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(54) **Method for formation and repair of a multilayer coating**

(57) In a method for formation of a multilayer coating wherein after application of an intercoat to a substrate surface, a sequence of colored basecoat containing color pigments, bright pigment-containing basecoat and clear coat is applied wet-on-wet to the intercoat and then cured according to a three-coat one-bake system, the method is characterized in that a spectral reflectance of said intercoat in a reflection region within a wavelength range from 300 nm to 700 nm is maintained within $\pm 15\%$ deviation from a spectral reflectance of said colored basecoat in a reflection region within a wavelength range from 300 nm to 700 nm.

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Description**BACKGROUND OF THE INVENTION**5 FIELD OF THE INVENTION

[0001] The present invention relates to a method for formation of a multilayer coating according to a three-coat one-bake system in which after application of an intercoat on a substrate surface, a colored basecoat, a bright pigment-containing basecoat and a clear coat are sequentially applied onto the intercoat by a wet-on-wet technique, and also to a
10 method for repair of the multilayer coating.

RELATED ART

[0002] Application of a topcoat containing a bright pigment such as aluminum flake or mica flake to a substrate, e.g.,
15 an automotive body, has been conventionally known. In applying such a bright pigment-containing topcoat, a two-coat one-bake film-forming method is typically utilized in which a basecoat containing a bright pigment and a color pigment is applied to the substrate followed by the wet-on-wet application of a clear coat thereon and then a single baking process is performed to cure all the coats simultaneously.

[0003] However, there are instances where the incorporation of the bright pigment and color pigment in the same coat
20 leads to the insufficient provision of a bright appearance. In such instances, a three-coat two-bake film-forming method may be utilized wherein a colored basecoat containing a color pigment is applied to the substrate and dried once by a baking process, and then a bright pigment-containing basecoat is applied onto the colored basecoat, followed by the wet-on-wet application of a clear coat thereon. Since a bright pigment-containing base layer is formed on a colored base layer containing the color pigment, the bright pigment can fully exhibit its brightening effect to result in the provision of a well-designed multilayer coating.
25

[0004] However, in the above-described three-coat two-bake system, the baking process must be carried out twice
during the topcoating, which inevitably complicates a coating system and prolongs the time period required for the coating process. This has led to the recent proposal of a three-coat one-bake system in which a colored basecoat, a bright pigment-containing basecoat and a clear basecoat are all applied by a wet-on-wet technique followed by a single baking
30 process.

[0005] There are other instances where the formation of the above-described multilayer coating on a surface of a substrate having relatively complicated profiles, such as an automotive body, results in the non-uniformity in thickness of the multilayer coating, which causes a difference in hue of a thinner portion from the remaining portion.

[0006] During application of the above-described multilayer coating on a substrate such as an automotive body, some
35 foreign matter may be accidentally incorporated therein to impair its film appearance. Such a defective site of the multilayer coating, if discovered, generally undergoes repairs in the following manner: The multilayer coating is polished locally as with a sandpaper to a depth reaching an intercoat to remove the defective site therefrom, and then a sequence of a colored basecoat, bright pigment-containing basecoat and a clear coat is applied onto the exposed intercoat surface.

[0007] In this repairing procedure, the sequence of coats is simultaneously applied to a region located in the vicinity
40 of the repaired portion. In such a region, the repair multilayer coating overlies the previously-formed, original multilayer coating. In some cases, this has caused the difference in hue of the film site where the multilayer coating is double-applied from the remaining site, leading to the non-uniform film appearance.

45 **SUMMARY OF THE INVENTION**

[0008] It is an object of the present invention to provide a method for formation of a multilayer coating, which can solve
the above-described conventional problems and which can reduce the difference in hue of a film site where a thinner colored basecoat portion locates from the remaining film site to thereby provide a uniform film appearance.

[0009] It is another object of the present invention to provide a method for repair of a multilayer coating, which can
50 solve the above-described conventional problems and which can reduce the difference in hue of the double-coated film site from the remaining film site to thereby provide a uniform film appearance.

[0010] The method for formation of a multilayer coating, in accordance with the present invention, involves applying
55 an intercoat to a substrate surface, applying to the intercoat a sequence of a colored basecoat containing a color pigment, a bright pigment-containing basecoat and a clear coat by a wet-on-wet technique, and allowing the sequence of coats to cure according to a three-coat one-bake system. The method is characterized in that a spectral reflectance of the intercoat in a reflection region within a wavelength range from 300 nm to 700 nm is maintained within ± 15 % deviation from a spectral reflectance of the colored basecoat in a reflection region within a wavelength range from 300 nm

to 700 nm.

[0011] The spectral reflectance as specified in the present invention for each of the intercoat and colored basecoat is a spectral reflectance in the reflection region within a wavelength range from 300 nm to 700 nm, i.e., given by an average reflectance value in the reflection region within a wavelength range from 300 nm to 700 nm. In an exemplary case where the reflection region of the intercoat within the 300 nm - 700 nm wavelength range appears in the 400 nm - 700 nm wavelength region, the spectral reflectance of the intercoat is given by an average reflectance value in the 400 nm - 700 nm wavelength region. Likewise, in a case where the reflection region of the colored basecoat within the 300 nm - 700 nm wavelength range appears in the 600 nm - 700 nm wavelength region, the spectral reflectance of the colored basecoat is given by an average reflectance value in the 600 nm - 700 nm wavelength region.

[0012] For exemplary purposes, a subjective coat is applied onto a JIS-specified contrast chart to a film thickness insufficient to completely hide the chart. Spectral reflectance curves are obtained for the film sites respectively on white and black surfaces. The reflection region can be defined by a wavelength region in which for a given wavelength, a difference in reflectance between the film sites does not fall below 1 %. The reflection region generally appears in the 400 nm - 700 nm wavelength region for a white or grey intercoat, in the 650 nm - 700 nm wavelength region for a red intercoat, in the 600 nm - 700 nm wavelength region for an orange intercoat, in the 550 nm - 700 nm wavelength region for a yellow intercoat, and in the 400 nm - 500 nm wavelength region for a blue intercoat.

[0013] In the present invention, a such-defined spectral reflectance of the intercoat is set within ± 15 % deviation from a spectral reflectance of the colored basecoat.

[0014] The method used to determine the spectral reflectance, while not particularly limited, generally utilizes a spectrophotometer. The spectral reflectance can be determined by using an integrating sphere, for example. In determining the spectral reflectance, a sample coat may be applied to a substrate to a film thickness sufficient to be unaffected by surface characteristics of the substrate.

[0015] In the present invention, a spectral reflectance of the aforementioned intercoat is controlled within ± 15 % deviation, more preferably within ± 10 % deviation from a spectral reflectance of the aforementioned colored basecoat.

When such a relationship is satisfied, the difference in hue (color difference) of a film site having a thinner colored basecoat portion or a double-coated film site, if present, from the remaining film site can be effectively reduced to result in the provision of a multilayer coating having a uniform film appearance.

[0016] In accordance with the present invention, a multilayer coating can be formed whose film appearance is rendered uniform to such an extent that no color difference is visually perceived even in a case where a colored basecoat incorporated therein has thickness variations ranging over ± 30 % of its average film thickness.

[0017] The multilayer coating of the present invention is obtained by the practice of the above-described method for formation of a multilayer coating in accordance with the present invention.

[0018] One embodiment of the multilayer coating in accordance with the present invention is illustrated as including a repaired portion. Characteristically, the multilayer coating is double-applied in a region surrounding the repaired portion. In accordance with the present invention, a multilayer coating can be provided whose film color is rendered even to such an extent that no color difference is visually perceived even in a case where the multilayer coating is double-applied in the region surrounding the repaired portion.

