the primary coating and the top coat formulation (S) for forming the secondary coating. The method comprises the following steps:

(i) applying the working base coat formulation (P) to the surface of an article to be coated, wherein the base coat formulation (P) is as defined above, preferably as described above as the first, second, or third embodiment of the coating formulation (P), preferably the first embodiment of the coating formulation (P),

(ii) allowing formation of the primary coating,

(iii) applying the top coat formulation (S) on the primary coating obtained by step (ii), wherein the top coat formulation is as defined above, preferably as described above as a two-component top coat formulation (S) containing or consisting of

b1) a binder containing composition (S1) as described above as the first, preferably the second, more preferably the third or fourth embodiment of the compositions S1 including their aspects, and

b2) a curing agent containing composition (S2) as defined above, containing 40-60% (w/w), preferably 48-52% (w/w) of an isocyanate group containing curing agent as defined above, preferably an isocyanate group containing prepolymer such as obtainable by BASF AG under the trade designation Basonat® HB 275 B", the rest being the at least one organic solvent of b2ii) as described above, preferably a mixture of butyl acetate and

methoxypropyl acetate,

wherein the mixing ratio of S1:S2 is selected to achieve a degree of cross linking of the binder component b1i) of between 90-200%,

(iv) allowing formation of the secondary coating,

wherein the steps (i)-(iv) are performed in the indicated sequence.

[0089] The present invention further relates to a method for preparing a multilayered, preferably an at least tri-layered film coating on a surface of an article, wherein the composite coating formulation as described above is used, comprising the base coat formulation (P) for forming the primary coating, the top coat formulation (S) for forming the secondary coating, and the color coat formulation (I) for forming the intermediate coating. The method comprises the following steps:

(i) applying the working base coat formulation (P) to the surface of an article to be coated, wherein the base coat formulation (P) is as defined above, preferably as described above as the first, second, or third embodiment of the coating formulation (P), preferably the first embodiment of the coating formulation (P),

(ii) allowing formation of the primary coating,

(iii) applying the working color coat formulation (I) on the primary coating obtained by step (ii),

(iv) allowing formation of the intermediate coating,

(v) applying the top coat formulation (S) on the intermediate coating obtained by step (iv), wherein the top coat formulation is as defined above, preferably as described above as a two-component top coat formulation (S) containing or consisting of

b1) a binder containing composition (S1) as described above as the first, preferably the second, more preferably the third or fourth embodiment of the compositions S1 including their aspects, and

b2) a curing agent containing composition (S2) as defined above, containing 40-60% (w/w), preferably 48-52% (w/w) of an isocyanate group containing curing agent as defined above, preferably an isocyanate group containing prepolymer such as obtainable by BASF AG under the trade designation Basonat® HB 275 B", the rest being the at least one organic solvent of b2ii) as described above, preferably a mixture of butyl acetate and methoxypropyl acetate,

wherein the mixing ratio of S1:S2 is selected to achieve a degree of cross linking of the binder component b1i) of between 90-200%,

(vi) allowing formation of the secondary coating,

wherein the steps (i)-(vi) are performed in the indicated sequence.

[0090] The method of the invention also considers embodiments wherein the method steps which provide the primary coating (steps (i) and (ii)) are performed at least two times before performing step (iii). This has the advantage, that a relatively thick base coating can be obtained, which is for example desired in applications where a filling and levelling of irregularities/unevenness like scratches on a surface, e.g. a painted surface to be coated is required.

[0091] The method of the invention also considers embodiments wherein the method steps which provide the secondary coating (steps (iii) and (iv), or (v) and (vi) respectively) are performed at least two times in order to obtain a relatively thick top coating layer. This allows the formation of glossy coating showing a strong resistance behavior against mechanical stresses, e.g. abrasive impacts when polishing the coated surface and chemical stresses, e.g. when contacted with fuels and lubricants.

[0092] The method of the invention also considers embodiments wherein the method steps which provide the intermediate coating (steps (iii) and (iv) of the method for preparing an at least tri-layered film coating) are performed at least two times before performing step (v) in order to obtain a relatively thick color coating. This allows the formation of colored surfaces with any desired color effects.

[0093] The method steps (ii) and (iv), or (ii), (iv) and (vi) respectively, relate to the film forming reaction steps after the respective working coat formulation has been applied. Said film forming reaction steps include the exposure of the applied formulation to conditions which allow drying, i.e. evaporating the solvents contained in the applied formulation, and/or curing, i.e. formation of cross linked binder polymers. Preferably, said steps are performed under ambient conditions. To enhance film formation, said steps can be performed at a temperature between 30-100°C, preferably between 40-80°C.

[0094] The method steps (i) and (iii), or (i), (iii) and (v) respectively, relate to the application of the working coat formulation. Said applications steps can be performed by a variety of methods known in the art. Preferably, the application steps are performed by dipping, e.g. single or multiple dipping operations, spray application, brush application and/or roller application.

[0095] The method of the invention provides a multilayered film coating exhibiting a unique property profile, which is desired in a wide variety of coating applications, especially for car styling and paint-repair purposes.

[0096] The method of the invention can be applied *inter alia* to provide an article with a new styling, to provide resistance to a surface of an article against adverse environmental impacts and to repair defects on a surface, e.g. defects in paint work.

