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(74) Agent: **OHTANI, Tamotsu**; OHTANI PATENT OFFICE,
Bridgestone Toranomon Bldg., 6F. 25-2, Toranomon
3-chome, Minato-ku, Tokyo 105-0001 (JP).

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(71) Applicant (for all designated States except US): **NIPPON
PAINT CO., LTD.** [JP/JP]; 2-1-2, Oyodokita, Kita-ku, Os-
aka-shi, Osaka 531-8511 (JP).

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(72) Inventors; and

(75) Inventors/Applicants (for US only): **TANAKA, Yasuo**
[JP/JP]; c/o NIPPON PAINT CO., LTD., 4-1-15, Mi-
namishinagawa, Shinagawa-ku, Tokyo 140-8675 (JP).
KAWABE, Yoshiki [JP/JP]; c/o NIPPON PAINT CO.,
LTD., 1-30, Nihookimachi, Minami-ku, Hiroshima-shi,
Hiroshima 734-0057 (JP). **KOIZUMI, Atsushi** [JP/JP];
c/o NIPPON PAINT CO., LTD., 19-17, Ikedanakamachi,
Neyagawa-shi, Osaka 572-8501 (JP).

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(54) Title: WATER-BORNE PRIMER SURFACER

(57) Abstract: A water-borne primer surfacer which comprises (a) a water-dispersible vinyl-modified polyester resin, (b) a water-soluble epoxy-modified polyester resin and (c) a melamine resin is provided. A multi-layer coating film exhibiting excellent property for designing and excellent functions can be formed even when a primer film, a base coat and a clear coat are formed in accordance with the three -coat one -bake coating process.

WO 2009/060992 A1

DESCRIPTION

WATER-BORNE PRIMER SURFACER

5 TECHNICAL FIELD

The present invention relates to a water-born primer surfacer. More particularly, the present invention relates to a water borne primer surfacer which forms a multi-layer coating film exhibiting excellent property for designing and excellent functions even when a primer film, a
10 base coat and a clear coat are formed in accordance with the three-coat one-bake coating process.

BACKGROUND ART

In the field of the coating material and, in particular, in the field of
15 the automotive coating, it is strongly required recently that organic solvent-borne coating materials be replaced with water-borne coating materials and steps of coating be decreased so that tasks such as saving of resources, saving of cost and decrease in the load on the environment (for example, VOC and HAPs) can be achieved. As for the decrease in the
20 steps of coating, the three-coat two-bake coating process, in which, after an electrodeposition coating film is formed and baked, a primer film is formed and baked and a base coat and a clear coat are formed and baked, has been widely used in conventional procedures of coating and finishing of automobiles. Recently, the three-coat one-bake coating process, in
25 which, after an electrodeposition coating film is formed and baked, a primer surfacer, a base coating material and a clear coating material are

applied in accordance with the wet-on-wet process and the obtained uncured coating film having a multi-layer structure is baked together, has been developed.

In general, a coating film plays the role on designing such as
5 improving the appearance and the role on functions such as protecting articles for coating. In particular, the primary surfacer is required to exhibit the excellent property for the designing and excellent functions. For example, it is required for the primer surfacer for automobiles that a coating film exhibiting satisfactory properties such as the excellent
10 property to hide roughness of the electrodeposition coating film (the property to hide the substrate) and chipping resistance be formed.

To satisfy the above requirements for the coating film, it has been heretofore conducted that a specific organic solvent-borne primer surfacer is used and, after the primer surfacer is applied and baked, a base coating
15 material and a clear coating material are applied to form a multi-layer coating film. Minute roughness on the substrate such as a steel plate and an electrodeposition coating film can be hidden and the chipping resistance can be increased in accordance with the above process. Coating technologies which can achieve the conversion into water-based
20 coating materials and the application to the three-coat one-bake coating process described above have been developed, recently. For example, in Patent Reference 1, a water-borne primer surfacer containing a specific polyester resin is disclosed, and a primer film exhibiting excellent adhesion with coating films formed on the primer film can be formed by
25 using the water-borne primer surfacer.

However, the decrease in the appearance of an article having the

multi-layer coating film due to the effect of the roughness of the substrate, which has been the problem of the three-coat one-bake coating process, is not improved by the above coating technologies, and it is necessary for obtaining an excellent appearance of the coating film that the substrate be suitably controlled. Therefore, a primer surfacer and a coating process which can form a multi-layer coating film exhibiting a sufficient hiding effect, excellent property for designing and excellent functions even when the coating film is formed in accordance with the three-coat one-bake coating process, has been desired.

[Patent Reference 1] Japanese Patent Application Laid-Open No. 2002-126637

DISCLOSURE OF THE INVENTION

[Problems to be Overcome by the Invention]

The present invention has an object of providing a water-borne primer surfacer which forms a primer film exhibiting excellent smoothness and excellent property for dispersing pigments and a multi-layer coating film exhibiting excellent appearance and excellent functions such as water resistance and chipping resistance even when a primer film, a base coat and a clear coat are formed in accordance with the three-coat one-bake coating process, a process for forming the multi-layer coating film and a coated article having the multi-layer coating film.

[Means for Overcoming the Problems]

The present inventors had found that, when a multi-layer coating film was formed in accordance with a three-coat one-bake process, i.e., in accordance with a process comprising step (1) in which an article for

coating having an electrodeposition coating film is coated with a water-borne primer surfacer to form an uncured primer film, step (2) in which the uncured primer film is coated with a water-borne base coating material to form an uncured base coat, step (3) in which the uncured base coat is coated with a clear coating material to form an uncured clear coat, and step (4) in which the uncured primer film, the uncured base coat and the uncured clear coat are simultaneously cured by heating, sufficient effect of hiding the substrate could be obtained by increasing the concentration of the solid components in the primer film before the base coating material is applied. However, since the skin of the surface of the film formed with the water-borne primer surfacer becomes poor (the smoothness is decreased) in accordance with the above coating process, it is difficult that the appearance of the multi-layer coated film is improved in accordance with this process.

As the result of further intensive studies by the present inventors, it was found that, when a specific water-borne primer surfacer was used, a primer film exhibiting excellent property for hiding the substrate and excellent smoothness could be formed, and a multi-layer coating film exhibiting excellent water resistance and excellent chipping resistance could be formed.

The present invention provides:

(1) A water-borne primer surfacer which comprises (a) a water-dispersible vinyl-modified polyester resin, (b) a water-soluble epoxy-modified polyester resin and (c) a melamine resin;

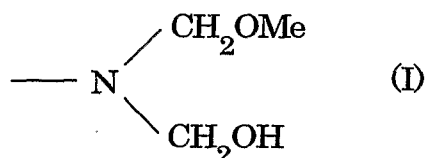
(2) A water-borne primer surfacer according to (1), wherein

the water-dispersible vinyl-modified polyester resin of component

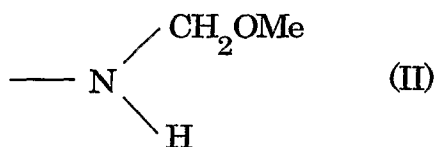
(a) is a polyester resin having an acid value of 20 to 100 mg KOH/g, a degree of neutralization of 70 to 100% and a weight-average molecular weight of 10,000 to 150,000, and

the water-soluble epoxy-modified polyester resin of component (b) is
 5 a polyester resin having an acid value of 25 to 50 mg KOH/g, a degree of neutralization of 70 to 100% and a weight-average molecular weight of 5,000 to 30,000;

(3) A water-borne primer surfacer described in any one of (1) and (2), wherein the melamine resin of component (c) is at least one melamine
 10 resin selected from melamine resins of a methylol type having, as a reactive group, a group expressed by formula (I):



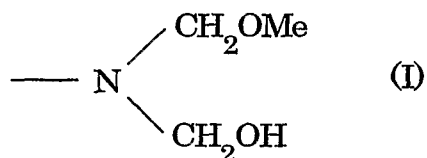
melamine resins of an imino type having, as a reactive group, a group expressed by formula (II):



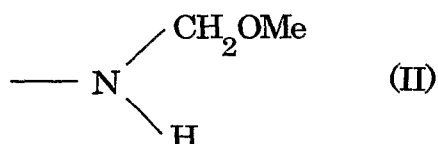
15 and melamine resins of a methylol/imino type having, as reactive groups, both of the group expressed by formula (I) and the group expressed by formula (II);

(4) A water-borne primer surfacer described in any one of (1) and (2),
 20 wherein the melamine resin of component (c) comprises a combination of at least one melamine resin selected from melamine resins of a methylol

type having, as a reactive group, a group expressed by formula (I):

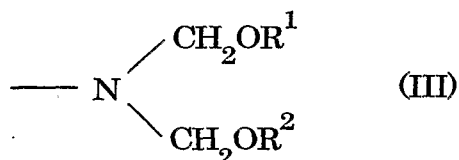


melamine resins of an imino type having, as a reactive group, a group expressed by formula (II):



5

and melamine resins of a methylol/imino type having, as reactive groups, both of the group expressed by formula (I) and the group expressed by formula (II), and a melamine resin of a complete alkyl ether type having, as a reactive group, a group represented by general formula (III):



10

R^1 and R^2 each independently representing an alkyl group having 1 to 4 carbon atoms; and

an amount of the melamine resin of a complete alkyl ether type is 60% by mass or smaller based on an entire amount of the melamine resin of component (c);

15

(5) A water-borne primer surfacer described in any one of (1) to (4), which further comprises (d) a water-soluble epoxy resin;

(6) A water-borne primer surfacer described in (5), wherein

a ratio of amounts by mass of the water-dispersible vinyl-modified

polyester resin of component (a) to the water-soluble epoxy-modified polyester resin of component (b) is 5:95 to 95:5, the amounts being expressed as amounts of solid components of the resins;

an amount of the melamine resin of component (c) is 25 to 100% by mass based on a sum of amounts of the water-dispersible vinyl-modified polyester resin of component (a) and the water-soluble epoxy-modified polyester resin of component (b), the amounts being expressed as amounts of solid components of the resins; and

an amount of the water-soluble epoxy resin of component (d) is 3 to 25% by mass based on a sum of amounts of the water-dispersible vinyl-modified polyester resin of component (a), the water-soluble epoxy-modified polyester resin of component (b) and the melamine resin of component (c), the amounts being expressed as amounts of solid components of the resins;

(7) A water-borne primer surfacer described in any one of (5) and (6), which further comprises (e) crosslinked resin particles, and an amount of the crosslinked resin particles of component (e) is 3 to 40% by mass based on a sum of amounts of the water-dispersible vinyl-modified polyester resin of component (a), the water-soluble epoxy-modified polyester resin of component (b), the melamine resin of component (c) and the water-soluble epoxy resin of component (d), the amounts being expressed as amounts by mass of solid components of the resins;

(8) A water-borne primer surfacer described in any one of (1) to (7), which further comprises (f) pigments, and an amount of the pigments of component (f) is 20 to 70% by mass, the amount being expressed as a pigment weight concentration (PWC);

(9) A water-borne primer surfacer described in any one of (1) to (8), which is a water-borne primer surfacer used for a process for forming a multi-layer coating film, wherein the process for forming a multi-layer coating film comprises step (1) in which an article for coating having an electrodeposition coating film is coated with the water-borne primer surfacer to form an uncured primer film, step (2) in which the uncured primer film is coated with a water-borne base coating material to form an uncured base coat, step (3) in which the uncured base coat is coated with a clear coating material to form an uncured clear coat, and step (4) in which the uncured primer film, the uncured base coat and the uncured clear coat are simultaneously cured by heating;

(10) A process for forming a multi-layer coating film which comprises step (1) in which an article for coating having an electrodeposition coating film is coated with a water-borne primer surfacer to form an uncured primer film, step (2) in which the uncured primer film is coated with a water-borne base coating material to form an uncured base coat, step (3) in which the uncured base coat is coated with a clear coating material to form an uncured clear coat, and step (4) in which the uncured primer film, the uncured base coat and the uncured clear coat are simultaneously cured by heating, wherein a water-borne primer surfacer described in any one of (1) to (8) is used as the water-borne primer surfacer;

(11) A process for forming a multi-layer coating film described in (10), wherein a base coating material comprising an acrylic emulsion is used as the water-borne base coating material;

(12) A process for forming a multi-layer coating film described in any one of (10) and (11), wherein preheating is conducted between step (1) and

step (2) and/or between step (2) and step (3); and

(13) A coated article having a multi-layer coating film which is formed in accordance with a process described in any one of (10) to (12).

