in this invention are vinyl acetate; olefins such as ethylene, propylene, and the like; conjugated dienes having 4-10 carbon atoms; aromatic hydrocarbons having vinylene groups, such as styrene; alkyl maleates; and alkyl esters of acrylic acid having 2-18 carbon atoms in the alkyl group. Small amounts of ethylenically unsaturated carboxylic acids can also be present, such as acrylic acid, methacrylic acid, crotonic acid, maleic acid, itaconic acid, and the like.

Crosslinking agents used with the hydroxyl-functional copolymers can be aminoplast resins or organic polyisocyanates. Preferred are aminoplasts such as alkoxymethyl melamines.

The aminoplasts are the alkylated products of amino resins, the latter prepared by the condensation of at least one aldehyde with at least one of urea, N,-N'-ethyleneurea, dicyandiamide, and an aminotriazine such as a melamine or a guanamine. Among the aldehydes that can be used are formaldehyde and its revertable polymers, acetaldehyde, crotonaldehyde, and acrolein.

The preferred aminoplasts are formed by alkylating the amino resins with from one to six alkanol molecules, each containing 1-6 carbon atoms. The alkanols can be straight-chain, branched, or cyclic. The most preferred members of this class are the methylated melamine-formaldehyde resins such as hexamethoxymethylmelamine.

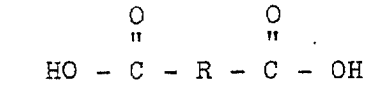
The organic polyisocyanates that can be used as the crosslinker include aliphatic, cycloaliphatic, alkaryl, aralkyl, heterocyclic, and aryl di- or tri-isocyanates. Oligomers of these can also be used. Preferred from these classes are hexamethylene di-isocyanate or its trimer, methylene-bis-(4-cyclohexyl isocyanate), and isophorone di-isocyanate.

The relative amount of cross-linker to film-forming resin will depend largely on the amount of hydroxyl monomer in the copolymer. Normally, however, high solids enamel compositions have acceptable physical and chemical properties when the stoichiometrically necessary amount of cross-linker is from 5-50% of the total binder weight.

The alkyd resins which are useful as the film-forming resins of this invention are well known as including esterification products having fatty acid or oil constituents. The resins are usually the reaction product of a fatty acid or its glyceride, a polyol, and a polybasic acid. Alternatively, the alcoholosis product of a fatty acid glyceride and a polyol can first be formed and then further reacted with a polyol and polybasic acid by well-known methods to produce resins having a weight average molecular weight, determined by gel permeation chromatography, of about 500-10000. The alkyd resins can be formed from various mixtures of several different fatty acids, polyols, and polyacids.

The fatty acid glycerides are found in castor oil, dehydrated castor oil, coconut oil, cottonseed oil, peanut oil, tung oil, linseek oil, soya oil, etc. The fatty acids derived from these and like oils are straight-chain monocarboxylic acids having a total of 8 to 12 carbon atoms. The acids can be saturated or mono- or polyunsaturated. When the acids are unsaturated, derived from the so-called drying oils, crosslinking is also effected through air oxidation.

The polybasic acids that are used generally are dicarboxylic acids having the general formula



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wherein R is alkylene, vinylene, aromatic, carboxylic, or heterocyclic. Anhydrides or dialkyl esters of these acids can also be used. Examples of such acids are glutaric, adipic, pimelic, succinic, maleic, itaconic, phthalic, isophthalic, terephthalic, cumidic, hexahydrophthalic, tetrahydrothphthalic, and the like.

The polyols that can be used are, for example, any of the various diols such as ethylene glycol; propylene glycol; 1,3 propane diol; 1,2-butanediol, 2,3 butane diol; and 1,4 butanediol. Triols, such as glycerine, or other higher functional alcohols can also be used. The diols are preferred.

The crosslinker used with these alkyd resins can be any of the aminoplasts or organic polyisocyanates described earlier. As with the acrylic resins, from about 5-50% by weight of the crosslinker, based on the combined weights of the crosslinker and alkyd resin, are used in the enamel compositions.