[0019] An article of the present invention is characterized as having the multilayer coating of the present invention.

[0020] The method for repair of a multilayer coating in accordance with the present invention is directed to repairing the multilayer coating formed by applying a sequence of a colored basecoat containing a color pigment, a bright pigment-containing basecoat and a clear coat onto an intercoat-applied substrate. The method involves polishing the multilayer coating to a level of the intercoat to remove a defective portion therefrom, and applying a sequence of the colored basecoat containing a color pigment, bright pigment-containing basecoat and clear coat onto the exposed intercoat surface and its adjacent region. The method is characterized that a spectral reflectance of the intercoat in a reflection region within a wavelength range from 300 nm to 700 nm is maintained within ± 15 % deviation, more preferably within ± 10 % deviation from a spectral reflectance of the colored basecoat in a reflection region within a wavelength range from 300 nm to 700 nm.

[0021] The spectral reflectance as defined in the aforesaid forming method of the present invention is similarly used in this repairing method of the present invention.

[0022] The method for formation of a multilayer coating, multilayer coating, article and method for repair of a multilayered coating, respectively in accordance with the present invention, are below described in more detail.

INTERCOAT

[0023] In the present invention, the intercoat may be formed by applying an intercoat composition onto a substrate surface followed by baking. The intercoat composition may be applied to the substrate surface over which an undercoat has been previously formed. The general purposes of the intercoat is to hide any defect present at the underlying surface to thereby insure surface smoothness (improved appearance) of a topcoat which will be subsequently applied over

the intercoat, as well as to improve film properties (e.g., impact resistance and chipping resistance). The intercoat composition generally contains various types of organic or inorganic color pigments, extender pigments and the like.

[0024] Examples of color pigments which can be incorporated in the intercoat composition include organic pigments such as azo chelate pigments, insoluble azo pigments, condensed azo pigments, phthalocyanine pigments, indigo pigments, perinone pigments, perylene pigments, dioxane pigments, quinacridone pigments, isoindolinone pigments, metal complex pigments and the like; and inorganic pigments such as lead chromate, yellow iron oxide, red iron oxide, carbon black, titanium dioxide and the like. Examples of extender pigments include calcium carbonate, barium sulfate, clay, talc and the like. A grey or white intercoat composition is typically employed which contains carbon black and titanium dioxide as primary pigments. In a particular case, a so-called colored intercoat composition can be used which contains a selected combination of various color pigments.

[0025] In the present invention, a spectral reflectance of the intercoat in a reflection region within a wavelength range from 300 nm to 700 nm is maintained within ± 15 % deviation from a spectral reflectance of the colored basecoat in a reflection region within a wavelength range from 300 nm to 700 nm, as stated above. The spectral reflectance of the intercoat formed can be controlled to fall within the above-specified range by suitably adjusting the types and amounts of the color pigments incorporated in the intercoat composition.

[0026] The type of film-forming resin for use in the intercoat composition, while not particularly limited, is generally thermosetting. Examples of useful film-forming resins include acrylic resins, polyester resins, alkyd resins, epoxy resins, urethane resins and the like. These resins are used in combination with a curing agent such as an amine resin and/or blocked isocyanate resin. From the viewpoints of applicability and pigment dispersibility, the use of the alkyd resin and/or polyester resin in combination with the amino resin is preferred.

[0027] After application onto the substrate surface, the intercoat composition is heated for cure to a temperature generally in the approximate range of 100 - 180 °C, more preferably in the approximate range of 120 - 160 °C. If the temperature is elevated excessively, the intercoat film shows a trend of increasing its hardness. On the other hand, if it is lowered excessively, curing may be caused to occur insufficiently. A curing period may be varied depending upon the curing temperature selected. In the event that the temperature is set within 120 °C - 160 °C range, a suitable curing period may generally be from about 10 minutes to about 30 minutes.

[0028] Although a film thickness of the intercoat is not particularly limited, its dry film thickness is preferably in the approximate range of 20 - 60 μm , more preferably in the approximate range of 30 - 40 μm .

COLORED BASECOAT

[0029] In the present invention, the colored basecoat composition containing a color pigment is applied onto the intercoat while in either a cured or uncured condition.

[0030] The color pigments which can be incorporated in the colored basecoat composition are similar to those used in the above-described intercoat composition, and include organic pigments such as azo chelate pigments, insoluble azo pigments, condensed azo pigments, phthalocyanine pigments, indigo pigments, perinone pigments, perylene pigments, dioxane pigments, quinacridone pigments, isoindolinone pigments, metal complex pigments and the like; and inorganic pigments such as lead chromate, yellow iron oxide, red iron oxide, carbon black, titanium dioxide and the like, for example. Examples of useful extender pigments include calcium carbonate, barium sulfate, clay, talc and the like.

[0031] A film-forming resin incorporated in the colored basecoat composition is not particularly specified. Any generally-known film-forming thermosetting resin can be employed. Specific examples of film-forming resins include acrylic resins, polyester resins, alkyd resins, epoxy resins, urethane resins and the like. These resins are used in combination with a curing agent such as an amino resin and/or a blocked isocyanate resin. From the viewpoints of applicability and pigment dispersibility, the use of the alkyd resin and/or polyester resin in combination with the amino resin is preferred.

[0032] A film thickness of the colored basecoat is not particularly limited. The colored basecoat may be applied onto the intercoat to a dry film thickness preferably in the approximate range of 10 - 30 μm , more preferably in the approximate range of 15 - 25 μm .

Bright pigment-CONTAINING BASECOAT

[0033] In the present invention, after application of the above-described colored basecoat, the bright pigment-containing basecoat is further applied thereonto by a wet-on-wet technique.

[0034] Examples of bright pigments incorporated in this basecoat composition includes bright pigments such as mica flake, interference mica flake, white mica flake, aluminum flake, graphite, flaky color pigments and the like; and bright pigments made of metals, such as aluminum, copper, zinc, iron, nickel and tin, or alloys thereof. These bright pigments may be provided in various forms, preferably in the form of flake. Particularly preferred are those bright pigments having an average particle size of 2 - 50 μm and a thickness of 0.1 - 3 μm .

[0035] The bright pigment-containing basecoat composition may further contain a color pigment. Examples of such

color pigments have been earlier listed in the descriptions of the intercoat and colored basecoat compositions.

[0036] The amount of bright pigment incorporated in the basecoat composition is not particularly specified, but may be generally in the approximate range of 0.1 % - 20 %, preferably in the range of 0.5 % - 18 %, more preferably in the range of 1 % - 15 %, as expressed in PWC (pigment weight content). The excessively higher bright pigment content leads likely to the provision of a poorer film appearance. On the other hand, the excessively low content may result in the insufficient provision of decorative effect.

[0037] A film-forming resin incorporated in the bright pigment-containing basecoat composition is not particularly specified. Any generally-known film-forming thermosetting resin can be employed. Specifically, at least one hydroxyl-containing thermosetting resin selected from the group consisting of an acrylic resin, polyester resin, alkyd resin and epoxy resin can be employed. These thermosetting resins can be used in combination with a curing agent such as an amino resin and/or a blocked isocyanate resin. From the viewpoints of weather resistance, pigment dispersibility and applicability, the use of the hydroxyl-containing acrylic resin in combination with the amino resin is preferred.

