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HAMMER FINISH FROM AQUEOUS COMPOSITION CONTAINING NON-LEAFING ALUMINUM PARTICLES

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14 Claims. (Cl. 260—29.4)

This application is a continuation application of my earlier application having the Serial No. 788,787, filed January 26, 1959, and now abandoned, entitled, Water Soluble Hammer Finish.

This invention relates to a coating composition which is capable of producing a hammer finish on a substrata comprising a mixture of a water-soluble potentially thermosetting polymethyl ether of a polymethylol melamine, a water-soluble ammonium salt of a copolymer of an ethylenically unsaturated carboxylic acid and an alkyl ester of an alpha, beta-ethylenically unsaturated monocarboxylic acid containing small amounts of a non-leafing aluminum particle. More particularly, this invention relates to a coating composition capable of producing a hammer finish on a substrata comprising a mixture of (1) 50% to 10% by weight of a water-soluble potentially thermosetting polymethyl ether of a polymethylol melamine, (2) 50% to 90% by weight of a water-soluble ammonium salt of a copolymer comprising (a) 5% to 50% by weight of an ethylenically unsaturated carboxylic acid and (b) 50% to 95% by weight of an alkyl ester of an alpha, beta-ethylenically unsaturated monocarboxylic acid, and (3) from about 1% to about 10% by weight based on the total weight of (1) and (2) of a non-leafing aluminum particle.

One of the objects of the present invention is to produce a water-soluble coating composition which is capable of producing a hammer finish on a substrate, particularly a metal substrate. A further object of the present invention is to produce a coating composition which is capable of producing on a substrata a continuous film having a hammer finish effect from a water-soluble coating composition, thereby eliminating the hazards of fire and explosion in the application of such a finish. These and other objects of the present invention will be discussed in greater detail hereinbelow.

Hammer finishes in coating compositions are well known and are so called because these finishes have the appearance of a sheet of metal which has been beaten with a ball peen hammer. When a coating of this type is viewed at a grazing angle, slight undulations can be seen but the finish is fundamentally smooth when contrasted with wrinkle finishes. For this reason, hammer finishes are much easier to wipe clean since there are no pockets in which dirt may be retained. The optical illusion on which the hammered effect depends results from the controlled orientation of very fine aluminum particles which are present in the film. In the center of these hammer marks, these metallic particles tend to lie flat and partially overlap one another whereas near the outer periphery of the mark, the thin particles stand more or less on edge. When the particles lie flat, they reflect more light and thus give a bright metallic look to such spots. In the surrounding areas where they stand up, the coating has a darker appearance. It is frequently the practice to incorporate small amounts of pigment into such finishes for the purpose of adding color and to accentuate the contrast of the dark and the light areas. These coating compositions are best applied by use of a spray gun. The non-leafing aluminum

particles used in the composition of the present invention are minute aluminum flakes which become scattered in random positions throughout the film. These aluminum particle compositions are available commercially and are frequently supplied to the paint manufacturer as a 65% solids paste wet with solvent. The particle size must be extremely small in order to produce the proper effect. It is usually finer than about 400 mesh although slightly larger sizes such as 325 mesh size provides a slightly more brilliant glitter but is apt to give a rougher, sandy surface. Only small quantities are used in the coating compositions because excessive amounts result in a dull gray appearance. As a consequence, one should use between about 1% and 10% by weight based on the total weight of the resinous components in the instant composition. It is preferred to use between about 3% and 6% by weight. The addition of color pigmentation should be limited so as not to mask the aluminum and must be very finely ground. It is neither necessary nor desirable to grind the aluminum particles. It is sufficient simply to stir the aluminum into the coating compositions with good agitation in order to insure that all of the lumps are being broken up.

The hammer finish coating compositions of the present invention will have utility as a coating composition primarily on metallic sub-strata such as vacuum cleaner housings, automobiles, elevator interiors, office furniture such as desks, chairs, lamps and the like.

