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54 **Durable multilayer coating.**

57 A laminate comprises, in consecutive order, a metal substrate, with or without a primer layer for powder coating ; a powder coating layer and a fluorine resin top coat ; in which the powder coating layer is formed by applying onto the metal substrate (with or without a primer layer), a composite powder coating composition containing mother powder particles comprising a film-forming binder resin which is solid at room temperature and heat-meltable and a pigment, together with microparticles of a resin containing, as an essential component, methyl methacrylate and having an average diameter of 0.001 to 10  $\mu\text{m}$ , in an amount of 0.05 to 40% by weight of the total powder coating composition ; and then baking the formed coating.

The present invention relates to a durable laminate and more specifically, a super-durable laminate comprising in consecutive order, a metal substrate, a powder coating layer and a fluorine resin top coat, the laminate being specifically excellent in interlaminar adhesion and showing the desired properties of said powder coating and fluorine resin coat in full.

5        Though a top coat composition based on a fluorine resin is useful in giving a coating with excellent weather resistance and corrosion resistance, but is very poor in adhesion towards substrate or under coat on said substrate. Therefore, in the actual application as in colored steel plate for roofing material and the like, an epoxy resin which is excellent in adhesion towards substrate and in processability, is first applied on as a surface primer coating, on which a fluorine resin based coating composition is applied to have a laminated coating.  
10        However, heretofore proposed epoxy primer compositions are all solvent type coating compositions, resulting coatings with at most about 5 microns thickness. Therefore, should the coating be mechanically damaged during transportation or processing step, cut would often reach to the substrate, resulting a marked loss in corrosion resistance of the coating. It is hardly possible to prepare the thicker coating with this solvent type epoxy primer coating composition without the fear of occurrence of cracks, sagging and the like.

15        On the other hand, a powder coating is in general believed to be suitable for thicker coating, and however, in the combination of fluorine resin coating and powder coating, it is generally poor in interlaminar adhesion and especially in the case of epoxy powder coating, such combination has never been practically used because of their extremely poor interlaminar adhesion properties.

20        Under the circumstances, the inventors have previously found a surprising fact that adhesion of fluorine resin coating towards powder coating is greatly improved when a particular powder coating composition comprising a particular epoxy resin, i.e. bisphenol A type epoxy resin, and a particular hardening agent, i.e. phenolic hardening agent, is selectively used as said powder coating and applied for patent on it ( as Japanese Patent Application No. 196133/87, now published as Publication (unexamined) No. 40329/89). In that invention, a thicker powder coating based on an epoxy resin having comparatively good processing properties is first  
25        applied on said primer coating, and the interlaminar adhesion between the coatings is likewise excellent.

Therefore, the resulted laminate is specifically useful as roofing material and others which require improved corrosion resistance under severe environmental conditions. However, the powder coating for the said epoxy primer coating was only limited to the composition comprising a particular epoxy resin and a particular hardening agent and there was additional problem of resulting only matte surface coating. It is, therefore, an object  
30        of the invention to provide a laminate comprising in consecutive order, a metal substrate, a powder coating layer and a fluorine resin top coat, the powder coating being freely selected from various kinds depending on the properties desired and the resulted laminate being excellent in interlaminar adhesion and properties and especially durability.

35        An additional object of the invention is to provide a super-durable laminate which is far excellent in processability, corrosion resistance and weather resistance as compared with those of heretofore proposed laminates.

#### Summary of the invention

40        According to the invention, the abovementioned objects may be attained with a laminate consisting, in consecutive order, of a metal substrate with or without a primer layer for powder coating, a powder coating layer and a fluorine resin top coat, characterized in that the powder coating layer is formed by applying onto the metal substrate with or without a primer layer, a composite powder coating composition comprising mother powder particles comprising a film-forming binder resin which is solid at room temperatures and heat-meltable and pigment,  
45        added with microparticles of a resin containing as an essential component methyl methacrylate and having an average diameter of 0.001 to 10 microns, in an amount of 0.05 to 40 % by weight of the total powder coating composition, and then subjecting the formed coating to a baking, thus formed powder coating layer being specifically excellent in durability.

50        In this invention, such metal plate as steel plate, galvanized steel sheet, aluminium plate, aluminium-galvanized steel sheet, stainless steel sheet and the like, with or without a primer for powder coating can be advantageously used as a substrate. As the primer, any of the known primers for powder coating, based on polyester resin, epoxy resin, acrylic resin, urethane resin or the like may be satisfactorily used as desired.

55        The powder coating to be applied on said substrate comprises mother powder particles based on a film-forming binder resin which is solid at room temperatures and is heat-meltable, added with microparticles of a resin containing as an essential constituting monomer methyl methacrylate, and having an average diameter of 0.001 to 10 microns. The amount of said resin microparticles may be in a range of 0.05 to 40% by weight, preferably 0.1 to 20% by weight of the total weight of the composite powder coating.

