

PATENT SPECIFICATION

(11) 1236 128

NO DRAWINGS

- (21) Application No. 35987/69 (22) Filed 17 July 1969
 (31) Convention Application No. 754958 (32) Filed 23 Aug. 1968 in
 (33) United States of America (US)
 (45) Complete Specification published 23 June 1971
 (51) International Classification C 09 d 3/14 3/74
 (52) Index at acceptance



C3P 11A 11C10 11C13A 11C14B 11C17 11C18 11C2
 11C20B 11C20C 11C20D1 11C20D2 11C20D3
 11C6B 11C8A 11C8B 11C8C 11C9 11D2A3 11D8
 11K7 11K8 11P1C 11P1E3 11P3 11P6A 11P6G
 8A 8C10 8C13A 8C14B 8C17 8C18 8C2 8C20B
 8C20C 8C20D1 8C20D2 8C20D3 8C6B 8C8A
 8C8B 8C8C 8C9 8D2A 8D2B2 8D3A 8D8 8K11
 8K7 8K8 8P1C 8P1E3 8P3 8P6A 8P6G
 B2E 185 18Y 19Y 204 209 20Y 327 349 360 380 382
 383 38X 38Y 390 391 392 39Y 40Y 410 412
 413 417 41X 41Y 420 441 442 44Y 452 453 456
 461 498 510 522 532 543 555 55Y 565 566 567
 568 56Y 590 59X 59Y 600 602 60Y 62X 62Y
 630 648 65Y 708 753 775 776 777 77Y
 C3F 335 37Y 38Y 391 39Y 500 51Y 520 530 531 540
 545 54X 57Y 603 621 626 632 654 720 722

(54) COATING COMPOSITION

(71) We, E. I. DU PONT DE NEMOURS AND COMPANY, a corporation organised and existing under the laws of the State of Delaware, United States of America, of Wilmington, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to polymeric coating compositions which can be applied to a variety of substrates, and in particular, to coating pigmented compositions that are useful in refinishing lacquer coatings.

A great need exists for a coating composition that can be used to repair damaged lacquer coatings, in particular, acrylic lacquer coatings which are widely used in the auto industry. A coating composition of this type would find wide use in the repair of damaged autos and trucks and in the production of autos and trucks where portions of the vehicle often require touch-up painting after assembly. Methacrylate coating compositions are well known in the art as shown by United States Patent Nos. 2,934,509 and 2,934,510. Coating compositions formed from cellulose acetate butyrate and a methacrylate polymer have been successfully used on metal substrates as shown in U. S. Patent No. 2,849,409. Polymers containing oxazoline dry-

ing oils have been used as coatings and are disclosed in U. S. Patent Nos. 3,208,981 and 3,248,397. The coating compositions of these prior art patents are excellent for many uses but do not have the properties preferred for a repair composition.

The coating compositions of this invention have the necessary balance of properties which allows pigmentation with a wide variety of pigments and which have excellent adherence to a lacquer coating, particularly an acrylic lacquer coating, without sanding or buffing the coating before application. Also, these coating compositions are resistant to weathering, resistant to solvents, such as gasoline, and resistant to water spotting which makes them well suited for use as an exterior finish or refinish for automobiles and trucks.

According to the present invention, therefore, we provide a coating composition comprising from 5 to 45% by weight of a film-forming material which consists of

(a) from 40 to 60% by weight, based on the weight of the film-forming material, of an acrylic oxazoline containing polymer which consists of units of

(1) from 30 to 70% by weight based on the weight of the polymer of methyl methacrylate,

(2) less than 35% by weight of an ester of an α,β - olefinically unsaturated mono-

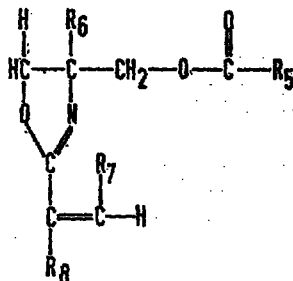
[Price 25p]

carboxylic acid and a C_2 to C_{12} saturated aliphatic monohydric alcohol,

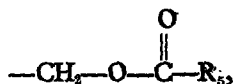
(3) less than 10% by weight acrylonitrile, and

- 5 (4) 15 to 35% by weight of an oxazoline compound having the formula:

Formula 1



- 10 in which R_5-CO- is a fatty acid acyl radical containing from 4 to 22 carbon atoms derived from a saturated or unsaturated fatty acid, R_6 is H, a C_1 to C_4 alkyl group or



- 15 R_7 is H, or a C_1 to C_4 alkyl group and R_8 is the residue of a saturated or unsaturated fatty acid containing from 4 to 22 carbon atoms minus the carboxyl group and the α -carbon atom,
- 20 (b) from 40 to 60% by weight, based on the weight of the film-forming material, of cellulose acetate butyrate that has a viscosity of 0.5—20 seconds at 25°C. measured according to ASTM D-1343-56 and a butyryl content of from 30 to 55% by weight; and
- 25 (c) from 0 to 10% by weight, based on the weight of the film-forming material, of an organic plasticizer which is either a polymeric plasticizer, a monomeric plasticizer or
- 30 a mixture of a polymeric plasticizer and a monomeric plasticizer;

wherein the film-forming material is in solution in a volatile organic liquid which includes at least one solvent for the film-forming material.

35 From 40—60% by weight, and preferably 40—49% by weight, based on the weight of the film-forming material, of an acrylic oxazoline containing polymer is used to form the coating compositions of this invention.

40 The acrylic oxazoline containing polymer used in the coating compositions is prepared by conventional solution polymerization methods. The monomers are mixed with suitable solvents, such as ethyl acetate, isopropyl alcohol, toluene, and butyl alcohol. A polymerization catalyst is then added to the mixture, such as tertiary butyl peroxide, cumene

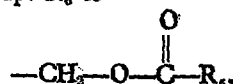
hydroperoxide, benzoyl peroxide and azobisisobutyronitrile. The amount of catalyst used is from 0.1 to 2% by weight of the monomers present. The reaction mixture is then refluxed until the polymerization is completed which can be checked by a polymer solids determination.

55 From 30 to 70% by weight, based on the weight of the polymer, of methyl methacrylate is used to prepare the acrylic oxazoline polymer. Preferably, 53 to 57% by weight of methyl methacrylate is used to form a high quality polymer. Less than about 35% by weight, based on the weight of the polymer, of an ester of an α,β -olefinically unsaturated carboxylic acid and a C_2 to C_{12} saturated monohydric alcohol is used to prepare the acrylic oxazoline polymer. Preferred are esters of acrylic and methacrylic acid, such as ethyl acrylate, propyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, lauryl acrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate, octyl methacrylate, and lauryl methacrylate. Lower alkyl acrylate and methacrylate esters in which the alkyl group has 2—6 carbon atoms are particularly preferred for forming a polymer with excellent physical properties. Ethyl acrylate is one particularly preferred ester used in an amount of from 13 to 17% by weight based on the weight of the polymer.

Up to 15% by weight of styrene can be substituted for part or all of the α,β -olefinically-unsaturated monocarboxylic acid ester of the polymer without adversely affecting the properties of the coating compositions.

Less than 10% by weight, based on the weight of the polymer, of acrylonitrile is used to form the acrylic oxazoline polymer and preferably, 3—7% by weight of acrylonitrile is used to form a high quality polymer.

60 From 15 to 35% by weight, based on the weight of the polymer, and preferably from 23 to 27% by weight of an oxazoline compound, previously defined by the structural Formula 1 (above) is used to prepare the acrylic oxazoline polymer. Preferably, the oxazoline compound is a reaction product of 1 mole of tris - (hydroxymethyl) - amino-methane and 3 moles of tall oil fatty acid which is subsequently reacted with formaldehyde. This oxazoline drying oil is described in U. S. Patent No. 3,248,397, which is hereby incorporated by reference; the compound is currently sold under the trademark of "Chemacoil TA 100". In relating the structural Formula 1 to the above reaction product, R_5 is the hydrocarbon residue of tall oil fatty acid, R_6 is the hydrocarbon residue of tall oil fatty acid less the alpha- CH_2 group. R_7 is



and R_7 is H.

From 40 to 60% by weight, and preferably from 48 to 55% by weight, based on the weight of the film-forming material of the coating composition, of cellulose acetate butyrate is used to form the coating compositions of this invention. The cellulose acetate butyrate has a viscosity of from 0.5 to 20.0 seconds and preferably, a viscosity of from 1 to 4 seconds measured at 25°C. and determined according to the method of ASTM D-1343-56. The butyryl content of the cellulose acetate butyrate is from 30 to 55% by weight. To form a particularly high quality coating composition, the cellulose acetate butyrate has a butyryl content of from 35 to 45% by weight.

