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Reflective photographic material.

There is disclosed a reflective photographic material having photosensitive emulsion layers applied on at least one side of a support film of thermoplastic resin essentially comprised of polyester resin that contains white pigment containing 90% by weight or more of surface-treated titanium oxide having an average particle size of 0.1 μm to 0.5 μm and including substantially no particles whose size is 50 μm or more. The disclosed photographic material shows excellent whiteness, opacity, gloss and resolving power. A permeation of a photographic processing liquid through the cut edge of the support of said photographic material does not take place.

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REFLECTIVE PHOTOGRAPHIC MATERIAL

BACKGROUND OF THE INVENTION

The present invention relates to a reflective photographic material. Unlike the so-called transmission-type photographic material wherein a photographic image is projected thereon by means of transmitted light and its projected image is utilized, the present reflective photographic material means a photographic material as usually called a photographic paper wherein an opaque material is used as a support thereof and a photographic layer is provided thereon and a photographic image formed on the photographic layer is usually enjoyed directly by means of reflected light.

Hitherto, a polyethylene-coated paper wherein a layer of polyethylene in which white pigment and others are kneaded is provided on a base paper made from pulp has been generally used as a support for the reflective photographic material. On the reflective photographic material wherein a polyethylene-coated paper is used as a support, however, the

brightness, the sharpness and the beauty caused by the formers of a photographic image are remarkably deteriorated by the roughness on the surface of an adjoining support of base paper that causes a glossy surface having a coarse wavy form on the photographic image. Further, the cut edges of a base paper are not coated though both sides of a support of base paper are covered by a water-proof polyethylene thin film and therefore, there have been disadvantages that developing liquid and others permeate the base paper through its cut edges and they reach a photographic layer through a change with the passage of time, resulting in a bad influence on the photographic image obtained.

As a method for overcoming aforesaid disadvantage, there have been proposed some methods which do not employ a base paper but employ only a thermoplastic resin film as a support.

In each of Japanese Patent Publication Open to Public Inspection No. 114921/1974 and Japanese Patent Examined in a polystyrene type resin film is disclosed but these films have disadvantages that they are hard and fragile. From the viewpoint of physical properties such as a mechanical strength and others of this film, polyester resins such as polyethylene terephthalate and others are excellent and as the technology employing this polyester resins, there are disclosed some methods wherein barium sulfate is added to polyester resins and then they are stretched, in British Patent Nos. 1,563,591

and 1,563,592. In this method, however, it is impossible to obtain sufficient whiteness as a support for the reflective photographic material. This is evidenced by the examples in the patents wherein fluorescent brightener and other pigment are used abundantly. Further, as a result of stretching, vacant spaces are produced around the barium sulfate particles and thereby the resolving power for images obtained after the coating of photographic layer becomes insufficient. In Japanese Patent Examined Publication No. 4910/1981, on the other hand, there is disclosed a technology wherein barium sulfate and titanium oxide are used in combination. In the aforesaid patent, olefin type resins, styrene type resins, vinylchloride type resins, polyacrylate type resins, polycarbonate type resins as well as saturated polyester type resins are stated to be preferable but it is impossible to apply to polyester type resins for the following two reasons. The first reason is that the desirable whiteness can not be obtained without stretching because an index of refraction of barium sulfate is close to that of polyester resin and there is no disclosure about the occasion of adding to polyester type resin in the patent. The second reason is that titanium oxide, if it is added to polyester type resins and stretched, causes the vacant spaces to be produced around the particles and thereby the desirable whiteness can not be obtained and the resolving power on the photographic image is insufficient

as stated above. As mentioned above, no satisfaction has been obtained as a reflective photographic material.

SUMMARY OF THE INVENTION

The present invention has been devised for the purpose of overcoming the aforesaid disadvantages and the object of the present invention is to provide a reflective photographic material wherein there is no permeation of photographic processing liquid and others through the cut edge of a support of the reflective photographic material and whiteness, opacity, glossiness and further the resolving power on the photographic image thereof are excellent.