5 THE EFFECT OF THE INVENTION

In accordance with the present invention, a water borne primer surfacer which forms a multi-layer coating film exhibiting excellent property for designing and excellent functions even when a primer film, a base coat and a clear coat are formed in accordance with the three-coat
10 one-bake coating process can be provided.

THE MOST PREFERRED EMBODIMENT TO CARRY OUT THE INVENTION

The water-borne primer surfacer of the present invention comprises
15 (a) a water-dispersible vinyl-modified polyester resin and (b) a water-soluble epoxy-modified polyester resin as the resin components forming a coating film. In other words, the water-borne primer surfacer of the present invention comprises hydrophilic polyester resins as the resin forming a coating film, and a water-dispersible polyester resin and a
20 water-soluble polyester resin are used in combination as the hydrophilic polyester resins. The water-soluble resin means a resin which can be dissolved in water. The water-dispersible resin means a resin which can form a system finely dispersed in water such as an emulsion and a suspension although the resin is not soluble in water.

25 It can be decided whether the resin used in the present invention (the polyester resins described above and (d) the water-soluble epoxy

resin) is water-soluble or water-dispersible by the absence or the presence, respectively, of turbidness when the resin is mixed with water, i.e., in accordance with the turbidimetry. It is preferable that the examination is made using water alone as the solvent although hydrophilic solvents
5 such as butylcellosolve may be contained in water as long as the content of the hydrophilic solvent is small (about 5% by weight based on the amount of the mixed fluid of the resin and water).

The water-dispersible vinyl-modified polyester resin of component (a) used in the present invention is a water-dispersible polyester resin in
10 which chains of a fatty acid having a vinyl polymer portion are bonded. It is preferable that 15 to 45% by mass of the water-dispersible vinyl-modified polyester resin of component (a) is the vinyl polymer portion, and 10 to 50% by mass of the vinyl polymer portion is a constituting unit derived from an α,β -ethylenically unsaturated monomer
15 having carboxyl group.

The water-dispersible vinyl-modified polyester resin of component (a) can be obtained, for example, by condensation of a vinyl-modified fatty acid having a vinyl polymer portion, which can be obtained by radical polymerization of an α,β -ethylenically unsaturated monomer having
20 carboxyl group and other copolymerizable α,β -ethylenically unsaturated monomers in the presence of an unsaturated fatty acid, [hereinafter, referred to as (a-1) a vinyl-modified fatty acid] and a polyester resin having hydroxyl group which will be described below [hereinafter, referred to as (a-2) a polyester resin having hydroxyl group].

25 Examples of the unsaturated fatty acid include fatty acids derived from various types of (semi)drying oils and non-drying oils such as tung

oil, linseed oil, soybean oil, safflower oil, castor oil, dehydrated castor oil, rice bran oil, cotton seed oil and coconut oil. The unsaturated fatty acid may be used singly or in combination of two or more.

It is preferable that the amount of the unsaturated fatty acid is in the range of 20 to 70% by mass and more preferably in the range of 30 to 60% by mass based on the amount the entire raw materials used for producing the vinyl-modified fatty acid of component (a-1). By using the vinyl-modified fatty acid obtained by using the unsaturated fatty acid in an amount in the above range, the dispersion stability of the water-dispersible vinyl-modified polyester resin of component (a), the storage stability of the water-borne primer surfacer of the present invention and the physical properties such as the water resistance of the multi-layer coating film obtained by using the water-borne primer surfacer of the present invention can be improved.

Examples of the α,β -unsaturated ethylenically unsaturated monomer having carboxyl group described above include α,β -ethylenically unsaturated monocarboxylic acids such as acrylic acid, methacrylic acid and crotonic acid, α,β -ethylenically unsaturated dicarboxylic acids such as maleic acid, fumaric acid and itaconic acid, anhydrides of acids such as maleic acid and itaconic acid and monoester compounds of these acid anhydrides. It is preferable that at least one of the above α,β -unsaturated ethylenically unsaturated monomers having carboxyl group is used. It is more preferable that methacrylic acid is used since the physical properties of the obtained coating film are made excellent.

It is preferable that the α,β -unsaturated ethylenically unsaturated monomer having carboxyl group is used in an amount such that 10 to 50%

by mass of the vinyl polymer portion in the obtained water-dispersible vinyl-modified polyester resin of component (a) is the constituting unit derived from the α,β -unsaturated ethylenically unsaturated monomer having carboxyl group. When the amount is in the above range, the property for dispersion in water of the water-dispersible vinyl-modified polyester resin of component (a) is improved, and the storage stability of the water-borne primer surfacer of the present invention can be improved. Moreover, a coating film suppressing whitening can be obtained after the coating film is dried.

Among the vinyl-modified fatty acid of component (a-1), a vinyl-modified fatty acid having a vinyl polymer portion having carboxyl group and an aryl group [hereinafter, referred to as a vinyl-modified fatty acid having an aryl group] is preferable. The water-borne primer surfacer exhibiting excellent storage stability can be obtained by using a vinyl-modified polyester resin which is obtained by the condensation of the vinyl-modified fatty acid having an aryl group and the polyester resin having hydroxyl group of component (a-2).

The vinyl-modified fatty acid having an aryl group can be obtained, for example, by radical polymerization of an α,β -ethylenically unsaturated monomer having carboxyl group, an α,β -ethylenically unsaturated monomer having an aryl group and other copolymerizable α,β -ethylenically unsaturated monomers in the presence of the unsaturated fatty acid.

Examples of the α,β -ethylenically unsaturated monomer having an aryl group described above include styrene and styrene derivatives having functional groups such as alkyl groups at various positions of the aromatic

ring of styrene. Examples of the styrene derivative include tertiary-butylstyrene, α -methylstyrene and vinyltoluene.

The amount of the α,β -ethylenically unsaturated monomer having an aryl group is not particularly limited. It is preferable that the amount of the α,β -ethylenically unsaturated monomer having an aryl group is 20% by mass or greater and more preferably 30 to 70% by mass based on the amount of the entire α,β -ethylenically unsaturated monomers used for the polymerization to obtain the vinyl polymer portion having carboxyl group and an aryl group. When the amount of the α,β -ethylenically unsaturated monomer having an aryl group is in the above range, the property for dispersion in water of the water-dispersible vinyl-modified polyester resin of component (a) is improved, and the storage stability of the water-borne primer surfacer of the present invention is further improved.

As described above, other copolymerizable α,β -ethylenically unsaturated monomers can be used for producing the vinyl-modified fatty acid of component (a-1) in combination with the α,β -ethylenically unsaturated monomer having carboxyl group and the α,β -ethylenically unsaturated monomer having an aryl group. As the other copolymerizable α,β -ethylenically unsaturated monomer, α,β -ethylenically unsaturated monomers other than the α,β -ethylenically unsaturated monomer having carboxyl group and the α,β -ethylenically unsaturated monomer having an aryl group can be used. Examples of the other copolymerizable α,β -ethylenically unsaturated monomer include alkyl esters of (meth)acrylic acid such as methyl (meth)acrylate, ethyl (meth)acrylate, n-butyl (meth)acrylate, i-butyl (meth)acrylate, t-butyl

(meth)acrylate, 2-ethylhexyl (meth)acrylate and cyclohexyl (meth)acrylate.

As the other copolymerizable α,β -ethylenically unsaturated monomer, hydroxyalkyl esters of (meth)acrylic acid such as 2-hydroxyethyl (meth)acrylate and 2-hydroxypropyl (meth)acrylate can also be used
5 as long as the object of the present invention can be achieved. α,β -Ethylenically unsaturated monomers having the nonionic surface active property such as methoxypolyethylene glycol mono(meth)acrylate, polyethylene glycol mono(meth)acrylate and propylene glycol polyethylene
10 glycol mono(meth)acrylate can also be used.

The vinyl-modified fatty acid of component (a-1) can be produced in accordance with a process such as the solution polymerization process and the bulk polymerization process.

In accordance with the solution polymerization, for example, the
15 vinyl-modified fatty acid of component (a-1) is obtained by intermittently or continuously adding the above α,β -ethylenically unsaturated monomer such as the α,β -ethylenically unsaturated monomer having carboxyl group and the above unsaturated fatty acid dropwise or by adding the entire monomers at once into an organic solvent in the presence of a
20 polymerization initiator under the atmosphere of an inert gas and by keeping the temperature at about 70 to 150°C. The polymerization initiator may be added into the organic solvent in advance as described above or may be added in combination with the α,β -ethylenically unsaturated monomer and the unsaturated fatty acid when the monomers
25 are added dropwise.

Examples of the organic solvent used in the solution polymerization

include aromatic solvents such as toluene and xylene, ketone-based solvents such as methyl ethyl ketone and methyl isobutyl ketone, and ester-based solvents such as ethyl acetate and butyl acetate. Alcohol-based solvents such as isopropanol and n-butanol and glycol
5 ether-based solvents such as ethylcellosolve and butylcellosolve may be used as long as the solvents do not adversely affect the condensation of the vinyl-modified fatty acid of component (a-1) and the polyester resin having hydroxyl group of component (a-2).

Examples of the polymerization initiator which can be used in the
10 solution polymerization include organic peroxides such as t-butyl peroxybenzoate, di-t-butyl peroxide, t-butyl peroxy-2-ethylhexanoate and benzoyl peroxide, and azo compounds such as 2,2'-azobisisobutyronitrile and 2,2'-azobis-2-methylbutyronitrile. The organic peroxides described above are preferable.

15 When the vinyl-modified fatty acid of component (a-1) is produced in accordance with the solution polymerization, a chain transfer agent may be used, where necessary. As the chain transfer agent, alkyl mercaptans such as t-dodecyl mercaptan, normal-dodecyl mercaptan and normal-octyl mercaptan and α -methylstyrene dimer are preferable.

20 In accordance with the bulk polymerization, for example, the vinyl-modified fatty acid of component (a-1) is obtained by mixing the above α,β -ethylenically unsaturated monomer such as the α,β -ethylenically unsaturated monomer having carboxyl group and the above unsaturated fatty acid under heating without using organic
25 solvents while the monomers are intermittently or continuously added dropwise or the entire monomers are added at once.

In this process, the water-dispersible vinyl-modified polyester resin of component (a) can be directly produced by polymerizing the α,β -ethylenically unsaturated monomer and the unsaturated fatty acid in the presence of the polyester resin having hydroxyl group of component (a-2) which will be described below in accordance with the bulk polymerization.

The polyester resin having hydroxyl group of component (a-2) will be described in the following. The polyester resin having hydroxyl group of component (a-2) is a polyester having hydroxyl group among polyesters obtained by condensation using polybasic acids and polyhydric alcohols as the main components. The polyester resin having hydroxyl group of component (a-2) may have a linear structure or a branched structure and may be modified with urethane or silicone in accordance with the application.

As the polybasic acid used for producing the polyester resin having hydroxyl group of component (a-2), polybasic acids having 2 to 4 carboxyl groups in one molecule are preferable. Examples of the polybasic acid include phthalic acid, isophthalic acid, terephthalic acid, succinic acid, maleic acid, itaconic acid, fumaric acid, tetrahydrophthalic acid, hexahydrophthalic acid, methyltetrahydrophthalic acid, adipic acid, sebacic acid, azelaic acid, himic acid, trimellitic acid, methylcyclohexenetricarboxylic acid, pyromellitic acid and anhydrides of these acids.

