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METHOD FOR FINISHING A CEMENT BASE MATERIAL

The present invention relates to a method for finishing a cement base material by means of a paint-finishing composition. More particularly, the present invention relates to the use, in such a method of a  
5 paint-finishing composition containing a special fluorinated polymer, whereby a paint-finish of a cement base material having improved durability is obtainable.

Cement base materials such as concrete materials, asbestos slates, calcium silicate materials or plaster-slag materials are widely used in the field of building  
10 and construction materials. A method for paint-finishing is known wherein a cured paint film of a finishing material is formed on such a cement base material with an intermediate coating interposed  
15 between the base material and the paint film, primarily for the purpose of imparting a beautiful outer appearance.

As such a finishing material, it has been common to use an acryl urethane paint, an acryl  
20 melamine paint, a polyester paint, a thermoplastic acrylic resin paint or the like. However, there have been various problems in the use of these finishing materials. For instance, cracks or blisters are likely to be formed in the paint film of  
25 the finishing material, or in an extreme case, peeling or paint-off is likely to be caused, by exudation of an alkali from the base material or by the action of the sun light, wind and rain, whereby the outer appearance is likely to be impaired. Thus, there has been a  
30 drawback that it is required to repaint the finishing material frequently.

The present inventors have conducted extensive researches to overcome the above problems and as a result, have found that the durability of the paint finish can be remarkably improved by using a finishing material composed of a composition containing a certain specific fluorinated polymer. Thus, the present invention has been accomplished based on this discovery.

The present invention provides a method for finishing a cement base material comprising:

(a) forming on the cement base an intermediate coating comprising a layer containing an epoxy resin, a phenol alkyd resin, a synthetic rubber, an ethylene-vinyl acetate copolymer, a vinyl chloride copolymer sol or a urethane-modified epoxy resin paint, said intermediate coating having an outer surface; and

(b) forming on said outer surface a cured paint layer of a solution or dispersion comprising:

100 parts by weight of a solvent-soluble fluorinated polymer containing cure sites which are hydroxyl groups, epoxy groups, carboxyl groups, acid amide groups, ester groups, unsaturated bonds, active hydrogen atoms or halogen atoms, and having an intrinsic viscosity of from 0.05 to 2.0 dl/g as measured at 30°C in tetrahydrofuran;

from 0.1 to 100 parts by weight of a curing agent, and

from 5 to 500 parts by weight of a colouring agent.

Now, the present invention will be described in detail with reference to the preferred embodiments.

In the present invention, it is important to use as the finishing material, a composition containing the specific fluorinated polymer. The fluorinated

polymer has cure sites and an intrinsic viscosity of from 0.05 to 2.0 dl/g, preferably from 0.07 to 0.8 dl/g, as measured at 30°C in tetrahydrofuran, and it is a solvent-soluble type. If the polymer does not have cure  
5 sides, the paint film thereby obtained will be poor in its durability. If the intrinsic viscosity is too low, and the mechanical strength of the paint film tends to be low, and if the intrinsic viscosity is too high, the concentration of the solution will have to be decreased  
10 to adjust the viscosity of the composition, whereby the processability will be impaired. Further, a solvent-insoluble polymer is not suitable for use since it is difficult to form a uniform paint film with such a polymer.

15 In the method of the present invention, not only a polymer obtained by addition polymerization but also a polymer obtained by condensation polymerization may be used as the fluorinated polymer. As the polymer obtained by addition polymerization, there may be  
20 mentioned a polymer or copolymer obtained by addition polymerisation of a fluorine - containing unsaturated compound. As the polymer obtained by condensation polymerization, there may be mentioned an epoxy resin having fluorine-containing bifunctional groups or a  
25 condensation product of a fluorine-containing diol, dibasic acid, dibasic acid anhydride or diisocyanate which contains ester bonds, urethane bonds or urea bonds.