Either or both layers of the dual-layer enamel coating of this invention can be produced from a polyester film-forming material also. Polyester resins used herein are prepared by the condensation reaction of polybasic acids and polyols. The weight-average molecular weight of these resins, which can be prepared by any of the conventionally known processes for polyester production, should be about 500-10000, as determined by gel permeation chromatography.

The polyols used in preparation of the polyesters are preferably diols that can be either aliphatic or aromatic. Suitable diols include ethylene glycol; propylene glycol; 1,3 propane diol, any of the butanediols; neopentyl glycol; 2,2,4-

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trimethyl- 1,3-pentane diol; 2,2-diethylpropane-1,3-diol; 2-methyl-2-propylpropane-1,3-diol; decamethylene glycol; dodecamethylene glycol; monoethyl ether of glycerine, alpha, beta-alkyl ethers of glycerol, and the like. Triols or other more highly functional polyols can also be used.

The polybasic acids used are normally dibasic carboxylic acids that are either aliphatic (saturated or not). or aromatic. Suitable acids include, for example malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic, sebacic, brasylic, maleic, fumaric, diphenic, tetrachlorophthalic, phthalic, terephthalic, isophthalic, cyclohexane-1,2-dicarboxylic acid, p-phenylene diacetic, naphthalene dicarboxylic acid, beta-methyl adipic acid, trimethyl adipic acid, and the like.

Anhydrides, acid chlorides, or dialkyl esters of the above acids can also be used. Preferred polyesters are formed from both aliphatic and aromatic acids with mixtures of polyols. Blends of polyester resins, some formed only from polyols and aromatic acids, some formed only from polyols and aliphatic acids, can also be used.

Crosslinkers used with the polyester resins can be the same as those described for the hydroxyl-functional acrylic or alkyd systems.

Although the preferred film-forming resins for use in the present dual-layer enamel systems are hydroxyl-functional acrylic, polyester, or alkyd resins, it is to be understood that any conventionally used film-forming constituents, with appropriate crosslinkers, can be used. For example, resins that are epoxy-functional can be used, crosslinked with a diacid, and conversely, resins that are acid-functional can be crosslinked with an epoxy resin. Other variations of the resins are also possible.

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Each of the coating layers of the present dual-layer enamel system is formed from a high-solids composition containing at least 50% by weight of binder constituents (film-forming resins and crosslinker) based on the combined weight of binder and solvent. The solvents that can be used are typically organic, inert to the binder constituents, and sufficiently volatile to be easily evaporated during the curing process when the film-forming resins are completing crosslinking. Specific examples are toluene, acetone, ethyl acetate, methyl isobutyl ketone, methylethyl ketone, and ethyl alcohol. Any of the other conventionally used cycloaliphatic or aromatic hydrocarbons, esters, ethers, ketones, or alcohols are also suitable.

The coating compositions can be formulated by conventional means. For example, the acrylic resins useful in this invention are typically formed by co-polymerizing the monomers in one of the above inert organic solvents in the presence of a free-radical forming initiator. The crosslinking agent and mill base, for the pigmented layer, are then blended into the composition.

The coating composition for either layer or both layers can optionally contain an ultraviolet light stabilizer, an antioxidant or both. The ultraviolet light stabilizer can be present in an amount of 1-20% by weight, based on the weight of the binder; the anti-oxidant can be present in an amount of 0.1-5% by weight, based on the weight of the binder.

Typical ultraviolet light stabilizers are benzophenones, triazoles, triazines, benzoates, lower alkyl thiomethylene-containing phenols, substituted

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benzenes, organophosphorous sulfides, and substituted methylene malontriles. Particularly useful are the hindered amines and nickel compounds shown in U.S. Patent 4,061,616 (December 6, 1977).

Typical antioxidants are tetra-kis alkylene (di-alkyl hydroxy aryl) alkyl ester alkanes, reaction product of p-amino diphenylamine and glycidyl methacrylate, and alkyl hydroxyphenyl groups bonded through carboalkoxy linkages to a nitrogen atom of a heterocyclic nucleus containing an imidodicarbonyl group or an imidodithiocarbonyl group.