As the polyhydric alcohol used for producing the polyester resin having hydroxyl group of component (a-2), polyhydric alcohols having 2 to 6 hydroxyl groups in one molecule are preferable. Examples of the polyhydric alcohol include ethylene glycol, propylene glycol, neopentyl

glycol, butanediol, pentanediol, 1,4-cyclohexanedimethanol, trimethylol-ethane, trimethylolpropane, glycerol, trisisocyanurate and pentaerythritol.

When the polyester resin having hydroxyl group of component (a-2)
5 is produced, animal oils, plant oils, fatty acids obtained by hydrolysis of animal oils and plant oils and "CARDURA (a registered trade name) E" (glycidyl ester of a branched aliphatic monocarboxylic acid, manufactured by SHELL Company) may be used in combination with the polybasic acid described above as long as the object of the present invention can be
10 achieved.

Examples of the animal oil, the plant oils and the fatty acid obtained by hydrolysis of the animal oil and the plant oil include coconut oil, hydrogenated coconut oil, rice bran oil, tall oil, soybean oil, castor oil, hydrogenated castor oil and fatty acids obtained by hydrolysis of the above
15 oils. It is preferable that the amount of the animal oil, the plant oil and the fatty acid obtained by hydrolysis of the animal oil and the plant oil does not exceed 50% by mass of the amount of the polyester resin having hydroxyl group of component (a-2) from the standpoint of the storage stability of the water-borne primer surfacer.

20 The polyester resin having hydroxyl group of component (a-2) can be produced by condensation using the polybasic acid and the polyhydric alcohol as the main components. For example, the melting process or the solvent process can be applied under the condition such that the amount of the polyhydric alcohol exceeds the amount of the polybasic acid.

25 As the polyester resin having hydroxyl group of component (a-2), a urethane-modified polyester resin may be used. The urethane-modified

polyester resin is obtained by synthesizing the polyester having hydroxyl group as described above, followed by modifying the obtained polyester having hydroxyl group by polyaddition of tolylene diisocyanate, methylenebisphenyl isocyanate and, occasionally, polyisocyanate such as
5 an adduct of hexamethylene diisocyanate and trimethylpropane (TMP-modified HDI).

It is preferable that the polyester resin having hydroxyl group of component (a-2) has a hydroxyl value of 50 to 300 mg KOH/g and more preferably 100 to 250 mg KOH/g. When the hydroxyl value is within the
10 above range, the condensation of the vinyl-modified fatty acid of component (a-1) and the polyester resin having hydroxyl group of component (a-2) proceeds smoothly, and the water resistance and the durability of the obtained coating film are excellent.

The water-dispersible vinyl-modified polyester resin of component
15 (a) used in the present invention can be produced, for example, by condensation of the vinyl-modified fatty acid of component (a-1) and the polyester resin having hydroxyl group of component (a-2) by mixing the components, followed by heating the obtained mixture. In the production, a polybasic acid, examples of which are shown in the production of the
20 polyester resin having hydroxyl group of component (a-2), may be further added.

The temperature of the condensation described above is not particularly limited. It is preferable that the temperature is 170 to 210°C. From the standpoint of the reaction rate, it is preferable that a
25 suitable temperature is selected in accordance with the type of the α,β -ethylenically unsaturated monomer having carboxyl group.

The condensation takes place between hydroxyl group in the polyester resin having hydroxyl group of component (a-2) and carboxyl group in the vinyl-modified fatty acid of component (a-1). The vinyl-modified fatty acid of component (a-1) has carboxyl group derived from the unsaturated fatty acid and carboxyl group derived from the vinyl polymer portion. It is preferable that the condensation takes place between carboxyl group derived from the unsaturated fatty acid and hydroxyl group in the polyester resin having hydroxyl group of component (a-2) since the property for dispersion in water of the obtained water-dispersible vinyl-modified polyester resin of component (a) is more excellent.

In particular, it is preferable that carboxyl group derived from the vinyl polymer portion is carboxyl group derived from methacrylic acid since the reactivity of the carboxyl group is smaller than the reactivity of carboxyl group derived from the unsaturated fatty acid, and carboxyl group derived from the unsaturated fatty acid alone takes part in the condensation.

As another process different from the above process, the water-dispersible vinyl-modified polyester resin of component (a) may be produced by adding monomers such as the unsaturated fatty acid and the α,β -ethylenically unsaturated monomer having carboxyl group described above in the presence of the polyester resin having hydroxyl group of component (a-2), where necessary, after adding a small amount of an organic solvent, followed by mixing the components and elevating the temperature to allow the condensation to proceed.

As still another process, the water-dispersible vinyl-modified

polyester resin of component (a) may be produced by adding a monomer such as the α,β -ethylenically unsaturated monomer having carboxyl group described above to a polyester obtained by condensation of the polyester resin having hydroxyl group of component (a-2) and the unsaturated fatty acid, followed by mixing the components to allow the polymerization to proceed.

As still another process, the water-dispersible vinyl-modified polyester resin of component (a) may be produced by polymerization of a vinyl polymer having carboxyl group with a polyester resin obtained by condensation of the polyester resin having hydroxyl group of component (a-2) and the unsaturated fatty acid.

It is preferable that the water-dispersible vinyl-modified polyester resin of component (a) has an acid value of 20 to 100 mg KOH/g and more preferably 25 to 60 mg KOH/g. When the acid value is smaller than 20 mg KOH/g, the property for dispersion in water is decreased, and the appearance of the coating film tends to become poor. When the acid value exceeds 100 mg KOH/g, the water resistance and the durability tend to be decreased. It is preferable that the hydroxyl value is 20 to 150 mg KOH/g and more preferably 40 to 150 mg KOH/g. When the hydroxyl value is smaller than 20 mg KOH/g, the hardness of the coating film is decreased, and the adhesion with the substrate tends to become insufficient. When the hydroxyl value exceeds 150 mg KOH/g, the water resistance tends to be decreased.

As for the degree of neutralization of the water-dispersible vinyl-modified polyester resin of component (a), the entire carboxyl group in the resin may be neutralized, or a portion of the carboxyl group in the

resin may be neutralized. It is preferable that the degree of neutralization is 70 to 100% and more preferably 80 to 100%. When the degree of neutralization is smaller than the above range, the hydrophilicity is decreased. Therefore, the excellent property for dispersion in water becomes difficult to be obtained, and the appearance of the coating film tends to become poor.

In the present specification, the degree of neutralization of a resin means the value expressed by the percentage showing the fractional amount (the unit: mole) of neutralized carboxyl group in the entire amount (the unit: mole) of carboxyl group in 1 g of the resin (as the solid components). For example, the degree of neutralization is 100% when the entire carboxyl groups in the resin is neutralized. When a portion of the carboxyl group in the resin is neutralized, the degree of neutralization is the value obtained by dividing the amount (the unit: mole) of the neutralized carboxyl group by the amount (the unit: mole) of the entire carboxyl group in the resin, followed by expressing the obtained result as the percentage.

Examples of the neutralizing agent used for neutralizing carboxyl group include ammonia; primary monoamines such as ethylamine, propylamine, butylamine, benzylamine, monoethanolamine, neopentanolamine, 2-aminopropanol and 3-aminopropanol; secondary monoamines such as diethylamine, diethanolamine, di-n-propanolamine, di-isopropanolamine, N-methylethanolamine and N-ethylethanolamine; tertiary monoamines such as dimethylethanolamine, trimethylamine, triethylamine, tiisopropylamine, methyldiethanolamine dimethylaminoethanol; amino compounds such as diethylenetriamine, hydroxyethyl-

aminoethylamine, ethylaminoethylamine and methylaminopropylamine; and hydroxides of alkali metals such as sodium hydroxide, potassium hydroxide and lithium hydroxide. From the standpoint of the workability, tertiary monoamines are preferable.

5 It is preferable that the amount of the vinyl polymer portion described above is adjusted in the range of 15 to 45% by mass of the water-dispersible vinyl-modified polyester of component (a) used in the present invention. When the amount of the vinyl polymer portion is smaller than 15% by mass, the dispersion of pigments tends to become
10 insufficient. When the amount exceeds 45% by mass, the property for dispersion in water is decreased, and the appearance of the coating film tends to become poor.

 It is preferable that the weight-average molecular weight of the water-dispersible vinyl-modified polyester of component (a) is in the range
15 of 10,000 to 150,000 and more preferably in the range of 30,000 to 100,000. When the weight-average molecular weight is smaller than 10,000, the hardness of the coating film is decreased, and the adhesion with the substrate tends to become insufficient. When the weight-average molecular weight exceeds 150,000, the viscosity of the resin tends to
20 become great, and there is the possibility that the concentration of the solid components in the coating material is required to be decreased unnecessarily. The weight-average molecular weight is obtained by the measurement in accordance with the gel permeation chromatography (GPC) and expressed as the value of the corresponding polystyrene used
25 as the reference.

 The water-borne primer surfacer of the present invention exhibits

the excellent property for dispersion of pigments which is derived from the vinyl polymer portion in the water-dispersible vinyl-modified polyester resin of component (a). Since pigments are uniformly dispersed in the primer film, the primer film exhibiting excellent property for designing
5 can be formed by using the primer surfacer. The use of colored pigments which tend to show non-uniformity markedly can be facilitated due to the above excellent property for dispersion of pigments, and a multi-layer coating film exhibiting more excellent property for designing can be formed by the combination with colored pigments in the base coat and the
10 clear coat. The hydrophilic property of the primer film can be enhanced by the use of the water-dispersible vinyl-modified polyester resin of component (a).

The water-soluble epoxy-modified polyester resin of component (b) used in the present invention is a polyester resin having epoxy group and
15 soluble in water. The water-soluble epoxy-modified polyester resin of component (b) can be obtained by modifying a polyester resin having 2 or more hydroxy groups in one molecule [hereinafter, referred to as (b-2) a polyester resin having hydroxyl group] with (b-1) an epoxy resin.

As the epoxy resin of component (b-1), epoxy resins conventionally
20 used in the field of coating materials can be used. Examples of the epoxy resin include epoxy resins of the bisphenol type such as EPICOAT 828, 834, 836, 1001, 1004 and 1007 and DX-225 (manufactured by SHELL KAGAKU Company), ARALDITE GY-260, 6071 and 6084 (manufactured by CIBA GEIGY Company), DER-330, 331, 660, 661 and 66
25 (manufactured by DOW CHEMICAL Company), and EPICRON 800, 830, 850, 860, 1050 and 4050 (manufactured by DAINIPPON INK KOGYO Co.,

Ltd.); epoxy resins of the phenol novolak type such as DEN-431 and 438 (manufactured by DOW CHEMICAL Company); epoxy resins of the polyglycol type such as ARALDITE CT508 (manufactured by CIBA GEIGY Company) and DER 732 and 736 (manufactured by DOW CHEMICAL Company); epoxy resins of the ester type, epoxy resins of the chain aliphatic type; epoxy resins of the alicyclic type; and epoxy resins of the polyol type. The above epoxy resins may have halogen atoms.

The polyester resin having hydroxy group of component (b-2) can be obtained, for example, by polycondensation (esterification) of a polyhydric alcohol and a polybasic acid or an anhydride thereof. The polyester can be produced in accordance with the same process as that used for producing the polyester having hydroxyl group of component (a-2). Examples of the polyhydric alcohol, the polybasic acid and the anhydride thereof include the compounds described as the examples of the corresponding compounds in the production of the polyester resin having hydroxyl group of component (a-2). For example, the polyhydric alcohol described above and the polybasic acid or the anhydride thereof described above are brought into reaction with each other in amounts such that the ratio of the amounts by mole of the hydroxyl group in the polyhydric alcohol to the carboxyl group in the polybasic acid is in the range of 1.2 to 1.8.

The water-soluble epoxy-modified polyester resin of component (b) can be synthesized by the reaction of the epoxy resin of component (b-1) and the polyester resin having hydroxyl group of component (b-2). Examples of the reaction include the addition reaction, the condensation reaction and the grafting reaction. More specifically, examples of the

reaction include the reaction between epoxy group in the epoxy resin of component (b-1) and carboxyl group or hydroxyl group in the polyester resin of component (b-2) and, when a polyisocyanate compound is used, the reaction of the polyisocyanate compound with epoxy resin of component (b-1) and hydroxyl group in the polyester resin having hydroxyl group of component (b-2).