The polymer or copolymer will contain cure sites such as hydroxyl groups, epoxy groups, carboxyl groups,  
30 acid amide groups, ester groups, unsaturated bonds, active hydrogen atoms or halogen atoms.

As such a fluorinated polymer, an addition polymerization type polymer such as a copolymer of a fluoroolefin with a hydrocarbon-type vinyl ether may  
35 preferably be used from the viewpoints of the weather resistance and the mechanical properties of the cured paint.

film and its availability.

As the fluoroolefin-vinyl ether copolymer preferably used in the present invention, there may be mentioned a copolymer comprising from 30 to 70 molar % of fluoroolefin units and from 70 to 30 molar % of vinyl ether units. Tetrafluoroethylene and chlorotrifluoroethylene may be mentioned as a preferred fluoroethylene component, and an alkyl vinyl ether containing a straight-chained, branched or cyclic alkyl group having from 2 to 8 carbon atoms may be mentioned as a preferred vinyl ether component.

As a comonomer which introduces cure sites to such a copolymer, a vinyl ether containing a functional group such as hydroxyalkyl vinyl ether or a glycidyl vinyl ether is preferably used. Such a copolymer preferably contains not more than 30 molar % of the hydroxyalkyl vinyl ether or glycidyl vinyl ether units.

The above-mentioned copolymer may be prepared by conducting copolymerization of a mixture of monomers in a predetermined ratio in the presence or absence of a polymerization medium by using a polymerization initiator or by application of a polymerization initiating source such as ionizable radiation.

According to the present invention, a curing agent such as a polyfunctional compound reactive with the cure sites of the fluorinated polymer is incorporated in the composition containing the fluorinated polymer in a proportion of from 0.1 to 100 parts by weight, preferably from 0.5 to 50 parts by weight, relative to 100 parts by weight of the polymer. Further, a curing assistant or a curing catalyst may optionally be incorporated.

For instance, in the case of a fluorinated polymer having hydroxyl groups as the cure sites, a diisocyanate or a titanium alkoxide is

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preferably used as the curing agent to obtain a composition which is curable at a normal temperature. If it is desired to obtain a heat curable composition, a melamine curing agent, a urea resin curing agent or a polybasic acid curing agent which is commonly used in a heat curable acrylic paint, may effectively be used as the curing agent. As the melamine curing agent, there may be mentioned butylated melamine, methylated melamine or an epoxy-modified melamine. The degree of the modification may be selected within a range of from 0 to 6 depending upon the particular purpose. Likewise, the self-condensation degree may optionally be selected. As the urea resin, there may be mentioned methylated urea or butylated urea. As the polybasic acid curing agent, a long-chained aliphatic dicarboxylic acid, an aromatic polybasic carboxylic acid or its anhydride or a block polyisocyanate is useful. When a melamine curing agent or a urea curing agent is used, it is possible to facilitate the curing by an addition of an acidic catalyst. As another example, in the case of a fluorinated polymer having epoxy groups as the cure sites, an amine, a carboxylic acid, a phenol or an alcohol is useful as the curing agent. In this case, a polyhydroxy compound, particularly a non-aromatic diol, is useful as curing assistant.

It is desirable that such a curing system is optionally selected depending upon the nature of the base material. For instance, a normal temperature curing system is preferably employed for on-the-spot application as in the case of the paint finish of a concrete structure, and a heat curing system may be employed without trouble when the application is carried out in a factory as in the case of the paint finish of asbestos slate plates.

In the present invention, it is important that a coloring agent is incorporated in the composition in an amount of from 5 to 500 parts by weight, preferably from 10 to 200 parts by weight, relative to 100 parts by weight of the fluorinated polymer. The coloring agent serves not only to impart a beautiful outer appearance but also to prevent the penetration of the ultra-violet ray in the sun light by its shielding effect, whereby the deterioration of the intermediate coating will be prevented and the durability of the paint finish will be improved.

If the amount of the coloring agent is too small, no adequate effectiveness will be obtained. On the other hand, an excessive amount tends to lead to deterioration of the paint film and a decrease of the durability.