In the preparation of the water-soluble copolymers used in the composition of the present invention, one of the essential reactants is an alpha, beta-ethylenically unsaturated carboxylic acid. This class of acids includes not only the monocarboxylic acids but includes as well the polycarboxylic acids. Amongst the monocarboxylic acids which may be used to prepare the copolymers of the present invention are such acids as acrylic, beta-benzoyl acrylic, methacrylic, cinnamic, crotonic and the like. Amongst the alpha, beta-unsaturated polycarboxylic acids which may be used in the preparation of the copolymers used in the present invention are the maleic, fumaric, itaconic, citraconic, mesaconic, aconitic; and the halogenated acids such as halogenated maleic, chloromaleic acid and the like. Quite obviously, these acids may be used either singly or in combination with one another. Whenever available, anhydrides of these acids may be used either singly or in combination with one another or with the acids.

As a second essential component to the water-soluble copolymers used in the present invention, there are the alkyl esters of the alpha, beta-unsaturated monocarboxylic acid such as methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, octyl acrylate, decyl acrylate, lauryl acrylate, ethyl methacrylate, butyl methacrylate, heptyl methacrylate, decyl methacrylate, propyl crotonate, butyl crotonate, nonyl crotonate, and the like. These akyl esters may be used either singly or in combination with one another.

There are certain other polymerizable vinyl monomers such as those containing the polymerizable $CH_2=C<$ groups which may be used to advantage with the alpha, beta unsaturated carboxylic acids and the alkyl esters of the alpha, beta-ethylenically unsaturated monocarboxylic acids. Included in such groups are such polymerizable vinyl compounds as styrene, ortho-, meta- or para-alkyl styrenes such as the o-, m- or p-methyl, ethyl, propyl and butyl styrenes, 2,4-dimethyl styrene, 2,3-dimethyl styrene, 2,5-dimethyl styrene, vinyl naphthenate, acrylonitrile, methacrylonitrile, halo ring or side chain styrenes such as α-chloro styrene, ortho-, meta- or para-chloro styrenes, 2,4-dichloro styrene, 2,3-dichloro sty-

rene, 2,5-dichloro styrene or the alkyl side chain styrenes such as α-methyl styrene, α-ethyl styrene and the like. Additionally, one may make use of such polymerizable vinyl monomers as acrylamide, methacrylamide, ethacrylamide, ethylenebisacrylamide, N-tertiarybutylacrylamide and the like. These additional monomers may be used either singly or in combination with one another or may be left out of the composition entirely. The amount of monomer of diminished water solubility will vary considerably and directly in amount with the available hydrophilic groups in the polymer. When 50% of acrylic acid is used in the polymer, larger amounts of a monomer such as styrene may be used whereas when 5% of acrylic acid is used, little or no styrene should be used. As a result of this limitation, it is generally advisable to use not more than 25% by weight of these polymerizable monomers in the total weight of the ultimate copolymer comprising the ethylenically unsaturated acid and the alkyl ester of the ethylenically unsaturated monocarboxylic acid.

The copolymers used in the present invention are rendered water-soluble by reaction with ammonium hydroxide to form the ammonium salt of the copolymer. The amount of ammonium hydroxide used to produce the water-soluble salt of the copolymer may be varied over a fairly wide range. For instance, one may use a sufficient amount of ammonium hydroxide to form the half salt by using ½ mol equivalent of ammonium hydroxide per mol of carboxyl groups available in the copolymer as produced. One may furthermore use a full equivalent of ammonium hydroxide per mol equivalent of carboxyl group present in the copolymer as prepared. Still further, one could use an excess of ammonium hydroxide to insure complete salt formation in amounts up to and even exceeding 4 mol equivalents of ammonium hydroxide per mol of carboxyl group present in the copolymer.