[0038] A ratio in weight of the film-forming resin to the curing agent (film-forming resin/curing agent ratio) is preferably in the range of 90/10 - 10/90, more preferably in the range of 80/20 - 50/50. If the amount of curing agent is excessively small, a curing level may be reduced. On the other hand, if it becomes excessively larger, the formation of a harder and more brittle film may result.

[0039] It is preferred that the bright pigment-containing basecoat composition further contains a rheological control agent. The use of rheological control agent is purposed to form a mottle-free and sagging-free film in a satisfactory fashion. Thixotropes can generally be used as the rheological control agent.

[0040] Examples of rheological control agents include polyamide-based rheological control agents such as a swelled dispersion of aliphatic amide, fatty amide, phosphates of long-chain polyaminoamide; and polyethylene-based rheological control agents such as a colloidal dispersion of swelled polyethylene oxide and the like.

[0041] Other rheological control agents include organic bentonite-based rheological control agents such as organic smectite clay and montmorillonite; inorganic pigments such as aluminum silicate and barium sulfate; and flake pigments which can develop viscosity when taking particular shapes. Preferred are those rheological control agents which impose little influence on the gloss and color development of a resulting film.

[0042] The preferred rheological control agents for use in the present invention include non-crosslinked or crosslinked resin particles which rely their viscosity-modifying function on the interaction between polar groups incorporated therein.

[0043] Preferably, the crosslinked resin particles are insoluble to an organic solvent for use in the coating composition and have an average particle size in the range of 0.02 - 0.5 μm . If the average particle size becomes excessively larger, their dispersion stability may be lowered. Preferred crosslinked resin particles can be obtained by emulsion polymerizing an emulsifiable resin synthesized using a monomer having oppositely charged ionic groups in a molecule as one of polyol moieties, such as an alkyd or polyester resin, with an ethylenically unsaturated monomer in an aqueous medium with the aid of a polymerization initiator.

[0044] The aforementioned monomer having oppositely charged ionic groups in a molecule may be represented by $\text{-N}^+\text{-R-COO}^-$, or $\text{-N}^+\text{-R-SO}_3^-$ and has a minimum of two hydroxyl groups. From a viewpoint of resin synthesis, the use of a hydroxyl-containing aminosulfonic acid type amphoteric compound is preferred. A specific example of such a compound is bis-hydroxyethyl taurine.

[0045] Preferred for use in the aforementioned emulsifiable resin synthesized using the monomer having oppositely charged ionic groups in a molecule is a polyester resin which has an acid value of 30 - 150 mgKOH/g, preferably of 40 - 150 mgKOH/g, as well as having a number-average molecular weight of 500 - 5,000, more preferably of 700 - 3,000. If the acid value and number-average molecular weight become excessively larger, a handling quality of the resin may decrease. On the other hand, if they become excessively smaller, the emulsifiable resin may be caused to fall off from a resulting coating film. The reduced solvent resistance of the coating film may also result.

[0046] In the synthesis of crosslinked resin particles, a monomer having two or more free-radically polymerizable ethylenically unsaturated groups in a molecule may preferably be incorporated as the ethylenically unsaturated monomer that undergoes emulsion polymerization. Such a monomer having two or more free-radically polymerizable ethylenically unsaturated groups in a molecule may be incorporated in the amount of 0.1 - 10 weight %, based on a total weight of all monomers. The incorporation of this monomer results in the successful synthesis of crosslinked resin particles which have a sufficient crosslinking level to become insoluble to an organic solvent.

[0047] The aforementioned crosslinked resin particles contain neither of a low-molecular modifier and a protective colloid which may otherwise act to reduce a film performance, and have a suitable level of crosslinking. The blend of such crosslinked resin particles in a coating composition thus results in the provision of a coating film having improved resistance to water and solvent and increased gloss.

[0048] The amount by weight of the rheological control agent is preferably in the range of 0.01 - 15 parts, more preferably in the range of 0.1 - 12 parts, most preferably in the range of 0.2 - 9 parts per 100 parts of solid resin in the coating composition. If the amount of the rheological control agent is excessively large, a resulting coating film may provide

a poorer appearance. On the other hand, if it is excessively small, the expected effect of controlling a viscosity may be reduced or lost to possibly result in the occurrence of intercoat bleeding or inversion in the multilayer coating.

[0049] Besides the aforementioned ingredients, the bright pigment-containing basecoat composition according to the present invention can additionally contain other ingredients such as curing catalysts, UV absorbers, antioxidants, surface modifiers and other additives.

[0050] In the formulation of the bright pigment-containing basecoat composition of the present invention, its total solids content is maintained preferably within the range of 20 - 70 % by weight, more preferably within the range of 30 - 50 % by weight. If the total solids content falls outside the preferred range, the stability of basecoat composition may be reduced. During the application of the composition, its total solids content is controlled preferably within the range of 10 - 60 % by weight, more preferably within the range of 20 - 50 % by weight. If the content goes beyond this preferred range, the composition may be excessively increased in viscosity to result in the provision of a poorer film appearance. On the other hand, if the content falls below the preferred range, the composition may be excessively reduced in viscosity to result in the occurrence of appearance imperfections such as intercoat bleeding and mottling in the resulting multilayer coating.

[0051] The thickness of the bright pigment-containing basecoat is not particularly specified, since it is suitably chosen depending upon the particular end use of the multilayer coating. However, the thickness may generally be in the range of 5 - 35 μm , preferably in the range of 7 - 25 μm . If the excessively large thickness is chosen, the basecoat film may be reduced in image sharpness. Non-uniform coating or sagging of the basecoat composition may also occur during the application thereof. On the other hand, the choice of excessively small thickness may result in not only the failure to hide an underlying surface but also the breakage of the basecoat film.

[0052] The bright pigment-containing basecoat composition for use in the present invention is preferably liquid-based. Any type of liquid-based coating composition can be employed which is either organic solvent-based type, or water-based type (e.g., water-soluble type, aqueous dispersion type or emulsion type) or non-aqueous dispersion type.

[0053] Where the bright pigment-containing basecoat composition is water-based, a thermosetting film-forming resin, as specifically described in U.S. Patent Nos. 5,151,125 and 5,183,504, can be used. Particularly useful in providing a good finish and appearance performance is a thermosetting film-forming resin described in the above-referenced U.S. Patent No. 5,183,504 as consisting of an acrylic resin containing acrylamide, hydroxyl and acidic groups in combination with a melemine resin.

[0054] The water-based bright pigment-containing basecoat composition, if used, is preferably heated and maintained at a temperature within the range of 60 - 100 $^{\circ}\text{C}$ for a time duration of 2 - 10 minutes before it is coated with the clear coating composition. This procedure serves to provide a good finish.

[0055] When the multilayer coating of the present invention is formed on a substrate such as an automotive body, the bright pigment-containing basecoat composition can preferably be applied as by electrostatic or air spraying. This basecoat composition may preferably be applied in two stages rather than a single stage to suppress the occurrence of non-uniform surface brightness.

CLEAR COAT

[0056] The type of the film-forming resin of the clear coat, while not particularly specified, may be thermosetting. Specifically, such film-forming resins as acrylic, polyester, epoxy and urethane resins can be used. These resins are generally used in combination with a curing agent such as an amino resin and/or a blocked isocyanate resin. Either a combination of the amino resin with acrylic and/or polyester resin, or the acrylic and/or polyester resin having a curing system of carboxylic acid and epoxy is preferably used to impart the improved transparency and increased resistance to acid etching.

