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(54) Reflection-photographic element and process of preparation thereof.

(57) A reflection-photographic element having a light-sensitive silver halide photographic emulsion layer coated on at least one side of a support that is made of a white polyester film having no more than 20% transmittance for all visible light and which contains titanium dioxide particles having an average size of 0.1 - 0.5 µm; at least the side of said support which is coated with said emulsion layer has a center-plane-average roughness of no more than 0.12 µm and said side is substantially free of projections that are at least 1.0 µm high as measured from the center plane; and a process of preparation thereof.

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REFLECTION-PHOTOGRAPHIC ELEMENT AND PROCESS OF PREPARATION THEREOF

Field of the Invention

The present invention relates to a reflection-photographic element which, rather than utilizing a projected photographic image obtained by transmitted light (i.e., a transmission-photographic element), forms a photographic image on a photographic layer on an opaque support material and permits direct viewing of the image by reflected light. A typical example of reflection-photographic elements is one which is generally referred to as photographic paper.

Background of the Invention

Polyethylene-coated paper has been conventionally used as a base for reflection-photographic elements and it consists of pulp-made raw paper coated with a polyethylene layer containing a white pigment. One disadvantage of polyethylene-coated paper is that a reflection-photographic element using it as a base has a grained and rippled glossy surface due to the asperities of the surface of raw paper and this impairs greatly the brightness and sharpness of a photographic image and, hence, the aesthetic appeal that is desirably attained by these attributes. Another disadvantage is that although both sides of the base are coated with a water-impermeable polyethylene layer, the edges that are produced by cutting are uncoated and processing solutions such as developer will get into and remain in the base to cause discoloration of the final print.

In order to eliminate these disadvantages, several methods have been proposed that employ bases or supports that are solely made of thermoplastic resin films instead of pulp-made raw paper. Japanese Patent Application (OPI) No. 114921/1974 (the term "OPI" as used herein means an "unexamined published Japanese patent application") and Japanese Patent Publication No. 5104/1980 disclose methods that are characterized by incorporation of white pigments in polystyrene-based resin films. These films, however, have the disadvantage of being hard and brittle. In terms of the physical properties of films such as mechanical strength, and polyesters such as polyethylene terephthalate are superior to other thermoplastic resins and techniques that employ such polyesters are described in British Patent Nos. 1,563,591 and 1,563,592 and are characterized by adding barium sulfate to the polyester and thereafter stretching the film. However, these methods are unable to provide a sufficient degree of whiteness to justify the use of the stretched film as a support for reflection-photographic elements. This is clear from the fact that a brightener and other pigments are used in large amounts in the working examples of these patents. Another problem is that stretching of the film creates boids around the particles of barium sulfate, thereby lowering the resolution of an image to be formed after a photographic layer is coated on the film. Japanese Patent Publication 4901/1981 proposes a technique that uses barium sulfate in combination with titanium dioxide. While various thermoplastic resins can be used, this patent states that saturated polyester-based resins are also advantageous in addition to olefinic resins, styrene-based resins, vinyl chloride based resins, polyacrylate based resins, polycarbonate based resins, etc. In practice, however, the method described in Japanese Patent Publication No. 4901/1981 is not suitable for application to polyester-based resins for the following two reasons. First, barium sulfate has a refractive index that is so close to the value of polyesters that a desired degree of whiteness is not attainable unless the film is stretched. Furthermore, this patent gives no working example of the case where barium sulfate is incorporated in polyester based resins. Secondly, if the film of a polyester based resin that contains titanium dioxide in an untreated form is stretched, boids will occur around the particles of titanium dioxide, making it impossible to attain a desired degree of whiteness. Furthermore, as already mentioned, such boids are detrimental for the purpose of ensuring high resolution of photographic images.