[0097] Therefore, the invention also relates to methods for providing to a surface of an article, preferably a metallic surface or a painted surface,

- Resistance/protection against adverse environmental impacts such as chemical and/or mechanical destruction,
- A new styling,
- A glossy finish, and to

a method for

- Repairing defects on a surface of an article, e.g. defects in paint work,

wherein both methods comprising the steps of

- (i) applying the working base coat formulation (P) and the working coating formulation (S) or the working coating formulation (S) to a surface of an article according to anyone of the above mentioned methods,
- (ii) allowing formation of the primary coating and the top coating or the top coating according to anyone of the above mentioned methods.

[0098] The present invention further relates to a multilayered film coating obtained by or obtainable by a method as described above using the composite coating formulation of the invention as described above.

[0099] The multilayered film coating includes a primary film coating and a secondary/top film coating. In addition to the primary film coating and the secondary/top film, the multilayered film coating optionally further includes an intermediate film coating, which is arranged between the primary film coating and the secondary/top film, and preferably provides the coloring layer.

[0100] The primary film coating directly adheres to the surface to be coated. The intermediate film coating directly adheres to the primary film coating. The secondary/top film coating directly adheres to the primary film coating if no intermediate layer is present, or to the intermediate film layer.

[0101] In a preferred embodiment, the multilayered film coating of the invention is obtained by or obtainable by a method as described above using the composite coating formulation of the invention which comprises or consists of the following formulations:

a) a base coat formulation (P) as described above as the first, second, or third embodiment of the coating formulation (P), preferably the first embodiment of the coating formulation (P),

b) a two-component top coat formulation (S) containing or consisting of

b1) a binder containing composition (S1) as described above as the first, preferably the second, more preferably the third or fourth embodiment of the compositions S1 including their aspects, and

b2) a curing agent containing composition (S2) as defined above, containing 40-60% (w/w), preferably 48-52% (w/w) of an isocyanate group containing curing agent as defined above, preferably an isocyanate group containing prepolymer such as obtainable by BASF AG under the trade designation Basonat® HB 275 B", the rest being the at least one organic solvent of b2ii) as described above, preferably a mixture of butyl acetate and methoxypropyl acetate,

wherein the mixing ratio of S1:S2 is selected to achieve a degree of cross linking of the binder component b1 i) of between 90-200%.

[0102] The multilayered film coating of the invention as described above possesses an outstanding property profile.

[0103] The primary rubber based coating of the multilayered film coating of the invention, which is directly adhered to the surface shows on a wide variety of surfaces, a durable, in particular edge durable, adherence and is pliable and flexible over a wide temperature range, such as a temperature range, a vehicle, including cars, airplanes, boats and the like, is subjected to. The primary coating film possesses sufficiently high cohesive strength so as to render the dried film

extremely tough and durable, and with sufficiently high adhesive strength so as to render the coating resistant to premature failure or release.

5 [0104] The secondary/top coating of the multilayered film coating of the invention is directly and firmly bonded to the cured/formed primary coating layer. Due to the uniformly curing/drying of the previously applied top coat formulation (S) as described herein, no bubble formation occurs between the top coat layer and the subjacent primary coating or intermediate coating. Instead, the top coating layer provides the primary coating with slip and toughness properties. It is not possible to separate the top coating layer from the subjacent primary coat or intermediate coat by peeling or skimming. Due to its outstanding cohesive strength, the top coating layer also enhances the weatherproofness of the overall coating as well as that of the coated article. The secondary/top coating layer does not impair the pliability and flexibility characteristics of the primary coating and does not decrease its adhesive/peel strength. Further, the flexibility of the primary coating does not impair the toughness, glossy finish and the high peel strength of the top coating layer. Instead, it could be observed that each of the layers in the multilayered film coating of the invention retains its good physical properties. Moreover, when applied to a painted/varnished surface of a vehicle component, the adherence of the primary coating to the coated surface is even improved if the primary coating layer itself is coated with the top coating formulation. Thus, with respect to the desired characteristics of the single coating layers, the combination of the primary coating and the secondary coating does not only lead to an addition of the respective properties; instead the combination of the coatings in the multilayered film coating of the invention generates a synergistic effect.

10 [0105] The multilayered film coating of the invention, or the composite coating formulation, respectively is suitable to coat plastically or elastically deformable surfaces. This includes deformable components on vehicles, electric cables, communication cables, rubber hoses, rubberized tool handles, plastic bottles and the like.

15 [0106] With the multilayered film coating of the invention it is now possible to provide a durable surface coating for a number of surfaces, the coating having/providing

- 25 - Balanced bonding properties to provide on the one hand a long term air-tight seal, protection against mechanical and weather conditions, and on the other hand to allow removing of the coating by easy peeling with hand;
- Pliability and flexibility over a wide range of temperatures;
- Protection against chemical destruction and adverse environmental conditions, in particular against organic solvents, e.g. fuels; road salt, salt water, acids, alkali, surfactants and moisture
- 30 - Corrosion resistance for metals, in particular ferrous metals
- Protection against mechanical impacts like those causing stone-chipping, scratches and the like,
- Toughness to withstand adverse environmental impacts, e.g. impacts occurring during use of the coated article, e.g. those occurring in car washes.
- Durable glossy finish with good slip and haptics properties which are desired, e.g. in the field of car styling,

35 [0107] The multilayered film coating of the invention is further characterized in that it is peelable by hand wherein integrity of the film coating layers to each other is not destroyed when peeled off by hand under ambient conditions.