This adding amount may be cut in proportion to the decrease in average diameter of said resin micropar-

5 ticles, and however, from the standview of production easiness, the lower limit of the average diameter of said microparticles should be about 0.001 micron. At that particle size, about 0.05% by weight to the total weight of the composite powder coating of such microparticles should be added to secure the intended objects and effects of the present invention. If the particle size exceeds over the upper limit of 10 microns, then the amount of resin microparticles should be increased up to more than 40% by weight for better adhesion toward a top coat applied. However, at that time, there results adverse effects on the coating appearance and the like and hence, such a higher amount should be avoided in the present invention.

10 As the binder resin of the mother powder particles, any of the known film-forming resins which are solid at room temperatures and heat-meltable, as acrylic resin, polyester resin, epoxy resin and the like may be successfully used. To this binder resin, pigment, hardening agent and other conventional additives may be optionally added. There is no particular limit on the average diameter of such mother powder particles and however, preference is given to a range of 30 to 50 microns, from the standviews of application characteristics, coating surface appearance and the like. The present microparticles may be composed of any kind of resins providing containing methyl methacrylate component. However, from the production and practical points of view, preference is given to such resin as vinyl resin (including acrylic resin), epoxy resin, polyester resin, melamine resin and the like, and especially vinyl resin. The last-mentioned resin is specifically preferred, because it is easily prepared by varying its composition at will. Thus, a various combination of polymerizable vinyl monomers may be directly polymerized by using an emulsion polymerization, suspension polymerization or the like, to obtain the resin microparticles or such monomers may be polymerized by means of solution polymerization, mass polymerization or the like and thus obtained resin is pulverized and shieved. The resin microparticles may be of either crosslinked or non-crosslinked type and the particles may have spherical, fibrous or plate form.

25 In preparing vinyl resin microparticles, methyl methacrylate is essential in this invention and however, the following vinyl monomers may be advantageously co-used each separately or in the combination of 2 or more, i.e. 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, polyethyleneglycol mono(meth)acrylate, polypropyleneglycol mono(meth)acrylate, (meth)acrylic acid, itaconic acid, maleic acid, fumaric acid, crotonic acid, glycidyl (meth)acrylate, -methyl glycidyl (meth)acrylate, N-glycidyl acrylamide, vinyl sulfonic acid glycidyl, (methyl) glycidyl ether of allyl alcohol and the like.

30 Besides them, the following may be used as desired, i.e. methyl acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, cyclohexyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, octyl (meth)acrylate, 2-ethyloctyl (meth)acrylate, dodecyl (meth)acrylate, benzyl (meth)acrylate, phenyl (meth)acrylate, dialkyl fumarate, dialkyl itaconate, styrene, (meth) acrylonitrile, vinyl toluene, -methyl styrene, (meth) acrylamide, methylol (meth) acrylamide, vinyl acetate, vinyl propionate, lauryl vinyl ether, halogen-containing vinyl monomers and the like. Regarding an average grain diameter of such resin microparticles, there is no particular conditions, providing being smaller than the average diameter of mother powder particles and however, for the reasons hereinbefore stated, it should preferably be in a range of 0.001 to 10 microns and more preferably 0.01 to 5 microns.

40 The present resin microparticles are thus characterized by containing as an essential constituting component methyl methacrylate. The content of this particular monomer in said resin is not absolutely limitative, but rather fluctuate depending on the properties of binder resin, mixing easiness and the like. It is, however, preferred to select in a range of 10 to 100%, in solid weight ratio, of the total resin weight.

In the present powder coating, the abovementioned resin microparticles are contained so that the microparticles are present at least on the surface of the respective mother powder particles. For this end, the resin microparticles are added to the mother powder particles at any stage of the preparation of the latter particles.

45 To corroborate the fact that resin microparticles are maintained in solid form and located on the surface of the respective mother powder particles, in the most preferable embodiment, the resin microparticles are added with the mother powder particles. Addition of resin microparticles to the mother powder particles may be carried out by using various mixing measures. In the first method, the mother particle resin, hardening agent and optional pigment and other additives are melt-kneaded and during or after pulverization step, the resin microparticles are mixed in Super mixer, Henschel mixer or the like. In the second method, the mother powder particles obtained by wet dispersion means and the resin microparticles are mixed well in Hybritizer, Ball mill or the like. In another method, the mother particles are coated with the resin microparticles and fused to form a continuous film thereupon.

55 Therefore, the term "contain" as used herein shall denote every embodiments as herein above mentioned. However, the invention can never be limited in any sense by the preparation method used, and it is also possible to have the composite powder coating by using a comparatively larger quantity of resin microparticles in, for example, melting or granulating step of powder particles, thereby placing the resin microparticles at least on the surface of the respective mother powder particles, or by using the combination of said processes.