With a view to solving these problems, Japanese Patent Application (OPI) No. 118746/1986 proposed a reflection-photographic element comprising an emulsion layer coated on a film that had surface-treated particles of titanium dioxide (average size, 0.1 - 0.5 μm) incorporated in a polyester and which was adjusted to have a film thickness and transmittance for all visible light within certain ranges. This technique provided to effective in improving the degree of whiteness and the resolving power of the reflection-photographic element but, on the other hand, the smoothness of the surface of the support film was insufficient and the presence of occasional high spots reduced the gloss of the film. Such high spots occur on account of insufficient dispersion of titanium oxide particles. Ordinary titanium dioxide cannot be sufficiently kneaded with polyesters to achieve a state in which it is uniformly dispersed. If kneading is effected under vigorous conditions, the molecular weight of the polyester is reduced as a result of thermal decomposition and it is not possible to attain the melt viscosity necessary to disperse titanium dioxide particles.

In order to solve these problems, the present inventors conducted intensive studies and finally reached the present invention.

Summary of the Invention

An object, therefore, of the present invention is to provide a reflection-photographic element that ensures an enhanced degree of whiteness and improved resolution of photographic images and which produces improved gloss in the absence of any defective high spots. Another object of the present invention is to provide a process of preparation of a white polyester film.

The first object of the present invention can be attained by a reflection-photographic element having a light-sensitive silver halide photographic emulsion layer coated on at least one side of a support that is made of a white polyester film having no more than 20% transmittance for all visible light and which contains titanium dioxide particles having an average size of 0.1 - 0.5 µm. This element is characterized in that at least the side of said support which is coated with said emulsion layer has a center-plane-average roughness of no more than 0.12 µm and that said side is substantially free of projections that are at least 1.0 µm high as measured from the center plane. Alternatively, this element is characterized in that at least said support is substantially free from particles of a size of at least 3 µm.

The second object of the present invention can be attained by a process of preparation of a white polyester film which comprises: at least one of classification and wet grinding of titanium dioxide particles for their average size to be 0.1 - 0.5 µm and their size less than 3 µm; kneading polyester with said titanium dioxide particles; extruding the composition; and stretching the extruded composition to be a film.

Detailed Description of the Invention

The term "center-plane-average roughness" as used herein may be defined as follows. If a portion with area SM is sampled from the center plane of a specific curved roughness profile and if two rectangular co-ordinate axes, x-axis and y-axis, are placed on the center plane of the sampled portion, with z-axis crossing the center plane at right angles, then the center-plane-average roughness (SRa) is expressed by the following equation and indicated in microns (µm):

$$SRa = \frac{1}{SM} \int_0^{LX} \int_0^{LY} \left| f(X,Y) \right| dX,dY$$

where LXLY = SM and Z = f(X,Y).

The values of the center-plane-average roughness and the height of a projection as measured from the center plane can be determined with a three-dimensional surface roughness meter (Model SE-30H of Kosaka Laboratory Co., Ltd.) by measuring an area of 5 mm^2 with a diamond stylus (4 μm^{ϕ}) for a cutoff value of 0.25 mm at a magnification of 20 in the horizontal direction and a magnification of 2,000 in the direction of height. The measuring stylus is preferably advanced at a rate of about 0.5 mm/sec.

The expression "substantial freeness of projections that are at least 1.0 µm high as measured from the center plane" means that when one to ten measurements are made under the conditions described above for the projections that result from the inherent asperities of the support film (in other words, projections with a height of at least 1.0 µm that result from the deposition of foreign matter on the support are not counted in), no projections having a height of at least 1.0 µm will be detected.

The support to be used in the present invention is such a support film that at least the side of this support which has a photographic emulsion layer coated thereon has a center-plane-average roughness of no more than 0.12 µm and that said side is substantially free of projections that are at least 1.0 µm high as measured from the center plane. The reflection-photographic element of the present invention which employs this support film offers a high degree of smoothness and gloss.

If either one of the two conditions set forth above is not satisfied (i.e., the center-plane-average roughness exceeds 0.12 µm or projections that are at least 1.0 µm high as measured from the center surface are substantially present), the support film will present a grainy surface even after it is coated with a photographic emulsion layer and the resulting photographic element will lack gloss.