[0057] In the formulation of the clear coating composition, its solids content is maintained preferably within the range of 20 - 60 % by weight, more preferably within the range of 35 - 55 % by weight. During the application, its solids content may preferably be controlled within the range of 10 - 50 % by weight, more preferably within the range of 20 - 50 % by weight.

[0058] Preferably, the clear coating composition is applied onto the aforementioned bright pigment-containing coat while in an uncured condition as by electrostatic or air spraying.

[0059] The clear coating composition is applied to a dry film thickness generally in the approximate range of 10 - 60 μm , preferably in the approximate range of 20 - 50 μm . The choice of excessively large film thickness may lead to the occurrence of unfavorable popping or sagging during the application of the composition. On the other hand, the excessively small film thickness may result in the failure to hide, for example, irregularities of the underlying surface.

[0060] Since the clear coating composition is applied onto the bright pigment-containing basecoat by a wet-on-wet technique, it preferably contains the rheological control agent as described earlier. Examples of useful rheological control agents are listed in the earlier descriptions given to explain the bright pigment-containing basecoat composition. The amount by weight of the rheological control agent incorporated in the clear coating composition is preferably in the

range of 0.01 - 10 parts, more preferably in the range of 0.02 - 8 parts, most preferably in the range of 0.03 - 6 parts, based on 100 parts of the solid resin in the coating composition. If the amount of the rheological control agent becomes excessively large, a poorer film appearance may result. On the other hand, if it becomes excessively small, the expected effect of controlling a viscosity may be reduced or lost to possibly result in the occurrence of intercoat bleeding or inversion in the multilayer coating.

[0061] The clear coating composition may be of any type, such as an organic solvent-based type, water-based type (e.g., water-soluble type, aqueous dispersion type or emulsion type), non-aqueous dispersion type or powder type. It may further contain curing catalysts and surface conditioners, when needed.

10 UNDERCOAT

[0062] In the present invention, prior to the sequential application of the intercoat and the multilayer coating of the present invention, an undercoat may be formed on a substrate surface. In the case of a conductive substrate such as a steel plate, an electrocoating composition can be used to form the undercoat. This electrocoating composition may be cationic or anionic. For its superior corrosion resistance, the cationic electrocoating composition is preferably used to better protect the multilayer coating from corrosion.

MULTILAYER COATING

[0063] In accordance with the present invention, the sequential application of the aforementioned colored basecoat, bright pigment-containing basecoat and clear coat results in formation of the multilayer coating. The total film thickness of the multilayer coating, while suitably varied depending upon the particular end use thereof, is generally in the range of 30 - 300 μm , preferably in the range of 50 - 250 μm . If the film thickness is excessively increased, the reduced film properties such as in thermal cycling may result. On the other hand, the excessively reduced film thickness may lead to a decrease in strength of the film itself.

SUBSTRATE

[0064] The material type of the substrate to which the intercoat and multilayer coating are sequentially applied is not particularly limited, and may be wood, metals, glass, cloth, plastic, or foams, for example. The present invention can be favorably applied to metal substrates and cast products, particularly favorably to metal products which can be cationically electrocoated.

[0065] Illustrative of such metal products are substrates made of iron, copper, aluminum, tin, zinc or alloys containing any of those metals. Examples of specific metal substrates include bodies and parts of passenger cars, trucks, motorcycles, buses and the like. It is particularly preferred that these metal substrates are chromated or phosphated.

Repairing METHOD

[0066] The repairing method of the present invention is a method which can repair the above-described multilayer coating of the present invention. In the event that any defect that adversely affects a film appearance, such as cratering and pinholing, is found in the multilayer coating formed in accordance with the present invention, such a defective site can be repaired in accordance with the present repairing method. In accordance with the repairing method of the present invention, repairing can be effected by polishing the multilayer coating to a level of the intercoat to remove a defective portion therefrom, and applying a sequence of the colored basecoat, bright pigment-containing basecoat and clear coat onto the exposed intercoat surface and its adjacent region. The coating compositions for use in the repairing method may be the same as or different from those used to form the original multilayer coating, so long as they can present a hue and a film appearance similar to those of the original multilayer coating.

[0067] The polishing step may be performed by first polishing a film site with a coarse-grain sandpaper of about # 400 to remove a defective portion, and then repolishing the same film site with a fine-grain sandpaper of about # 1,000 to effect surface preparation.

[0068] After the polishing step, the aforementioned coating compositions are sequentially applied onto the prepared surface and its adjacent region to form a repair multilayer coating. Application of the repair coating compositions can be achieved by various conventional means, but generally by spraying such as hand or air spraying. After application of the repair coating compositions, a baking process is generally performed to cure the repair multilayer coating.

[0069] In accordance with the present repairing method, the repair multilayer coating is formed on the exposed intercoat surface and its adjacent region. Accordingly, the repair multilayer coating formed at the adjacent region overlies the original multilayer coating. However, a difference in hue of such a double-coated region from the remaining single-coated region can be effectively reduced to such an extent that a film appearance becomes indiscernible between the

two regions, if the present repairing method is properly practiced.

[0070] In accordance with the present invention, a difference in film color either between the region where a thinner colored basecoat locates and the remaining region or between the double- and single-coated regions can be effectively reduced so that a uniform film appearance is obtained over the entire region.

[0071] The multilayer coating for application to substrates such as an automotive body is demanded to present various colors. In accordance with the present invention which requires the spectral reflectance of the intercoat to be maintained within the ranged deviation from that of the colored basecoat, the use of a single type of intercoat in combination with any one of various multilayer coatings having different colors satisfies the above-stated demand. This enables formation of various types of multilayer coatings in an efficient and economical fashion.

[0072] Also in accordance with the repairing method of the present invention, multilayer topcoatings can be repaired in an effective and economical manner without an appreciable color difference between the double-coated and single-coated regions.

BRIEF DESCRIPTION OF THE DRAWINGS

[0073]

Figure 1 is a graph showing a relationship of the colored basecoat thickness to the color difference ΔE ;

Figure 2 is a sketch showing the spectral reflectance curve of the colored basecoat;

Figure 3 is a sketch showing the spectral reflectance curve of the ultra light gray intercoat;

Figure 4 is a sketch showing the spectral reflectance curve of the light gray intercoat;

Figure 5 is a sketch showing the spectral reflectance curve of the gray intercoat;

Figure 6 is a sectional view showing one embodiment of the multilayer coating formed on the intercoat; and

Figure 7 is a sectional view showing the polished portion of the multilayer coating and its adjacent region.

PREFERRED EMBODIMENTS

[0074] The following specific examples illustrate the present invention. All parts and percentages in the examples are by weight unless otherwise specified.

PREPARATION OF CROSSLINKED RESIN PARTICLES

[0075] A reaction vessel equipped with a stirrer, heating unit, thermometer, nitrogen inlet tube, cooling condenser and decanter was charged with 213 parts of bis-hydroxyethyl taurin, 208 parts of neopentyl glycol, 296 parts of phthalic anhydride, 376 parts of azelaic acid and 30 parts of xylene, and subsequently heated. Water produced during the reaction was azeotropically removed with xylene. In about 3 hours from the initiation of reflux, the reaction mixture was elevated in temperature to 210 °C. The reaction was continued with successive stirring and dewatering until a carboxylic acid equivalent acid value reached 135 mgKOH/g. After the reaction mixture was cooled to 140 °C, 500 parts of "Cardura E10" (product name; glycidyl ester of versatic acid manufactured by Shell Chemical Co., Ltd.) was added dropwise over 30 minutes. After 2 hours of stirring, the reaction was terminated. As a result, an amphoteric polyester resin was obtained having an acid value of 55 mgKOH/g, hydroxyl value of 91 mgKOH/g and number average molecular weight of 1,250.