As the coloring agent, an inorganic pigment, especially a calcined pigment is preferred from the viewpoint of the prevention of discoloration, although an organic type pigment such as phthalocyanine blue may also be used.

In the method of the present invention, the intermediate coating serves as a medium for the adhesion of the paint film of the finishing material with the cement base material, and it also serves to cover voids on the surface of the base material and to prevent exudation of an alkali from the base material. For such an intermediate coating, a layer of an epoxy resin paint, a phenol alkyd resin paint and synthetic rubber paint which are commonly used for such a purpose, and an ethylene-vinyl acetate copolymer paint, a vinyl chloride copolymer sol paint and a urethane-modified epoxy resin paint is used.

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Such an intermediate coating may not necessarily be a single layer formed as a covering layer on the base material, and may have a multi-layered structure wherein a base layer made of the above-mentioned material is formed in direct contact with the base material and an additional layer of an epoxy resin paint or a thermoplastic acrylic resin paint containing cement is formed thereon, or a pattern-forming layer of an epoxy resin paint or a thermoplastic acrylic paint containing a fine aggregate material such as lime stone sand or silica sand or a filler such as clay or talc is formed on a similar base layer.

According to the present invention, a paint finish having superior durability is obtainable. Accordingly, the present invention is extremely useful particularly in the field of ceramic construction materials.

Now, the present invention will be described in further detail with reference to Examples. However, it should be understood that the present invention is by no means limited to these specific examples.

#### EXAMPLE 1:

A white paint composition having the following composition was prepared by using a fluorinated polymer comprising chlorotrifluoroethylene, cyclohexyl vinyl ether and hydroxybutyl vinyl ether in molar ratios of 50, 40 and 10%, respectively, and having a hydroxyl group value of 50 mgKOH/g and an intrinsic viscosity of 0.23 dl/g as measured at 30°C in tetrahydrofuran.

|    |                                                        |                     |
|----|--------------------------------------------------------|---------------------|
|    | The above-mentioned fluorinated polymer                | 100 parts by weight |
| 25 | Titanium oxide                                         | 42 "                |
|    | Xylene/methyl isobutyl ketone (50/50)<br>mixed solvent | 200 "               |

To the white paint composition, 18 parts by weight of an isocyanate curing agent (Colonate EH, manufactured by Nippon Polyurethane Co.) was added and uniformly mixed. By means of a spray machine, the mixture thereby obtained was applied onto a slate plate having a thickness of 6 mm which was preliminarily prepared by applying the following paints to form an intermediate coating having a double layered structure. The coated slate plate was left for one week at room temperature, and then subjected to various tests for the paint film properties. In each test, no abnormality in the paint film was observed and it was confirmed that the paint finish had superior durability.

Formation of the intermediate coating

- First layer: a paint film of an ethylene-vinyl acetate copolymer paint
- 15 Second layer: an epoxy resin emulsion paint containing 60% by weight of cement

Tests for the paint film properties

- (1) Accelerated weather resistance test  
(in accordance with JIS A-1415)
- 20 Sunshine Weather Meter
- Black panel temperature: 63°C
- Humidity : 50% RH
- Water spray : water was continuously sprayed for 12 minutes every hour

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(2) Warming-cooling repeating test

(in accordance with JIS A-6910)

Cycle: Immersion in water : 18 hours

Low temperature storage: 3 hours  
(-20°C)

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High temperature storage: 3 hours  
(50°C)

(3) Alkali resistance test

Immersion in a saturated slaked lime aqueous solution

(4) Gloss

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60° - 60° specular gloss

EXAMPLES 2 to 8 and COMPARATIVE EXAMPLES 1 and 2

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Paint films having the compositions identified in Tables 1 and 2 were prepared and they were subjected to various property tests. The results thereby obtained are shown in Table 3. It is evident from the results that the paint finish of the cement base materials according to the present invention is superior to the paint finish obtained by the conventional methods.