In accordance with the present invention, the support is considered to be "substantially free from particles of a size of at least 3 μm" if the number of particles of a size of at least 3 μm is no more than 0.1% of the total number of particles observed in a particle size distribution that is obtained by performing image processing on the picture from ten visual fields of a cross section of the support film as examined with an electron microscope at a magnification of 10,000. If particles no smaller than 3 μm are present on the film surface or in its vicinity, occasional high spots or defective projections will occur on the film surface and some of them which are large will remain as defective points even after an emulsion layer is coated on the support. If the number of such defective points increases, a grainy surface that lacks gloss will result. Even particles smaller than 3 μm will produce high spots if they are present in areas near the film surface, so preferably particles of at least 2 μm, more preferably those of at least 1 μm, should be absent from the support for use in the present invention.

The titanium dioxide powder having an average particle size of 0.1 - 0.5 μm which is to be used in the present invention may be of the rutile or anatase type, but anatase titanium dioxide is preferred because of the bluish color it presents.

The titanium dioxide for use in the present invention has a refractive index (n = 2.5 - 2.75) which is far greater than that of the polyester to be used in the present invention (for instance, polyethylene terephthalate has a refractive index of ca. 1.66). Because of this great difference in refractive index, the titanium dioxide particles, when used in the support of the reflection-photographic element, will exhibit enhanced light reflecting ability, thereby producing a photographic image at high resolution.

The titanium dioxide particles to be used in the present invention may be subjected to a suitable surface treatment, such as an inorganic treatment which involves depositing one or more inorganic compounds on the surface of titanium dioxide particles that are selected from among hydroxides, hydrated oxides, phosphates, basic sulfates, etc. of metals such as Al, Ce, Mg, Ti, Sb, Si, Sn, Zn and Zr. This inorganic treatment may be performed either individually or in combination with an organic treatment which involves allowing organic compounds to be absorbed on the surface of titanium dioxide particles and exemplary organic compounds include metal salts of aliphatic acids, various coupling agents, alcohols, amines, siloxane polymers, various ester compounds, and phosphoric acid compounds.

The only requirement that should be met by the support for use in the present invention is that it is such a film that at least the side which is coated with a photographic emulsion layer has a center-plane-average roughness of no more than 0.12 μm and that it is substantially free of projections with a height of 1.0 μm or more as measured from the center plane. While there is no particular limitation on the method that can be used to prepare such a film, a typical method will proceed as follows: titanium dioxide particles, before being added to a polyester, are subjected to classification by a wet or dry process and/or grinding by a wet process, so as to eliminate any coarse particles that will produce unwanted surface projections; the so treated TiO_2 particles are then mixed with the polyester to form a feed composition, which is subsequently shaped into a film.

Classification by a wet process consists of suspending the titanium dioxide particles in water or some other fluids that will not dissolve titanium dioxide, and then rejecting particles larger than a specified size by making use of the difference in the rate of settlement that depends on particle size. This method is divided into two types, gravitational settlement and centrifugal settlement, according to the way in which particles settle. Either type of method can be adopted in the present invention but the method of gravitational settlement is preferred because it guarantees high precision and permits the use of a simple apparatus. The concentration of the suspension of titanium dioxide particles is not limited to any particular value but it is generally in the range of 100 - 700 g/ℓ. A dispersant such as sodium hexametaphosphate may be added to the suspension.

Classification by a dry process is a technique in which particles larger than a specified size are rejected by making use of the difference in the behavior of particles of different sizes suspended in a gas such as air. In practice, this technique may be implemented by air elutriation or by such means as an air separator or a cyclone.

For the purposes of the present invention, classification by a wet process is preferred over classification by a dry process for several reasons including the precision of classification and ease of handling.

Grinding by a wet process is an operation in which titanium dioxide is ground into fine particles in a fluid such as water that dose not dissolve titanium dioxide. In this method, grinding machines such as a ball mill, a vibration mill and a sand mill are commonly employed and a grinder of the sand mill type is particularly effective. Media to be used include glass beads, alumina beads, zirconia beads and Ottawa sand. Many sand mills are commercially available for this purpose. The residence time in sand mills generally ranges from about 3 to 30 minutes.