[0076] A mixture of 10 parts of the amphoteric polyester resin thus obtained, 140 parts of deionized water, 1 part of dimethyl ethanolamine, 50 parts of styrene and 50 parts of ethylene glycol dimethacrylate was stirred rigorously in a beaker made of stainless steel to prepare a monomer dispersion. Also, an aqueous initiator was prepared by mixing 0.5 parts of azobiscyanovaleric acid, 40 parts of deionized water and 0.32 parts of dimethyl ethanolamine.

[0077] A reaction vessel equipped with a stirrer, heating unit, thermometer, nitrogen inlet tube and cooling condenser was charged with 5 parts of the amphoteric polyester resin as obtained above, 280 parts of deionized water and 0.5 parts of dimethyl ethanolamine, and subsequently heated to 80 °C. 251 parts of the monomer dispersion and 40.82 parts of the aqueous initiator were concurrently added dropwise to the mixture over 60 minutes. The reaction was continued for another one hour and then terminated.

[0078] As a result, an emulsion was obtained which contained crosslinked resin particles having a particle size of 55 nm as determined by a dynamic light scattering method.

[0079] Xylene was added to the resin emulsion, and water was removed by azeotropic distillation under a reduced pressure to substitute xylene for the medium, so that a xylene solution containing the particles of crosslinked resin was obtained having a solids content of 20 % by weight.

PREPARATION OF COATING COMPOSITIONS

[0080] Coating compositions for use in examples and comparative examples were prepared from the following formulations A through F.

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(A) Formulation A

[0081] The following ingredients were formulated into an ultra light brown colored basecoat composition.

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Ingredients	Parts by weight
TYPAKE R-820 ¹⁾	30.0
TAROX LLX-LO ²⁾	0.2
DEGUSSA CARBON FW200P ³⁾	0.11
thermosetting acrylic resin ⁴⁾	40.6 (20.3)
UBAN 20N60 ⁵⁾	14.5 (8.7)
acrylic surfactant	0.2
crosslinked resin particles ⁶⁾	7.5 (1.5)
n-butanol	2.0
butyl acetate	3.6
toluene	1.3
<u>Total</u>	<u>100.01</u>

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¹⁾White pigment manufactured by Ishihara Sangyo Co. Ltd.

²⁾Brown pigment manufactured by Titan Kogyo Co., Ltd.

³⁾Black pigment manufactured by Degussa AG.

⁴⁾Manufactured by Nippon Paint Co., Ltd. and having a hydroxyl value of 45, acid value of 15, number-average molecular weight of 21,000 and solids content of 50 %.

⁵⁾Butylated melamine resin having a solids content of 60 %, manufactured by Mitsui Tohatsu Co., Ltd.

⁶⁾Prepared in the above-described preparation example and having a solids content of 20 %.

(B) Formulation B

[0082] The following ingredients were formulated into a mica flake-containing basecoat composition.

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Ingredients	Parts by weight
PEARLGRACE SME-90-9 ⁷⁾	3.0
thermosetting acrylic resin ⁸⁾	38.4 (23.0)
UBAN 20N60 ⁵⁾	25.3 (15.2)
RIPONOX NC-60 ⁹⁾	0.2
crosslinked resin particles ⁶⁾	12.5 (2.5)
n-butanol	3.0
butyl acetate	3.0
xylol	8.4
toluene	6.2
<u>Total</u>	<u>100.0</u>

⁵⁾Butylated melamine resin having a solids content of 60 %, manufactured by Mitsui Tohatsu Co., Ltd.
⁶⁾Prepared in the above-described preparation example and having a solids content of 20 %.
⁷⁾Mica flake manufactured by Nippon Koken Co., Ltd.
⁸⁾Manufactured by Nippon Paint Co., Ltd. and having a hydroxyl value of 50, acid value of 15, number-average molecular weight of 15,000 and solids content of 60 %.
⁹⁾Surface modifier manufactured by Lion Yushi Co., Ltd.

(C) Formulation C

[0083] "SUPERLAC O-150 CLEAR" (acrylic-melamine resin paint manufactured by Nippon Paint Co., Ltd.) was used as the formulated clear coating composition.

(D) Formulation D

[0084] "ORGA P-GRAY" (polyester-melamine resin paint manufactured by Nippon Paint Co., Ltd.) was used as the formulated gray intercoat composition.

(E) Formulation E

[0085] The formulations D and F were blended in a ratio of 1:2 to formulate a light gray intercoat composition.

(F) Formulation F

[0086] The following ingredients were formulated into an ultra light gray intercoat composition.

Ingredients	Parts by weight
TYPAKE R-820 ¹⁾	30.0
CARBON BLACK MA100 ¹⁰⁾	0.001
thermosetting polyester resin ¹¹⁾	30.0 (21.0)
UBAN 128 ¹²⁾	15.0 (9.0)
crosslinked resin particles ⁶⁾	12.5 (2.5)
RESIMIX RL-4 ¹³⁾	0.1
n-butanol	4.0
SOLVESSO 100	8.4
<u>Total</u>	<u>100.001</u>

¹⁾White pigment manufactured by Ishihara Sangyo Co. Ltd.

⁶⁾Prepared in the above-described preparation example and having a solids content of 20 %.

¹⁰⁾Black pigment manufactured by Mitsubishi Carbon Co., Ltd.

¹¹⁾Manufactured by Nippon Paint Co., Ltd. and having a hydroxyl value of 90, acid value of 8, number-average molecular weight of 1,800 and solids content of 70 %.

¹²⁾Butylated melamine resin having a solids content of 60 %, manufactured by Mitsui Cytech Co., Ltd.

¹³⁾Surface modifier manufactured by Mitsui Tohatsu Co., Ltd.

MEASUREMENT OF SPECTRAL REFLECTANCE

[0087] A spectral reflectance was measured, according to the below-stated procedure, for coating films obtained from the above-formulated colored basecoat composition (Formulation A), gray intercoat composition (Formulation D), light gray intercoat composition (Formulation E) and ultra light gray intercoat composition (Formulation F).

[0088] A cationic electrodeposition paint "POWERTOP U-50" (product of Nippon Paint Co., Ltd.) was electrocoated on a 0.8 mm thick, 10 cm x 30 cm plate of zinc phosphated dull steel panel to a dry film thickness of 20 μm, followed by baking at 160 °C for 30 minutes. Each of the aforementioned coating compositions was spray coated on the electrocoated film to a dry film thickness of 45 μm, followed by baking at 140 °C for 20 minutes.

[0089] A spectrophotometer (product of Hitachi Seisakusho Co., Ltd.; model number U-3200) equipped with an integrating sphere was utilized to measure a reflectance of each sample film. Figures 2 through 5 show spectral reflectance curves for the sample films. Figure 2 shows a spectral reflectance curve for the colored basecoat film, Figure 3 for the ultra light gray intercoat film, Figure 4 for the light gray intercoat film and Figure 5 for the gray intercoat film. As can be seen from Figures 2 - 5, a reflection region was observed in the wavelength range from about 400 nm to about 700 nm for either of the sample films. Accordingly, the reflectance values in the 400 nm - 700 nm wavelength range were averaged to give a value for the spectral reflectance specified in the present invention, as shown by broken lines in Figures 2 - 5. As shown in Figure 2, the spectral reflectance of the colored basecoat film was determined to be 69 %. As shown in Figure 3, the spectral reflectance of the ultra light gray intercoat film was determined to be 70 %. As shown in Figure 4, the spectral reflectance of the light gray intercoat film was determined to be 60 %. As shown in Figure 5, the spectral reflectance of the gray intercoat film was determined to be 29 %.