An organic plasticizer in amounts up to 10% by weight, based on the weight of film-forming material, is used in the coating compositions. Preferably, from 3 to 6% by weight of organic plasticizer is used which provides a coating composition with excellent durability. Polymeric plasticizers which are particularly useful are epoxidized soya bean oil, oil free and oil modified alkyds and polyesters, such as, polyorthophthalate esters, polyalkylene adipate esters or polyarylene adipate esters.

Monomeric plasticizers can also be used such as benzylbutyl phthalate, dibutyl phthalate, triphenyl phosphate, 2-ethylhexylbenzyl phthalate, dicyclohexyl phthalate, diallyl phthalate, dibenzyl phthalate, butylcyclohexyl phthalate, mixed benzoic acid and fatty oil acid esters of pentaerythritol, diethyleneglycol dibenzoate, tetrabutylthiodisuccinate, butyl phthalate, butyl glycolate, acetyltributyl citrate, dibenzyl sebacate, tricresyl phosphate, N-ethyl toluene sulfonamide, the di-2-ethylhexyl ester of hexamethylene diphthalate, di(methylcyclohexyl) phthalate. One preferred group of plasticizers is the phthalate esters with butylcyclohexyl phthalate being particularly preferred since it forms a coating with excellent balance of properties.

Blends of polymeric plasticizers and monomeric plasticizers can be used. Preferably, a weight ratio of 1:1 of monomeric to polymeric plasticizer can be used.

The coating compositions of this invention have a solids content of film-forming ingredients of from 5 to 45% by weight, and preferably, from 20 to 40% by weight. Examples of the volatile solvents and diluents which are used in formulating the coating compositions are: toluene, xylene, butyl ace-

tate, acetone, methylisobutyl ketone, methyl-ethyl ketone, butyl alcohol, and other aliphatic, cycloaliphatic and aromatic hydrocarbons, esters, ethers, ketones, and alcohols, such as are conventionally used in coating compositions.

Preferably, pigments are used in the coating compositions in an amount of from 0.1—20.0% pigment volume concentration; more preferably, a pigment volume concentration of from 0.3—6.0% is used. Examples of the great variety of pigments which may be used in the coating compositions are metal oxides, preferably titanium dioxide, or zinc oxide, metal hydroxides, metal flakes, chromates, such as lead chromate, sulfides, sulfates, carbonates, carbon black, silica, talc, china clay, organic dyes, and lead and iron blues, organic reds, and maroons.

The coating compositions can be applied to a variety of substrates, for example, wood, glass and metal, by any of the usual application methods, such as spraying, dipping, flow-coating and brushing. These coatings can be air dried or can be baked, for example, for 10 to 50 minutes at 125—175°C. The resulting coatings or films can be rubbed or polished in accordance with conventional techniques, if desired, to improve smoothness or gloss or both.

The coating compositions are particularly useful in repairing lacquer coatings and in particular acrylic lacquer coatings. The compositions have excellent adhesion and durability when dry and can be pigmented to blend the refinished area with the adjacent areas of the coating which makes the refinished area unnoticeable. Also, the coating compositions can be used to coat articles which are mass produced, as in the automobile industry.

The dried coatings of the compositions of this invention are characterized by increased freedom from water spotting and have excellent craze resistance in combination with outstanding durability and gloss retention. Coatings of this invention also have good gasoline resistance and improved adhesion as compared with conventional methyl methacrylate polymer lacquers.

In order that the invention may be more fully understood, the following Example is given by way of illustration only.

The parts and percentages are by weight unless otherwise specified.