It is preferable that the weight-average molecular weight of the water-soluble epoxy-modified polyester resin of component (b) is 5,000 to 30,000 and more preferably 10,000 to 25,000. When the weight-average molecular weight is smaller than 5,000, the hardness of the coating film tends to be decreased, and the adhesion with the substrate tends to become insufficient. When the weight-average molecular weight exceeds 30,000, the viscosity of the resin tends to be increased, and there is the possibility that the concentration of the solid components in the coating material is required to be decreased unnecessarily. It is preferable that the hydroxyl value is 75 to 200 mg KOH/g and more preferably 80 to 150 mg KOH/g. When the hydroxyl value is smaller than 75 mg KOH/g, the hardness of the coating film tends to be decreased, and the adhesion with the substrate tends to become insufficient. When the hydroxyl value exceeds 200 mg KOH/g, the viscosity of the resin tends to be increased, and there is the possibility that the concentration of the solid components in the coating material is required to be decreased unnecessarily. It is preferable that the acid value is 25 to 50 mg KOH/g and more preferably 27 to 40 mg KOH/g. When the acid value is smaller than 25 mg KOH/g, the property for dispersion in water is decreased, and the appearance of the coating film tends to become poor. When the acid value exceeds 50

mg KOH/g, the viscosity of the resin tends to be increased, and there is the possibility that the concentration of the solid components in the coating material is required to be decreased unnecessarily. Moreover, the storage stability of the coating material tends to be decreased. As for
5 the degree of neutralization of the water-soluble epoxy-modified polyester resin of component (b), the entire carboxyl group in the resin may be neutralized, or a portion of the carboxyl group may be neutralized. It is preferable that the degree of neutralization is 70 to 100% and more preferably 80 to 100%. When the degree of neutralization is smaller than
10 the above range, the hydrophilicity is decreased. Therefore, the excellent property for dissolution in water is difficult to be obtained, and the appearance of the coating film tends to become poor.

When the water-borne primer surfacer comprising the water-soluble epoxy-modified polyester resin of component (b) is used, a
15 multi-layer coating film exhibiting excellent chipping resistance and water resistance can be formed. The hydrophilicity of the primer film is also enhanced by using the water-borne primer surfacer comprising the water-soluble epoxy-modified polyester resin of component (b).

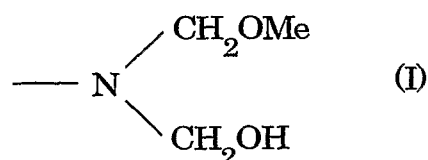
Heretofore, the surface tends to become hydrophobic when the
20 preheating treatment is conducted after a water-dispersible coating material is applied. When the coating film is formed with the water-borne coating material comprising the water-soluble epoxy-modified polyester resin of component (b), the surface of the coating film can be kept hydrophilic even after the coating film is treated by preheating. The
25 water-borne primer surfacer of the present invention utilizes this effect. By increasing the concentration of the solid components in the primer film

by the preheating treatment, the excellent effect of hiding the substrate can be obtained. Even when the smoothness of the surface of the primer film becomes temporarily poor due to the above treatment, water in the water-borne coating material coating the primer film in accordance with the wet-on-wet process is transferred to the primer film since the hydrophilicity of the surface of the coating film can be maintained, and the smoothness of the surface of the finally obtained primer film (the interface with the base coat) is improved. In the present invention, the hydrophilic effect of the primer film described above is obtained since the water-soluble epoxy-modified polyester resin of component (b) is used in combination with the water-dispersible vinyl-modified polyester resin of component (a) as the resins for forming the coating film.

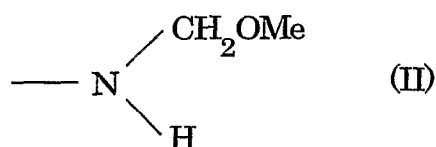
In the water-borne primer surfacer of the present invention, it is preferable that the ratio of the amounts by mass of the water-dispersible vinyl-modified polyester resin of component (a) to the water-soluble epoxy-modified polyester resin of component (b) is 5:95 to 95:5, expressed as the amounts of the solid components. When the amount of the water-dispersible vinyl-modified polyester resin of component (a) is smaller than the above range, the property for dispersion of pigments becomes poor. Therefore, the effect of hiding the substrate with the primer film is insufficient, and the property for designing of the multi-layer coating film tends to become poor. When the amount of the water-soluble epoxy-modified polyester resin of component (b) is smaller than the above range, the primer film before application of the base coating material tends to be hydrophobic. Therefore, the smoothing effect of the interface between the primer film and the base coat due to the

transfer of water is suppressed, and the smoothness of the surface of the base coat tends to become poor. Moreover, the water resistance and the chipping resistance are decreased. From the above standpoints, it is more preferable that the ratio of the amount by mass of the water-dispersible vinyl-modified polyester resin of component (a) to the water-soluble epoxy-modified polyester resin of component (b) is 10:90 to 90:10 and most preferably 15:85 to 85:15, expressed as the amounts of the solid components.

In the present invention, (c) a melamine resin is used as the curing agent. The melamine resin of component (c) can be obtained by polymerizing methylolmelamine obtained by the reaction of melamine and formaldehyde, followed by etherification of methylol group with an alcohol. In the present invention, water-soluble melamine resin is preferable from the standpoint of the properties of the coating film and the hydrophilicity of the coating material. It is preferable that the melamine resin of component (c) is at least one melamine resin selected from melamine resins of the methylol type having, as the reactive group, a group expressed by formula (I):

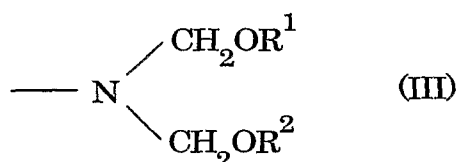


melamine resins of the imino type having, as the reactive group, a group expressed by formula (II):



and melamine resins of the methylol/imino type having, as the reactive groups, both of the group expressed by formula (I) and the group expressed by formula (II). Since the melamine resin having the group expressed by general formula (I) and/or the group expressed by general formula (II) exhibits the excellent property for curing, a multi-layer coating film exhibiting excellent properties such as the excellent chipping resistance can be obtained.

From the standpoint of the designing, it is preferable that, as the melamine resin of component (c), the melamine resin of the methylol type, the melamine resin of the imino type or the melamine resin of the methylol/imino type is used in combination with the melamine resin of the complete alkyl ether type having, as the reactive group, a group represented by general formula (III):



In general formula (III), R¹ and R² each independently represent an alkyl group having 1 to 4 carbon atoms. Since the reaction rate of the melamine resin of the complete alkyl ether type is smaller than those of other melamine resins, the curing time can be adjusted by using the melamine resin of the complete alkyl ether type in combination, and the multi-layer coating film exhibiting excellent smoothness of the interface

between the primer film and the base coat can be formed. When the melamine resin of the complete alkyl ether type is used in combination, it is preferable that the content of the melamine resin of the complete alkyl ether type is 60% by mass or smaller and more preferably 10 to 50% by mass based on the amount of the entire melamine resin of component (c).
5 When the content exceeds 60% by mass, the properties of the coating film tend to become poor.

It is preferable that the degree of polymerization of the melamine resin of component (c) is 3.0 or smaller and more preferably 1.5 or smaller.

10 The degree of polymerization is a value showing the degree of condensation of the melamine resin. When the degree of polymerization exceeds 3.0, the property for hiding the substrate tends to become poor. It is preferable that the fraction of the single nucleus species is 50% or greater and more preferably 60% or greater. The fraction of the single
15 nucleus species is the fraction of the melamine resin having a single nucleus, i.e., having the degree of polymerization of 1.0, in the entire melamine resin. When the above fraction is smaller than 50%, the property for hiding the substrate tends to become poor.

Examples of the commercial product of the melamine resin include
20 CYMEL (a registered trade name) 235, 267, 303, 325 and 350 and MICOAT (a registered trade name) M506 (all manufactured by MITSUI CYTEC Co. Ltd.).

It is preferable that the content of the melamine resin of component (c) is 25 to 100% by mass based on the sum of the amounts of the
25 water-dispersible vinyl-modified polyester resin of component (a) and the water-soluble epoxy-modified polyester resin of component (b), expressed

as the content of the solid components. When the content is smaller than 25% by mass, the chipping resistance and the water resistance are decreased. When the content exceeds 100% by mass, there is the possibility that the appearance becomes poor. From the above
5 standpoint, it is more preferable that the content is 30 to 80% by mass.

The water-borne primer surfacer of the present invention may further comprise (d) a water-soluble epoxy resin. The water-soluble epoxy resin is a compound having at least one hydrophilic portion and at least two epoxy groups in one molecule. In particular, compounds having
10 ether bond or hydroxyl group as the hydrophilic portion are preferable.

Preferable examples of the water-soluble epoxy resin of component (d) include ethylene glycol diglycidyl ether, polyethylene glycol diglycidyl ether, propylene glycol diglycidyl ether and polypropylene glycol diglycidyl ether. The above compound may be used singly or in combination of two
15 or more. When the water-borne primer surfacer of the present invention comprises the water-soluble epoxy resin of component (d), the chipping resistance of the coating film is improved.

Examples of the commercial product of the water-soluble epoxy resin of component (d) include diglycidyl ethers of ethylene glycol or
20 polyethylene glycol such as EX-810, EX-811, EX-851, EX-821, EX-830, EX-832, EX-841 and EX861 in the "DENACOL (a registered trade name)" series manufactured by NAGASE CHEMTEX Co., Ltd., 40E, 100E, 200E and 400E in the "EPOLITE" series manufactured by KYOEISHA KAGAKU Co., Ltd., and 212 and 214 in the "EPOLEAD (a registered
25 trade name) NT" series manufactured by DAICEL KAGAKU Co., Ltd.; and diglycidyl ethers of propylene glycol or polypropylene glycol such as

EX-911, EX-941, EX-920, EX-921 and EX-931 in the "DENACOL (a registered trade name)" series manufactured by NAGASE CHEMTEX Co., Ltd., 70P, 200P and 400P in the "EPOLITE" series manufactured by KYOEISHA KAGAKU Co., Ltd., and 228 in the "EPOLEAD (a registered trade name) NT" series manufactured by DAICEL KAGAKU Co., Ltd.

It is preferable that the content of the water-soluble epoxy resin of component (d) is 3 to 25% by mass based on the sum of the amounts of the water-dispersible vinyl-modified polyester resin of component (a), the water-soluble epoxy-modified polyester resin of component (b) and the melamine resin of component (c), expressed as the content of the solid components. When the content is smaller than 3% by mass, the chipping resistance is insufficient. When the content exceeds 25% by mass, the stability of the coating material is poor. From the above standpoint, it is more preferable that the content is 5 to 20% by mass and most preferably 7 to 15% by mass.

The water-borne primer surfacer of the present invention may further comprise (e) crosslinked resin particles. The crosslinked resin particles of component (e) used in the present invention are fine particles comprising a polymer which is crosslinked so that the polymer is insoluble in the organic solvent for the coating material. In particular, fine particles having the property such that the particles are dispersed in the water-borne primer surfacer with stability, i.e., having the hydrophilic property, are preferable. For the crosslinked resin particles of component (e), particulate acrylic resins having carboxyl group are used. In general, the particles of an acrylic resin having carboxyl group are obtained as a dispersion in water.

For producing a water dispersion of the crosslinked resin particles of component (e), in general, an ethylenically unsaturated monomer having at least one carboxyl group in one molecule (hereinafter, referred to as an ethylenically unsaturated monomer having carboxyl group) and
5 other ethylenically unsaturated monomers are polymerized in accordance with the emulsion polymerization in an aqueous medium.