One preferred combination of ultraviolet light stabilizer and antioxidant is 2-hydroxy-4-dodecyloxy benzophenone or a substituted 2(2'-hydroxyphenyl) benzotraizole and tetra-kis methylene 3(3',5'-dibutyl-4'-hydroxyphenyl) propionate methane.

The coating compositions for either layer or both layers may optionally contain additives to control rheology during and after application of the composition to a substrate. Examples of such rheology control agents include additives containing fumed silica, such as disclosed in U.S. Patent No. 4,238,387 to Antonelli et al., and polymer microparticles, such as disclosed in U.S. Patents No. 4,220,679 to Backhouse and 4,180,619 to Markhlouf. The fumed silica can be present in an amount of 1 to 15% by weight, based on the weight of the coating composition. The polymer microparticles may be present in an amount of at least 10% of the aggregate weight of film-forming polymer and polymer microparticles. Combinations of such additives may also be used.

The coating composition of each layer of this invention can be applied to a substrate by any well-known means, but spraying is preferred. The pigmented base layer is first applied to a substrate and preferably cured to a degree sufficient to effect substantial solvent evaporation and crosslinking. Curing is normally carried out

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by baking or heating the layer for 10-60 minutes at 50°-200°C. Before baking, it is often preferable to allow the base layer to flash at room temperature, 23°C, for up to 15 minutes. This facilitates the flake orientation.

The transparent top layer is applied directly over the base layer, preferably after the base layer is cured. It is important that the solvents of the transparent top layer do not attack the base layer. This attack, or strike-in, can cause the film-forming resins of the two layers to combine at the layers' interface, and can destroy the desired flake orientation in the base layer. As stated above, it is preferably to cure the base layer such that crosslinking occurs to a degree sufficient to make the base layer immune to attack from the solvent in the top layer.

After the top layer is applied, baking is carried out as with the base layer, with optional flashing of the coating before the bake, to completely cure both layers. The top layer not only provides depth to the coating, enhancing the metallic glamor, but also increases the gloss and distinctness-of-image over values obtainable if only a single pigmented layer were used. The metallic glamor is evident, however, even when no transparent top layer is used.

The following Example illustrates the invention.

EXAMPLE

Control Coating A

A conventional acrylic solution lacquer can be prepared according to Example 1 of U.S. Patent 3,823,205, with the exception that the pigment dispersion is made by blending together the following two mill bases:

Mill Base 1, prepared by blending

	Parts by Weight
Aluminum Flake	3.2
Polymethyl Methacrylate	12.8
Toluene/Acetone (70/30)	25.8
	41.8

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Mill Base 2, prepared by sand grinding

	Parts by Weight
Monastral® Blue Pigment	0.85
Polymethyl Methacrylate	1.45
Toluene/Acetone (70/30)	4.37
	6.67

This lacquer coating has an aluminum flake/binder ratio of 1.5/100 and an aluminum flake/chromatic pigment weight ratio of 3.75/1.0. The lacquer is thinned to 12% volume solids with a conventional solution lacquer thinner and is sprayed onto a primed aluminum panel. Four coats are applied to the panel, three passes per coat, allowing a flash of two minutes between coats and a flash of ten minutes after the last coat is applied. The coating is then baked for 20 minutes at about 155°C.

Control Coating B

A pigmented high-solids enamel coating is prepared by conventional means to have the following final composition:

	Parts by Weight
Acrylic Polymer Solution, prepared by conventional means, wherein the polymer solution has a weight solids content of 74%, the polymer is a copolymer of methyl methacrylate, n-butyl acry acrylate, and 2-hydroxyethyl acrylate having a weight average molecular weight of 3000 and a glass transition temperature of -10°C	70
Hexamethoxymethylmelamine	30
Methylethyl Ketone	107.6
Aluminum Flake Pigment	1.23
Monastral® Blue Pigment	0.33
	209.16

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The enamel coating has a binder solids content of 65% by weight, based on weight of binder and solvent, and has an aluminum flake/binder weight ratio of 1.5/100 and a chromatic pigment/binder weight ratio of 0.4/100. The enamel is sprayed onto a primed aluminum panel in four coats, two passes per coat, allowing a flash of two minutes between coats and a flash of thirty minutes after the last coat is applied. The coating is then baked for thirty minutes at 71°C and for thirty additional minutes at 163°C.