[0090] Next, a color difference meter (product of Minolta Co., Ltd.; model number CR-200) was utilized to numerically determine a hue of each sample film according to the L*a*b* Color Notation System. Numerical values for L*, a* and b* are listed in Table 1. The difference in spectral reflectance of each intercoat film from the colored basecoat film is also given in Table 1.

Table 1

	Film Color			Difference in Spectral Reflectance from Colored Basecoat
	L Value	a Value	b Value	ΔRa (% Average)
Gray Intercoat	59.60	-0.84	-4.00	40
Light Gray Intercoat	80.60	-0.72	-2.51	9
Ultra Light Gray Intercoat	85.75	-0.45	-1.10	1
Colored Basecoat	86.50	-0.50	+4.70	(Control)

[0091] As apparent from Table 1, the light gray intercoat film and the ultra light gray intercoat film exhibit reflectances within $\pm 15\%$ deviation from the reflectance of the colored basecoat film to demonstrate that they meet the condition required for the intercoat in accordance with the present invention, relative to the above-specified colored basecoat.

EVALUATION OF VISUAL COLOR DIFFERENCE BETWEEN FILM SITES HAVING DIFFERENT FILM THICKNESSES

[0092] The above-described procedure was followed to form on to a dull steel panel a cationic electrocoating film on which each of the aforementioned intercoat compositions (Formulations D - F) was subsequently spray coated to a dry film thickness of 35 μm , followed by baking at 140 $^{\circ}\text{C}$ for 20 minutes. The colored basecoat composition (Formulation A) was then spray coated on each intercoat film such that a dry film of the colored basecoat was proportionally varied in thickness from 5 to 30 μm along its length.

[0093] Each sample film was determined in hue at the sites where the colored basecoat have different thicknesses, and the difference in hue of each site from the reference site where the thickness of colored basecoat measured 30 μm was determined as ΔE .

[0094] Figure 1 is a graph showing a relationship between the film thickness of colored basecoat and ΔE . In Figure 1, Example 1 indicates a curve for the sample film having the ultra light gray intercoat, Example 2 for the sample film having the light gray intercoat, and Comparative Example 1 for the sample film having the gray intercoat. The ΔE value at or below which no color difference was visually perceived was chosen to be 0.5. At $\Delta E = 0.5$, a film thickness was 11 μm in the case of Example 1, 15 μm in the case of Example 2 and 20 μm in the case of Comparative Example 1. This demonstrates that a marked color difference is not perceived visually even toward the film site where the colored basecoat has a rather small thickness, if the intercoats of Examples 1 and 2 are utilized.

EVALUATION OF VISUAL COLOR DIFFERENCE BETWEEN DOUBLE- AND SINGLE-COATED FILM SITES

[0095] A cationic electrodeposition paint "POWERTOP U-50" (product of Nippon Paint Co., Ltd.) was electrocoated on a 0.8 mm thick, 10 cm x 30 cm plate of zinc phosphated dull steel panel to a dry film thickness of 20 μm , followed by baking at 160 $^{\circ}\text{C}$ for 30 minutes. Then, each of the intercoat compositions (Formulations D through F). was spray coated on the electrocoated paint film to a dry film thickness of 30 μm , followed by baking at 140 $^{\circ}\text{C}$ for 20 minutes to form three types of sample intercoat films.

[0096] Next, the colored basecoat composition (Formulation A) was diluted to a #4 Ford cup viscosity of 18 seconds (at 20 $^{\circ}\text{C}$), and then spray coated on each intercoat film in two stages by an electrostatic air spray equipment "AUTO REA" (product of Lansberg Co., Ltd.) to provide a dry film thickness of 20 μm . After a 5-minute interval, the mica flake-containing basecoat composition (Formulation B) previously diluted to a #4 Ford cup viscosity of 15 seconds (at 20 $^{\circ}\text{C}$) was applied wet-on-wet to the colored basecoat in two stages by AUTO REA to provide a dry film thickness of 15 μm . After another 5-minute interval, the clear coating composition (Formulation C) previously diluted to a #4 Ford cup viscosity of 20 seconds (at 20 $^{\circ}\text{C}$) was spray coated wet-on-wet on the mica flake-containing basecoat to provide a dry film thickness of 30 μm , followed by baking at 140 $^{\circ}\text{C}$ for 20 minutes. As a result, three types of sample films (Examples 3 and 4 and Comparative Example 2) were obtained.

[0097] Figure 6 is a view illustrating a sectional structure of the multilayer coating formed in the manner as stated above. Formed on the substrate 1, zinc phosphated dull steel panel, is the electrodeposition coat 2 on which the intercoat 3 is applied. Formed on the intercoat 3 is the multilayer coating 7 consisting of the colored basecoat 4, mica flake-containing basecoat 5 and clear coat 6 which were applied according to a three-coat one-bake system.

[0098] For illustrative purposes, a portion of multilayer coating that extended inwardly from an edge of the coated dull steel panel by a distance of 10 cm was assumed to need repair. In order to remove that portion, wet polishing was done using a sandpaper (#400) to a depth reaching the intercoat 3. A colored basecoat, mica flake-containing basecoat and clear coat, as similar in respective compositions to those described above, were sequentially applied wet-on-wet by hand spraying onto an exposed intercoat surface and its adjacent region to respective film thicknesses similar in dimension to those described above, followed by baking.

[0099] Figure 7 is a sectional view illustrating a condition of the multilayer coating which underwent repairs. As shown in Figure 7, the portion subjected to polishing is flattened down to a level of the intercoat 3 for complete removal thereof from the original multilayer coating 7. Thereafter, the repair multilayer coating 11 consisting of colored basecoat 8, mica flake-containing basecoat 9 and clear coat 10 is applied to overlie the exposed surface of intercoat 3 and its adjacent region. As shown in Figure 7, at the region adjacent the repaired portion, the repair multilayer coating 11 overlies the original multilayer coating 7, so that the intercoat 3 is at the region double-coated with the multilayer coating.

[0100] The sample films which underwent repairs in the manner as stated above were then evaluated for film appearance, i.e., surface roughness and decorative effect, using the following ratings. The rating results are listed in Table 2.

- 5: excellent
- 4: good
- 3: fair
- 2: slightly poor
- 1: very poor

[0101] The color difference of the double-coated region from the remaining single-coated region was evaluated visually using the following ratings. Also, those two regions were determined in hue to calculate a color difference ΔE . The results are shown in Table 2.

- 5: no appreciable change observed
- 4: slight change observed
- 3: slight changes observed locally
- 2: significant changes observed locally
- 1: significant color change observed

Table 2

Intercoat		Exp. 3	Exp. 4	Comp. Exp. 2
Gray (Conventional)				○
Light Gray			○	
Ultra Light Gray		○		
Film Appearance	Surface roughness	5	5	5
	Decorative Effect	5	4	3
Double-coated Site	Visual Color Diff.	5	4	2
	Color Diff.(ΔE)	0.3	0.6	1.0

[0102] As can be appreciated from the results shown in Table 2, the sample films of Examples 3 and 4, which respectively incorporates the ultra light gray intercoat and the light gray intercoat whose spectral reflectances in their respective reflection regions within a wavelength range from 300 nm to 700 nm are maintained within $\pm 15\%$ deviation from the spectral reflectance of the colored basecoat film, exhibit the improved film appearance and marked reduction in visual color difference between the double-coated and single-coated regions, compared to the sample film of Comparative Example 2. Therefore, the efficient and economical repairing can be achieved which prevents the occurrence of non-uniform film appearance at the double-coated region to insure the uniform film appearance over an entire region.