Aforesaid object of the present invention may be attained by a reflective photographic material wherein photosensitive photographic emulsion layers are provided on at least one side of a support of thermoplastic resin film primarily composed of polyester resin containing white pigment that contains 90% by weight or more of surface-treated titanium oxide having an average particle size of $0.1\mu\text{m}$ - $0.5\mu\text{m}$ and having substantially no particles whose size is $50\mu\text{m}$ or more.

A thermoplastic resin primarily composed of polyester resin used in the present invention (hereinafter referred to as "the resin of the present invention") includes thermoplastic resin composed only of polyester, as a matter of course, and other ones wherein other polymer, additives and

others are added thereto within a range that does not practically change the resin characteristics of polyester that is principal ingredient.

As polyester resin used in the invention, there are cited polymer of condensate between aromatic dicarboxylic acid such as terephthalic, isophthalic, phthalic, and naphthalenedicarboxylic acids, and glycol such as ethylene glycol, 1,3-propanediol, and 1,4-butanediol, including polyethylene terephthalate, polyethylene-2,6-dinaphthalate, polypropylene terephthalate, and polybutylene terephthalate; and their copolymers. Among them, polyethylene terephthalate (hereinafter referred to as PET) is preferable. In general, film made from PET resin is excellent not only in water-impermeability, smoothness, mechanical properties such as tensile and tear strengths, and thermal dimension stability, but also in chemical resistance during development processing.

The intrinsic viscosity of the polyester resin of the invention measured at 20°C in a mixed solvent of phenol and tetrachloroethane (60:40 in weight) is preferably 0.4 to 1.0, and especially preferably 0.5 to 0.8.

White pigment used in the invention is composed of 90% by weight or more of surface-treated titanium oxide having an average particle size of 0.1 to 0.5 μ m, and substantially containing no particles not smaller than 50 μ m. Said surface treatment of titanium oxide particles is referred to at least one of those

with oxygen bond-or hydroxyl group bond-carrying aluminum compounds (such as alumina) or silicon compounds (such as silicic acid), metallic soaps, surfactants, coupling agents and polyhydric alcohol or, the above treatment plus the post-treatment with metallic soaps, surfactants, coupling agents polyhydric alcohol or the like for the purpose of giving to titanium oxide particles the affinity to the resin of the invention.

As a surface-treatment in the present invention, the surface-treatment with an oxygen bond- or hydroxyl group bond-carrying aluminum compound and/or silicon compound is preferable. Aluminum compounds, (when calculated in the form of Al_2O_3), are to be used in the amount of, for example, 0.5-20% by weight and preferably of 0.5-5% by weight against titanium oxide. Silicon compounds, (when calculated in the form of SiO_2), are to be used in the amount of, for example, 0.1-20% by weight and preferably of 0.5-5% by weight against titanium oxide. Titanium oxide treated with SiO_2 and Al_2O_3 at the same time is especially useful in the invention.

The amount of aluminum compounds to be used is free but at least 0.1% by weight of silicon compounds against titanium oxide should be deposited together with aluminum compounds. These methods for treatment are disclosed in British Patent No. 1164849 or in West German OLS Patent No. 1167442.

After the aforesaid surface-treatment, further treatment with metallic soap, surfactant, coupling agent or polyhydric

alcohol is also preferable and they may be employed individually or in combination. As a surfactant, any of anion type, cation type and nonion type surfactants may be used. Metallic soaps described below are especially useful. Anion type surfactant means higher fatty acid and its metallic salt, ester sulfate, sulfonate and ester phosphate. As higher fatty acid and its metallic soap, lauric acid, palmitic acid, stearic acid, behenic acid, sodium laurate, calcium palmitate, zinc stearate, calcium stearate, magnesium stearate and others may be used. As ester sulfate, alkylester sulfate such as sodium lauryl sulfate, sodium cetyl sulfate, triethanol lauryl sulfate, lauryl sulfate and oleyl sulfate etc.; polyoxyethylene alkylether ester sulfate such as sodium polyoxyethylenepheryl sulfate, ammonium polyoxyethylene phenyl sulfate and others; and polyoxyethylene alkylarylether ester sulfate such as sodium polyoxyethylene-nonylphenyl sulfate, ammonium polyoxyethylene nonylphenyl sulfate and others may be used. As sulfonate, alkylaryl sulfonate such as dibutyl-naphthalene sulfonate, dioctyl-naphthalene sulfonate, dinaphthylmethane sodium disulfonate and others, and higher fatty acid alkylolamide sulfonate such as N-methyl N-oleyltaurine sodium or the like may be used. As ester phosphate, aminoalkyl ester phosphate and others may be used.