Dual-Layer High-Solids Enamel

1. A pigmented base-layer coating is prepared by conventional means to have the following composition:

	Parts by Weight
Acrylic Polymer Solution (described in Coating B)	70
Hexamethoxymethylmelamine	30
Methylethyl ketone	107.6
Aluminum Flake Pigment	14.76
Monastral® Blue Pigment	3.96
	226.32

This enamel composition has a binder solids content of 65% by weight, based on weight of binder and solvent, and has an aluminum flake/binder weight ratio of 18/100 and a chromatic pigment/binder weight ratio of 4.8/100.

2. An unpigmented top-layer coating composition is prepared as is the base layer but without pigmentation.

The pigmented base-layer enamel composition is sprayed onto a primed aluminum panel in one coat, two passes per coat, allowing a flash of 15 minutes after the coat is applied. The coating is then baked for thirty minutes at 71°C and for thirty additional minutes at about 93°C. The unpigmented top-layer enamel composition is then sprayed over the base-layer

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in four coats, two passes per coat, allowing a flash of two minutes between coats and a flash of fifteen minutes after the last coat is applied. The coating is then baked for thirty minutes at 71°C and for thirty additional minutes at 163°C.

The flake orientation index of the coatings on each of the three panels is determined using a goniophotometer as previously described. Control Coating A (a solution lacquer with conventional pigmentation levels) exhibits a flake orientation index of 52. Control Coating B (a high-solids enamel with conventional pigmentation levels) exhibits an index of 29. The dual-layer high-solids enamel having pigmentation levels within the range of the present invention exhibits a flake orientation index of 49.

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CLAIMS

1. An improved coating composition of the kind having

(1) binder constituents consisting essentially of a film-forming material and a crosslinker for the film-forming material wherein the film-forming material is selected from the group consisting of acrylic resins, polyester resins, and alkyd resins having a weight-average molecular weight of 500-10000;

(2) a solvent for the binder constituents in an amount of no more than 100% by weight of the binder; and

(3) chromatic and metallic-flake pigments;

wherein the improvement is characterized in that the metallic-flake pigment is present in the composition in an amount of 10-24% by weight, based on the weight of the binder constituents, and the chromatic pigment is present in an amount sufficient with the amount of the metallic-flake pigment to give a cured coating of this composition a flake orientation index of at least 40.

2. The composition of claim 1 wherein the film-forming material is a polyester resin.

3. The composition of claim 2 wherein the film-forming material is a polyester resin that is a mixture of the condensation products of (1) aliphatic diols and aliphatic dibasic acids, and (2) aliphatic diols and aromatic dibasic acids, and wherein the crosslinker is an aminoplast.

4. The composition of claim 1 wherein the film-forming material is an acrylic resin.

5. The composition of claim 4 wherein the film-forming material is a copolymer of an alkyl acrylate, alkyl methacrylate, and at least one of a hydroxy alkyl acrylate and hydroxy alkyl methacrylate, and wherein the crosslinker is an aminoplast.

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6. The composition of claim 1 in which the film-forming material is an alkyd resin.

7. The composition of claim 6 wherein the film-forming material is an alkyd resin that is the reaction product of a glyceride of a fatty acid, a diol, and a dicarboxylic acid.

8. The composition of claim 1, 2, 3, 4, 5, 6, or 7 wherein the amount of metallic-flake pigment is 10-20% by weight, based on the weight of the binder constituents.

9. The composition of claim 1, 2, 3, 4, 5, 6, or 7 containing an ultraviolet light stabilizer and an antioxidant.

10. The composition of claim 1, 2, 3, 4, 5, 6, or 7 containing 1 to 15% by weight fumed silica, based on the weight of the coating composition.

11. The composition of claims 1, 2, 3, 4, 5, 6, or 7 containing at least 10% by weight polymer microparticles, based on the aggregate weight of film-forming polymer and polymer microparticles.

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