As the second principal component of the composition mixture of the present invention, one will use the water-soluble potentially thermosetting polymethyl ethers of polymethylol melamines. The polymethyl ether will encompass the dimethyl ether, the trimethyl ether, the tetramethyl ether, the pentamethyl ether and the hexamethyl ether of polymethylol melamines. In preparing the polymethylol melamines, one must react at least 2 mols of formaldehyde and preferably at least 3 mols of formaldehyde with each mol of melamine under known reaction conditions in order to produce the water-soluble polymethylol melamine such as trimethylol melamine and the like. The preferred methyl ether of polymethylol melamine is the hexamethoxy-hexamethylol melamine. The ratio of the water-soluble potentially thermosetting polymethyl ether of polymethylol melamine to the water-soluble ammonium salt of the copolymer may be varied over a fairly wide range. For instance, one may use between about 10% to about 50% by weight of the methylol melamine material to a corresponding 90%–50% by weight of the water-soluble copolymer.

The water-soluble copolymers used in the composition of the present invention may be prepared by reacting alkyl esters of alpha, beta-unsaturated monocarboxylic acids and alpha, beta-unsaturated carboxylic acids in proportions which vary over a fairly wide range. For instance, one may use between about 50% and 95% by weight of the alkyl esters of the alpha, beta-unsaturated monocarboxylic acids to a correspondingly 50%–5% by weight of the alpha, beta-unsaturated carboxylic acids. Preferably, one would use about 75–90% by weight of the alkyl ester of the alpha, beta-ethylenically unsaturated monocarboxylic acid to about 25–10% by weight of the alpha, beta-ethylenically unsaturated carboxylic acid. If a third component of the class described hereinabove is to be utilized in the preparation of these water-soluble copolymers, it may be present in an amount up to about 25% by weight based on the total weight of the copolymer solids.

In the use of these mixtures of the thermosetting resin-forming reaction products with the water-soluble copolymers of the present invention, it is not imperative that a catalyst be used, although one may be used as a matter of choice. The catalyst used may be any of the conventional catalytic materials, many of which have been disclosed in the prior art and which are water soluble or at least water dispersible. The amount of catalyst which may be used obviously can be varied over a considerable range, as the prior art clearly teaches.

In order that the present invention may be more completely understood, the following examples are set forth in which all parts are parts by weight unless otherwise indicated. These examples are set forth primarily for the purpose of illustration and any specific enumeration of detail contained therein should not be interpreted as a limitation on the case except as is indicated in the appended claims.

Example 1

Into a suitable reaction vessel equipped with stirrer, thermometer and reflux condenser, there is introduced 67.5 parts of dioxane. The charge is heated gradually to the reflux temperature by heating on an oil bath. After the dioxane has reached reflux, a mixture of 378 parts of ethyl acrylate, 107.5 parts of acrylic acid, and 122 parts of a 1% solution of butyl mercaptan in ethyl acrylate are introduced in relatively small increments over a two-hour period. Concurrently but separately, over the same period of time, there is added 12.2 parts of cumene hydroperoxide. After the addition is completed, reflux is continued for about 5 hours. 200 parts of the copolymer thus prepared are dissolved in 220 parts of a mixture of 1 part of concentrated ammonia (29% NH_3) to 4 parts of water. An additional 80 parts of water is added to give an aqueous solution of 36% solids concentration of the copolymer. The solvent dioxane is used in the present example in an amount approximating 10% of the total charge. At the end of the polymerization reaction, this solvent may be stripped off under vacuum but it is preferred to leave said solvent in since its removal is not economically justifiable and since this solvent is completely water miscible.

Example 2

A hammer finish coating composition is prepared by blending a mixture of 289 parts of a 36% solids solution of the copolymer prepared according to Example 1, 43.5 parts of the dimethyl ether of trimethylol melamine, 403 parts of water and 3 parts of Reynolds 40–LN paste (an aluminum paste comprising 65% extra fine lining grade, non-leafing aluminum powder mixed with 35% of an organic solvent). After thorough mixing of these components, the viscosity is adjusted to the desired fluidity for spray coating and a sheet steel panel is sprayed and air dried for 20 minutes at room temperature and is then baked for 20 minutes at 300° F. The coating thus produced is hard, glossy, has an attractive hammer finish with good metallized color.