[0108] In contrast to other rubber based composite film coatings known in the art, removing the multilayered film coating of the invention by hand does not result in the formation of small pieces of removed coating material. Instead coating sheets can be obtained, having a size of 0.1 square meter or more, preferably 1 square meter or more, more preferably 2 square meter or more, if the multilayered film coating of the invention is peeled by hand under ambient conditions from a variety of surfaces, in particular painted surfaces of vehicle components. Even for a layperson it is easy to peel of the film by hand getting film sheets of even more than 2, 3 or 4 square meter. If removed from the surface, the layers of the multilayered film coating of the invention do not separate from each other, i.e. the layers remain attached to each other during peeling.

40 [0109] Further, the multilayered film coating of the invention can be removed by peeling without damaging the underlined surface structure, e.g. an original lacquer/finish/paint.

[0110] These adhesive properties/peeling characteristics allow the complete, i.e. residue-free removal of the multilayered film coating in a single operation step.

45 [0111] Therefore, the present invention further relates to a peelable multilayered surface coating obtained by or obtainable by a method as defined above, the coating having a property profile as described above.

[0112] The present invention further relates to an article coated with the composite coating formulation according to a method as described herein or with the coating formulation (S) each of which is as defined herein.

[0113] The present invention further relates to an article having a surface coat containing or consisting of a multilayered film coating, wherein the film coating is obtained by or obtainable by a method as described herein

50 [0114] As mentioned above, the composite coating formulation forms a multilayered film coating with good adherence properties on a wide variety of different surfaces. Preferably, the article or the surface to be coated is a painted/varnished or unpainted/unvarnished metal, a metal alloy and/or a plastic article/surface. A preferred article in connection with the present invention is a body component of a vehicle, preferably a painted or chrome plated component of a vehicle, e.g.

of a motorized vehicle such as a car, a watercraft, an aircraft or a motorbike.

[0115] A further preferred article in connection with the present invention is selected from an electric cable, a communication cable, a rubber hose or a tool handle.

[0116] A further preferred article in connection with the present invention is selected from furniture, sporting goods such as surfboards and car interior components.

[0117] A further preferred article in connection with the present invention is selected from swimming pool articles, window frames, front doors and garage doors.

[0118] A further preferred article in connection with the present invention is selected from pipelines, e.g. oil pipelines.

[0119] The invention further relates to a container such as an aerosol can, containing a binder containing composition (S1) and optionally a curing agent containing composition (S2) of the working top coat formulation (S) of the invention, wherein the composition (S1) is separated from composition (S2).

EXAMPLES

[0120] The following examples shall illustrate some aspects of the present invention and do not limit any subject matter of the invention.

Example 1: Top coat formulation (S)

[0121] Working binder containing composition (S1)

(i) 48% (w/w) binder component which is selected from a polyester polyol having a hydroxyl content of between about 5%,

(ii) 51-52% (w/w) of a mixture of organic solvents essentially comprising of xylene, toluene, butyl acetate, propyl acetate, methoxypropyl acetate and butylglykol acetate,

(iii) 0.3% (w/w) of a light-stabilizing/light-protecting/light-absorbing agent selected from 2-(2H-benzotriazol-2-yl)-4,6-diterpentyphenol.

(iv) 0.12% (w/w) of an additive which is selected from a mixture of a silicone glycol having a carbinol functionality, and a polyether modified poly-dimethylsiloxan,

(v) 0.04% (w/w) of an agent capable of catalyzing a polymerisation reaction of the binder component with an isocyanate group containing compound, wherein said agent is a mixture of butyltin derived compounds,

each referred to the amount of the binder containing composition (S1), being 100% (w/w).

Working curing agent containing composition (S2)

[0122]

(i) 50% (w/w) of an isocyanate group containing prepolymer,

(ii) 50% (w/w) of a mixture essentially comprising of Butyl acetate and methoxypropyl acetate,

each referred to the amount of the curing agent containing composition (S2), being 100% (w/w).

[0123] A working top coat formulation (S) of the composite coating formulation of the invention is prepared as follows:

In order to prepare 100g of composition (S1), 60g of a polyester polyol composition as manufactured by Synthopol Chemie Dr. Koch GmbH & Co. KG under the trade designation "Synthoester HD-165" having 80% (w/w) solids in xylene, are mixed with 31 g butyl acetate, 5g propyl acetate and 2g butylglykol acetate at room temperature (18-25°C). To the obtained mixture, 0.3g 2-(2H-benzotriazol-2-yl)-4,6-diterpentyphenol is added, followed by the addition of 0.7g of a silicone glycol containing composition obtained by Dow Corning Corporation under the trade designation "Dow Corning® 11" having 10% (w/w) solids in toluene, and 0.6g of a polyether modified poly-dimethylsiloxan containing composition, obtained by BYK-Chemie GmbH under the trade designation "BYK-331" having 10% (w/w) solids in methoxypropyl acetate.

[0124] To the obtained mixture, the mixture of butyltin derived compounds obtainable by Rohm and Haas under the trade designation "Metatin™ Katalysator 712 ES" is added under continuous stirring until a homogenous solution (S1) is obtained.

[0125] In order to prepare 100g composition (S2), 66.7g of a 75% solution of an isocyanate group containing prepolymer in butyl acetate, obtainable by BASF AG under the trade designation Basonat® HB 275 B", is mixed at room temperature with 8.3g butyl acetate and 25g methoxypropyl acetate.

[0126] Shortly before application, 100g of composition (S1) is mixed with 50g of composition (S2) to give 150g of the working top coat formulation (S).