EXAMPLE

A coating composition was formed by first preparing a polymer solution using the following components:

	Parts By Weight
5	
Portion 1	
Methyl amyl acetate	102.30
Xylol	152.00
10 Portion 2	
Methyl methacrylate monomer	224.80
"Chemacoil" TA-100 (reaction product of one mol of tris - (hydroxymethyl) - amino-methane with 3 mols of tall oil fatty acid which is subsequently reacted with one mole of formaldehyde using the process of U. S. Patent 3,248,397)	102.20
Cellosolve (trade mark) acetate	74.10
Dicumyl peroxide	4.10
Acrylonitrile	20.50
Ethyl acrylate monomer	61.30
25 Di - tertiary - butyl peroxide	6.20
Portion 3	
Toluene	74.10
Total	821.60

The multi-component portions were premixed before they were added. Portion 1 was charged into a conventional polymerization vessel equipped with stirrer, thermometer, means to introduce the reagents, and means of heating and cooling the reaction mixture and was heated with agitation to its reflux temperature which was about 132°C. to 135°C. Portion 2 was premixed only a short time before it was added since it was not stable and was added at an even and continuous rate over a 5-hour period with constant agitation while maintaining a reflux temperature of about 132 to 133°C. The mixture was held at its reflux temperature until a conversion of about 53.5% polymer solids was reached and a constant Gardner-Holt viscosity of Z_3-Z_4 is obtained. The mixture was then cooled to room temperature and Portion 3 added. The resulting mixture, which had a solids content of about 50%, was filtered to remove the coagulum that had formed during the reaction. The polymer contained 55% by weight methylmethacrylate, 15% by weight ethyl acrylate, 5% by weight acrylonitrile and 25% by weight of the oxazoline drying oil constituent.

A coating composition was then formulated by forming a pigment dispersion, mixing this dispersion with the above polymer solution and a cellulose acetate butyrate solution and diluting this mixture to a spray viscosity with solvents.

Formula Y Pigment Dispersion

	Parts By Weight
Polymer solution prepared above (50% solids)	188
Titanium dioxide pigment	580
Acetone	77
Toluene	129
Cellosolve acetate	26
Total	1000

The ingredients were premixed and charged into a conventional sand-grinding mill and ground to about a 0.3 mil fineness.

The coating composition was formed by mixing the following ingredients:

	Parts By Weight
Above prepared polymer solution (50% solids)	19.6
Formula Y Pigment dispersion	25.2
Cellulose acetate butyrate solution (25% solids, in acetone and toluene, 2 sec. viscosity measured at 25% polymer solids at 25°C. according to ASTM D-1343-56 and a butyryl content of 38% by weight)	53.7
Butylcyclohexyl phthalate	1.5
Total	100.0

The coating composition was reduced to a spray viscosity with acetone and toluene and a coating about 2 mils thick was sprayed onto each of the following sets of panels (15 panels per set); autobody steel panels which had been suitably primed; steel panels coated with acrylic lacquer and steel panels coated with a pigmented nitrocellulose lacquer.

The initial appearance of each of these sets of panels and adhesion of the lacquer to the various substrates were excellent.

Five panels of each of the above sets were subjected to a high-humidity-low temperature crack test which consisted of 24 cycles. In each cycle, the panels were subjected to (1) 100% relative humidity and 100°F. for 24 hours, (2) -10°F. for 24 hours and (3) room temperature for 4 hours. At the completion of each cycle, the panels were examined with a magnifying glass for cracks. At the end of the test, many of the above panels showed no cracking, while several had some slight insignificant cracks.

Ten panels of each of the sets were exposed outdoors in Florida at a 45° angle facing south. The panels were examined after 6 months and 12 months. After 12 months of weathering, each of the panels showed good color retention, excellent gloss, very little chalking and water spotting, and no loss of adhesion to the substrate.

Both the high humidity-cold crack test and the outdoor exposure test indicate that the acrylic lacquer composition of this invention is an excellent primary coating for metals and adheres well to an acrylic lacquer coating and a nitrocellulose lacquer coating even under severe testing conditions.

WHAT WE CLAIM IS:—

1. A coating composition which comprises from 5 to 45% by weight of a film-forming material in solution in a volatile organic liquid which includes at least one solvent for the film-forming material, said film-forming material consisting of

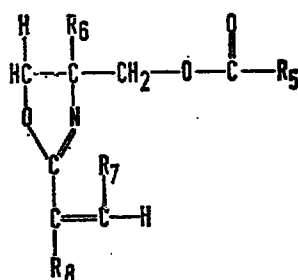
(a) from 40 to 60% by weight, based on the weight of the film-forming material, of an acrylic oxazoline polymer consisting of

(1) from 30 to 70% by weight, based on the weight of said polymer, of units derived from methyl methacrylate,