Examples of the ethylenically unsaturated monomer having carboxyl group preferably used in the above production include styrene derivatives, (meth)acrylic acid derivatives and unsaturated dibasic acids.
10 Among these monomers, (meth)acrylic acid derivatives are preferable, and acrylic acid, methacrylic acid, acrylic acid dimer and α -hydro- ω -((1-oxo-2-propenyl)oxy)poly(oxy(1-oxo-1,6-hexandiyl)) are more preferable.

The other ethylenically unsaturated monomer preferably used in the above production is an ethylenically unsaturated compound radical
15 copolymerizable with the ethylenically unsaturated monomer having carboxyl group. Examples of the other ethylenically unsaturated monomer include (meth)acrylates having no reactive functional groups (such as methyl acrylate, methyl methacrylate, ethyl acrylate and ethyl methacrylate), polymerizable aromatic compounds (such as styrene,
20 α -methylstyrene, vinyl ketone and vinyl naphthalene), unsaturated compounds having hydroxyl group (such as 2-hydroxyethyl acrylate and 2-hydroxyethyl methacrylate), polymerizable amides (such as acrylamide, methacrylamide, N-methylolmethacrylamide and N-methoxymethylacrylamide), polymerizable nitriles (such as acrylonitrile and
25 methacrylonitrile), vinyl halides (such as vinyl chloride, vinyl bromide and vinyl fluoride), α -olefins (such as ethylene and propylene), vinyl esters

(such as vinyl acetate and vinyl propionate) and dienes (such as butadiene and isoprene).

It is necessary that an ethylenically unsaturated compound having two or more radical polymerizable groups in the molecule be used as the other ethylenically unsaturated monomer so that crosslinks sufficient for making the formed crosslinked resin particles insoluble in a solvent is provided. Examples of the other ethylenically unsaturated monomer described above include esters of polymerizable unsaturated monocarboxylic acids with polyhydric alcohols (such as ethylene glycol diacrylate, ethylene glycol dimethacrylate, trimethylolpropane triacrylate and trimethylolpropane trimethacrylate), esters of polymerizable unsaturated alcohols with polybasic acids (such as diallyl terephthalate, diallyl phthalate and triallyl trimellitate), aromatic compounds substituted with two or more vinyl groups (such as divinylbenzene) and addition products of ethylenically unsaturated monomers having epoxy group with ethylenically unsaturated monomers having carboxyl group (such as reaction products of glycidyl acrylate or glycidyl methacrylate with acrylic acid, methacrylic acid, crotonic acid or maleic acid).

The other ethylenically unsaturated monomer may be used singly or in combination of two or more.

As for the relative amounts of the ethylenically unsaturated monomer having carboxyl group and the other ethylenically unsaturated monomer in the emulsion polymerization, the ethylenically unsaturated monomer having carboxyl group is used in an amount of 1 to 50% by mass and preferably 10 to 40% by mass, and the other ethylenically unsaturated monomer is used in an amount of 99 to 50% by mass and

preferably 90 to 60% by mass, both based on the amount of the entire ethylenically unsaturated monomers used for producing the crosslinked resin particles of component (e). In the other ethylenically unsaturated monomer described above, the amount of the ethylenically unsaturated compound having two or more radial polymerizable groups is 1 to 10% by mass, preferably 1 to 7% by mass and more preferably 1 to 5% by mass based on the amount of the entire ethylenically unsaturated monomers.

The emulsion polymerization is conducted by dissolving an emulsifier into water or, where necessary, an aqueous medium containing water and an organic solvent such as an alcohol, followed by adding the ethylenically unsaturated monomers and a polymerization initiator dropwise under heating and stirring. The ethylenically unsaturated monomers which has been emulsified by using an emulsifier and water in advance may be added dropwise.

Examples of the preferable polymerization initiator include azo-based compounds soluble in oils (such as azobisisobutyronitrile, 2,2'-azobis(2-methylbutyronitrile) and 2,2'-azobis(2,4-dimethylvaleronitrile), azo-based compounds soluble in water (such as anion-based 4,4'-azobis(4-cyanovaleric acid) and cation-based 2,2'-azobis(2-methylpropionamidine), redox-based peroxides soluble in oils (such as benzoyl peroxide, para-chlorobenzoyl peroxide, lauroyl peroxide and t-butyl perbenzoate) and redox-based peroxides soluble in water (such as potassium persulfate and ammonium peroxide).

As the emulsifier, emulsifiers conventionally used by those skilled in the art can be used. Reactive emulsifiers such as ANTOX MS-60 (manufactured by NIPPON NYUKAZAI Co., Ltd.), ELEMNOL (a

registered trade name) JS-2 (manufactured by SANYO KASEI KOGYO Co., Ltd.) and AQUALON (a registered trade name) HS-10 (manufactured by DAIICHI KOGYO SEIYAKU Co., Ltd.) are preferable.

For adjusting the molecular weight, chain transfer agents, for example, mercaptans such as lauryl mercaptan, and α -methylstyrene dimer are used, where necessary.

The temperature of the reaction is decided in accordance with the initiator. For example, it is preferable that the reaction is conducted at 60 to 90°C when the azo-based initiator is used and at 30 to 70°C when the redox-based initiator is used. The time of the reaction is, in general, 1 to 8 hours. The amount of the initiator is, in general, 0.1 to 5% by mass and preferably 0.5 to 2% by mass based on the amount of the entire unsaturated compounds.

The crosslinked resin particles prepared in an aqueous medium may be used in the form obtained by the preparation. The prepared crosslinked resin particles may also be used after isolating fine particles of the resin in accordance with a suitable process such as filtration, spray drying and freeze drying without further treatments or after being pulverized to a suitable particle size by a mill or the like.

It is preferable that the diameter of the crosslinked resin particles of component (e) is in the range of 0.01 to 10 μm and more preferably in the range of 0.01 to 1.0 μm . When the diameter of the particles is smaller than 0.01 μm , the effect of improving the workability is small. When the diameter of the particles exceeds 10 μm , there is the possibility that the appearance of the coating film becomes poor. The adjustment of the diameter of the particles can be conducted in accordance with a

conventional process widely known for those skilled in the art. For example, the diameter of the particles can be adjusted by pulverization by a mill as described above or by changing the composition of the monomer.

It is preferable that the water dispersion of the crosslinked resin particles of component (e) has an acid value of 5 to 80 mg KOH/g and more preferably 10 to 70 mg KOH/g. When the acid value is smaller than 5 mg KOH/g, the effect of improving the workability is small. When the acid value exceeds 80 mg KOH/g, the solubility in water is increased, and there is the possibility that the properties as the particles are lost.

The water dispersion of the crosslinked resin particles of component (e) can be used at a pH of 5 to 10 by neutralizing with a base. The water dispersion of the crosslinked resin particles of component (e) exhibits excellent stability when the pH is in the above range. It is preferable that the neutralization is conducted by adding a tertiary amine such as dimethylethanolamine and triethylamine before or after the polymerization.

When the water-borne primer surfacer of the present invention comprises the crosslinked resin particles of component (e), the appearance of the coating film is improved and mixing of components of the primer film and the base coat can be prevented when the primer film and the base film are formed in accordance with the wet-on-wet process.. Therefore, the transfer of water from the base coat can be achieved while the mixing of components of the coating films can be prevented, and the property for designing of the multi-layer coating film can be improved.

It is preferable that the amount of the crosslinked resin particles component (e) is 3 to 40% by mass based on the sum of the amounts of the

water-dispersible vinyl-modified polyester resin of component (a), the water-soluble epoxy-modified polyester of component (b), the melamine resin of component (c) and the water-soluble epoxy resin of component (d), expressed as the amount of the solid components. When the amount is smaller than 3% by mass, there is the possibility that mixing of the coating films takes place in the formation of the composite coating film of the primer film and the base coat in accordance with the wet-on-wet process using a water-borne base coating material. When the amount exceeds 40% by mass, there is the possibility that the smoothness of the multi-layer coating film becomes poor. From the above standpoint, it is more preferable that the amount is 5 to 30% by mass and most preferably 8 to 25% by mass.

The water-borne primer surfacer of the present invention may comprise (f) pigments. Examples of the pigment include coloring pigments and fillers. By adding the pigments, fine roughness on the surface of the electrodeposition coating film as the substrate for the primer film can be hidden, and the smoothness of the coating film can be improved. Examples of the coloring pigment include organic pigments such as azo lake-based pigments, diketopyrrolopyrrol-based pigments, benzimidazolone-based pigments, phthalocyanine-based pigments, indigo-based pigments, perylene-based pigments, quinophthalone-based pigments, dioxazine-based pigments, quinacridone-based pigments, isoindolinone-based pigments and metal complex compounds; and inorganic pigments such as lead yellow, yellow iron oxide, red iron oxide, titanium oxide and carbon black. Examples of the filler include barium sulfate, barium carbonate, calcium carbonate, magnesium carbonate,

silica and talc. It is preferable that the pigment weight concentration (PWC) of the above pigment is 20 to 70% by mass and more preferably 25 to 60% by mass.

The water-borne primer surfacer of the present invention may
5 comprise other additives as long as the effects of the present invention are not adversely affected. Examples of the additive include antissettling agents such as polyamide waxes and polyethylene waxes, ultraviolet light absorbents, antioxidants, leveling agents, surface conditioners such as silicones and organic macromolecules, antisagging agents, thickeners,
10 defoaming agents and organic compounds such as cellulose alkyl ethers. It is preferable that the amount of the additive is 15% by mass or smaller and more preferably 10% by mass or smaller based on the amount of the entire coating material, expressed as the amount of the solid components.

The process for obtaining the water-borne primer surfacer of the
15 present invention is not particularly limited, and any conventional process known to those skilled in the art such as mixing the above resins and pigments by a kneader or rolls or dispersing the above resins and pigments by a sand grind mill or a disper can be used.

When the water-borne primer surfacer of the present invention is
20 used in combination with a water-borne base coating material and a composite coating film is formed from the water-borne primer surfacer and the water-borne base coating material in accordance with the wet-on-wet process, water in the base coat can be transferred to the primer film. Due to the transfer of water, the viscosity of the primer
25 film on the face contacting the base coat is decreased, and the roughness is relaxed. As the result, the effect of improving the smoothness of the

surface of the base coat can be obtained. Specifically, this effect is exhibited when the water-borne primer surfacer is used as a water-borne primer surfacer for a process for forming a multi-layer coating film, wherein the process for forming a multi-layer coating film comprises:

5 step (1) in which an article for coating having an electrodeposition coating film is coated with the water-borne primer surfacer described above to form an uncured primer film,

 step (2) in which the primer film described above is coated with a water-borne base coating material to form an uncured base coat,

10 step (3) in which the uncured base coat described above is coated with a clear coating material to form an uncured clear coat, and

 step (4) in which the primer film, the base coat and the clear coat, which are described above, are simultaneously cured by heating to obtain a multi-layer coating film.

15 When the water-borne primer surfacer of the present invention is applied to the process for forming a multi-layer coating film comprising steps (1) to (4) described above, fine roughness on the surface of the electrodeposition coating film can be cancelled due to the effects described above based on the combination of the water-borne primer surfacer and
20 the water-borne base coating material, and the multi-layer coating film exhibiting excellent smoothness can be formed.

 In particular, when the preheating is conducted between step (1) and step (2) so that the amount of water in the water-borne primer film is decreased (the concentration of the solid components is increased) while
25 the primer film is kept uncured, mixing of the primer film formed by using the water-borne primer surfacer and the base coat formed by using the

water-borne base coating material can be prevented, and a more excellent effect of hiding the substrate can be obtained. Since the surface of the primer film formed with the water-borne primer surfacer of the present invention can maintain the hydrophilic property even after the preheating,
5 the multi-layer coating film exhibiting the excellent smoothness can be formed due to the transfer of water from the base coat.

When the preheating is conducted between step (2) and step (3) described above, water in the base coat can be transferred to the primer film during the preheating and, as the result, the smoothness of the
10 multi-layer coating film can be improved. The preheating may be conducted between step (1) and step (2) and between step (2) and step (3). In this case, the effect of conducting the preheating between step (1) and step (2) and the effect of conducting the preheating between step (2) and step (3) are both exhibited.