Example 2: Preparation of the multilayered film coating

[0127] A base coat formulation (P) as defined in anyone of the Tables 1-3 herein is applied, e.g. by spraying or dipping to a surface to be coated. The base coat formulation is allowed to dry at a temperature between 10-80°C for 10min-72hours until the applied formulation is hardened thereby obtaining the primary coating. Subsequently, a top coat formulation (S) as prepared in Example 1 herein is applied to the primary coating, e.g. by spraying or dipping. The top coat formulation is allowed to cure at a temperature between 10-80°C for 10min-72hours until the applied formulation is hardened thereby obtaining the secondary coating.

[0128] The following items are part of the description of the present invention:

ITEMS

[0129]

1. A composite coating formulation for forming a multilayered film coating on a surface of an article, the formulation comprising or consisting of

- c) a base coat formulation (P) for forming a primary coating
- d) a top coat formulation (S) for forming a secondary coating,

wherein the working base coat formulation (P) is a fluid rubber formulation comprising or consisting of

ai) a monomer component selected from an acrylate, (hydroxy-)C₁₋₃alkylacrylate, methacrylate, (hydroxy-)C₁₋₃alkylmethacrylate, acrylonitrile, styrene, butadiene, ethylene, butylene, vinylacetate, vinylhalogenid or a polymerisable mixture thereof, and/or

a ii) a copolymer component comprising or consisting of 2-8 monomeric building blocks selected from an acrylate, (hydroxy-)C₁₋₃alkylacrylate, methacrylate, (hydroxy-)C₁₋₃alkylmethacrylate, acrylonitrile, styrene, butadiene, ethylene, butylene, vinylacetate and/or a vinylhalogenid component, wherein halogenid means chloride, bromide, fluoride or iodide,

a iii) at least one organic solvent, and optionally

a iv) at least one additive selected from surfactants, wetting agents, thickeners, plasticizers, dispersing agents, coalescing agents, fillers and/or defoamers, and optionally

a v) at least one pigment,

wherein the working top coat formulation (S) comprises or consists of

b1) a binder containing composition (S1), comprising or consisting of

b1i) a binder component selected from a polyester polyol, a hydroxy-functionalized polyacrylate or mixtures thereof,

b1ii) at least one organic solvent, and optionally

b1iii) at least one light-stabilizing/light-protecting/light-absorbing agent, and optionally

b1iv) at least one additive selected from surfactants, wetting agents, thickeners and/or defoamers, and optionally

b1v) at least one agent capable of catalyzing a polymerisation reaction of the binder component with an isocyanate group containing compound, and optionally

b1vi) at least one pigment.

2. The composite coating formulation of item 1, wherein the monomer component of ai) is styrene, butadiene, C₁₋₃methacrylate, hydroxyethyl acrylate, acrylonitrile, hydroxypropyl acrylate, vinylchlorid and/or vinylacetate.

3. The composite coating formulation of item 1 or 2 wherein the copolymer component of aii) is a styrene/1,3-butadiene copolymer, a styrene/ethylene/butylene/styrene block copolymer and/or a vinylchloride copolymer.

4. The composite coating formulation of anyone of the preceding items, wherein the hydroxyl content of the binder component of b1 i) is 2-10%, 3-8% or 3-6%.

5. The composite coating formulation of anyone of the preceding items, wherein the at least one organic solvent of b1ii) is a non-polar aprotic solvent selected from aromatic hydrocarbons, carboxylic acid esters, or any mixtures thereof.

6. The composite coating formulation of anyone of the preceding items, wherein the at least one organic solvent of b1ii) is benzene, benzene mono- or di-substituted with a C₁₋₆alkyl, C₁₋₆oxoalkyl and/or aryl, C₁₋₆alkyl(glykol) formiate, C₁₋₆alkyl(glykol) acetate, C₁₋₆alkyl(glykol) propionate, C₁₋₆alkyl(glykol) butyrate, C₁₋₆alkoxy-C₁₋₆alkyl(glykol) formiate, C₁₋₆alkoxy-C₁₋₆alkyl(glykol)-acetate, C₁₋₆alkoxy-C₁₋₆alkyl(glykol) propionate, C₁₋₆alkoxy-C₁₋₆alkyl(glykol) butyrate or any mixture thereof.

7. The composite coating formulation of anyone of the preceding items, wherein the at least one organic solvent of b1ii) is xylene, toluene, butyl acetate, propyl acetate, methoxypropyl acetate, butylglykol acetate or any mixture thereof.

8. The composite coating formulation of anyone of the preceding items, wherein the at least one light- stabilizing/light-protecting/light-absorbing agent of b1iii) is an UV-light absorber of the hydroxyphenylbenzotriazole class.

9. The composite coating formulation of anyone of the preceding items, wherein the at least one additive of b1iv) is a silicone glycol and/or a poly-diC₁₋₆alkylsiloxan optionally modified with a polyester and/or a polyether.

10. The composite coating formulation of anyone of the preceding items, wherein the at least one additive of b1iv) is a mixture of a silicone glycol having a carbinol functionality and/or a polyether modified poly-dimethylsiloxan.

11. The composite coating formulation of anyone of the preceding items, wherein the at least one agent of b1v) capable of catalyzing a polymerisation reaction of the binder component with an isocyanate group containing compound is a dibutyltin compound and/or a tin-free carboxylate compound.

12. The composite coating formulation of anyone of the preceding items, wherein the content of the binder component b1i) is 20-80% (w/w), 30-70% (w/w), 30-60% (w/w) or 40-60% (w/w), referred to 100% (w/w) binder containing composition (S1).