Classification by a wet or dry process may be performed either independently or in combination with grinding by a wet process.

In the present invention, classification by a dry or wet process and/or grinding by a wet process may be performed either before or after the surface treatment of titanium dioxide particles. If the surface treatment consists of an inorganic and an organic treatment, classification and/or grinding may be carried out between the two surface treatments.

The polyester that can be used in the present invention may be a thermoplastic resin that is solely composed of a polyester. Alternatively, it may include other polymers and suitable additives to such an extent that the resin characteristics of the main component polyester will not be affected when used in practical applications.

Illustrative polyesters that can be used in the present invention include polymers of the condensation products of aromatic dicarboxylic acids (e.g., terephthalic acid, isophthalic acid, phthalic acid, and naphthalenedicarboxylic acid) and glycols (e.g., ethylene glycol, 1,3-propanediol, and 1,4-butanediol), such as polyethylene terephthalate, polyethylene-2,6-dinaphthalate, polypropylene terephthalate, polybutylene terephthalate, and copolymers thereof.

For the purpose of the present invention, polyethylene terephthalate (hereinafter abbreviated as PET) is preferably used as a polyester. PET films are impermeable to water, have a high degree of smoothness, display good mechanical characteristics in such aspects as tensile strength and tear strength, are high in dimensional stability, and offer high chemical resistance during development and other steps of photographic processing.

The polyester used in the present invention preferably has an intrinsic viscosity of 0.4 - 1.0, more preferably 0.5 - 0.8, when measured at 20 °C in a mixed solvent of phenol and 1,1,2,2-tetrachloroethane (60/40 in weight ratio).

In the present invention, titanium dioxide is preferably incorporated in the polyester in an amount of 10 - 50 parts by weight per 100 parts by weight of the polyester in order to satisfy the requirements for a higher degree of whiteness and stretchability of the support film. The range of 15 -30 parts by weight is more preferred. Titanium dioxide is preferably added in such an amount that the support film will have no more than 20% transmittance of all visible light.

Titanium dioxide may be used together with one or more inorganic pigments such as zinc oxide, barium sulfate, silica, talc and calcium carbonate, which are commonly employed as white pigments in the art. These optional white pigments are preferably used in amounts that do not exceed 10 parts by weight per 100 parts by weight of the polyester used in the present invention.

In accordance with the present invention, the titanium dioxide described above is mixed with the polyester in a molten state.

Kneading machines that may be used in the present invention for the purpose of uniformly dispersing titanium dioxide in the polyester include: continuous kneaders such as extruders having mixing rotors or blades, corotating or counterrotating twin-screw extruders, and single-screw continuous kneaders; and batch kneaders such as three-roll mills, Banbury mixers, Henschel mixers and kneaders. Corotating continuous twin-screw extruders are particularly advantageous since they allow continuous kneading operations under strong shearing force.

In the present invention, the polyester composition obtained by the kneading step described above may be shaped into a film after it has been formed into pellets. Alternatively, the composition in a molten state may be directly shaped into a film. In either method, the concentrations of pigments in the composition may be preliminarily adjusted to the final values. Alternatively, a master batch, or a composition having higher pigment concentrations, may be first prepared, which then is diluted before being shaped into a film.

Film shaping may proceed as follows: the polyester composition obtained by the kneading step is extruded in a molten state through a slit die, cast onto a chill surface such as a rotary drum to form an amorphous sheet, which is subsequently stretched biaxially (stretching in the longitudinal or transverse direction is followed by stretching in the transverse or longitudinal direction, or the film is stretched in the longitudinal and transverse directions simultaneously) at a temperature not lower than the glass transition temperature (Tg) of the polyester and not higher than 130 °C. In order to produce a film base that meets the requirements for high mechanical strength and dimensional stability, the stretching is preferably effected for a draw ratio of 4 to 16, more preferably 6 to 12, on the basis of area. The stretched film is preferably heat-set and heat-relaxed.