Example 3

Into a suitable reaction vessel equipped with stirrer, thermometer, reflux condenser and two graduated funnels, there is introduced 149.6 parts of dioxane and the charge is heated to reflux. To the refluxing charge, there is added a mixture of 64 parts of butyl acrylate, and 10.8 parts of acrylic acid in small increments over a period of about 2 hours. Separately but concurrently there is added a total of 6 parts of cumene hydroperoxide under the same conditions. After the addition of monomer and catalyst is completed, refluxing is continued for about 6 hours. The solvent is stripped off by means of vacuum distillation to give a clear, viscous

copolymer. An aqueous solution of the copolymer is prepared by dissolving said copolymer in 0.5 to 2.0 equivalents of dilute ammonium hydroxide to give a 40% solids solution of the copolymer.

Example 4

A blend of 2 parts of the copolymer in solution prepared according to Example 3 and 1 part of hexamethyl ether of hexamethylol melamine is prepared to give a liquid coating composition of 47.3% solids to which there is added 0.18 part of Reynolds 40–LN paste. After adjusting the coating compositions to the desired viscosity for spraying, a steel panel is sprayed with the coating composition, allowed to air dry for 20 minutes at room temperature followed by a bake for 20 minutes at 120° C., 15 minutes at 150° C. and 15 minutes at 200° C. The resulting film had good hiding power of the defects in the steel panel and a lustrous metallic hammer finish is produced which is hard and glossy.

Example 5

128 parts of dioxane are introduced into a suitable reaction vessel equipped with stirrer, thermometer, reflux condenser and a graduated funnel and are heated to the reflux temperature whereupon a mixture of 46 parts of n-octyl acrylate, and 18 parts of acrylic acid are added in small increments over about a two-hour period. 5.1 parts of cumene hydroperoxide are added concurrently but separately under the same increment addition conditions. The refluxing is continued after the addition is completed for a period of about 5½ to 6 hours. The dioxane is stripped off by a means of vacuum distillation to give a clear viscous copolymer. A completely clear solution of the copolymer in water is prepared by introducing ten parts of the copolymer into a mixture of 21.4 parts of dilute ammonium hydroxide (concentrated NH_4OH to H_2O, 1:4, respectively), 6 parts of ethanol and a sufficient amount of water to give 50 parts of solution. After stirring, the solution is completely clear.

Example 6

A 20% (solids) ammonium hydroxide solution of the copolymer of Example 5 is mixed with an 80% solids solution in water of the dimethyl ether of trimethylol melamine in a ratio of two parts of copolymer to 1 part of the methyl ether of the methylol melamine solids. 0.24 part of Reynolds 40–LN paste is added and thoroughly dispersed throughout the coating composition. The viscosity is adjusted for spraying use if necessary or desired, and a sheet steel panel is sprayed with the same. The film thus deposited is permitted to air dry for about 20 minutes at room temperature and the film is then baked for about 30 minutes at 300° F. The resulting finish has a hammer effect, is glossy, hard and has good hiding power.

For optimum operating conditions, the compositions of the present invention should have their spray viscosities adjusted to between about 3 and 6 minutes in a No. 4 Ford cup. The spray pressures that may be used with the composition of the present invention may be varied between about 30 pounds per square inch and 75 pounds per square inch.

I claim:

1. A composition of matter capable of producing a continuous film on a sub-strata with a hammer finish effect comprising an aqueous dispersion of a mixture of (1) 50% to 10% by weight of a water-soluble potentially thermosetting polymethyl ether of a polymethylol melamine, (2) 50% to 90% by weight of a water-soluble ammonium salt of a copolymer comprising (*a*) 5% to 50% by weight of an ethylenically unsaturated carboxylic acid and (*b*) 50% to 95% by weight of an alkyl ester of an alpha,beta-ethylenically unsaturated monocarboxylic acid, and (3) from about 1% to about 10% by weight based on the total weight of (1) and (2) of a non-leafing aluminum particle.