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Table 1

|                     |   | Base material | Intermediate coating |                         | Finishing material |                              |
|---------------------|---|---------------|----------------------|-------------------------|--------------------|------------------------------|
|                     |   |               | Materials            | Thickness $\mu\text{m}$ | Composition        | Film thickness $\mu\text{m}$ |
| Example             | 1 | A             | F/G                  | 10/1000                 | J                  | 40                           |
|                     | 2 | B             | F/G                  | 10/1000                 | J                  | 40                           |
|                     | 3 | C             | F/G                  | 10/1000                 | J                  | 40                           |
|                     | 4 | D             | H                    | 15                      | J                  | 40                           |
|                     | 5 | E             | F                    | 15                      | J                  | 40                           |
|                     | 6 | A             | H                    | 15                      | K                  | 20                           |
|                     | 7 | A             | H                    | 15                      | L                  | 20                           |
|                     | 8 | A             | H                    | 15                      | M                  | 20                           |
| Comparative Example | 1 | A             | H                    | 15                      | N                  | 60                           |
|                     | 2 | B             | F/G                  | 10/1000                 | N                  | 60                           |

**Notes:**

A: Slate plate

B: Concrete plate

C: Glass fiber-reinforced concrete plate

D: Plaster-slag plate

E: Light weight concrete plate

F: Ethylene-vinyl acetate copolymer

G: Epoxy resin containing 60% by weight of cement

H: Epoxy resin

J - N: See Table 2

Table 2

|   | Polymers                                                                                                                  |                     | Curing agents                                                                  |                   |
|---|---------------------------------------------------------------------------------------------------------------------------|---------------------|--------------------------------------------------------------------------------|-------------------|
|   | Composition                                                                                                               | Intrinsic viscosity | Kind                                                                           | Amount (Phr)      |
| J | Same as Example 1                                                                                                         | Same as Example 1   | Same as Example 1                                                              | Same as Example 1 |
| K | Copolymer of chlorotri-fluoroethylene, cyclo-hexyl vinyl ether and glycidyl vinyl ether in molar ratios of 52, 10 and 38% | 0.19                | Dimethyl cyclo-hexylamine hydrochloride                                        | 1                 |
| L | Condensation product of $\text{HOCH}_2(\text{CF}_2)_4\text{CH}_2\text{OH}$ with epichlorohydrin                           | 0.11                | Isocyanate curing agent (Desmodule N, manufactured by Sumitomo Bayer)          | 14                |
| M | Same as Example 1                                                                                                         | Same as Example 1   | Melamine curing agent* (Cymel <sup>®</sup> 303, manufactured by Mitsui Toatsu) | 6                 |
| N | Acryl urethane resin hydroxyl group value: 50 mgKOH/g                                                                     | --                  | Same as Example 1                                                              | 20                |

The coloring agent in each of J to N was the same as the one used in Example 1.