Though the mixture form may somewhat vary with the addition method used, this shall give no influence for the essential features of the present invention.

Thus obtained powder coating composition as applied by conventional application means on the surface of substrate and then over-coated with a fluorine resin. As already stated, adhesion of fluorine resin toward powder coating is in general no good and this is especially in the case of vinylidene fluoride type fluorine resin because of having no adhering functional groups. However, with the present powder coating composition, said adhesion is excellent, resulting an improved durable fluorine resin over coat.

The invention shall be now more fully explained in the following Examples and comparative Examples.

Unless otherwise being stated, all parts and percentages are by weight.

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#### Synthetic Example 1 ( Synthesis of resin microparticles A )

Into a reaction vessel fitted with a stirrer, a condenser, and a thermoregulator, were placed 380 parts of deionized water and 2 parts of nonionic surfactant MON2 (manufactured by Sanyo Kasei) and heated under stirring to 80°C to have a solution. To this, was added a solution of 1 part of ammonium persulfate (initiator) in 10 parts of deionized water and then dropwise added in 60 minutes a mixture of 61 parts of methyl methacrylate, 36 parts of styrene and 3 parts of n-butyl methacrylate. After completion of said addition, the combined was stirred at 80°C for 60 minutes to obtain an emulsion having a non-volatile content of 20% and an average particle diameter of 0.03 to 0.05 $\mu$ . This emulsion was spray-dried to obtain resin microparticles A.

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#### Synthetic Example 2 (Synthesis of resin microparticles B)

Into a reaction vessel fitted with a stirrer, a condenser and a thermoregulator, were placed 380 parts of deionized water and 2 parts of nonionic surfactant MON2 (manufactured by Sanyo Kasei) and heated under stirring to 80°C to obtain a solution. To this, was added a solution of 1 part of ammonium persulfate (initiator) in 10 parts of deionized water and then dropwise added in 60 minutes a mixture of 90 parts of methylmethacrylate, 33 parts of styrene, 46 parts of n-butyl methacrylate, and 20 parts of 2-hydroxyethyl methacrylate. After completion of said addition, the combined was further stirred at 80°C for 60 minutes to obtain an emulsion having a non-volatile content of 20% and an average particle diameter of 0.03 to 0.05 $\mu$ .

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This emulsion was subjected to spray-drying to obtain resin microparticles B.

#### Synthetic Example 3 (Synthesis of resin microparticles C)

Into a reaction vessel fitted with a stirrer, a condenser and a thermoregulator, were placed 380 parts of deionized water and 2 parts of nonionic surfactant MON2 (manufactured by Sanyo Kasei) and heated under stirring to 80°C to obtain a solution.

To this, was added a solution of 1 part of ammonium persulfate (initiator) in 10 parts of deionized water and then dropwise added in 60 minutes a mixture of 3 parts of lanryl methacrylate, 15 parts of methylmethacrylate and 82 parts of styrene. After completion of said addition, the combined was stirred at 80°C for 60 minutes to obtain an average particle diameter of 0.03 to 0.05 $\mu$ . This emulsion was then subjected to spray-drying to obtain resin microparticles C.

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#### Synthetic Example 4 (Synthesis of pulverized resin microparticles D)

Into a flask fitted with a dropping funnel, a stirrer and a thermometer, were placed 80 parts of xylene and heated to 130°C.

Using the dropping funnel, a mixture of 36 parts of methyl methacrylate, 10 parts of styrene, 24 parts of glycidyl methacrylate, 30 parts of t-butyl methacrylate and 6 parts of Kayaester O (initiator) was dropwise added at a constant speed in 3 hours to the flask and after standing for 30 minutes, a solution of 1 part of Kayaester O in 20 parts of xylene was added in 1 hour. Thereafter, the combined was maintained at 130°C for additional 2 hours and then the solvent was distilled an acrylic resin. Thus obtained acrylic resin was pulverized to obtain non-crosslinked resin microparticles D having an average diameter of 30 $\mu$ .

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#### Synthetic Example 5 (Preparation of epoxy coating composition E)

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100 parts of Epotohto YD-019 (epoxy resin, manufactured by Tohto Kasei), 3 parts of dicyandiamide and 40 parts of Titanium oxide CR50 were dry-mixed in Henshel Mixer (trade mark, Mitsui-Miike Seisakusho) and then the content was melt-dispersed at 100°C in Cokneader PR-46 (trade mark, Bus Co., Swiss).

After cooling, the resin mass obtained was pulverized by using Hammer mill and shieved by using 150 mesh metal net to obtain mother powder particles E.