2. A composition of matter capable of producing a continuous film on a sub-strata with a hammer finish effect comprising an aqueous dispersion of a mixture of (1) 50% to 10% by weight of a water-soluble potentially thermosetting polymethyl ether of a polymethylol melamine, (2) 50% to 90% by weight of a water-soluble ammonium salt of a copolymer comprising (*a*) 5% to 50% by weight of an alpha,beta-ethylenically unsaturated monocarboxylic acid and (*b*) 50% to 95% by weight of an alkyl ester of an alpha,beta-ethylenically unsaturated monocarboxylic acid, and (3) from about 1% to about 10% by weight based on the total weight of (1) and (2) of a non-leafing aluminum particle.

3. A composition of matter capable of producing a continuous film on a sub-strata with a hammer finish effect comprising an aqueous dispersion of a mixture of (1) 50% to 10% by weight of a water-soluble potentially thermosetting polymethyl ether of a polymethylol melamine, (2) 50% to 90% by weight of a water-soluble ammonium salt of a copolymer comprising (*a*) 5% to 50% by weight of acrylic acid and (*b*) 50% to 95% by weight of an alkyl ester of an alpha,beta-ethylenically unsaturated monocarboxylic acid, and (3) from about 1% to about 10% by weight based on the total weight of (1) and (2) of a non-leafing aluminum particle.

4. A composition of matter capable of producing a continuous film on a sub-strata with a hammer finish effect comprising an aqueous dispersion of a mixture of (1) 50% to 10% by weight of a water-soluble potentially thermosetting polymethyl ether of a polymethylol melamine, (2) 50% to 90% by weight of a water-soluble ammonium salt of a copolymer comprising (*a*) 5% to 50% by weight of acrylic acid and (*b*) 50% to 90% of butyl acrylate, and (3) from about 1% to about 10% by weight based on the total weight of (1) and (2) of a non-leafing aluminum particle.

5. A composition of matter capable of producing a continuous film on a sub-strata with a hammer finish effect comprising an aqueous dispersion of a mixture of (1) 50% to 10% by weight of a water-soluble potentially thermosetting polymethyl ether of a polymethylol melamine, (2) 50% to 90% by weight of a water-soluble ammonium salt of a copolymer comprising (*a*) 5% to 50% by weight of acrylic acid and (*b*) 50% to 90% of butyl acrylate and (*c*) up to 25% by weight of acrylamine, and (3) from about 1% to about 10% by weight based on the total weight of (1) and (2) of a non-leafing aluminum particle.

6. A composition of matter capable of producing a continuous film on a sub-strata with a hammer finish effect comprising an aqueous dispersion of a mixture of (1) 50% to 10% by weight of the hexamethyl ether of hexamethylol melamine, (2) 50% to 90% by weight of a water-soluble ammonium salt of a copolymer comprising (*a*) 5% to 50% by weight of acrylic acid and (*b*) 50% to 95% of butyl acrylate, and (3) from about 1% to about 10% by weight based on the total weight of (1) and (2) of a non-leafing aluminum particle.

7. A composition of matter capable of producing a continuous film on a sub-strata with a hammer finish effect comprising an aqueous dispersion of a mixture of (1) 50% to 10% by weight of a water-soluble potentially thermosetting polymethyl ether of a polymethylol melamine, (2) 50% to 90% by weight of a water-soluble ammonium salt of a copolymer comprising (*a*) 5% to 50% by weight of methacrylic acid and (*b*) 50% to 95% by weight of an alkyl ester of an alpha,beta-ethylenically unsaturated monocarboxylic acid, and (3) from about 1% to about 10% by weight based on the total weight of (1) and (2) of a non-leafing aluminum particle.

