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(71) Applicant: **NOF CORPORATION**

Tokyo 150 (JP)

(72) Inventors:

• **YOSHIDA, Tatsuro**
Ibaraki 305 (JP)

• **WATANABE, Kenji**
Ibaraki 300-44 (JP)

• **IKEDA, Tomoyuki**

Ibaraki 305 (JP)

• **ITO, Tetsuya**

Ibaraki 305 (JP)

• **GOTO, Yoshitaka**

Ibaraki 300-24 (JP)

(74) Representative:

Hallybone, Huw George et al

CARPMAELS AND RANSFORD

43 Bloomsbury Square

London WC1A 2RA (GB)

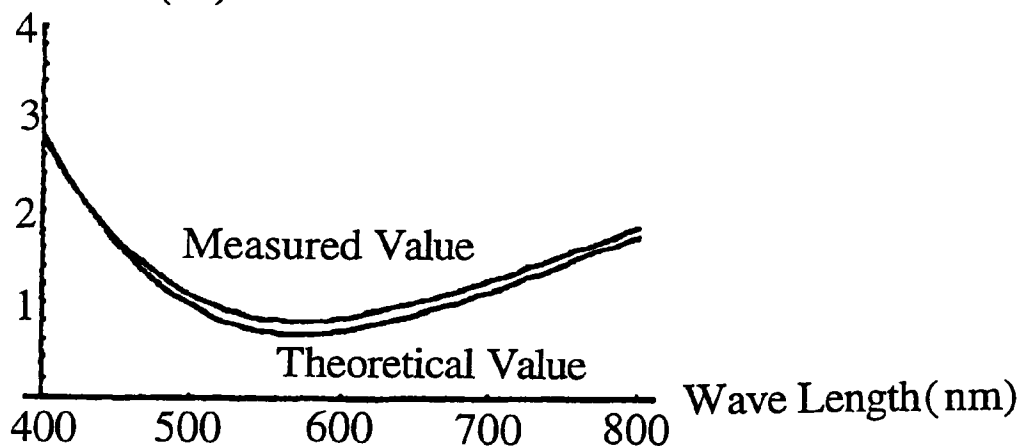
(54) **METHOD OF FORMING COATING FILM**

(57) A method for producing a coating film is provided, which enables continuous coating of a base having a large surface area, which achieves high productivity, and by which ultra-thin films having highly uniform film thickness. This method including the step of

continuously applying a coating liquid containing 0.05 to 40 wt % solid component to a base with a gravure roll to form a coating film having the dry thickness of 0.005 to 1 μm .

Fig. 1

Reflection (%)



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DescriptionFIELD OF INVENTION

5 The present invention relates to a method for continuously producing a ultra-thin coating film on a base such as a plastic film.

BACKGROUND ART

10 A variety of functions may be given to a base by forming an ultra-thin coating film having the dry thickness of not more than 1 μm on the base. For example, by applying solid components to a base such as a plastic film to produce a film having the dry thickness of about 0.1 μm functioning as an anti-reflection film, the surface reflection of the base can be decreased.

The ultra-thin coating films have conventionally been produced by vacuum coating, chemical vapor deposition (CVT), plasma polymerization, dipping, spin coating, Langmuir-Blodgett's technique, or the like. Among these, the vacuum coating method, CVT, and plasma polymerization method include vaporization of the solid components for application to a base. Accordingly, the coating process should be performed in a closed system, and thus coating of a base having a large surface area is difficult and results in low productivity. On the other hand, the dipping method, spin coating method, and Langmuir-Blodgett's technique enable the coating in an open system. However, it is difficult with these methods to coat a base having a large surface area. Further, the continuous production is impossible and the productivity is low.

As a method enabling coating of a base having a large surface area with high productivity, there are conventionally known roll coating method, gravure coating method, and the like. However, these methods have never been employed for industrially producing ultra-thin coating films.

DISCLOSURE OF THE INVENTION

It is an object of the present invention to provide a method for producing a coating film which enables continuous production of a coating film on a base having a large surface area, which results in high productivity, and which enables production of a ultra-thin coating film having highly uniform thickness.

According to the present invention, there is provided a method for producing a coating film comprising the step of continuously applying a coating liquid containing 0.05 to 40 wt % solid component to a base with a gravure roll to form a coating film having dry thickness of 0.005 to 1 μm .

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a graph showing measured and theoretical values of the spectral reflection of the anti-reflection film prepared in Example 1.

Fig. 2 is a graph showing measured and theoretical values of the spectral reflection of the anti-reflection film prepared in Example 2.