13. The composite coating formulation of anyone of the preceding items, wherein the binder containing composition (S1), comprises or consists of

b1i) 40-60% (w/w) of the binder component selected from a polyester polyol, a hydroxy-functionalized polyacrylate or mixtures thereof,

b1ii) 40-60% (w/w) of the at least one organic solvent,

b1iii) 0-2% (w/w) of the at least one light-stabilizing/light-protecting/light-absorbing agent,

b1iv) 0-2% (w/w) of the at least one additive selected from surfactants, wetting agents, thickeners and/or defoamers,

b1v) 0-2% (w/w) of the at least one agent capable of catalyzing a polymerisation reaction of the binder component with an isocyanate group containing compound, and optionally

b1vi) at least one pigment,

each referred to 100% (w/w) binder containing composition (S1).

14. The composite coating formulation of anyone of the preceding items, wherein the binder containing composition (S1), comprises or consists of

b1i) 40-60% (w/w) of the binder component selected from a polyester polyol, wherein the hydroxyl content of the binder component is 2-10%, 3-8% or 3-6%,

b1ii) 40-60% (w/w) of the at least one organic solvent, wherein the solvent is as defined in item 6 or 7,

b1iii) 0-2% (w/w) of the at least one light-stabilizing/light-protecting/light-absorbing agent,

b1iv) 0.01-1% (w/w) of the at least one additive selected from surfactants, wetting agents, thickeners and/or defoamers, wherein the additive is as defined in item 9 or 10,

b1v) 0-2% (w/w) of the at least one agent capable of catalyzing a polymerisation reaction of the binder component with an isocyanate group containing compound, wherein said agent is as defined in item 11, and optionally

b1vi) at least one pigment,

each referred to 100% (w/w) binder containing composition (S1).

15. The composite coating formulation of anyone of the preceding items, wherein the working top coat formulation (S) is a multi-component, preferably a two-component coating formulation further comprising

b2) a curing agent containing composition (S2), comprising or consisting of

b2i) at least one curing agent having at least two isocyanate groups or at least two blocked isocyanate groups wherein the isocyanate groups are blocked by a thermolabile protection group,

b2ii) at least one organic solvent.

16. The composite coating formulation of item 15, wherein the at least one curing agent of b2i) is a polyisocyanate compound based on an aliphatic diisocyanate.

17. The composite coating formulation of item 15 or 16, wherein the at least one organic solvent of b2ii) is a non-polar aprotic solvent selected from aromatic hydrocarbons, carboxylic acid esters or any mixture thereof.

18. The composite coating formulation of anyone of items 15 to 17, wherein the at least one organic solvent of b2ii) is benzene, benzene mono- or di-substituted with a C₁₋₆alkyl, C₁₋₆oxoalkyl, and/or aryl, C₁₋₆alkyl(glykol) formiate, C₁₋₆alkyl(glykol) acetate, C₁₋₆alkyl(glykol) propionate, C₁₋₆alkyl(glykol) butyrate, C₁₋₆alkoxy-C₁₋₆alkyl(glykol) formiate, C₁₋₆alkoxy-C₁₋₆alkyl(glykol) acetate, C₁₋₆alkoxy-C₁₋₆alkyl(glykol)-propionate, C₁₋₆alkoxy-C₁₋₆alkyl(glykol) butyrate or any mixture thereof.

19. The composite coating formulation of anyone of items 15 to 18, wherein the at least one organic solvent of b2ii) is xylene, toluene, butyl acetate, propyl acetate, methoxypropyl acetate, butylglykol acetate or any mixture thereof.

20. The composite coating formulation of anyone of items 15 to 19, wherein the content of the curing agent component b2i) is 5-80% (w/w), 10-70% (w/w), 20-60% (w/w) or 40-60% (w/w), referred to 100% (w/w) curing agent

containing composition (S2).

5 **21. The composite coating formulation** of anyone of items 15 to 20, wherein compositions (S1) and (S2) are mixed together immediately before application, wherein the mixing ratio of S1:S2 is selected to achieve a degree of cross linking of the binder component b1i) of between 60-200% or 100-200%.

22. The composite coating formulation of anyone of the preceding items, further comprising

10 c) a color coat formulation (I) for forming an intermediate coating, the working color coat formulation (I) comprising at least one pigment.

15 **23. A coating formulation (S)** for forming a top coating on a surface of an article, wherein the working top coat formulation (S) is as defined in anyone of items 14 to 21, wherein the surface is optionally plastically and/or elastically deformable.

24. A method for preparing a multilayered film coating on a surface of an article, using the composite coating formulation as defined in anyone of items 1 to 21 the method comprising the steps of

- 20 (i) applying the working base coat formulation (P) to the surface of an article to be coated,
(ii) allowing formation of the primary coating,
(iii) applying the top coat formulation (S) on the primary coating obtained by step (ii),
(iv) allowing formation of the secondary coating.

25 **25. A method for preparing a multilayered film coating** on a surface of an article, using the composite coating formulation as defined in item 22, the method comprising the steps of

- 30 (i) applying the working base coat formulation (P) to the surface of an article to be coated,
(ii) allowing formation of the primary coating,
(iii) applying the working color coat formulation (I) on the primary coating obtained by step (ii),
(iv) allowing formation of the intermediate coating,
(v) applying the top coat formulation (S) on the intermediate coating,
(vi) allowing formation of the secondary coating.

35 **26. The method** according to item 24 or 25, wherein method steps (i) and (ii) are performed at least two times before performing step (iii).

40 **27. The method** according to anyone of items 24 to 26, wherein the application of the working base coat formulation (P), the top coat formulation (S) and/or the color coat formulation (I) is performed by dipping, spray application, brush application and/or roller application.