15 In the process for forming a multi-layer coating film, the article for coating is not particularly limited. Examples of the article for coating include metals such as iron, copper, aluminum, tin and zinc, alloys containing the metals and cast products of the metals. Specific examples include bodies and other members of automobiles such as passenger cars,
20 trucks, motorcycles and basses. It is preferable that the above metals are chemically treated with a phosphate or a chromate before being treated by the electrodeposition coating.

In the process for forming a multi-layer coating film, a cationic electrodeposition coating material is applied to the article for coating so
25 that a cationic electrodeposition coating film is formed. The cationic electrodeposition coating material is not particularly limited, and a

conventional cationic electrodeposition coating material can be used. Examples of the electrodeposition coating material include coating materials comprising a cationic substrate resin and a curing agent.

The cationic substrate resin is not particularly limited. Examples
5 of the cationic substrate resin include amine-modified epoxy resin-based substrate resins described in Japanese Patent Application Publication Nos. Showa 54(1979)-4978 and Showa 56(1981)-34186; amine-modified polyurethane polyol resin-based substrate resins described in Japanese Patent Application Publication No. Showa 55(1980)-115476, amine-
10 modified polybutadiene-based substrate resins described in Japanese Patent Application Publication No. Showa 62(1987)-61077 and Japanese Patent Application Laid-Open No. Showa 63(1988)-86766, amine-modified acrylic resin-based substrate resins described in Japanese Patent Application Laid-Open No. Showa 63(1988)-139909 and Japanese Patent
15 Application Publication No. Heisei 1(1989)-60516, and substrate resins based on resins having sulfonium group described in Patent Application Laid-Open No. Heisei 6(1994)-128351. As the cationic substrate resin other than the resins described above, substrate resins based on resins having phosphonium group can be used. Among the above cationic
20 substrate resins described above, amine-modified epoxy resin-based substrate resins are preferable.

Examples of the curing agent include amino resins and blocked polyisocyanate compounds. However, the curing agent is not limited to the compounds described above.

25 In the process for forming a multi-layer coating film, after the electrodeposition coating film is cured by heating, the water-borne primer

surfacers of the present invention is applied, and the primer film is formed. The process for application of the primer surfacer is not particularly limited. The primer surfacer can be applied, for example, by using an air electrostatic spray gun which is widely called "a react gun", or an electrostatic coating machine of the rotating atomization type, which is widely called "a micro-micro ($\mu\mu$) bell", "a micro (μ) bell" or "a metabell". Among the above machines, the electrostatic coating machine of the rotating atomization type is preferable.

It is preferable that the thickness of the primer film is 5 to 50 μm after being dried although the thickness is varied depending on the application. When the thickness exceeds the above range, problems such as sagging of the coating material during the coating operation and formation of pin holes and craters at the time of the baking occasionally arise. When the thickness is smaller than the above range, there is the possibility that the appearance becomes poor.

In the process for forming a multi-layer coating film, the base coat is formed by applying the water-borne base coating material while the primer film remains in the uncured condition (i.e., in accordance with the wet-on-wet process). In the present specification, the uncured condition means not only the condition without the preheating but also the condition after the preheating.

The preheating is a step in which, after the primer surfacer is applied, the formed primer film is treated under a condition such that the applied primer surfacer is not cured. For example, the formed primer film is left standing or heated at a temperature between the room temperature and a temperature lower than 100°C for 1 to 10 minutes. In

the process for forming a coating film of the present invention, this step can be conducted for adjusting the content of the solid components. In particular, when the water-borne primer surfacer of the present invention is used, it is preferable that the content of the solid components is 70% or greater and more preferably 75% or greater before the water-borne base coating material is applied. When the content of the solid components in the primer surfacer is 70% or greater, the excellent effect of hiding the substrate can be obtained. In accordance with conventional processes, the smoothness of the surface of the primer film is lost, and the property for designing of the multi-layer coating film becomes poor when the content of the solid components is 70% or greater. In contrast, when the water-borne primer surfacer of the present invention is used and the water-borne base coating material is applied in accordance with the wet-on-wet process, the smoothness of the interface of the primer film and the base coat is improved, and the multi-layer coating film exhibiting the excellent property for designing can be obtained.

The base coating material is not particularly limited as long as the base coating material is a water-borne base coating material. Examples of the base coating material include coating materials containing a water-borne resin exhibiting the property for forming a coating film, a curing agent, pigments and other additives. Examples of the water-borne resin exhibiting the property for forming a coating film include acrylic resins, polyester resins, alkyd resins, epoxy resins and urethane resins. The form of the water-borne resin exhibiting the property for forming a coating film is not particularly limited. Examples of the form include the form dispersible in water (the emulsion type) and the form

soluble in water.

It is preferable that an acrylic emulsion and/or a water-soluble acrylic resin is used as the water-borne base coating material from the standpoint of workability in coating and the properties of the coating film
5 such as weatherability and water resistance. Among the above materials, the acrylic emulsion is more preferable.

The base coating material may comprise a curing agent such as a melamine resin and an epoxy resin. Among these curing agents, the melamine resin is preferable from the standpoint of the properties of the
10 obtained coating film and the cost. From the standpoint of improving the curing property at low temperatures, it is preferable that a blocked isocyanate resin, a carbodiimide compound or an oxazoline compound is added in combination with the above components.

The base coating material may suitably comprise the agent for
15 adjusting viscosity described above and other additives so that mixing with the clear coat is prevented and the sufficient workability in the coating operation is surely exhibited.

The water-borne base coating material may be used as a metallic base coating material by adding a bright pigment or as a base coating
20 material of the solid type by adding coloring pigments such as red, blue or black pigments and, where necessary, fillers without adding bright pigments. The bright pigment is not particularly limited. Examples of the bright pigment include non-colored or colored metallic bright materials such as metals and alloys, mixtures of these metallic bright
25 materials, interfering mica powder, colored mica powder, white mica powder, graphite and colorless and colored flat pigments. Non-colored or

colored metallic bright materials such as metals and alloys and mixtures of these metallic bright materials are preferable since the property for dispersion is excellent and a coating film exhibiting excellent transparent feel can be formed. Examples of the metal include aluminum, aluminum
5 oxide, copper, zinc, iron, nickel and tin.

The shape of the bright pigment is not particularly limited. The pigment may be colored. For example, a scale-like shape having an average diameter of particles (D_{50}) of 2 to 50 μm and a thickness of 0.1 to 5 μm is preferable, and a scale-like shape having an average diameter of
10 particles of 10 to 35 μm is more preferable due to the excellent bright feel. The pigment weight concentration (PWC) of the bright pigment in the base coating material is, in general, 23% by mass or smaller. When PWC exceeds 23% by mass, the appearance of the coating film becomes poor. It is preferable that PWC is 0.01 to 20% by mass and more preferably 0.01
15 to 18% by mass.

As the pigment other than the bright pigment, the coloring pigments and the fillers described for the water-borne primer surfacer of the present invention can be used. As the pigment, a single pigment or a combination of two or more pigments selected from bright pigments,
20 coloring pigments and fillers can be used. The pigment weight concentration (PWC) of the entire pigments including the bright pigments and other pigments in the water-borne base coating material is, in general, 0.1 to 50% by mass and preferably 0.5 to 40% by mass. When PWC exceeds 50% by mass, the appearance of the coating film becomes poor.
25 Examples of the other additives used in the water-borne base coating material and the process for preparing the water-borne base coating

material are the same as those described as the examples of the other additives and the process, respectively, for the water-borne primer surfacer.

As the process for applying the water-borne base coating material, the process described as the examples for the process for applying the water-borne primer surfacer can be used. When the water-borne base coating material is applied to a body of an automobile, coating is conducted using air electrostatic spray guns in multi-stages and preferably in two stages. It is also preferable that a coating process using a combination of the air electrostatic spray gun and the electrostatic coating machine of the rotating atomization type is conducted.

It is preferable that the thickness of the base coat after being dried is 5 to 35 μm although the thickness is varied depending on the application. When the thickness exceeds the above range, occasionally, a decrease in the sharpness of reflection takes place and problems in the coating such as uneven coating and sagging occasionally arise. When the thickness is smaller than the above range, there is the possibility that uneven coloring takes place.

As described above, when the effect of hiding the substrate is expected to be obtained, the primer film before the coating with the water-borne base coating material is adjusted at a condition such that the concentration of the solid components is as great as 70% or greater. Even when the surface of the primer film temporarily exhibits poor smoothness as the result of this condition, water in the water-borne base coating material is transferred to the primer film when the primer film is coated with the water-borne base coating material in accordance with the

wet-on-wet process, and the surface of the primer film (the interface between the primer film and the base coat) is made smooth. Since the primer surfacer of the present invention is hydrophilic and the change of the hydrophilic property into the hydrophobic property is prevented even
5 after the preheating of the primer film, the transfer of water described above tends to take place easily, and the property for hiding the substrate and the smoothness of the surface can be achieved simultaneously. The primer surfacer of the present invention suppresses mixing of the components of the coating films although the transfer of water takes place.
10 As the result, the feel of gloss is not decreased, and the multi-layer coating film exhibiting the excellent property for designing can be formed. Moreover, since the excellent property for dispersion of pigments can be exhibited in combination with the effect of preventing the mixing, coloring pigments can be used also in the primer film. Therefore, improvements
15 in the appearance can be achieved by the combination of the coloring pigments in the primer film and the coloring pigments in the base coat, and the multi-layer coating film exhibiting the excellent property for designing can be formed.

In the process for forming the multi-layer coating film described
20 above, a clear coating material is applied while the base coat is still in the uncured condition, and a clear coat is formed. The clear coat is formed so that roughness and glare of the base coat due to bright pigments is made smooth when the metallic base coating material containing the bright pigment is used, and the base coat is protected. The clear coating
25 material is not particularly limited. Examples of the clear coating material include coating materials comprising a resin for forming a

coating film, a curing agent and other additives.

The resin for forming a coating film is not particularly limited. Examples of the resin for forming a coating film include acrylic resins, polyester resins, epoxy resins and urethane resins. The above resin is
5 used in combination with a curing agent such as an amino resin and/or a blocked isocyanate resin. From the standpoint of the transparency or the resistance to acid etching, it is preferable that a combination of an acrylic resin and/or a polyester resin with an amino resin or an acrylic resin having carboxylic acid-epoxy curing system and/or a polyester resin is
10 used.

Since the clear coating material is applied after the water-borne base coating material has been applied and is still in the uncured condition, it is preferable that the clear coating material comprises an agent for adjusting the viscosity as an additive so that mixing and
15 inversion of the layers and sagging of the coating material are prevented. The amount of the agent for adjusting the viscosity is 0.01 to 10 parts by mass, preferably 0.02 to 8 parts by mass and more preferably 0.03 to 6 parts by mass based on 100 parts by mass of the solid resin components in the clear coating material. When the amount of the agent for adjusting
20 the viscosity exceeds 10 parts by mass, the appearance becomes poor. When the amount is smaller than 0.1 part by mass, the effect of controlling the viscosity is not obtained, and problems such as sagging of the coating material may arise.

As for the form of the clear coating material, any of the materials of
25 the organic solvent type, the water-borne type (the aqueous solution type, the aqueous dispersion type or the emulsion type), the non-aqueous

dispersion type and the powder type can be used. Where necessary, curing agents and surface conditioners may be used.

As the process for preparation and the process for application of the clear coating material, conventional processes can be conducted. The thickness of the clear coat after being dried is 10 to 70 μm although the thickness is varied depending on the application. When the thickness exceeds the above range, a decrease in the sharpness of reflection occasionally takes place, and problems such as uneven coating and sagging of the coating material occasionally arise during the coating.

When the thickness is smaller than the above range, there is the possibility that the appearance becomes poor.

In the process for forming a multi-layer coating film described above, the primer film, the base coat and the clear coat which are described above are simultaneously cured by heating, and the multi-layer coating film can be obtained.