Cation type surfactant means amine salt and quaternary ammonium salt. As amine salt, tertiary amine salt such as

triethanonamine chloride or the like; secondary amine salt such as N-laurylbenzyl amine chloride or the like; and primary amine salt such as laurylamine acetate or the like may be used. As quaternary ammonium salt, alkyltrimethyl ammonium chloride such as stearyltrimethylammonium chloride or the like; and alkyldimethylbenzyl ammonium chloride such as lauryldimethylbenzyl ammonium chloride or the like may be used.

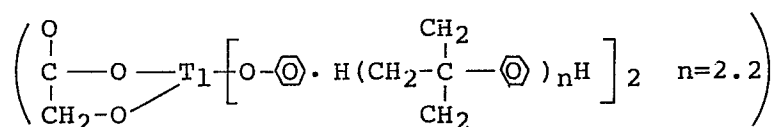
Nonion type surfactant means polyethyleneglycol derivatives and polyhydric alcohol derivatives. Polyethyleneglycol derivatives include polyoxyethyleneoctylphenylether such as polyoxyethyleneoylel ether, polyoxyethylene laurylether polyoxyethylenecetyl ether, polyoxyethylenestearyl ether or the like; polyoxyethylenealkylaryl ether such as polyoxyethyleneoctylphenyl ether, polyoxyethyleneonylphenyl ether or the like; polyoxyethylene fatty acid amide such as polyoxyethylenestearyl amide, polyoxyethyleneoylel amide or the like; and polyoxyethylenepolypropyleneglycol ether such as polyoxyethylenepolyoxypropylenecetyl ether or the like. As polyhydric alcohol derivatives, sorbitan fatty acid ester such as sorbitanmonolaurate, sorbitan-monopalmitate, sorbitan-monostearate, sorbitantriorate or the like; and polyethylene sorbitan fatty acid ester such as polyoxyethylene sorbitan-monolaurate, polyoxyethylene sorbitan-monopalmitate,

polyoxyethylene sorbitan-triorate or the like may be used.

An amount of these surfactants for the treatment is preferably about 0.01-10% by weight against titanium oxide.

As coupling agents, alkyl titanate is typical and as alkyl titanate, isopropyltitanate salt such as isopropyltriisostearoyltitanate, isopropyltrioctanoyltitanate, isopropyltri (dioctylpyrophosphate)-titanate, isopropylmethacryldiisostearoyltitanate, isopropyltrimethacrylisostearoyltitanate, isopropyltridodecylbenzensulfonyltitanate, isopropylldiacrylisostearoyltitanate, isopropyltri(dioctylphosphate)titanate, isopropyl-4-aminobenzenesulfonyldi(dodecylbenzenesulfonyl) titanate, isopropyltrimethacryltitanate, isopropyltricumylphenyltitanate, isopropylldi(4-aminobenzoyl)isostearoyltitante, isopropyltriacryltitanate, isopropyltri(N-ethylaminoethylamino)titanate, isopropyltri(2-aminobenzoyl)titanate, isopropyltri (butyl,octylpyrophosphate)titanate di(octyl hydrogen)phosphate addition compound, di(butyl, methylpyrophosphate)isopropyltitanate di(dioctyl, hydrogen) phosphite addition compound, titanium oxyacetate salt such as titaniumisostearatemethacrylaceteoxyacetate, titaniumacrylateisostearateoxyacetate, titaniumdimethyacrylateoxyacetate, titaniumdi(cumulphenylate)oxyacetate