Fig. 3 is a graph showing measured and theoretical values of the spectral reflection of the anti-reflection film prepared in Example 3.

Fig. 4 is a graph showing measured and theoretical values of the spectral reflection of the anti-reflection film prepared in Comparative Example 1.

PREFERRED EMBODIMENTS OF THE INVENTION

In the method for producing a coating film of the present invention, a coating liquid containing 0.05 to 40 wt % solid components is continuously applied to a base with a gravure roll.

The type of the coating liquid used in the present method is not particularly limited as long as the coating liquid is of a liquid type, and may include a solution, a dispersion, a colloidal solution (sol), or mixtures thereof. The solid components in these types of coating liquids are the solutes, dispersoids, or colloids, respectively. The liquid components thereof are the solvents or dispersion media, respectively. The coating liquid contains 0.05 to 40 wt %, preferably 0.1 to 20 wt % solid components. By setting the content of the solid components to not lower than 0.05 wt %, evaporation of the liquid components is facilitated, whereas by setting the content of the solid components to not higher than 40 wt %, the dry thickness of the resulting coating film becomes uniform.

The components constituting the solid components are not particularly limited, and may include, for example, polymerizable monomers, polymers, or mixtures thereof. The solid components may additionally contain inorganic

compounds.

The polymerizable monomers may either be monofunctional or polyfunctional polymerizable monomers, and may preferably be, for example, (meth)acrylic acid and alkyl esters thereof; unsaturated polybasic acid such as fumaric acid, maleic acid, citraconic acid, mesaconic acid, itaconic acid, or tetrahydrophthalic acid, or alkyl esters of these unsaturated polybasic acids; vinyl esters of fatty acids; styrenes; vinyl alkyl ethers; or vinyl alkyl ketones. Specific examples of the polymerizable monomers may include methyl (meth)acrylate, 1,6-hexanediol di(meth)acrylate, dipentaerythritol hexa(meth)acrylate, 2-(perfluorooctyl)ethyl (meth)acrylate, perfluorooctylmethylethylene glycol di(meth)acrylate, 4,4,5,5-tetrafluorooctane-1,2,7,8-tetraol tetra(meth)acrylate, diisopropyl fumarate, vinyl acetate, vinyl propionate, styrene, α -methyl styrene, aryl acetate, dodecyl vinyl ether, triethylene glycol divinyl ether, vinyl methyl ketone, and vinyl ethyl ketone.

In making the polymerizable monomers be contained in the solid components, a polymerization initiator may also be added to the solid components. The polymerization initiator may suitably be selected depending on the polymerizable monomers used, and may be, for example, an azo radical polymerization initiator such as azobisisobutyronitrile, azobiscyclohexanecarbonitrile, or azobisvaleronitrile; an organic peroxide radical polymerization initiator such as benzoyl peroxide, tert-butyl hydroperoxide, cumene hydroperoxide, or diacyl peroxide; or a photopolymerization initiator such as a benzoin compound including benzoin, benzoin methyl ether, benzoin ethyl ether, or benzoin isopropyl ether; a carbonyl compound including benzophenone, acetophenone, or Michler's ketone; an azo compound including azobisisobutyronitrile or azodibenzobenzoyl; or mixtures of α -diketone and tertiary amines. The mixing ratio of the polymerization initiator to 100 parts by weight of the polymerizable monomers is preferably 0.01 to 10 parts by weight.

The polymers mentioned above are not particularly limited, and may preferably be homopolymers or copolymers of the above-mentioned monofunctional polymerizable monomers. Examples of such homopolymers may include poly(methyl (meth)acrylate), poly(2-(perfluorooctyl)ethyl (meth)acrylate), poly(diisopropyl fumarate), polyvinyl acetate, polyvinyl propionate, polystyrene, poly(α -methylstyrene), polyaryl acetate, polydodecyl vinyl ether, polyvinyl methyl ketone, and polyvinyl ethyl ketone.

The inorganic compounds mentioned above may preferably be metals, metal oxides, metal sulfides, metal halides, or silicon compounds. Specifically, fine powders of zinc oxide, titanium oxide, magnesium fluoride, or silica gel are particularly preferred.

The content of the polymerizable monomers, polymers, or inorganic compounds in the solid components is not particularly limited. The solid components may be composed only of the polymerizable monomers and/or the polymers.

The solid components may further contain additives such as a slipping agent, a leveling agent, a defoaming agent, a surface active agent, a color-breakup preventing agent, dyes, pigments, a UV absorber, an antioxidant, a polymerization inhibitor, or a metal filler. The mixing ratios of such additives may be adjusted for each additive.