8. A composition of matter capable of producing a continuous film on a sub-strata with a hammer finish effect comprising an aqueous dispersion of a mixture of

(1) 50% to 10% by weight of a water-soluble potentially thermosetting polymethyl ether of a polymethylol melamine, (2) 50% to 90% by weight of a water-soluble ammonium salt of a copolymer comprising (*a*) 5% to 50% by weight of methacrylic acid and (*b*) 50% to 95% by weight of butyl acrylate and (3) from about 1% to about 10% by weight based on the total weight of (1) and (2) of a non-leafing aluminum particle.

9. A composition of matter capable of producing a continuous film on a sub-strata with a hammer finish effect comprising an aqueous dispersion of a mixture of (1) 50% to 10% by weight of a water-soluble potentially thermosetting polymethyl ether of a polymethylol melamine, (2) 50% to 90% by weight of a water-soluble ammonium salt of a copolymer comprising (*a*) 5% to 50% by weight of methacrylic acid and (*b*) 50% to 95% by weight of ethyl acrylate, and (3) from about 1% to about 10% by weight based on the total weight of (1) and (2) of a non-leafing aluminum particle.

10. A composition of matter capable of producing a continuous film on a sub-strata with a hammer finish effect comprising an aqueous dispersion of a mixture of (1) 50% to 10% by weight of a water-soluble potentially thermosetting polymethyl ether of a polymethylol melamine, (2) 50% to 90% by weight of a water-soluble ammonium salt of a copolymer comprising (*a*) 5% to 50% by weight of an ethylenically unsaturated carboxylic acid and (*b*) 50% to 95% of an alkyl ester of acrylic acid, and (3) from about 1% to about 10% by weight based on the total weight of (1) and (2) of a non-leafing aluminum particle.

11. A composition of matter capable of producing a continuous film on a sub-strata with a hammer finish effect comprising an aqueous dispersion of a mixture of (1) 50% to 10% by weight of a water-soluble potentially thermosetting polymethyl ether of a polymethylol melamine, (2) 50% to 90% by weight of a water-soluble ammonium salt of a copolymer comprising (*a*) 5% to 50% by weight of an ethylenically unsaturated carboxylic acid and (*b*) 50% to 95% by weight of an alkyl ester of methacrylic acid, and (3) from about 1% to about 10% by weight based on the total weight of (1) and (2) of a non-leafing aluminum particle.

12. A composition of matter capable of producing a continuous film on a sub-strata with a hammer finish effect comprising an aqueous dispersion of a mixture of (1) 50% to 10% by weight of a water-soluble potentially thermosetting polymethyl ether of a polymethylol melamine, (2) 50% to 90% by weight of a water-soluble ammonium salt of a copolymer comprising (*a*) 5% to 50% by weight of an ethylenically unsaturated carboxylic acid and (*b*) 50% to 95% of butyl acrylate, and (3) from about 1% to about 10% by weight based on the total weight of (1) and (2) of a non-leafing aluminum particle.

13. A composition of matter capable of producing a continuous film on a sub-strata with a hammer finish effect comprising an aqueous dispersion of a mixture of (1) 50% to 10% by weight of a water-soluble potentially thermosetting polymethyl ether of a polymethylol melamine, (2) 50% to 90% by weight of a water-soluble ammonium salt of a copolymer comprising (*a*) 5% to 50% by weight of an ethylenically unsaturated carboxylic acid and (*b*) 50% to 95% of ethyl acrylate, and (3) from about 1% to about 10% by weight based on the total weight of (1) and (2) of a non-leafing aluminum particle.

14. A composition of matter capable of producing a continuous film on a sub-strata with a hammer finish effect comprising an aqueous dispersion of a mixture of (1) 50% to 10% by weight of a water-soluble potentially thermosetting polymethyl ether of a polymethylol melamine, (2) 50% to 90% by weight of a water-soluble ammonium salt of a copolymer comprising (*a*) 5% to 50% by weight of acrylic acid and (*b*) 50% to 95% of ethyl acrylate, and (3) from about 1% to about 10% by weight based on the total weight of (1) and (2) of a non-leafing aluminum particle.

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