titaniumdi(dioctylpyrophosphate)oxyacetate, titanium diacrylate-oxyacetate, titanium di(butyl, octylpyrophosphate)di(dioctyl, hydrogenphosphite)oxyoxyacetate, titanium di(butyl, octylpyrophosphate)di(dioctyl, hydrogenphosphite)oxyoxyacetate,



titanium di(butyl, octylpyrophosphate)di(dioctyl, hydrogenphosphite)oxyacetate addition compound and ethylene titanate such as diisostearylethylene titanate, di(dioctylphosphate)ethylene titanate, 4-aminobenzensulfonyldodecylbenzensulfonyl ethylenetitanate, di(dioctylpyrophosphate)ethylenetitanate, di(butyl, methylpyrophosphate ethylenetitanate di(dioctyl, hydrogenphosphite)addition compound, tetraisopropyl di(dioctylphosphite)titanate, tetraoctyloxytitanium di(di-tridecylphosphite), tetra(2 diacryloxy-methyl-1-butoxy)titanium di(di-tridecyl)phosphite addition compound may be used. The amount of these alkyl titanate for surface-treatment of titanium oxide is to be 0.1-3% by weight against titanium oxide and 0.2-1.5% by weight is especially preferable. As polyhydric alcohol, the one having two hydroxyl groups in one molecule such as ethylene glycol, propylene glycol, 1,3-dihydroxy

butane, 1,4-dihydroxy butane, pentamethylene glycol, 2,5-dihydroxy-hexane, 2,4-dihydroxy-2-methyl pentane, heptamethylene glycol, dodecamethylene glycol and others, the one having three hydroxyl groups in one molecule such as trimethylol ethane, trimethylol propane, glycerol, 2,4-dihydroxy-3-hydroxymethyl pentane, 1,2,6-hexanetriol, 2,2-bis(hydroxymethyl)-3-butanol and others and the one having 4 hydroxyl groups in one molecule such as pentaerythritol and others may be used.

Besides the above, an amine, p-diketone chelate and the like may also advantageously be used as the surface treating agents in the invention.

As for such amines which may be used therein, a primary amine such as ethanol amine, laurylamine, butanolamine or the like, a secondary amine such as diethanolamine, N-methylauryl amine, N-methylethanolamine or the like, a tertiary amine such as triethanolamine, N,N-dimethylaurylamine, N,N,-dibutylpropanol amine or the like may be included, for example.

An amount of these amines to be used in a coating process is preferably of the order of from about 0.01% by weight to 10% by weight of titanium oxide used.

The useful β -diketone chelates include, for example, an acetylacetone chelate such as acetylacetonecalcium, acetylacetonaluminium, acetylacetone magnesium or the like, a

benzoylacetone chelate such as benzoylacetonepotassium, benzoylacetonecopper, benzoylacetonealuminium or the like, a benzoyltrifluoracetone chelate such as benzoyltrifluoracetonesodium, benzoyltrifluoracetone magnesium or the like, a furoylacetone chelate such as furoylacetonealuminium, furoylacetone calcium, furoylacetone titanium or the like, a trifluoracetylacetone chelate such as trifluoracetylacetone manganese, trifluoracetylacetonecobalt, trifluoracetylacetonebarium or the like, a dibenzoylmethane chelate such as dibenzoylmethane magnesium, dibenzoylmethane indium, dibenzoylmethane calcium or the like.

An amount of these β -diketone chelates to be used in a coating process is preferably of the order of from about 0.01% by weight to 10% by weight of titanium oxide used.

The processes for coating the abovementioned surface treating agents of the invention over to the surfaces of titanium/oxide/particles include, for example, a process in which titanium oxide is dipped in a solution prepared by dissolving the surface treating agent of the invention into a solvent, and the solvent is removed by an evaporation, and the remaining matter is dried up; another process in which titanium oxide is sprayed with a solution prepared by dissolving the surface treating agent of the invention into a solvent, and the solvent is removed therefrom, and the remaining matter is dried up; a further process in which the

surface treating agent of the invention is finely liquid-grained and they are mixed up in titanium oxide; and the like processes. Among the abovementioned processes, the first-mentioned process is preferred to apply.