The liquid components of the coating liquid are not particularly limited, and may be selected taking the solubility or dispersibility of the solid components, wettability in respect to the base, and evaporation during coating into account. Specific examples of the liquid components may include hexane, toluene, xylene, benzotrifluoride, diisopropyl ether, dichloroethane, methyl ethyl ketone, butyl acetate, isopropyl alcohol, and butanol.

In the method of the present invention, the base to which the coating liquid is applied is not particularly limited as long as the coating liquid can be applied by gravure coating method, and may be a plastic film or a paper coated with a resin. Examples of the plastic film may include films of polyethylene, polypropylene, polymethylpentene, polyethylene terephthalate, polybutyleneterephthalate, polymethyl methacrylate, polystyrene, polycarbonate, triacetyl cellulose, polyurethane, polysulfone, polyether sulfone, polyether ether ketone, and polyvinyl acetate.

In the method of the present invention, the method for continuously applying the coating liquid to the base is not particularly limited as long as it is a method employing a gravure roll. For example, a direct system wherein the coating liquid is directly applied to the base with a gravure roll, or an off-set system wherein an off-set roll is disposed between the gravure roll and the base, may be employed.

The gravure roll used for application is not particularly limited, but preferably has 10 to 300 mesh per centimeter, and the mesh depth of 5 to 500 μm . By setting the number of mesh to not more than 300 per centimeter and setting the mesh depth to not less than 5 μm , the wet thickness of the coating film is prevented from becoming too thin, thereby facilitating the formation of the coating film, and defects of the coating film due to the insufficiency of the coating liquid supply are prevented. On the other hand, by setting the number of mesh to not less than 10 per centimeter and setting the mesh depth to not more than 500 μm , excess supply of the coating liquid is prevented, and formation of a coating liquid pool between the base and the gravure roll or the off-set roll is prevented, thereby improving the uniformity of the coating surface and facilitating the evaporation of the liquid components. However, even if the number and the depth of the mesh are outside the range defined above, acceptable effects of the present invention may be obtained.

The configuration of the cells on the gravure roll surface is not particularly limited, and gravure rolls having cells in the form of pyramids, lattice or slanted lines may be used.

For applying the coating liquid to the base, the direction of rotation of the gravure roll may be forward or reverse direction with respect to the direction of application. The ratio of the rotation speed of the gravure roll with respect to the

speed of the application to the base is preferably 0.001 to 500. Setting the speed ratio to not less than 0.001 makes it possible to prevent the wet thickness of the coating film from becoming too thin, and to prevent defects of the coating film due to insufficient supply of the coating liquid. Setting the speed ratio to not more than 500 makes it possible to prevent excess supply of the coating liquid to thus prevent formation of a coating liquid pool between the base and the gravure roll or the off-set roll, thereby improving the uniformity of the coating surface and facilitating the evaporation of the liquid components. However, even if the speed ratio is outside the range defined above, acceptable effects of the present invention may be obtained.

The thickness of the coating film immediately after the application of the coating liquid to the base, i.e. the wet film thickness, is preferably 0.025 to 1000 μm . By setting the wet film thickness to not less than 0.025 μm , the formation of a uniform coating film is prevented from becoming too difficult. On the other hand, by setting the wet film thickness to not more than 1000 μm , the evaporation of the solvent is facilitated. With the method of the present invention, the dry thickness of the coating film to be obtained may be easily adjusted by selecting an appropriate gravure roll and suitably regulating the conditions for the application to thereby adjust the wet thickness of the coating film. Since evaporation of the liquid components in the applied coating film starts immediately after the application of the coating liquid, it is difficult to directly measure the wet thickness of the coating film. However, the wet film thickness may be calculated indirectly from the thickness of the dried coating film and the change in the volume of the coating liquid. For example, the change in the volume of the coating liquid may be determined by putting the coating liquid in a vessel such as a Schale, and measuring the volumes of the coating liquid before and after drying. The wet film thickness may also be calculated from the amount of the coating liquid used for the application and the coated area.

In the method of the present invention, the coating liquid is applied to the base to form a coating film having the dry thickness of 0.005 to 1 μm . The dry film thickness is the film thickness after the evaporation of the liquid components, or, when a coating liquid containing the solid components including polymerizable monomers is used for the application, after the evaporation of the liquid components and the completion of the polymerization. There is no limitation to the dispersion of the dry film thickness, but it is preferred for producing industrially superior products that the standard deviation of the dry film thickness is within 25 % of the average dry film thickness.