28. An article having a surface coat comprising or consisting of a multilayered film coating, wherein the film coating is obtained by or obtainable by a method as defined in anyone of items 24 to 27.

45 **29. The article or the method** according to anyone of items 24 to 28, wherein the article is a body component of a vehicle such as a motorized vehicle.

30. The article or the method according to anyone of items 24 to 28, wherein the article is selected from an electric cable, a communication cable, a rubber hose, a tool handle or a pipeline, e.g. an oil pipeline.

50 **31. The article or the method** according to anyone of items 24 to 30, wherein the article or the surface to be coated of the article is a metal, a metal alloy and/or a plastic article/surface.

55 **32. The article or the method** according to anyone of items 24 to 31, wherein the surface to be coated of the article is a varnished surface.

33. A peelable multilayered surface coating obtained by or obtainable by a method as defined in anyone of items 24 to 27.

34. A method for providing resistance against chemical destruction, mechanical destruction and/or for providing a glossy finish of a film coating essentially comprising of rubber, the method comprising

- (i) applying a working coating formulation (S) as defined in any one of items 1 to 22 on the rubber film coating,
- (ii) allowing formation of a top coating.

35. A container, containing a binder containing composition (S1) and an optionally a curing agent containing composition (S2) of a working top coat formulation (S), wherein the composition (S1), the composition (S2) and the working top coat formulation (S) are as defined in any one of items 1 to 22, and wherein composition (S1) is separated from composition (S2).

36. The container of item 35, being an aerosol can.

Claims

1. A composite coating formulation for forming a multilayered film coating on a surface of an article, the formulation comprising or consisting of

- a) a base coat formulation (P) for forming a primary coating
- b) a top coat formulation (S) for forming a secondary coating,

wherein the working base coat formulation (P) is a fluid rubber formulation comprising or consisting of

- ai) a monomer component selected from an acrylate, (hydroxy-)C₁₋₃alkylacrylate, methacrylate, (hydroxy-)C₁₋₃alkylmethacrylate, acrylonitrile, styrene, butadiene, ethylene, butylene, vinylacetate, vinylhalogenid or a polymerisable mixture thereof, and/or
- a ii) a copolymer component comprising or consisting of 2-8 monomeric building blocks selected from an acrylate, (hydroxy-)C₁₋₃alkylacrylate, methacrylate, (hydroxy-)C₁₋₃alkylmethacrylate, acrylonitrile, styrene, butadiene, ethylene, butylene, vinylacetate and/or a vinylhalogenid component, wherein halogenid means chloride, bromide, fluoride or iodide,
- a iii) at least one organic solvent, and optionally
- a iv) at least one additive selected from surfactants, wetting agents, thickeners, plasticizers, dispersing agents, coalescing agents, fillers and/or defoamers, and optionally
- a v) at least one pigment,

wherein the working top coat formulation (S) comprises or consists of

- b1) a binder containing composition (S1), comprising or consisting of

- b1i) a binder component selected from a polyester polyol, a hydroxy-functionalized polyacrylate or mixtures thereof, preferably having a hydroxyl content of 2-10%, 3-8% or 3-6%,
- b1ii) at least one organic solvent, and optionally
- b1iii) at least one light-stabilizing/light-protecting/light-absorbing agent, and optionally
- b1iv) at least one additive selected from surfactants, wetting agents, thickeners and/or defoamers, and optionally
- b1v) at least one agent capable of catalyzing a polymerisation reaction of the binder component with an isocyanate group containing compound, and optionally
- b1vi) at least one pigment.

2. The composite coating formulation of claim 1 wherein the copolymer component of a ii) is a styrene/butadiene, a styrene/ethylene/butylene/styrene block copolymer and/or a vinylchloride copolymer.

3. The composite coating formulation of claim 1 or 2, wherein the at least one organic solvent of b1ii) is a non-polar aprotic solvent selected from aromatic hydrocarbons, carboxylic acid esters, or any mixtures thereof, such as xylene, toluene, butyl acetate, propyl acetate, methoxypropyl acetate, butylglykol acetate or any mixture thereof.

4. The composite coating formulation of any one of the preceding claims, wherein the at least one light-stabiliz-

ing/light-protecting/light-absorbing agent of b1iii) is an UV-light absorber of the hydroxyphenyl benzotriazole class.

5 **5. The composite coating formulation** of anyone of the preceding claims, wherein the at least one additive of b1iv) is a silicone glycol optionally having a carbinol functionality and/or a poly-diC₁₋₆alkylsiloxan optionally modified with a polyester and/or a polyether.

10 **6. The composite coating formulation** of anyone of the preceding claims, wherein the at least one agent of b1v) capable of catalyzing a polymerisation reaction of the binder component with an isocyanate group containing compound is a dibutyltin compound and/or a tin-free carboxylate compound.

7. The composite coating formulation of anyone of the preceding claims, wherein the content of the binder component b1i) is 20-80% (w/w), 30-70% (w/w), 30-60% (w/w) or 40-60% (w/w), referred to 100% (w/w) binder containing composition (S1).