The composition from which a film is to be formed is preferably passed through a filler of an appropriate grade.

The film base of the present invention has a thickness of 50 - 300 µm, preferably 75 - 250 µm. If the base is thinner than 50 µm, it does not have a sufficient body to withstand wrinkke formation. If the base is thicker than 300 µm, great inconvenience in handling will result.

The film base of the present invention may contain conventional additives such as brighteners dyes, uv absorbers and antistats provided that they do not have any detrimental effect on the objects of the present invention.

The film base of the present invention which has been shaped, opacified and whitened by the procedures described above is then coated with at least one light-sensitive photographic emulsion layer. If necessary, the application of light-sensitive photographic emulsion layers may be preceded by a treatment for surface activation (e.g., corona treatment) and/or provision of subbing layers.

Particularly useful methods for coating light-sensitive silver halide photographic emulsion layers are extrusion coating and curtain coating techniques which permit two or more layers to be coated simultaneously. The coating speed may be selected at any desired value but to achieve a high production rate, 50 m/min and faster speeds are preferred.

The reflection-photographic element of the present invention may be applied to any photographic elements that employ a base and it may be applied to either black-and-white photography or color photography. There also is no particular limitation on photographic constituent layers, and light-sensitive photographic emulsion layers, intermediate layers, protective layers, filter layers, backcoat layers and other constituent layers may be disposed in any number and in any order.

Any ordinary silver halide emulsion layes may be employed as photographic emulsion layers and preferred emulsions are silver chloride, silver bromide, silver chlorobromide, silver iodobromide and silver chloroiodobromide emulsions. Couplers for forming color image may be incorporated in these photographic emulsion layers. It is also possible to incorporate as binders non-gelatin hydrophilic polymers such as polyvinyl alcohol and polyvinyl pyrrolidone. The above-mentioned silver halide emulsion layers may be optically sensitized with suitable dyes such as cyanine and merocyanine dyes. Preferably, other photographic addenda such as antifoggants, chemical sensitizers (e.g., those using gold and sulfur compounds), hardeners and antistats may be incorporated. Therefore, the reflection-photographic element of the present invention is effective not only in black-and-white development but also in color development.

The following examples are provided for the purpose of further illustrating the present invention but are in no way to be taken as limiting.

EXAMPLE 1

An anatase titanium dioxide powder having an average particle size of 0.37 µm was mixed with water to make a slurry having a TiO_2 concentration of 400 g/ℓ. The slurry was left to stand for a predetermined time and coarse particles of TiO_2 (≧1 µm) were rejected by gravitational settlement.

To the suspension, an aqueous solution of aluminum sulfate and a solution of sodium hydroxide were added in that order, thereby forming a hydrated alumina coating on the surface of TiO_2 particles. The deposit of hydrated alumina was 1.0 wt% of TiO_2 as calculated for Al_2O_3.

To the suspension of alumina-coated TiO_2 particles, an aqueous solution of polydimethylsiloxane was added in such an amount that the deposit of polydimethylsiloxane would be 0.6 wt% of TiO_2. Thereafter, the suspension was filtered and dried.

A formulation consisting of 20 parts by weight of the so prepared TiO_2, 0.05 parts by weight of a brightener ("Leucopur EGM" of Sandoz, Inc.) and 80 parts by weight of polyethylene terephthalate having an intrinsic viscosity of 0.80 was charged into a corotating twin-screw kneader/extruder (Model ZCM 53/60 of Automatic Material Handling, Inc.), in which the ingredients were melted, kneaded and shaped into pellets.

The pellets were vacuum-dried at 180 °C for 6 hours, melted in an extruder, and extruded through a slit die onto a chilling rotary drum to form an amorphous sheet 1.4 mm thick. The sheet was first stretched at a draw ratio of 2.6 in the longitudinal direction at 95 °C and then at a draw ratio of 3.0 in the transverse direction at 110 °C. The stretched sheet was heat-set at 210 °C, relaxed by 0.5% in the transverse direction, and cooled to produce a white opaque film support having a thickness of 180 µm.