As a method for causing surface-treated titanium oxide of the present invention to be dispersed and contained in thermoplastic resins, a method for causing surface-treated titanium oxide to be added and dispersed in glycols such as ethylene glycol and others to make slurry and for causing the slurry to be added to polymer-forming precursor, a method for melting and mixing by the use of the kneader such as a

mixer, a mixer, a heating and kneading roll, a double-shaft screw kneader and a kneader and a method for adding and mixing polymer materials when they are melted and formed, are given and in those methods, there is no restriction for the timing and the order of adding thereof, namely, they may be added any time during the period that ends up with film-forming.

As titanium oxide used in the invention, titanium oxide (IV) of rutile and/or anatase form is useful. Since the titanium oxide used in the invention is much higher than the resin of the invention in refractive index (2.5 to 2.75 versus 1.66 for PET), it can give to the photographic image excellent light reflectivity and resolving power on photographic image used in the support of a photographic material.

Titanium oxide used in the invention has an average particle size from 0.1 μ m, to 0.5 μ m, and substantially contains no particles not smaller than 50 μ m. If an average particle size exceeds the range of the invention, effective reflectivity, opacity and whiteness are hard to be obtained. Even in case of titanium oxide with an average particle size within the range of 0.1 to 0.5 μ m, its particles would occasionally be reaggregated together in the resin of the invention to form secondary particles even larger than 50 μ m, causing various problems such as the lack of tear strength during forming a stretching of the film; the loss of smoothness, glossiness as well as mechanical strength of the polyester-based film; and further, the occurrence of white spot-like defects on the photographic image when a photographic layer is provided, which is not desirable as a photographic material. The titanium oxide used in the invention, therefore, for the preferred embodiment, shall not only contain no particles larger than 50 μ m substantially but also be dispersed into the resin of the invention and formed so as to not be reaggregated to particles larger than 50 μ m.

The content of the above white pigment in the resin of the invention is preferably 10 to 50 parts by weight per 100 parts by weight of the resin, and especially preferably 15 to 30 parts by weight per 100 parts by weight of resin, in terms of whiteness, stretchability and the like of the support film.

As white pigment usable in combination with said titanium oxide of the invention in the white pigment of the invention, there are cited one or plural kinds of inorganic pigments such as barium sulfate, silica, talc, and calcium carbonate. It is preferable that the dose of such white pigment dose not exceed 10 parts by weight per 100 parts by weight of resin of the invention.

In the support of the invention, other additives normally used such as, for example, fluorescent brightener, dyes, ultraviolet ray absorbing agent, antistatic agent or the like are allowed to be contained therein within the range that does not harm the object of the invention.

To make the support film for the reflective photographic material of the invention, the resin of the invention is mixed with said white pigment of the invention, melted, extruded through a slit die, and quenched with a rotating drum or the like to obtain an amorphous sheet. The obtained sheet may be stretched lengthwise and widthwise in the order of respective direction or simultaneously, at a temperature between the glass transition point (T_g) and 130°C . The stretching ratio is preferably from 4 to 16 on the basis of area, for the purpose of satisfying the mechanical strength and dimensional stability of the support film. Then the film is preferably heat-set and annealed.

The thickness of the support film of the invention is preferably 50 to 300 μ m, and further preferably 75 to 250 μ m. A film thinner than 50 μ m would be apt to wrinkle because of its poor stiffness. A film thicker than 300 μ m would be hard to handle because of its thickness which is too thick.

It is preferable that the transmission factor for whole visible light of the support of the invention is 20% or less for the sufficient visual opacity and whiteness and 10% or less is more preferable. Accordingly, both the content of white pigment and the stretching ratio of the support film material are selected so that the thickness of the support of the invention will preferably be 50-300 μ m and more preferably 75-250 μ m and the transmission factor for whole visible light is 20% or less and preferably 10% or less.

In the invention, photo-sensitive emulsion layers are applied onto at least one side of the support film made in the above manners and opaqued and whitened. In this case, before applying of such photo-sensitive emulsion layers, certain surface active treatment such as corona discharging and/or coating of subbing layer may be given to the support at need.