The coating film having the dry thickness of 0.005 to 1 μm may be formed by, for example, drying the wet coating film, i.e. the coating film immediately after the application of the coating liquid. The method for drying the wet coating film is not particularly limited, and may be carried out by spraying a gas such as air or nitrogen to the wet coating film at the room temperature or a higher temperature in a drying furnace. When the polymerizable monomers are contained in the solid components, the liquid components may be dried before or simultaneously with the curing by polymerization, whereas when the polymerizable monomers are not contained in the solid components, the liquid components may be dried before the produced coating film is rolled up. Some types of the liquid components used will evaporate immediately after coating, so that the separate drying process may not be required in this case.

The method for polymerizing the polymerizable monomers in the applied coating liquid containing the solid component including the polymerizable monomers may suitably be selected from such methods as irradiation with active energy rays such as ultraviolet rays or electron beams or heating, depending on the kind of the polymerizable monomers.

With the method of the present invention, since the coating liquid of the particular concentration is continuously applied to the base with a gravure roll, a base having a large surface area can be coated, ultra-thin films having the dry thickness of not more than 1 μm can be produced continuously, and high productivity is achieved. Further, with the method of the present invention, industrially useful ultra-thin films having highly uniform thickness can be produced. In addition, the dry thickness of the ultra-thin film may be adjusted easily by selecting a suitable gravure roll and regulating the application conditions.

EXAMPLES

The present invention will now be explained in more detail with reference to Examples, but the present invention is not limited thereto.

Preparation Example 1

400 g of (perfluorooctyl)methylethylene glycol diacrylate (polymerizable monomer) as a solid component and 4600 g of trifluoromethylbenzene as a liquid component were mixed to prepare coating liquid A containing 8 wt % solid component.

Preparation Example 2

100 g of poly(2-(perfluorooctyl)ethyl acrylate) (polymer) as a solid component and 4900 g of trifluoromethylbenzene

as a liquid component were mixed to prepare coating liquid B containing 2 wt % solid component.

Preparation Example 3

5 178 g of trimethylolpropanetriacrylate (polymerizable monomer) as a solid component, 2 g of "DAROCUR 1116" (trade name, acetophenone compound) manufactured by E. MELCK CORPORATION as a polymerization initiator, 600 g of an inorganic compound "XBA-ST SILICA SOL" (trade name) manufactured by NISSAN CHEMICAL INDUSTRIES CO., LTD. (containing 180 g of colloidal silica as a solid component, and 270 g of xylene and 150 g of n-butanol as liquid components), and 4580 g of toluene as a liquid component were mixed to prepare coating liquid C containing 6.72 wt
10 % solid components.

Preparation Example 4

15 2500 g of (perfluorooctyl)methylethyl glycol diacrylate (polymerizable monomer) as a solid component and 2500 g of trifluoromethylbenzene as a liquid component were mixed to prepare coating liquid D containing 50 wt % solid components.

Preparation Example 5

20 0.5 g of poly(2-(perfluorooctyl)ethyl acrylate) (polymer) as a solid component and 4999.5 g of trifluoromethylbenzene as a liquid component were mixed to prepare coating liquid E containing 0.01 wt % solid component.

Example 1

25 The coating liquid A prepared in Preparation Example 1 was applied to a PET (polyethylene terephthalate) film as a base under the following conditions. "MICROGRAVURE COATER" (trade name) manufactured by YASUI SEIKI CO., LTD. as a gravure roll coater, and "MICROGRAVURE ROLLER" (trade name) having 110 mesh per centimeter and the mesh depth of 70 μm manufactured by YASUI SEIKI CO., LTD. as a gravure roll were employed. The coating liquid A was applied at the application rate of 20 m/min. with the MICROGRAVURE ROLL rotating at 10 m/min. in the direction
30 opposite to the coating direction. Immediately after the application, the applied coating liquid was irradiated with the electron beam having the absorbed dose of 20 Mrad from an electron beam irradiator (manufactured by IWASAKI ELECTRIC CO., LTD.) at the accelerating voltage of 125 kV and beam current of 60 mA for polymerizing the polymerizable monomer, thereby obtaining anti-reflection film F. The resulting anti-reflection film F and the coating liquid A used for application were subjected to various tests below for evaluation.