As for the temperature of the curing by heating, a cured coating film having a great degree of crosslinking can be obtained by the heating at 110 to 180°C and more preferably 120 to 160°C. When the temperature of the curing by heating is higher than 180°C, the obtained coating film tends to become hard and fragile. When the temperature is lower than 110°C, the curing tends to be insufficient. It is suitable that the time of the curing is 10 to 60 minutes when the temperature of the curing is 120 to 160°C although the time of the curing is varied depending on the temperature of the curing. The thickness of the multi-layer coating film obtained in accordance with the process for forming a coating film of the present invention is, in general, 30 to 300 μm and preferably 50

to 250 μm . When the thickness exceeds 300 μm , the physical properties of the film such as the properties under repeated cycles of heating and cooling become poor. When the thickness is smaller than 30 μm , strength of the film itself is decreased.

5

EXAMPLES

The present invention will be described more specifically with reference to examples in the following. However, the present invention is not limited to the examples. "Part" and "%" in the following descriptions
10 mean "part by mass" and "% by mass", respectively, unless otherwise mentioned.

[Preparation Example 1] (Preparation of (a) a water-dispersible vinyl-modified polyester resin)

15 Preparation of (a-1) a vinyl-modified fatty acid

Into a 3 liter four-necked flask equipped with a stirrer, a thermometer, a reflux condenser and an inlet for nitrogen gas, a fatty acid shown in Table 1 in an amount also shown in Table 1 and 650 parts of xylene were placed, and the temperature was elevated at 130°C under
20 stirring. To the stirred mixture, a mixture of the vinyl-polymerizable monomers and the polymerization initiator was added over 3 hours, and the obtained mixture was heated at 130°C for one night. After the temperature was lowered to 80°C, 350 parts of methyl ethyl ketone was added, and a solution of Vinyl-modified fatty acid A of component (a-1)
25 was obtained. The content of the non-volatile components in the solution was 50% by mass.

Table 1

Raw material		
	fatty acid of castor oil	356
5	styrene	172
	i-butyl methacrylate	257
	methacrylic acid	215
Polymerization initiator		
10	t-butyl peroxybenzoate	30

The number in the table are expressed by part by mass.

Preparation of (a-2) a polyester resin having hydroxyl group

15 Into a 3 liter four-necked flask equipped with a stirrer, a thermometer, a reflux condenser having a dehydration trap and an inlet for nitrogen gas, raw materials shown in Table 2 in amounts also shown in Table 2 and 0.5 parts by mass of dibutyltin oxide were placed, and the condensation with dehydration was conducted by elevating the

20 temperature at 220°C. During the reaction, a portion of the reaction solution of the resin was taken out and diluted with butyl cellosolve so that a solution having a content of the non-volatile components of 60% by mass was obtained. The reaction was continued until the acid value of the obtained solution reached the value shown in Table 2, and Polyester

25 resin having hydroxyl group A of component (a-2) which was a raw material for a water-dispersible vinyl-modified polyester resin of component (a) was obtained as a solid substance.

Table 2

Raw material		
5	isophthalic acid	161
	adipic acid	330
	fatty acid of soybean	53
	neopentyl glycol	101
	1,6-hexanediol	44
10	trimethylolpropane	311
Properties		
	hydroxyl value	192
	acid value	9.7
15	weight-average molecular weight	9200

The numbers on the raw materials in the table are expressed by part by mass.

20 Preparation of (a) a water-dispersible vinyl-modified polyester resin

Into a 3 liter four-necked flask equipped with a stirrer, a thermometer, a reflux condenser having a dehydration trap and an inlet for nitrogen gas, raw materials shown in Table 3 in amounts also shown in Table 3 were placed. The temperature was slowly elevated at 180°C, and the condensation with dehydration was conducted by removing xylene and methyl ethyl ketone by distillation. During the reaction, a portion of the reaction solution of the resin was taken out and diluted with butyl cellosolve so that a solution having a content of the non-volatile

components of 50% by mass was obtained. The reaction was continued until the acid value of the obtained solution reached 16.5 mg KOH/g. After the reaction was completed, the reaction mixture was stirred at 150°C for 1 hour and, after triethylamine was added at 90°C, the obtained
5 mixture was stirred at the same temperature for 1 hour. Then, an ion-exchanged water was added in an amount such that the concentration of the non-volatile components was adjusted at 40% by mass, and a water dispersion of Water-dispersible vinyl-modified polyester resin A of component (a) having the properties shown in Table 3 was obtained.

10 As the result of examination of water-dispersible vinyl-modified polyester resin A of component (a) obtained above in accordance with the turbidity method, it was confirmed that the product was a water-dispersible resin.

15 Turbidity method (another method for examining whether a material is soluble in water or dispersible in water)

The examination was conducted in accordance with the following procedures (i) to (iii):

(i) A resin for the examination was mixed with 100 g of a mixed
20 solvent of water and butylcellosolve, and a mixed fluid was prepared so that the fluid contained 40% by weight of the resin for the examination as expressed by the content of the solid components, 55% by weight of water and 5% by weight of butylcellosolve.

(ii) A printed character of No. 5 size was placed on the bottom of a
25 glass beaker containing the mixed fluid prepared above, and a person having a vision of 1.5 attempted to read the printed character at a position

0.5 m above the character.

(iii) When the mixed fluid was transparent to the degree such that the character of No. 5 size could be read, the resin was decided to be “soluble in water”. When the mixed fluid was not transparent to the degree such that the character of No. 5 size could be read, the resin was decided to be “dispersible in water”.

The properties of Water-dispersible vinyl-modified polyester resin A are shown in Table 3.

Table 3

Preparation Example 1

Raw material

Vinyl-modified fatty acid A 760

Polyester resin having hydroxyl group A 240

Basic compound

triethylamine 48

Properties

hydroxyl value (mg KOH/g) 138

acid value (mg KOH/g) 32.5

degree of neutralization (% by mole) 80

weight-average molecular weight 57,000

form of resin dispersible
in water

(b) Water-soluble epoxy-modified polyester resin

A commercial epoxy-modified polyester resin shown in the following was used.

5 An epoxy-modified polyester resin (manufactured by DAINIPPON INK KAGAKU KOGYO Co., Ltd.; the trade name: WATERSOL (a registered trade name); S-370; the hydroxyl value: 100; the acid value: 40; the weight-average molecular weight: 17,000; the uniform liquid type; the content of the solid components: 55%)

10 When the above resin was examined in accordance with the turbidity method described above, it was found that the resin was soluble in water.

(c) Melamine resin

15 Commercial melamine resins shown in the following were used.

 Melamine resin A (manufactured by MITSUI CYTEC Co., Ltd.; the trade name: CYMEL (a registered trade name) 325; the imino type having methyl group; the number of the nucleus: 1)

 Melamine resin B (manufactured by MITSUI CYTEC Co.,
20 Ltd.; the trade name: CYMEL (a registered trade name) 303; the complete alkyl type having methyl group; the number of the nucleus: 1)

(d) Water-soluble epoxy resin

 A commercial epoxy resin (manufactured by NAGASE CHEMTECH
25 Co., Ltd.; the trade name: DENACOL (a registered trade name) EX-861) was used.

When the above epoxy resin was examined in accordance with the turbidity method described above, it was found that the resin was soluble in water.

5 [Preparation Example 2] (Preparation of (e) crosslinked resin particles)

Into a 500 ml reactor equipped with an inlet for nitrogen gas, a stirrer, a condenser, a temperature controller and a dropping funnel, 185 parts of deionized water was placed, and the temperature was elevated at 83°C. Into the dropping funnel, 20 parts of ACRONIX (a registered trade
10 name) M-5300 (manufactured by TOA GOSEI KAGAKU Co., Ltd.), 5.9 parts of dimethylethanolamine and 80 parts by styrene were placed, and a monomer solution was prepared. Then, the prepared monomer solution was added dropwise into the reactor over 2 hours. Simultaneously with the addition of the monomer solution, a solution prepared by neutralizing
15 1 part of 4,4'-azobis-4-cyanovaleric acid with 0.55 parts of dimethylethanolamine, followed by dissolving the obtained product into 40 parts of deionized water was added dropwise as the initiator. After being stirred at 83°C for 1 hour, the reaction mixture was cooled, and a milk white emulsion was obtained. The obtained emulsion of the crosslinked
20 resin particles had a content of the solid components of 30%, and the diameter of the particles was 100 nm (in accordance with the laser light scattering method).

[Examples 1 to 12 and Comparative Examples 1 and 2] (Preparation of
25 primer surfacers and multi-layer coating films)

Preparation of primer surfacers

Into a stainless vessel, a water-dispersible vinyl-modified polyester resin of component (a) in a specific amount and pigments in specific amounts, which are shown in Table 1, and glass beads in the same amount as the amounts of the above components were placed, and a dispersion was prepared by using a paint shaker for 2 hours. To the prepared dispersion, a water-soluble epoxy-modified polyester resin of component (b), a melamine resin of component (c), a water-soluble epoxy resin of component (d) and crosslinked resin particles of component (e) in respective specific amounts were added, and the resultant mixture was stirred for 5 minutes. Then, the glass beads were removed, and the viscosity was adjusted with ion-exchanged water so that the viscosity measured by using a Ford cup No. 4 was 50 seconds (20°C). Water-borne primer surfacers were prepared as described above.

Preparation of multi-layer coating films

A dull finished steel plate which had been treated with zinc phosphate was treated by electrodeposition coating using POWER TOP (a registered trade name) U-50 (a cationic electrodeposition coating material manufactured by NIPPON PAINT Co., Ltd.) to form a coating film having a thickness of 30 μm after being dried, and the formed coating film was baked at 160°C for 30 minutes. The obtained plate was coated with the water-borne primer surfacer prepared above in accordance with the rotating atomization coating process to form a coating film having a thickness of 20 μm , and the obtained coating film was preheated at 80°C for 3 minutes. The concentration of the solid components in the preheated coating film was 85% by mass. The measurement of the concentration of the solid components in the water-borne primer film after

being preheated was conducted as described in the following.

An aluminum foil having a size of 150×100 mm the mass of which had been measured in advance was coated with the water-borne primer surfacer and the obtained coating film was preheated under the same conditions as those in the corresponding procedures using the dull finished steel plate, and an uncured primer film was obtained. The aluminum foil on which the uncured primer film was formed was quickly folded, and the mass was measured. The concentration of the solid components was calculated from the obtained result.

After the preheating described above, AQUAREX AR-2100 (a water-borne base coating material manufactured by NIPPON PAINT Co., Ltd.) was applied in accordance with the air spray coating process to form a coating film having a thickness of 12 μm , and the formed coating film was baked at 80°C for 3 minutes. The obtained coated steel plate was coated with MACFLOW (a registered trade name) 1820 CLEAR (a clear coating material manufactured by NIPPON PAINT Co., Ltd.) in accordance with the spray coating process to form a coating film having a thickness of 35 μm , and the coated steel plate was baked at 140°C for 30 minutes. Multi-layer coating films were obtained as described above.

Test materials for evaluation of the skin of the base coat were obtained by baking the steel plates obtained after the application of the base coating material at 140°C for 30 minutes.