This film support had a transmittance of 5.0% for all visible light.

The center-plane-average roughness of this film support and the maximum height of projections from the center plane were measured by the methods described herein. The results are shown in Table 1.

The film support was coated with a subbing layer consisting of a terpolymer of styrene, butadiene and maleic anhydride and subjected to a corona discharge treatment. Thereafter, a silver halide photographic emulsion that was in common use in color photographic paper was coated on the support to give a dry thickness of 15 µm, thereby preparing sample No. 1 of reflection-photographic element.

The degree of whiteness of this sample, its resolving power, the number of defective projections and its gloss were measured by the methods described below. The results are shown in Table 1.

Degree of whiteness

The unexposed sample was developed and the spectral reflectance of the white background was measured at 380 -780 nm with a spectrophotometer Model 320 of Hitachi, Ltd. The data obtained was calculated in accordance with JIS Z 8722 (1982) to determine the degree of whiteness (L value).

Resolving power

A chart for resolving power measurement that was composed of very narrow and closely spaced lines was printed on the sample of reflection-photographic element, which developed by standard procedures. The difference in optical density of the printed image of closely spaced lines was measured with a microdensitometer PDM-5 of Konica Corp. and the resolving power of the sample was calculated by the following equation:

$$\text{Resolving power (\%)} = \frac{\text{Difference between Dmax and Dmin of printed image containing 5 lines per millimeter}}{\text{Difference between Dmax and Dmin of printed image containing 0.1 line per millimeter}} \times 100$$

Defective projections

The number of surface projections that were visible per unit area (100 cm²) of the sample was counted and evaluated by the following criteria:

0 - 5 projection/100 cm^2	◎ , the highest degree of smoothness
6 - 30 projections/100 cm^2	O , high degree of smoothness
31 - 100 projections/100 cm^2	Δ , low degree of smoothness
101 and more projections/100 cm^2	x , The lowest degree of smoothness

Samples rated O and ◎ would be satisfactory for practical purposes and were considered to be useful as reflection-photographic elements having improved gloss. On the other hand, samples rated Δ and x had an apparently grainy texture and lacked gloss.

Gloss

Using a digital variable angle glossmeter Model VG-1D of Nipon Denshoku Kogyo Co., Ltd., a black sample that had been obtained by development following 5-sec exposure under a candescent lamp was subjected to gloss measurement through angles of 20° - 20°.

COMPARATIVE EXAMPLE 1

A formulation consisting of 20 parts by weight of an anatase titanium dioxide powder having an average particle size of 0.37 µm, 0.05 parts by weight of a brightener ("Leucopur EGM" of Sandoz, Inc.) and 80 parts by weight of polyethylene terephthalate having an intrinsic viscosity of 0.80 was melted, kneaded and shaped into pellets as in Example 1. The pellets were processed into a white opaque film support 180 µm thick by the same method as that employed in Example 1.

The three-dimensional roughness characteristics of this film were measured and the results are shown in Table 1.

As in Example 1, an emulsion layer was coated on the support film to prepare sample No. 2 of reflection- photographic element. The degree of whiteness of this sample, its resolving power, the number of defective projections and its gloss were measured as in Example 1, and the results are also shown in Table 1.

COMPARATIVE EXAMPLE 2

Sample No. 3 was prepared as in Comparative Example 1 except that 20 parts by weight of the anatase titanium dioxide powder having an average particle size of 0.37 µm was replaced by a mixture of 10 parts by weight of an anatase titanium dioxide powder having an average particle size of 0.37 µm and 5 parts by weight of a silica powder having an average particle size of 0.25 µm. The degree of whiteness of this sample, its resolving power, the number of defective projections and its gloss were measured, and the results are shown in Table 1.