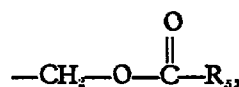
(2) less than 35% by weight of units derived from an ester of an α,β - olefinically - unsaturated monocarboxylic acid and a saturated aliphatic monohydric alcohol containing from 2 to 12 carbon atoms,

(3) less than 10% by weight of units derived from acrylonitrile, and

(4) from 15 to 35% by weight of units derived from a compound having the structural formula:—



where $\text{R}_5 - \text{CO} -$ is a fatty acid acyl radical containing from 4 to 22 carbon atoms derived from a saturated or unsaturated fatty acid, R_6 is H, a C_1 to C_4 alkyl group or



R_7 is H or a C_1 to C_4 alkyl group and R_8 is the residue of a saturated or unsaturated fatty acid containing from 4 to 22 carbon atoms minus the carboxyl group and the α - carbon atom;

(b) from 60 to 40% by weight, based on the weight of the film-forming material, of cellulose acetate butyrate having a viscosity of from 0.5 to 20 seconds at 25°C. measured

according to ASTM D-1343-56 and a butyryl content of from 30 to 5% by weight, and

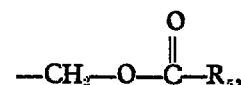
(c) from 0 to 10% by weight, based on the weight of the film-forming material, of an organic plasticizer which is a polymeric plasticizer, a monomeric plasticizer or a mixture of a polymeric plasticizer and a monomeric plasticizer.

2. A coating composition according to claim 1 which contains pigments in a pigment volume concentration of from 0.1 to 20%.

3. A coating composition according to claim 1 or 2 in which the α,β - olefinically - unsaturated monocarboxylic acid is acrylic acid or methacrylic acid.

4. A coating composition according to claim 1 or 2 in which said ester is an alkyl methacrylate or an alkyl acrylate in which the alkyl group has from 2 to 6 carbon atoms.

5. A coating composition according to any of claims 1 to 4 in which in the structural formula R_5 is a tall oil fatty acid residue, R_6 is a tall oil fatty acid residue less the alpha $-\text{CH}_2-$ group, R_7 is H and R_8 is



6. A coating composition according to claim 1 or 2 containing from 30 to 40% by weight, based on the weight of the coating composition, of a film-forming material consisting of

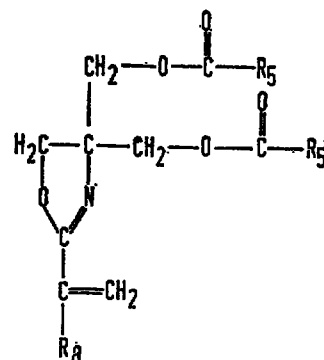
(a) from 40 to 49% by weight, based on the weight of the film-forming material, of an acrylic oxazoline polymer consisting of

(1) from 53 to 57% by weight, based on the weight of the polymer, of units derived from methyl methacrylate,

(2) from 13 to 17% by weight of units derived from ethyl acrylate,

(3) from 3 to 7% by weight of units derived from acrylonitrile, and

(4) from 23 to 27% by weight of units derived from a compound having the formula:



Both the high humidity-cold crack test and the outdoor exposure test indicate that the acrylic lacquer composition of this invention is an excellent primary coating for metals and adheres well to an acrylic lacquer coating and a nitrocellulose lacquer coating even under severe testing conditions.

WHAT WE CLAIM IS:—

1. A coating composition which comprises from 5 to 45% by weight of a film-forming material in solution in a volatile organic liquid which includes at least one solvent for the film-forming material, said film-forming material consisting of

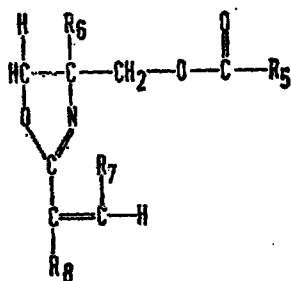
(a) from 40 to 60% by weight, based on the weight of the film-forming material, of an acrylic oxazoline polymer consisting of

(1) from 30 to 70% by weight, based on the weight of said polymer, of units derived from methyl methacrylate,

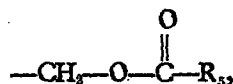
(2) less than 35% by weight of units derived from an ester of an α,β - olefinically - unsaturated monocarboxylic acid and a saturated aliphatic monohydric alcohol containing from 2 to 12 carbon atoms,