15 **8. The composite coating formulation** of anyone of the preceding claims, wherein the binder containing composition (S1), comprises or consists of

b1i) 40-60% (w/w) of the binder component selected from a polyester polyol, a hydroxy-functionalized polyacrylate or mixtures thereof,

20 b1ii) 40-60% (w/w) of the at least one organic solvent,

b1iii) 0-2% (w/w) of the at least one light-stabilizing/light-protecting/light-absorbing agent,

b1iv) 0-2% (w/w) of the at least one additive selected from surfactants, wetting agents, thickeners and/or defoamers,

25 b1v) 0-2% (w/w) of the at least one agent capable of catalyzing a polymerisation reaction of the binder component with an isocyanate group containing compound, and optionally

b1vi) at least one pigment,

each referred to 100% (w/w) binder containing composition (S1).

30 **9. The composite coating formulation** of anyone of the preceding claims, wherein the binder containing composition (S1), comprises or consists of

b1i) 40-60% (w/w) of the binder component selected from a polyester polyol, wherein the hydroxyl content of the binder component is 2-10%, 3-8% or 3-6%,

35 b1ii) 40-60% (w/w) of the at least one organic solvent, wherein the solvent is as defined in claim 3,

b1iii) 0-2% (w/w) of the at least one light-stabilizing/light-protecting/light-absorbing agent,

b1iv) 0.01-1% (w/w) of the at least one additive selected from surfactants, wetting agents, thickeners and/or defoamers, wherein the additive is as defined in claim 5,

40 b1v) 0-2% (w/w) of the at least one agent capable of catalyzing a polymerisation reaction of the binder component with an isocyanate group containing compound, wherein said agent is as defined in claim 6, and optionally

b1vi) at least one pigment,

each referred to 100% (w/w) binder containing composition (S1).

45 **10. The composite coating formulation** of anyone of the preceding claims, wherein the working top coat formulation (S) is a multi-component, preferably a two-component coating formulation further comprising

b2) a curing agent containing composition (S2), comprising or consisting of

50 b2i) at least one curing agent having at least two isocyanate groups or at least two blocked isocyanate groups wherein the isocyanate groups are blocked by a thermolabile protection group,

b2ii) at least one organic solvent.

11. The composite coating formulation of anyone of the preceding claims, further comprising

55 c) a color coat formulation (I) for forming an intermediate coating, the working color coat formulation (I) comprising at least one pigment.

12. **A coating formulation (S)** for forming a top coating on a surface of an article, wherein the working top coat formulation (S) is as defined in anyone of claims 8 to 10.

5 13. **A method for preparing a multilayered film coating** on a surface of an article, using the composite coating formulation as defined in anyone of claims 1 to 10 the method comprising the steps of

- (i) applying the working base coat formulation (P) to the surface of an article to be coated,
- (ii) allowing formation of the primary coating,
- 10 (iii) applying the top coat formulation (S) on the primary coating obtained by step (ii),
- (iv) allowing formation of the secondary coating.

14. **A method for preparing a multilayered film coating** on a surface of an article, using the composite coating formulation as defined in claim 11, the method comprising the steps of

- 15 (i) applying the working base coat formulation (P) to the surface of an article to be coated,
- (ii) allowing formation of the primary coating,
- (iii) applying the working color coat formulation (I) on the primary coating obtained by step (ii),
- (iv) allowing formation of the intermediate coating,
- (v) applying the top coat formulation (S) on the intermediate coating,
- 20 (vi) allowing formation of the secondary coating.

15. **An article** having a surface coat comprising or consisting of a multilayered film coating, wherein the film coating is obtained by or obtainable by a method as defined in claim 13 or 14.

25 16. **A peelable multilayered surface coating** obtained by or obtainable by a method as defined in claim 13 or 14.

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EUROPEAN SEARCH REPORT

Application Number
EP 14 15 8451

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	EP 0 513 814 A1 (KANSAI PAINT CO LTD [JP]) 19 November 1992 (1992-11-19) * column 5, line 28 - line 40; claim 1 * -----	1	INV. B05D7/00
X	EP 0 512 562 A2 (KANSAI PAINT CO LTD [JP]) 11 November 1992 (1992-11-11) * examples 13-15 * -----	1,2,13, 15	
X	US 5 100 735 A (CHANG DAVID C K [US]) 31 March 1992 (1992-03-31) * examples 21-25 * -----	1,2,13, 15	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (IPC)
			B05D
Place of search The Hague		Date of completion of the search 19 November 2014	Examiner Slembrouck, Igor
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing claims for which payment was due.

- Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due and for those claims for which claims fees have been paid, namely claim(s):
- No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet B

- All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.
- As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.
- Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:
- None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:
2(completely); 1, 13, 15(partially)
- The present supplementary European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims (Rule 164 (1) EPC).



**LACK OF UNITY OF INVENTION
SHEET B**

Application Number

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The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

1. claims: 2(completely); 1, 13, 15(partially)

a composite coating formulation for forming a multilayered film coating on a surface of an article, the formulation comprising or consisting of

a) a base coat formulation (P) for forming a primary coating
b) a top coat formulation (S) for forming a secondary coating,

wherein the working base coat formulation (P) is a fluid rubber formulation comprising or consisting of

ai) a monomer component selected from an acrylate, (hydroxy-)C,-3 alkylacrylate, methacrylate, (hydroxy-)C,-3 alkylmethacrylate, acrylonitrile, styrene, butadiene, ethylene, butylene, vinylacetate, vinylhalogenid or a polymerisable mixture thereof, and/or

a ii) a copolymer component comprising or consisting of 2-8 monomeric building blocks selected from an acrylate, (hydroxy-)C,-3 alkylacrylate, methacrylate, (hydroxy-)C,-3 alkylmethacrylate, acrylonitrile, styrene, butadiene, ethylene, butylene, vinylacetate and/or a vinylhalogenid component, wherein halogenid means chloride, bromide, fluoride or iodide,

a iii) at least one organic solvent, and optional components,

wherein the working top coat formulation (S) comprises or consists of

b1) a binder containing composition (S1) comprising or consisting of

b1 i) a binder component selected from a polyester polyol, a hydroxy-functionalized polyacrylate or mixtures thereof,

b1 ii) at least one organic solvent, and optional components,

wherein the base coat formulation (P) is further specified;