Claims

1. In a method for formation of a multilayer coating wherein after application of an intercoat to a substrate surface, a sequence of colored basecoat containing color pigments, bright pigment-containing basecoat and clear coat is

applied wet-on-wet to the intercoat and then cured according to a three-coat one-bake system, the method is characterized in that a spectral reflectance of said intercoat in a reflection region within a wavelength range from 300 nm to 700 nm is maintained within ± 15 % deviation from a spectral reflectance of said colored basecoat in a reflection region within a wavelength range from 300 nm to 700 nm.

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2. The method according to claim 1 wherein said intercoat is a gray or white intercoat.

3. The method according to claim 1 or 2 wherein said substrate surface is undercoated before said intercoat is applied thereto.

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4. A multilayer coating formed by the method according to any one of claims 1 - 3.

5. The multilayer coating according to claim 4 wherein said multilayer coating has a repaired portion and wherein a multilayer coating is double-applied in a region adjacent said repaired portion.

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6. An article having the multilayer coating according to claim 4 or 5.

7. In a method of repairing a multilayer coating comprising a sequence of colored basecoat containing a color pigment, bright pigment-containing basecoat and clear coat applied onto an intercoat, wherein after the multilayer coating is polished down to a level of the intercoat to remove a defective portion therefrom, a colored basecoat containing color pigments, a bright pigment-containing basecoat and a clear coat are sequentially applied to form a repair multilayer coating which overlies an exposed surface of the intercoat and its adjacent region, the method is characterized in that a spectral reflectance of the intercoat in a reflection region within a wavelength range from 300 nm to 700 nm is maintained within ± 15 % deviation from a spectral reflectance of the colored basecoat in a reflection region within a wavelength range from 300 nm to 700 nm.

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8. The method according to claim 7 wherein said intercoat is a gray or white intercoat.

9. The method according to claim 7 or 8 wherein said substrate surface is undercoated before said intercoat is applied thereto.