\* "Cymel" is a Registered Trade Mark

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Table 3

|                       | Accelerated weather resistance test |                    |                              |                      | Warming-cooling cycle |                            | Alkali resistance |                 |
|-----------------------|-------------------------------------|--------------------|------------------------------|----------------------|-----------------------|----------------------------|-------------------|-----------------|
|                       | Exposure time (hrs)                 | Gloss relation (%) | Discoloration (yellow index) | Outer appearance     | Number of cycles      | Result                     | Number of days    | Result          |
| Example 1             | 1000                                | 102                | 3                            | Normal               | 2                     | Normal                     | 7                 | Normal          |
|                       | 2000                                | 105                | 4                            | "                    | 4                     | "                          | 10                | "               |
|                       | 4000                                | 93                 | 4                            | "                    | 10                    | "                          | 15                | "               |
|                       | 4000                                | 91                 | 4                            | "                    | 10                    | "                          | 15                | "               |
|                       | 4000                                | 90                 | 4                            | "                    | 10                    | "                          | 15                | "               |
|                       | 4000                                | 93                 | 4                            | "                    | 10                    | "                          | 15                | "               |
|                       | 4000                                | 89                 | 4                            | "                    | 10                    | "                          | 15                | "               |
|                       | 2000                                | 98                 | 4                            | "                    | 4                     | "                          | 7                 | "               |
| 7                     | 4000                                | 91                 | 4                            | "                    | 10                    | "                          | 15                | "               |
|                       | 2000                                | 94                 | 4                            | "                    | 4                     | "                          | 7                 | "               |
|                       | 4000                                | 86                 | 4                            | "                    | 10                    | "                          | 15                | "               |
|                       | 4000                                | 86                 | 4                            | "                    | 10                    | "                          | 15                | "               |
|                       | 1000                                | 65                 | 10                           | Normal               | 2                     | Fine blister formed        | 7                 | Cracks appeared |
|                       | 2000                                | 14                 | 28                           | Fine cracks appeared | 4                     | Substantial blister formed | 10                | Blister formed  |
|                       | 1000                                | 59                 | 9                            | Normal               | 2                     | Normal                     | 7                 | "               |
|                       | 2000                                | 17                 | 21                           | Fine cracks appeared | 4                     | Blister formed             | 10                | "               |
| Comparative Example 1 |                                     |                    |                              |                      |                       |                            |                   |                 |

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**EXAMPLE 9:**

The tests were conducted in the same manner as in Example 6 except that 25 phr of titanium oxide and 25 phr of calcined yellow pigment were used instead of 42 phr of titanium oxide. The results  
5 thereby obtained were substantially the same as those obtained in Example 6. In this case, the color difference  $\Delta E$  after the 4000 hours of accelerated weather resistance test was as small as 2.



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CLAIMS:-

1. A method for finishing a cement base material comprising:

(a) forming on the cement base an intermediate coating comprising a layer containing an epoxy resin, a phenol alkyd resin, a synthetic rubber, an ethylene-vinyl acetate copolymer, a vinyl chloride copolymer sol or a urethane-modified epoxy resin paint, said intermediate coating having an outer surface; and

(b) forming on said outer surface a cured paint layer of a solution or dispersion comprising:

100 parts by weight of a solvent-soluble fluorinated polymer containing cure sites which are hydroxyl groups, epoxy groups, carboxyl groups, acid amide groups, ester groups, unsaturated bonds, active hydrogen atoms or halogen atoms, and having an intrinsic viscosity of from 0.05 to 2.0 dl/g as measured at 30°C in tetrahydrofuran;

from 0.1 to 100 parts by weight of a curing agent, and

from 5 to 500 parts by weight of a coloring agent.

2. A method as claimed in claim 1 wherein the fluorinated polymer is a copolymer of a fluoroolefin with a hydrocarbon-type vinyl ether comprising from 30 to 70 molar % of fluoroolefin units, from 70 to 30 molar % of vinyl ether units, and not more than 30 molar % of hydroxy alkyl vinyl ether units.

3. A method as claimed in claim 1 or 2 wherein the composition used in (b) is curable at ambient temperature.

4. A method as claimed in any of claims 1 to 3 wherein the curing agent is a diisocyanate or a titanium alkoxide.

5. A method as claimed in any of claims 1 to 4

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wherein the coloring agent is an inorganic pigment.

6. A method as claimed in any of claims 1 to 5,  
wherein the intermediate coating comprises a second  
layer containing an epoxy resin or a thermoplastic acrylic  
5 resin containing cement on the surface of the first layer  
remote from the cement base material.

7. A method as claimed in any of claims 1 to 5  
wherein the intermediate coating comprises a second  
layer containing an epoxy resin or a thermoplastic  
10 acrylic resin containing limestone, silica, clay or talc  
on the surface of the first layer remote from the cement  
base material.

8. A method as claimed in claim 1, substantially  
as described in the Examples.

15 9. A cement base material whenever finished by a  
method as claimed in any of claims 1 to 8.

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