2. claims: 3-10(completely); 1, 13, 15(partially)

a composite coating formulation for forming a multilayered film coating on a surface of an article, the formulation comprising or consisting of

a) a base coat formulation (P) for forming a primary coating
b) a top coat formulation (S) for forming a secondary coating,

wherein the working base coat formulation (P) is a fluid rubber formulation comprising or consisting of

ai) a monomer component selected from an acrylate, (hydroxy-)C,-3 alkylacrylate, methacrylate, (hydroxy-)C,-3 alkylmethacrylate, acrylonitrile, styrene, butadiene, ethylene, butylene, vinylacetate, vinylhalogenid or a polymerisable mixture thereof, and/or

a ii) a copolymer component comprising or consisting of 2-8



**LACK OF UNITY OF INVENTION
SHEET B**

Application Number

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The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

monomeric building blocks selected from an acrylate, (hydroxy-)C,- 3 alkylacrylate, methacrylate, (hydroxy-)C,-3 alkylmethacrylate, acrylonitrile, styrene, butadiene, ethylene, butylene, vinylacetate and/or a vinylhalogenid component, wherein halogenid means chloride, bromide, fluoride or iodide, aiii) at least one organic solvent, and optional components, wherein the working top coat formulation (S) comprises or consists of b1) a binder containing composition (S1) comprising or consisting of b1 i) a binder component selected from a polyester polyol, a hydroxy-functionalized polyacrylate or mixtures thereof, b1 ii) at least one organic solvent, and optional components, wherein the top coat formulation (S) is further specified;

3. claims: 11, 14(completely); 1, 15(partially)

a composite coating formulation for forming a multilayered film coating on a surface of an article, the formulation comprising or consisting of a) a base coat formulation (P) for forming a primary coating b) a top coat formulation (S) for forming a secondary coating, wherein the working base coat formulation (P) is a fluid rubber formulation comprising or consisting of ai) a monomer component selected from an acrylate, (hydroxy-)C,- 3 alkylacrylate, methacrylate, (hydroxy-)C,-3 alkylmethacrylate, acrylonitrile, styrene, butadiene, ethylene, butylene, vinylacetate, vinylhalogenid or a polymerisable mixture thereof, and/or aii) a copolymer component comprising or consisting of 2-8 monomeric building blocks selected from an acrylate, (hydroxy-)C,- 3 alkylacrylate, methacrylate, (hydroxy-)C,-3 alkylmethacrylate, acrylonitrile, styrene, butadiene, ethylene, butylene, vinylacetate and/or a vinylhalogenid component, wherein halogenid means chloride, bromide, fluoride or iodide, aiii) at least one organic solvent, and optional components, wherein the working top coat formulation (S) comprises or consists of b1) a binder containing composition (S1) comprising or consisting of b1 i) a binder component selected from a polyester polyol, a hydroxy-functionalized polyacrylate or mixtures thereof, b1 ii) at least one organic solvent, and optional components,



**LACK OF UNITY OF INVENTION
SHEET B**

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The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

wherein the composite coating formulation further comprises a color coat formulation (I) for forming an intermediate coating;

4. claim: 12

a coating formulation (S) for forming a top coating on a surface of an article, wherein the working top coat formulation (S) comprises or consists of
 b1) a binder containing composition (S1) comprising or consisting of
 b1 i) 40-60% (w/w) of a binder component selected from a polyester polyol, a hydroxy-functionalized polyacrylate or mixtures thereof,
 b1 ii) 40-60% (w/w) of at least one organic solvent, and optional components;

5. claim: 16

a peelable multilayered surface coating obtained by a method comprising the steps of
 (i) applying the working base coat formulation (P) to the surface of an article to be coated,
 (ii) allowing formation of the primary coating,
 (iii) applying the top coat formulation (S) on the primary coating obtained by step (ii),
 (iv) allowing formation of the secondary coating,
 wherein the working base coat formulation (P) is a fluid rubber formulation comprising or consisting of
 ai) a monomer component selected from an acrylate, (hydroxy-)C,-3 alkylacrylate, methacrylate, (hydroxy-)C,-3 alkylmethacrylate, acrylonitrile, styrene, butadiene, ethylene, butylene, vinylacetate, vinylhalogenid or a polymerisable mixture thereof, and/or
 aii) a copolymer component comprising or consisting of 2-8 monomeric building blocks selected from an acrylate, (hydroxy-)C,-3 alkylacrylate, methacrylate, (hydroxy-)C,-3 alkylmethacrylate, acrylonitrile, styrene, butadiene, ethylene, butylene, vinylacetate and/or a vinylhalogenid component, wherein halogenid means chloride, bromide, fluoride or iodide,
 aiii) at least one organic solvent, and optional components,
 wherein the working top coat formulation (S) comprises or consists of
 b1) a binder containing composition (S1) comprising or consisting of
 b1 i) a binder component selected from a polyester polyol, a hydroxy-functionalized polyacrylate or mixtures thereof,



**LACK OF UNITY OF INVENTION
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The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

b1 ii) at least one organic solvent, and
optional components,

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**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

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