(a) Spectral Reflection of Anti-reflection Film

35 The spectral reflection of the anti-reflection film was measured by a UV spectrophotometer equipped with 5 degree specular reflectivity measuring attachment (U-best35) manufactured by JAPAN SPECTROSCOPIC CO., LTD. In this case, the measurement was effected on the surface coated with the coating liquid A, and the reverse side was roughened using a sandpaper for inhibiting reflection thereon. The results are shown in Fig. 1. The minimum spectral reflection r_m (%) and the wave length which indicated r_m (optical film thickness) λ_m (μm) are shown in Table 1.

(b) Volume Ratio of Solid Components in Coating Liquid

45 50 ml of a coating liquid was poured in a Schale having the radius of 50 mm, and the liquid components therein were evaporated. The remaining portion of the coating liquid was irradiated with electron beams having the absorbed dose of 5 Mrad from an electron beam irradiator at the accelerating voltage of 175 kV and beam current of 5 mA to obtain a film of the solid components. The dry thickness of the film of the solid components was measured, and the volume ratio of the coating liquid to the solid components v_w/v_d was calculated. The results are shown in Table 1.

(c) Refractive Index of Base and Solid Components

55 The refractive index n_1 of a base and the refractive index n_2 of the film of the solid components prepared in (b) above were measured, respectively, with Abbe's refractometer (manufactured by ATAGO CO., LTD.) . The results are shown in Table 1.

(d) Average Film Thickness and Standard Deviation of Thickness of Anti-reflection Film

It is known in an anti-reflection film that the refractive index n_1 of the base, the refractive index n_2 of the anti-reflection film, and the thickness d of the anti-reflection film satisfy the following formulae (1) and (2). In the formulae, r_t and λ_t stand for the minimum reflection and the optical film thickness, respectively, theoretically obtained by the formulae (1) and (2).

$$r_t(\%) = ((n_1 - n_2)^2 / (n_1 + n_2)^2) \times 100 \quad (1)$$

$$\lambda_t = 4 \times n_2 \times d \quad (2)$$

If the surface of the anti-reflection film is irregular, the average spectral reflection corresponding to the irregular film thickness is measured. As a result, the obtained measured value r_m is different from the theoretical value r_t , and the standard deviation σ with respect to the average film thickness may be calculated from the difference between the theoretical value and the measured value. The average film thickness d_{AV} of the anti-reflection film, the standard deviation σ (%) with respect to d_{AV} , and the theoretical reflection are shown in Table 1. Further, the spectral reflection obtained from the theoretical formulae is shown in Fig. 1.

(e) Wet Film Thickness

v_w/v_d obtained in (b) above is equal to the wet film thickness d_w / the dry film thickness d . The value of d_w obtained by calculation is shown in Table 1.

Example 2

The coating liquid B prepared in Preparation Example 2 was applied to a PET film as a base under the following conditions. The gravure roll coater used in Example 1 and "MICROGRAVURE ROLLER" (trade name) having 90 mesh per centimeter and the mesh depth of 100 μm manufactured by YASUI SEIKI CO., LTD. as a gravure roll were employed. The coating liquid B was applied at the application rate of 20 m/min. with the MICROGRAVURE ROLL rotating at 20 m/min. in the direction opposite to the coating direction. The applied coating liquid was subsequently dried by spraying hot air at 80 °C in a drying furnace of 2 m long, thereby obtaining anti-reflection film G. The resulting anti-reflection film G and the coating liquid B used for application were subjected to the same tests as in Example 1 for evaluation. The results of the measurements of r_m , λ_m , v_w/v_d , n_1 , n_2 , d_{AV} , r_t , and d_w are shown in Table 1 and Fig. 2. In this case, v_w/v_d was obtained by measuring the film thickness after drying without the irradiation process.

Example 3

The coating liquid C prepared in Preparation Example 3 was applied to a PET film as a base under the following conditions. The gravure roll coater used in Example 1 and "MICROGRAVURE ROLLER" (trade name) having 110 mesh per centimeter and the mesh depth of 70 μm manufactured by YASUI SEIKI CO., LTD. as a gravure roll were employed. The coating liquid C was applied at the application rate of 10 m/min. with the MICROGRAVURE ROLL rotating at 5 m/min. in the direction opposite to the coating direction. The applied coating liquid was immediately irradiated with ultraviolet rays at 950 mJ/cm² from a ultraviolet ray irradiator (manufactured by IWASAKI ELECTRIC CO., LTD.) for polymerizing the polymerizable monomer, thereby obtaining anti-reflection film H. The resulting anti-reflection film H and the coating liquid C used for application were subjected to the same tests as in Example 1 for evaluation. The results of the measurements of r_m , λ_m , v_w/v_d , n_1 , n_2 , d_{AV} , r_t , and d_w are shown in Table 1 and Fig. 3. In this case, v_w/v_d was obtained by measuring the film thickness after irradiating the dried coating liquid with the ultraviolet rays at 950 mJ/cm².