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FIG. 1

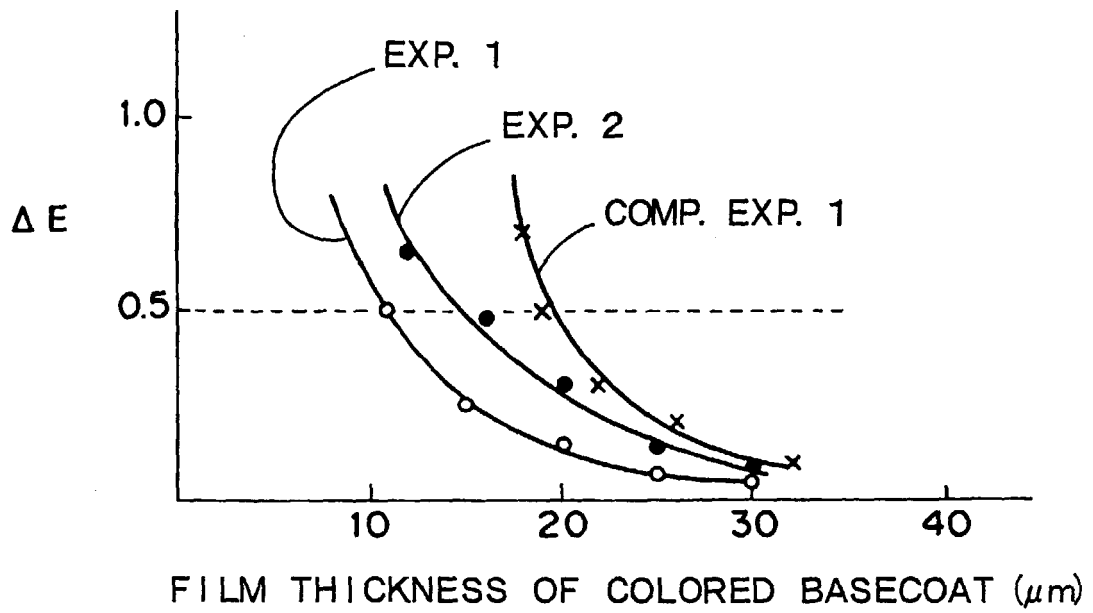


FIG. 2

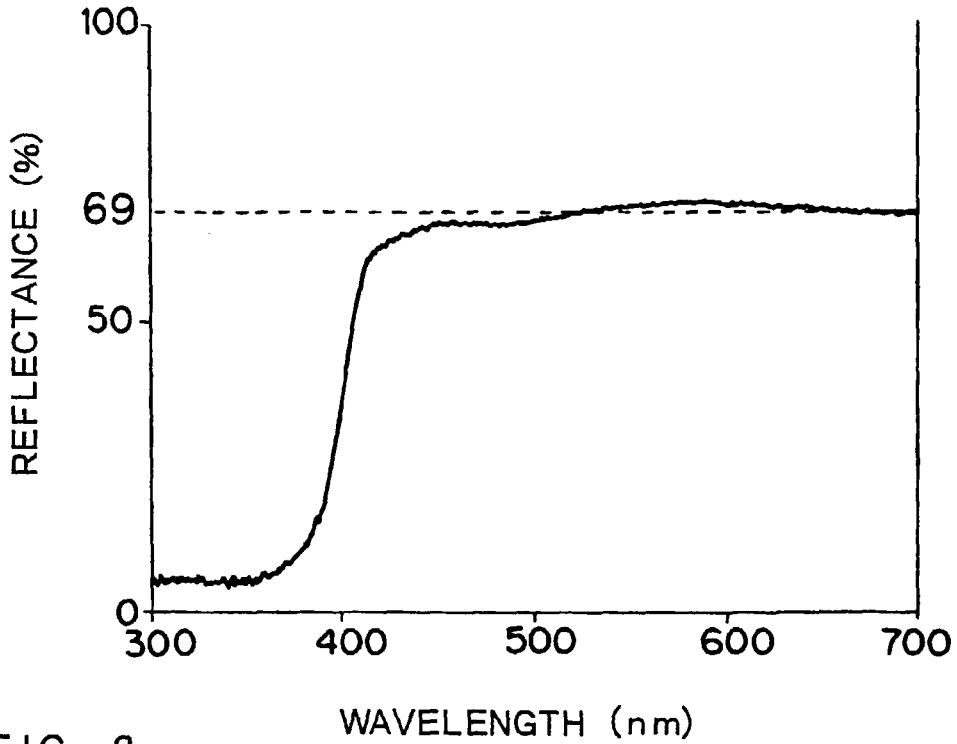


FIG. 3

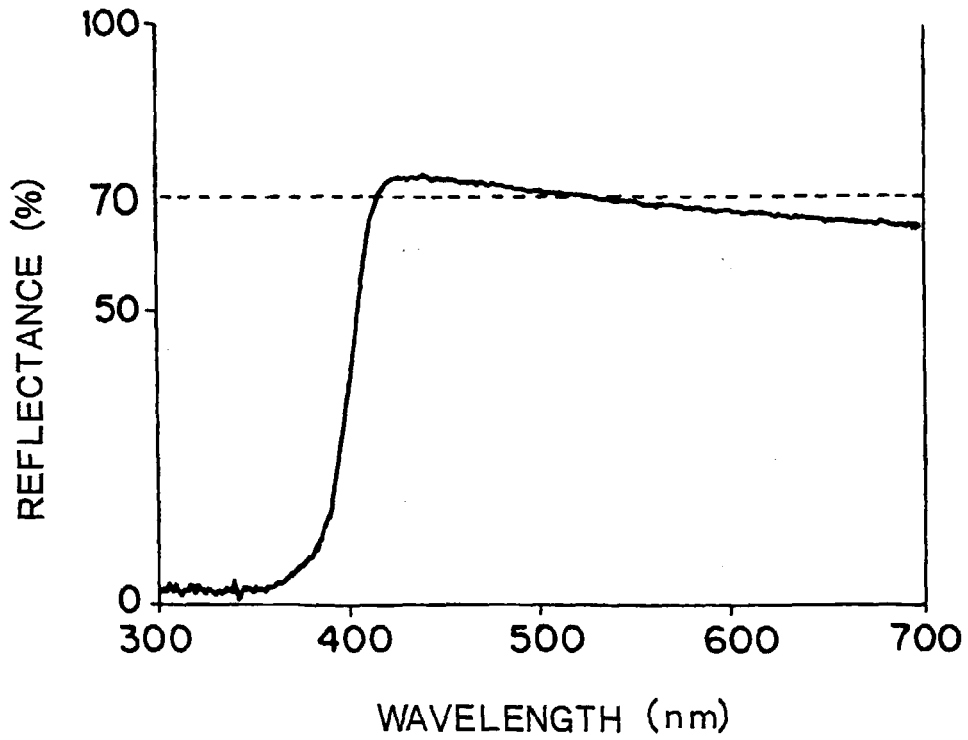


FIG. 4

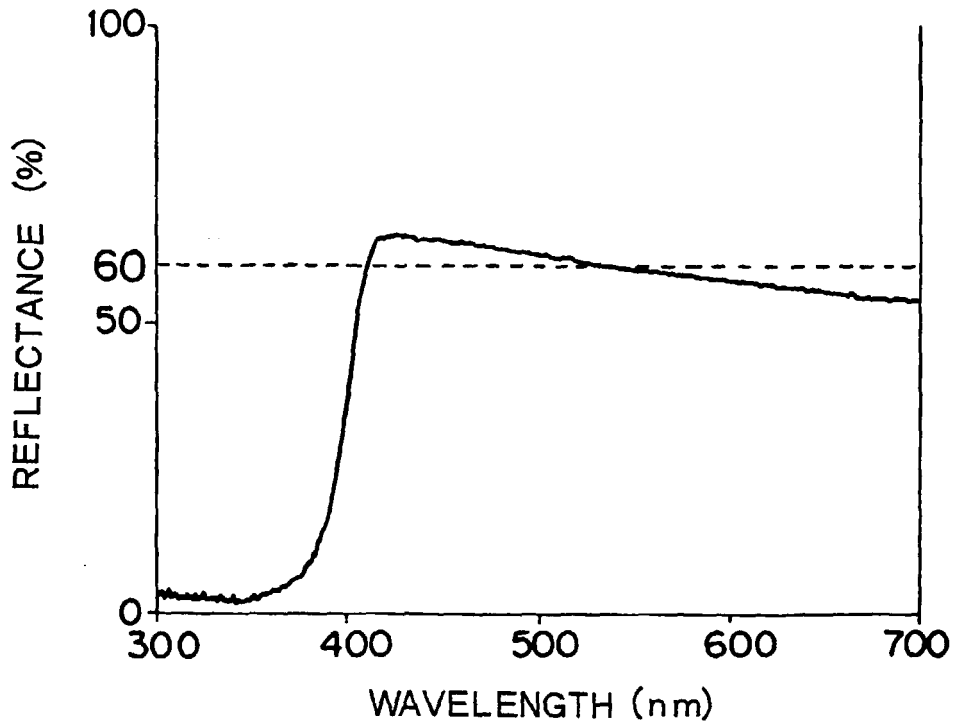


FIG. 5

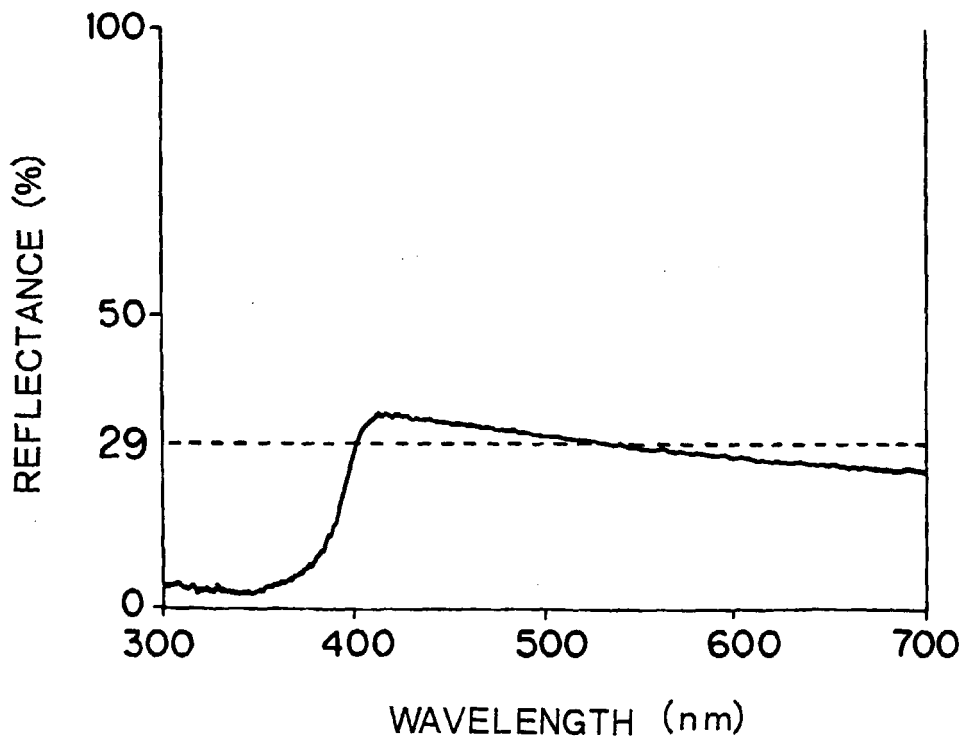


FIG. 6

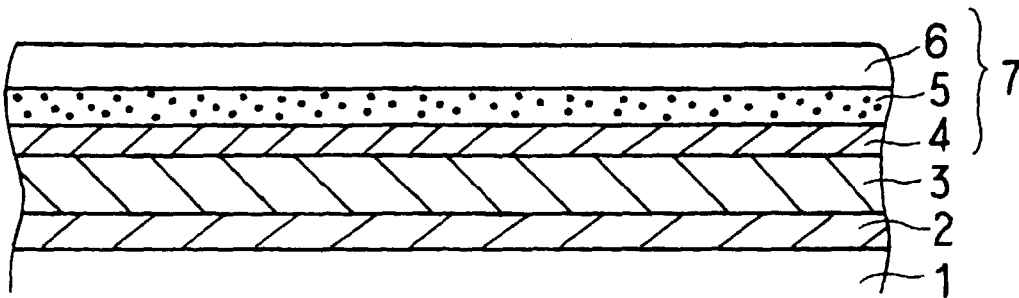


FIG. 7