EXAMPLE 2

Titanium dioxide, polyethylene terephthalate and a brightener were kneaded and formed into pellets as in Comparative Example 1; except that the blend emerging from the kneader was passed through a filter having a precision of 10 µm (capable of rejecting at least 90% of particles of a size of 10 µm and larger) before it was formed into pellets. The pellets were processed into a white opaque film support 180 µm thick by the same method as that employed in Example 1, except that the melt of pellets emerging from the extruder was passed through a filter having a precision of 5 µm (capable of rejecting at least 90% of particles of a size of 5 µm and larger).

The three-dimensional roughness characteristics of this film were measured and the results are shown in Table 1.

As in Example 1, an emulsion layer was coated on the support film to prepare sample No. 4 of reflection-photographic element. The degree of whiteness of this sample, its resolving power, the number of defective projections and its gloss were measured as in Example 1, and the results are also shown in Table 1.

TABLE 1

Sample No.	Center-plane-average roughness (µm)	Maximum height of projections (µm)	Degree of whiteness (L value)	Resolving power (%)	Defective projections	Gloss (%)
1 (sample of the invention)	0.06	0.5	92	71	◎	96
2 (comparative sample)	0.06	2.0	91	70	×	92
3 (comparative sample	0.15	2.0	88	66	×	78
4 (sample of the invention)	0.10	0.8	91	70	◎	96

One can see from Table 1 that the samples of the present invention were improved not only in the degree of whiteness and resolving power but also in smoothness (as evidenced by fewer defective projections) and gloss.

EXAMPLE 3

An anatase titanium dioxide powder having an average particle size of 0.35 µm was mixed with water to make a slurry having a TiO_2 concentration of 400 g/ℓ. The slurry was subjected to classification by gravitational settlement, with the size of particles to be rejected being adjusted for 1 µm, 3 µm, 5 µm or 10 µm.

Twenty parts by weight of the resulting four classes of TiO_2 particles were individually fed into a corotating twin-screw kneader/extruder (Model ZCM 53/60 of Automatic Material Handling, Inc.) together with 80 parts by weight of polyethylene terephthalate having an intrinsic viscosity of 0.80, and the respective charges were melted, kneaded and shaped into pellets.

In each run, the pellets were vacuum-dried at 180°C for 6 hours, melted in an extruder, and extruded through a slit die onto a chilling rotary drum to form an amorphous sheet 1.4 mm thick. The sheet was first stretched at a draw ratio of 2.6 in the longitudinal direction at 95°C and then at a draw ratio of 3.0 in the transverse direction at 110°C. The stretched sheet was heat-set at 210°C and cooled to produce a white opaque film support having a thickness of 180 µm. Each of the films obtained had a transmittance of 5.0% for all visible light.

A cross section of each film was examined with an electron microscope at a magnification of 10,000 and the picture of ten visual fields was processed with an image analyzer (Model TV-IP2000 of Japan Avionics Co., Ltd.) to obtain a particle size distribution. The percentage of the total particle count in each film which was occupied by particles having a size of at least 3 µm is shown in Table 2.

Each of the film supports was then coated with a subbing layer consisting of a terpolymer of styrene, butadiene and maleic anhydride and subjected to a corona discharge treatment. Thereafter, a silver halide photographic emulion in gelatin that was in common use in color photographic paper was coated on the support to give a dry thickness of 15 µm, thereby preparing sample Nos. 5 - 8 of reflection-photographic element. The degree of whiteness of these samples, their resolving power and the number of defective projections were measured as in Example 1. The results are shown Table 2.

TABLE 2

Sample No.	Particle size to be rejected by classification	No. of particles no smaller than 3μm (%)	Degree of whiteness (L value)	Resolving power (%)	Defective projections	Remarks
5	≧1μm	0	92	71	◎	sample of the invention
6	≧3μm	0.03	91	72	○	do.
7	≧5μm	0.26	92	71	Δ	comparative sample
8	≧10μm	1.4	91	71	×	do.

One can see from Table 2 that the samples of the present invention were improved not only in the degree of whiteness and resolving power but also in gloss as evidenced by fewer defective projections.

As will be understood from the foregoing explanation, only when the support that is within the scope of the present is used can a reflection-photographic element be realized that is improved in four aspects, i.e., the degree of whiteness, resolving power, the number of defective projections and gloss.