Comparative Example 1

The coating liquid D prepared in Preparation Example 4 was applied to a PET film as a base under the following conditions. The gravure roll coater used in Example 1 and "MICROGRAVURE ROLLER" (trade name) having 250 mesh per centimeter and the mesh depth of 13 μm manufactured by YASUI SEIKI CO., LTD. as a gravure roll were employed. The coating liquid D was applied at the application rate of 20 m/min. with the MICROGRAVURE ROLL rotating at 0.1 m/min. in the direction opposite to the coating direction. Immediately after the application, the applied coating liquid was irradiated with electron beams of the absorbed dose of 20 Mrad from an electron beam irradiator (manufactured by IWASAKI ELECTRIC CO., LTD.) at the accelerating voltage of 125 kV and beam current of 60 mA for polymerizing the polymerizable monomer, thereby obtaining anti-reflection film I. The resulting anti-reflection film I and the coating liquid

D used for application were subjected to the same tests as in Example 1 for evaluation. The results of the measurements of r_m , λ_m , v_w/v_d , n_1 , n_2 , d_{AV} , r_t , and d_w are shown in Table 1 and Fig. 4. In this case, v_w/v_d was obtained by measuring the film thickness after irradiating the dried coating liquid with the ultraviolet rays at 950 mJ/cm².

5 Comparative Example 2

The coating liquid E prepared in Preparation Example 5 was applied to a PET film as a base under the following conditions. The gravure roll coater used in Example 1 and "MICROGRAVURE ROLLER" (trade name) of having 20 mesh per centimeter and the mesh depth of 300 μm manufactured by YASUI SEIKI CO., LTD. as a gravure roll were employed. The coating liquid E was applied at the application rate of 1 m/min. with the MICROGRAVURE ROLL rotating at 100 m/min. in the direction opposite to the coating direction. However, the liquid component was not evaporated sufficiently, so that an anti-reflection film could not be produced. The value of d_w was calculated from the volume of the coating liquid used in the application and the area of the coated surface. The results are shown in Table 1.

Table 1

	r_m (%)	λ_m (μm)	v_w/v_d	n_1	n_2	d_{AV} (μm)	σ (%)	r_t (%)	d_w (μm)
Example 1	0.76	0.576	15.3	1.645	1.388	0.104	11	0.62	1.57
Example 2	0.63	0.580	62.1	1.645	1.364	0.104	15	0.37	6.49
Example 3	1.53	0.589	20.1	1.645	1.442	0.101	13	1.36	2.03
Comp.Ex. 1	1.55	0.596	2.22	1.645	1.388	0.092	30	0.62	0.433
Comp.Ex. 2									1100

Claims

1. A method for producing a coating film comprising the step of continuously applying a coating liquid containing 0.05 to 40 wt % solid component to a base with a gravure roll to form a coating film having dry thickness of 0.005 to 1 μm .
2. The method of claim 1 wherein, in said step of continuously applying said coating liquid, the coating liquid is applied so that wet film thickness is 0.025 to 1000 μm .
3. The method of claim 1 wherein standard deviation of the dry thickness of the coating film is within 25 % of average dry thickness of the coating film.
4. The method of claim 1 wherein said gravure roll has 10 to 300 mesh per centimeter and mesh depth of 5 to 500 μm .
5. The method of claim 1 wherein ratio of rotating rate of the gravure roll with respect to the rate of applying the coating liquid to the base is 0.001 to 500.
6. The method of claim 1 wherein said solid component in the coating liquid is a composition containing a polymerizable monomer.
7. The method of claim 1 wherein said solid component in the coating liquid is a composition containing a polymer.
8. The method of claim 6 or 7 wherein said solid component in the coating liquid is a composition further containing an inorganic compound.
9. The method of claim 6 further comprising the steps of evaporating liquid component of said coating liquid, and polymerizing said polymerizable monomer, after the step of continuously applying the coating liquid to the base.
10. The method of claim 7 further comprising the step of evaporating liquid component of said coating liquid.