(3) less than 10% by weight of units derived from acrylonitrile, and

(4) from 15 to 35% by weight of units derived from a compound having the structural formula:—



where R_5 -CO— is a fatty acid acyl radical containing from 4 to 22 carbon atoms derived from a saturated or unsaturated fatty acid, R_6 is H, a C_1 to C_4 alkyl group or



R_7 is H or a C_1 to C_4 alkyl group and R_8 is the residue of a saturated or unsaturated fatty acid containing from 4 to 22 carbon atoms minus the carboxyl group and the α - carbon atom;

(b) from 60 to 40% by weight, based on the weight of the film-forming material, of cellulose acetate butyrate having a viscosity of from 0.5 to 20 seconds at 25°C. measured

according to ASTM D-1343-56 and a butyryl content of from 30 to 5% by weight, and

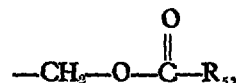
(c) from 0 to 10% by weight, based on the weight of the film-forming material, of an organic plasticizer which is a polymeric plasticizer, a monomeric plasticizer or a mixture of a polymeric plasticizer and a monomeric plasticizer.

2. A coating composition according to claim 1 which contains pigments in a pigment volume concentration of from 0.1 to 20%.

3. A coating composition according to claim 1 or 2 in which the α,β - olefinically - unsaturated monocarboxylic acid is acrylic acid or methacrylic acid.

4. A coating composition according to claim 1 or 2 in which said ester is an alkyl methacrylate or an alkyl acrylate in which the alkyl group has from 2 to 6 carbon atoms.

5. A coating composition according to any of claims 1 to 4 in which in the structural formula R_5 is a tall oil fatty acid residue, R_6 is a tall oil fatty acid residue less the alpha $-\text{CH}_2-$ group, R_7 is H and R_8 is



6. A coating composition according to claim 1 or 2 containing from 30 to 40% by weight, based on the weight of the coating composition, of a film-forming material consisting of

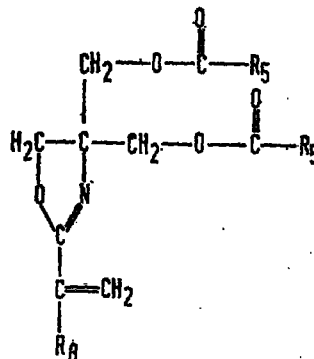
(a) from 40 to 49% by weight, based on the weight of the film-forming material, of an acrylic oxazoline polymer consisting of

(1) from 53 to 57% by weight, based on the weight of the polymer, of units derived from methyl methacrylate,

(2) from 13 to 17% by weight of units derived from ethyl acrylate,

(3) from 3 to 7% by weight of units derived from acrylonitrile, and

(4) from 23 to 27% by weight of units derived from a compound having the formula:



- where R_2 is a hydrocarbon residue of a tall oil fatty acid and R_{11} is a hydrocarbon residue of a tall oil fatty acid less the alpha $-\text{CH}_2-$ group
- 5 (b) from 48 to 55% by weight, based on the weight of the film-forming material, of cellulose acetate butyrate having a viscosity of from 1 to 4 seconds at 25°C. measured according to ASTM D-1343-56 and a butyryl content of from 35 to 45% by weight, and
- 10 (c) from 3 to 6% by weight of a phthalate ester plasticizer.
7. A coating composition according to any of claims 1 to 6 in which the plasticizer is
- 15 butylcyclohexyl phthalate.
8. A modification of the coating composition according to any of claims 1 to 7, in which up to 15%, by weight, of units derived from styrene are substituted for part or all of the units derived from the α, β - olefinically - unsaturated monocarboxylic acid ester.
9. A coating composition according to claim 1 substantially as herein described in the Example.
10. An article coated on at least one surface with a dried coalesced layer of a composition as claimed in any of the preceding claims.
11. An article coated with a paint layer and having a dried coalesced layer of a composition as claimed in any of claims 1 to 9 firmly adhered to said paint layer.
12. An article according to claim 10 or 11 formed of steel.
- 20
- 25
- 30
- A. A. THORNTON & CO.,
Chartered Patent Agents,
Northumberland House,
303/306, High Holborn,
London, W.C.1.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1971.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.



* C L H S *