Claims

1. A reflection-photographic element having a light-sensitive silver halide photographic emulsion layer coated on at least one side of a support that is made of a white polyester film having no more than 20% transmittance for all visible light and which contains titanium dioxide particles having an average size of 0.1 - 0.5 µm, at least the side of said support which is coated with said emulsion layer having a center-plane-average roughness of no more than 0.12 µm and said side being substantially free of projections that are at least 1.0 µm high as measured from the center plane.

2. A reflection-photographic element according to claim 1 wherein said titanium dioxide is of the anatase type.

3. A reflection- photographic element according to claim 1 or 2 wherein said titanium dioxide particles have been subjected to a surface treatment.

4. A reflection-photographic element according to claim 3 wherein said surface treatment is an organic treatment and/or an organic treatment, said inorganic treatment involving depositing one or more inorganic compounds on the surface of said titanium dioxide particles that are selected from among hydroxides, hydrated oxides, phosphates, basic sulfates of metals such as Al, Ce, Mg, Ti, Sb, Si, Sn, Zn and Zr, and said organic treatment involving allowing one or more organic compounds to be adsorbed on the surface of titanium dioxide particles that are selected from among metal salts of aliphatic acids, coupling agents, alcohols, amines, siloxane polymers, ester compounds, and phosphoric acid compounds.

5. A reflection-photographic element according to claim 1 wherein said polyester film is prepared from a composition that is obtained by mixing a polyester with titanium dioxide that has been preliminarily subjected to classification or wet grinding.

6. A reflection-photographic element according to claim 5 wherein said classification is conducted by a wet process.

7. A reflection-photographic element according to claim 6 wherein said wet classification is conducted by gravitational settlement.

8. A reflection-photographic element according to claim 1 wherein said polyester is a polymer of the condensation product of an aromatic dicarboxylic acid and a glycol.

9. A reflection-photographic element according to claim 8 wherein said polymer of the condensation product is polyethylene terephthalate, polyethylene-2,6-dinaphthalate, polypropylene terephthalate, polybutylene terephthalate or copolymers thereof.

10. A reflection-photographic element according to claim 1 or 5 wherein 10 - 50 parts by weight of titanium dioxide is incorporated in 100 parts by weight of the polyester.

11. A reflection-photographic element according to claim 1 wherein said polyester film has been stretched for a draw ratio of 4 - 16 on the basis of area.

12. A reflection-photographic element according to claim 11 wherein said polyester film has been heat-set and heat-relaxed after stretching.

13. A reflection-photographic element according to claim 1 wherein said support has a thickness of 50 - 300 µm.

14. A reflection-photographic element according to claim 1 wherein said titanium dioxide particles have a size of less than 3 µm.

15. A reflection-photographic element comprising a light-sensitive silver halide photographic emulsion layer coated on at least one side of a support that is made of a white polyester film having no more than 20% transmittance for all visible light and which contains titanium dioxide particles having an average size of 0.1 - 0.5 µm and having substantially a size of less than 3 µm.

16. A reflection-photographic element according to claim 15 wherein titanium dioxide particles have a size of less than 2 µm.

17. A reflection-photographic element according to claim 15 wherein titanium dioxide particles have a size of less than 1 µm.

18. A process of preparation of a white polyester film comprising, at least one of classificaton and wet grinding of titanium dioxide particles for their average size to be 0.1 - 0.5 µm and their size less than 3 µm, kneading polyester with said titanium dioxide particles,
extruding the composition, and
stretching the extruded composition to be a film.

19. A process of preparation of a white polyester film according to claim 15 wherein the stretching is biaxial drawing.

20. A support comprising a white polyester film having no more than 20% transmittance for all visible light and which contains titanium dioxide particles having an average size of 0.1 - 0.5 µm, at least the side of said support which is coated with a light-sensitive silver halide photographic emulsion layer having a center-plane-average roughness of no more than 0.12 µm and said side being substantially free of projections that are at least 1.0 µm high as measured from the center plane.