Fig. 1

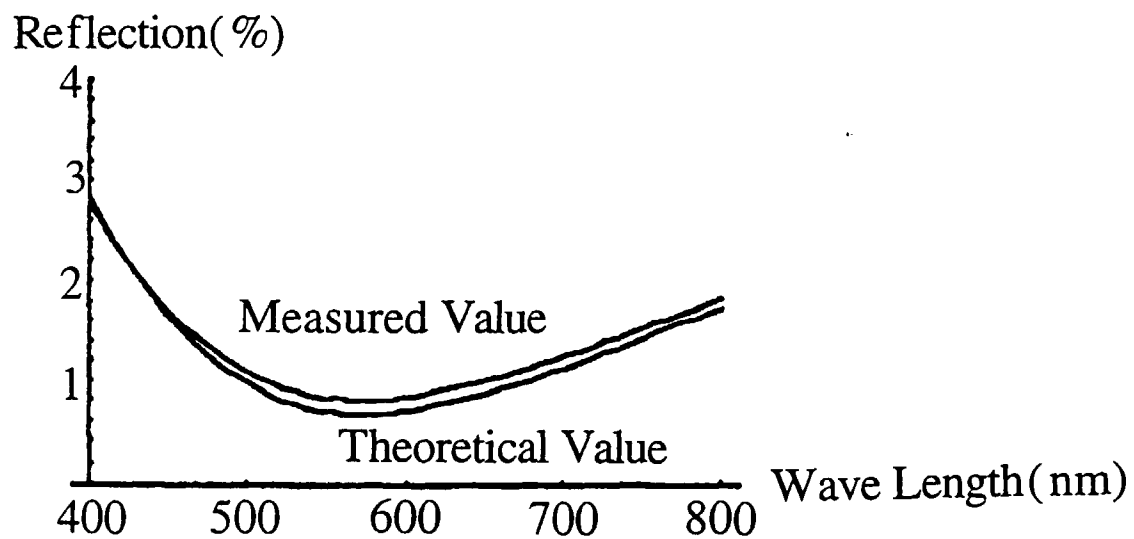


Fig. 2

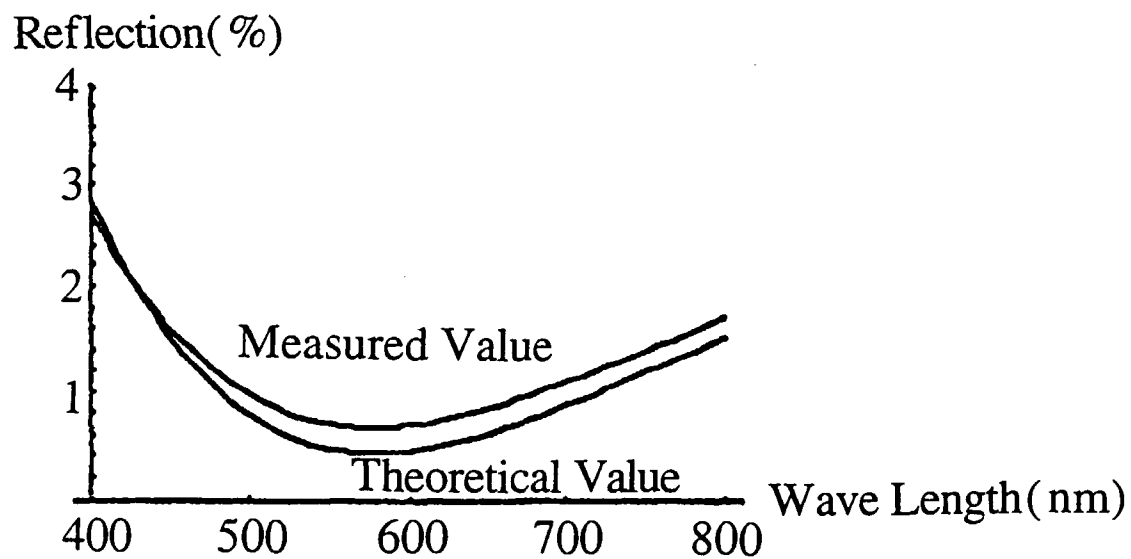


Fig. 3

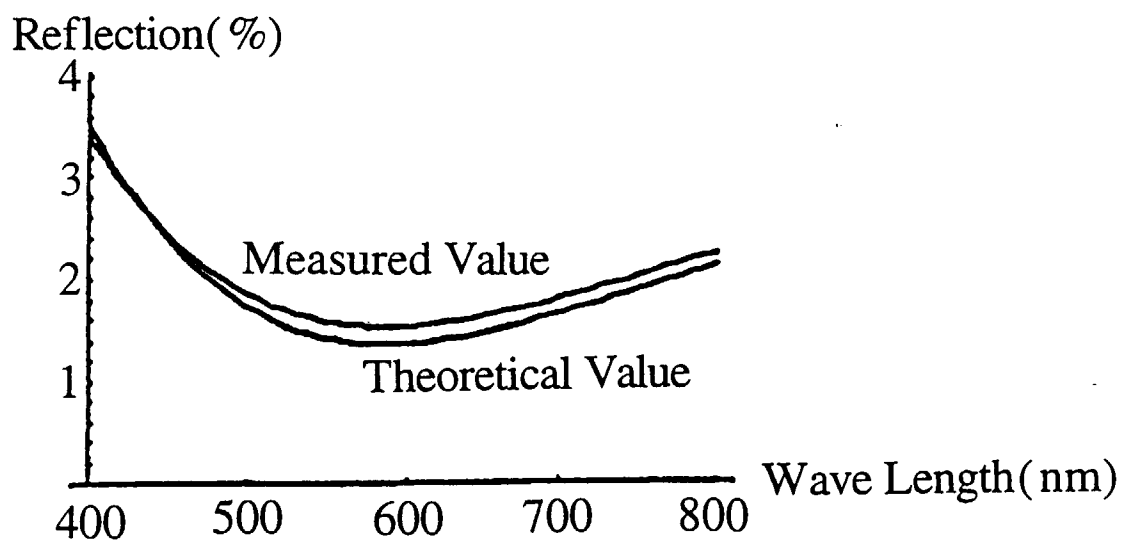
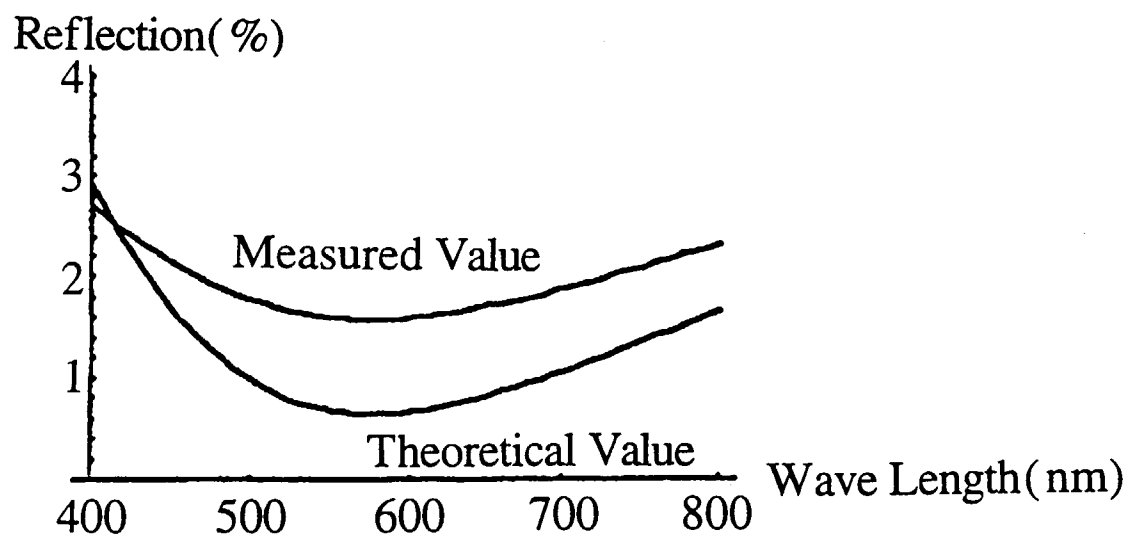


Fig. 4



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP97/01806

A. CLASSIFICATION OF SUBJECT MATTER		
Int. Cl ⁶ B05D1/28, B05D5/06		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
Int. Cl ⁶ B05D1/28, B05D5/06		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Jitsuyo Shinan Koho 1926 - 1997 Kokai Jitsuyo Shinan Koho 1971 - 1997 Toroku Jitsuyo Shinan Koho 1994 - 1997		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 1-176478, A (Kawasaki Steel Corp.), July 12, 1989 (12. 07. 89), Claim; example (Family: none)	1 - 10
A	JP, 55-3889, A (Energy Sciences, Inc.), January 11, 1980 (11. 01. 80) & DE, 2916940, A1 & US, 4537811, A & FR, 2424073, A1	1 - 10
A	JP, 53-59515, A (Toyo Ink Manufacturing Co., Ltd.), May 29, 1978 (29. 05. 78) (Family: none)	1 - 10
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
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Date of the actual completion of the international search		Date of mailing of the international search report
June 26, 1997 (26. 06. 97)		July 8, 1997 (08. 07. 97)
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Form PCT/ISA/210 (second sheet) (July 1992)