Table 4-1

Example		1	2	3	4	5	6	7
Comparative Example								
5	Vehicle							
	(a) water-dispersible vinyl-modified polyester resin	30	4	54	30	30	30	40
10	(b) water-soluble epoxy-modified polyester resin	30	54	4	30	30	30	40
	(c) melamine resin							
	(A)	20	20	20	20	20	40	20
	(B)	20	20	20	20	20	-	-
	(d) water-soluble epoxy resin	10	10	10	10	10	10	10
15	[sum of (a), (b), (c) and (d)]	110	108	108	110	110	110	110
	(e) Crosslinked resin particles	15	15	15	40	5	15	10
	Pigment							
20	titanium oxide	70	70	70	70	70	70	74
	carbon black	5	5	5	5	5	5	1
	barium sulfate	25	25	25	25	25	25	25
	[entire pigments]	100	100	100	100	100	100	100
25	Sum total	225	223	223	250	215	225	220

Table 4-2

Example		8	9	10	11	12		
Comparative Example							1	2
5	Vehicle							
	(a) water-dispersible vinyl-modified polyester resin	25	30	30	30	30	60	-
10	(b) water-soluble epoxy-modified polyester resin	25	30	30	30	30	-	60
	(c) melamine resin							
	(A)	25	20	20	20	20	20	20
	(B)	25	20	20	20	20	20	20
	(d) water-soluble epoxy resin	10	3	-	10	-	10	10
15	[sum of (a), (b), (c) and (d)]	110	103	100	110	100	110	110
	(e) Crosslinked resin particles	15	15	15	-	-	15	15
	Pigment							
20	titanium oxide	70	74	70	70	70	70	70
	carbon black	5	1	5	5	5	5	5
	barium sulfate	25	25	25	25	25	25	25
	[entire pigments]	100	100	100	100	100	100	100
25	Sum total	225	218	215	210	200	225	225

Using the obtained multi-layer coating films, the following measurements and tests were conducted. The results are shown in Table 5.

[Appearance of the skin of a base coat]

5 Using a test material for evaluation of the skin of a base coat which was prepared by baking at 140°C for 30 minutes after a base coating material was applied, the appearance of the skin of the base coat was evaluated in accordance with the following criterion:

 excellent: no roughness found on the surface, excellent gloss

10 good: no roughness found on the surface, good gloss

 fair: slight roughness found on the surface, poor gloss

 poor: roughness found on the surface, poor gloss

 The above criterion was applied also to the evaluation of the appearance of a multi-layer coating film described below.

15 [Appearance of a multi-layer coating film]

 (Gloss)

 The 20 degree gloss was measured using "PICOGLOSS MODEL 1500MC" manufactured by ERICHSEN Company.

 (Measurement of PGD)

20 The distinctness of gloss (Gd) of a composite coating film was measured using a portable gloss distinctness meter "PGD IV Type" manufactured by NIPPON SHIKISAI KENKYUSHO. The value of Gd indicates the distinctness of an image reflected on a surface. The greater the value, the more excellent the distinctness of the surface.

25 (Evaluation by visual observation)

 The evaluation was conducted in accordance with the same

criterion as that described for the evaluation of the appearance of the skin of a base coat.

[Properties of a coating film]

(Water resistance)

5 A coating film was dipped into warm water at 40°C for one day, and the change in the appearance was evaluated by visual observation in accordance with the following criterion:

 excellent: no change

 good: slightly whitened

10 fair: whitened

 poor: dissolved

(Chipping resistance)

 The test was conducted using Gravelometer (manufactured by SUGA SHIKENKI Co., Ltd.) for evaluation of chipping resistance under
15 the following condition:

 size of gravel: No. 7 gravel

 amount of gravel: 50 g

 distance: 35 cm

 air pressure: 4.0 kg/cm²

20 angle: 45°

 temperature of the test: -20°C

The result was evaluated by visual observation in accordance with the following criterion:

 excellent: absolutely no separation

25 good: slight separation found

 fair: separation of 1 mmφ or smaller found occasionally

poor: marked separation

Table 5-1

5	Example	1	2	3	4	5	6	7
	Comparative Example							
	Skin of base coat	good	good	good	good	good	good	good
10	Appearance of multi-layer coating film							
	gloss	88	88	88	89	88	86	89
	PGD	0.9	0.8	0.9	0.9	0.9	0.8	0.9
15	visual evaluation	excel- lent	excel- lent	excel- lent	excel- lent	excel- lent	good	excel- lent
	Properties of multi-layer coating film							
20	water resistance	excel- lent	excel- lent	good	excel- lent	excel- lent	excel- lent	good
	chipping resistance	excel- lent	excel- lent	good	excel- lent	excel- lent	excel- lent	good

25

Table 5-2

		8	9	10	11	12		
Example							1	2
Comparative Example								
5	Skin of base coat	good	good	good	fair	fair	poor	good
Appearance of multi-layer coating film								
10	gloss	87	89	88	85	86	83	82
	PGD	0.8	0.9	0.9	0.8	0.8	0.7	0.5
	visual evaluation	excel- lent	excel- lent	excel- lent	good	good	poor	poor
15	Properties of multi-layer coating film							
	water resistance	excel- lent	excel- lent	good	excel- lent	good	fair	good
20	chipping resistance	excel- lent	excel- lent	fair	excel- lent	fair	poor	good

INDUSTRIAL APPLICABILITY

In accordance with the present invention, the water borne primer surfacer which forms a multi-layer coating film exhibiting excellent property for designing and excellent functions even when a primer film, a base coat and a clear coat are formed in accordance with a three-coat one-bake coating process, is provided. By using the water-borne primer surfacer of the present invention, the preparation of the multi-layer coating film exhibiting the excellent properties of the coating film can be

achieved in combination with the conversion of a organic solvent-borne coating material to a water-borne coating material and the decrease in the steps of coating.

CLAIMS

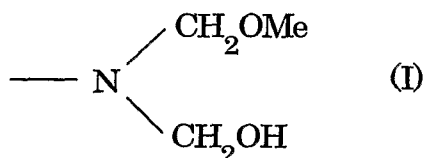
1. A water-borne primer surfacer which comprises (a) a water-dispersible vinyl-modified polyester resin, (b) a water-soluble epoxy-modified polyester resin and (c) a melamine resin.

2. A water-borne primer surfacer according to Claim 1, wherein

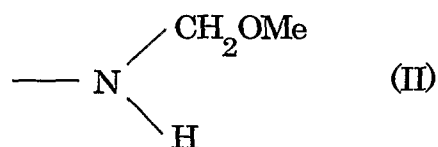
the water-dispersible vinyl-modified polyester resin of component (a) is a polyester resin having an acid value of 20 to 100 mg KOH/g, a degree of neutralization of 70 to 100% and a weight-average molecular weight of 10,000 to 150,000, and

the water-soluble epoxy-modified polyester resin of component (b) is a polyester resin having an acid value of 25 to 50 mg KOH/g, a degree of neutralization of 70 to 100% and a weight-average molecular weight of 5,000 to 30,000.

3. A water-borne primer surfacer according to any one of Claims 1 and 2, wherein the melamine resin of component (c) is at least one melamine resin selected from melamine resins of a methylol type having, as a reactive group, a group expressed by formula (I):



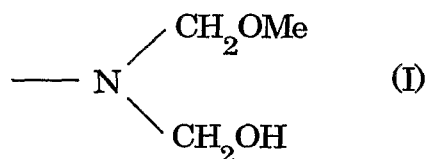
melamine resins of an imino type having, as a reactive group, a group expressed by formula (II):



and melamine resins of a methylol/imino type having, as reactive groups, both of the group expressed by formula (I) and the group expressed by formula (II).

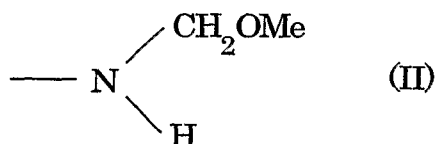
5

4. A water-borne primer surfacer according to any one of Claims 1 and 2, wherein the melamine resin of component (c) comprises a combination of at least one melamine resin selected from melamine resins of a methylol type having, as a reactive group, a group expressed by formula (I):



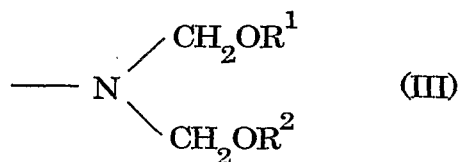
10

melamine resins of an imino type having, as a reactive group, a group expressed by formula (II):



and melamine resins of a methylol/imino type having, as reactive groups, both of the group expressed by formula (I) and the group expressed by formula (II), and a melamine resin of a complete alkyl ether type having, as a reactive group, a group represented by general formula (III):

15



R¹ and R² each independently representing an alkyl group having 1 to 4 carbon atoms; and

an amount of the melamine resin of a complete alkyl ether type is
 5 60% by mass or smaller based on an entire amount of the melamine resin of component (c).

5. A water-borne primer surfacer according to any one of Claims 1 to 4, which further comprises (d) a water-soluble epoxy resin.

10

6. A water-borne primer surfacer according to Claim 5, wherein

a ratio of amounts by mass of the water-dispersible vinyl-modified polyester resin of component (a) to the water-soluble epoxy-modified polyester resin of component (b) is 5:95 to 95:5, the amounts being
 15 expressed as amounts of solid components of the resins;

an amount of the melamine resin of component (c) is 25 to 100% by mass based on a sum of amounts of the water-dispersible vinyl-modified polyester resin of component (a) and the water-soluble epoxy-modified polyester resin of component (b), the amounts being expressed as amounts
 20 of solid components of the resins; and

an amount of the water-soluble epoxy resin of component (d) is 3 to 25% by mass based on a sum of amounts of the water-dispersible vinyl-modified polyester resin of component (a), the water-soluble epoxy-modified polyester resin of component (b) and the melamine resin of

component (c), the amounts being expressed as amounts of solid components of the resins.

7. A water-borne primer surfacer according to any one of Claims 5 and 6,
5 which further comprises (e) crosslinked resin particles, and an amount of the crosslinked resin particles of component (e) is 3 to 40% by mass based on a sum of amounts of the water-dispersible vinyl-modified polyester resin of component (a), the water-soluble epoxy-modified polyester resin of component (b), the melamine resin of component (c) and the water-soluble
10 epoxy resin of component (d), the amounts being expressed as amounts by mass of solid components of the resins.

8. A water-borne primer surfacer according to any one of Claims 1 to 7,
which further comprises (f) pigments, and an amount of the pigments of
15 component (f) is 20 to 70% by mass, the amount being expressed as a pigment weight concentration (PWC).

9. A water-borne primer surfacer according to any one of Claims 1 to 8,
which is a water-borne primer surfacer used for a process for forming a
20 multi-layer coating film, wherein the process for forming a multi-layer coating film comprises step (1) in which an article for coating having an electrodeposition coating film is coated with the water-borne primer surfacer to form an uncured primer film, step (2) in which the uncured primer film is coated with a water-borne base coating material to form an
25 uncured base coat, step (3) in which the uncured base coat is coated with a clear coating material to form an uncured clear coat, and step (4) in which

the uncured primer film, the uncured base coat and the uncured clear coat are simultaneously cured by heating.

10. A process for forming a multi-layer coating film which comprises step
5 (1) in which an article for coating having an electrodeposition coating film is coated with a water-borne primer surfacer to form an uncured primer film, step (2) in which the uncured primer film is coated with a water-borne base coating material to form an uncured base coat, step (3)
10 in which the uncured base coat is coated with a clear coating material to form an uncured clear coat, and step (4) in which the uncured primer film, the uncured base coat and the uncured clear coat are simultaneously cured by heating, wherein a water-borne primer surfacer described in any one of Claims 1 to 8 is used as the water-borne primer surfacer.

15 11. A process for forming a multi-layer coating film according to Claim 10, wherein a base coating material comprising an acrylic emulsion is used as the water-borne base coating material.

20 12. A process for forming a multi-layer coating film according to any one of Claims 10 and 11, wherein preheating is conducted between step (1) and step (2) and/or between step (2) and step (3).

13. A coated article having a multi-layer coating film which is formed in accordance with a process described in any one of Claims 10 to 12.

INTERNATIONAL SEARCH REPORT

International application No

PCT/JP2008/070629

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09D167/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2004/242756 A1 (KOMAZAKI SHIGERU [JP] ET AL) 2 December 2004 (2004-12-02) -----	
P,A	US 2008/139736 A1 (YAMADA SHINYA [JP] ET AL) 12 June 2008 (2008-06-12) -----	
A	US 2004/152856 A1 (LEE JU-KIL [KR] ET AL) 5 August 2004 (2004-08-05) -----	

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"P" document published prior to the international filing date but later than the priority date claimed

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

18 February 2009

Date of mailing of the international search report

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Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Lohner, Pierre

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/JP2008/070629

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