Synthetic Example 6 (Preparation of polyester coating composition F)

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100 parts of ER 6800 (polyester resin, manufactured by Nippon Polyester Co.), 36 parts of Kureran U1 (blocked isocyanate, manufactured by BASF) and 40 parts of Titanium oxide CR50 were dry-mixed in Henshel Mixer and then melt-dispersed at 100°C by using Cokneader PR-46 (Bus, Swiss). After cooling, thus obtained resin mass was pulverized by using Hammer mill and then shieved by using 150 mesh metal net to obtain mother powder particles F.

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Example 1

In Henshel mixer, 99.95 parts of the mother powder particles E obtained in Synthetic Example 5 and 0.05 parts of the resin microparticles A were dry-mixed for 30 seconds to obtain composite powder coating composition.

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Thus obtained powder coating composition was applied on a steel sheet by using an electrostatic spray equipment and the coating was baked at 180°C for 20 minutes to obtain a coating with 80 micron thickness.

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On this coating, Duraner C (fluorine coating composition, trade mark, Nippon Paint Co., Ltd) was applied by using a bar coater and then baked at 270°C for 1 minute to obtain a top coat with 20 micron thickness.

Thus obtained laminate was tested in respect of coating appearance and interlaminar adhesion between the powder coating layer and fluorine resin coating and test results were shown in Table 1. In every respects, the test results were excellent.

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Examples 2-8

Following the procedures of Example 1, various composite powder coating compositions were prepared and applied on test substrates. Thereafter, fluorine resin coatings were prepared as in Example 1. The similar tests were conducted and test results were shown in Table 1. In every Examples, test results were excellent.

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Comparative Example 1

Similar composite powder coating composition was prepared with the materials shown in Table 1 and the similar was prepared.

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However, in this experiment, there resulted poor adhesion between the powder coating layer and the fluorine resin layer.

Comparative Examples 2-4

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Following the procedures of Comparative Example 1, but using the materials shown in Table 1, various comparative composite powder coating compositions and experiments, the coatings were no good because of having poor levelling properties.

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Table 1 (1)

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Example No.	1	2	3	4	5
Mother powder resin	E p o x y				
resin microparticles	A	B	C	A	A
Adding amount of resin microparticles	0.05	0.1	0.1	10	40
average diameter of microparticles	0.05	0.05	0.05	0.05	0.05
Inter laminar adhesion with fluorine resin coating	○	◎	◎	◎	◎
levelling property	◎	◎	○	◎	○

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Adding amount of resin microparticles =  $\frac{\text{weight of resin microparticles}}{\text{weight of the composite powder coating}}$

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Inter laminar adhesion = tested by cross-cut adhesion test

◎ 100/100

○ 100/ 90 or more

X 100/ 50 or less

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Table 1 (2)

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Example No.	6	7	8
Mother powder resin	Polyester		
resin microparticles	C	C	C
Adding amount of resin microparticles	0.1	10	40
average diameter of microparticles	0.05	0.05	0.05
Inter laminar adhesion with fluorine resin coating	⊙	⊙	⊙
levelling property	⊙	⊙	○

Adding amount of resin microparticles =  $\frac{\text{weight of resin microparticles}}{\text{weight of the composite powder coating}}$

Inter laminar adhesion = tested by cross-cut adhesion test  
 ⊙ 100/100  
 ○ 100/ 90 or more  
 X 100/ 50 or less

Table 1 (3)

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Comp.Ex.	1	2	3	4
Mother powder resin	Polyester			
resin microparticles	A	D	C	C
Adding amount of resin microparticles	0.003	0.1	60	.60
average diameter of microparticles	0.05	30	0.05	0.05
Inter laminar adhesion with fluorine resin coating	X	○	⊙	⊙
levelling property	⊙	X	X	X

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Adding amount of resin microparticles =  $\frac{\text{weight of resin microparticles}}{\text{weight of the composite powder coating microparticles}}$

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Inter laminar adhesion = tested by cross-cut adhesion test

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- ⊙ 100/100
- 100/ 90 or more
- X 100/ 50 or less

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**Claims**

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1. A laminate comprising, in consecutive order, a metal substrate, with or without a primer layer for powder coating; a powder coating layer and a fluorine resin top coat; in which the powder coating layer is formed by applying onto the metal substrate (with or without a primer layer), a composite powder coating composition containing mother powder particles comprising a film-forming binder resin which is solid at room temperature and heat-meltable and a pigment, together with microparticles of a resin containing, as an essential component, methyl methacrylate and having an average diameter of 0.001 to 10  $\mu\text{m}$ , in an amount of 0.05 to 40% by weight of the total powder coating composition; and then baking the formed coating.
  2. A laminate according to claim 1, wherein the binder resin is an acrylic resin, polyester resin or epoxy resin.
  3. A laminate according to claim 1 or claim 2, wherein the fluorine resin is a vinylidene fluorine polymer.
  4. A laminate according to any one of the preceding claims wherein the primer layer, when preset, is composed of a polyester resin, epoxy resin, acrylic resin or urethane resin.