Reflective photographic materials of the invention may be applied to any reflective materials with a certain reflective support, regardless of black and white or color, and may be used for photographic structural layers regardless of the

number and the sequence of photographic layers including photo-sensitive emulsion layers, intermediate layers, protective layers, filter layers, and backcoat layers.

The photographic emulsion layer in the invention is a common silver halide photographic emulsion layer, which preferably contains an emulsion of silver chloride, silver bromide, silver chlorobromide, silver iodobromide, and/or silver chloriodobromide, for example. Such a layer is allowed to contain either couplers to build a color image, or a hydrophilic polymer other than gelatin such as polyvinyl alcohol and polyvinylpyrrolidone as a binder. In addition, said silver halide emulsion layer can be also sensitized by a cyanine or merocyanine dye at the photo-sensitive wavelength range, and can preferably be incorporated into with various other photographic additives including antifoggants; chemical sensitizers containing gold or sulfur; hardeners, and antistaic agents. Thus, the reflective photographic material of the invention is effective in processing of both black and white development, and coupler-containing or uncontained color development.

As described above, the reflective photographic material of the invention is very suitable for either showing or recording use due to excellence in resolving power as well as preservability for photographic image, whiteness, opacity and glossiness of the resulting photographic image, because of no

permeation of photographic processing liquid through the cut edge of the support.

EXAMPLES

Further description of the invention is given based on an example as follows, but the mode of embodiment of the invention is not limited to the example.

Example 1

A composition of 100 parts by weight of PET resin with an intrinsic viscosity of 0.74 (phenol/tetrachloroethane [60/40 wt/wt], 20°C), and 25 parts by weight of anatase-form titanium oxide with an average particle size of 0.24μm and maximum particle size of 0.72μm which had preliminarily surface-treated with alumina and silica, was melted, and extruded from a slit die onto a rotating quenching drum to make an amorphous sheet 1.6mm thick. The obtained sheet was stretched lengthwise through stretching at 90°C, and then trebled widthwise at 110°C, and heat-set at 220°C to make a film for the support of the invention. The thickness of the obtained film was 180μm. To evaluate its opacity, the transmission factor for whole visible light was measured with a digital turbidimeter (Model T-2600DA: Tokyo Denshoku Co., Ltd.). The results are shown in Table 1.

The above support film was subcoated on its one side, and was applied on the same side with a common gelatin-silver

halide photographic emulsion used commonly for color photographic paper so as to form an emulsion layer 15 μ m thick after drying. The sample No.1 among thus obtained samples of the reflective photographic material of the invention was print-exposed to be a dense-line chart for determining resolving power, and was subjected to a usual color developing treatment, and then the difference in the optical density on the dense-line printed image was determined with a microdensitometer (Model PDM-5; Konishiroku Photo Industry Co., Ltd.). The resolving power was defined as the ratio of the difference between the maximal and minimal densities on the 5 lines/mm-print image to the difference between the maximal and minimal densities on the 0.1 line/mm-print image in percentage.

The spectral reflectance over 380 to 780 nm of a white portion of the sample after developing treatment, was measured with a spectrophotometer (Model 320; Hitachi, Ltd.), and then the whiteness of the sample was calculated there-from according to JIS-Z-8722(1982). The reflectance at 20°/20° of the sample was obtained with a glossmeter according to JIS-Z-8741, Method 4, and the glossiness in percentage was determined. The results are shown in Table 1.

Sample No.2 of this example of the reflective photographic material of the invention was obtained in the same manner as for Sample 1, except for using rutile-form

titanium oxide surface-treated with alumina and zinc stearate and having an average particle size of $0.26\mu\text{m}$ and maximum particle size of $0.82\mu\text{m}$ instead of anatase-form titanium oxide surface-treated with alumina and silica in white pigment contained in film support for photographic use for Sample 1.

Sample No.3 of this example was obtained in the same manner as for Sample 1, except for using 25 parts by weight of anatase-form surface-untreated titanium oxide (IV)(average particle size $0.2\mu\text{m}$) instead of surface-treated titanium oxide for Sample 1.

Sample No.4 of this example was further obtained in the same manner as for Sample 1, except for using mixed white pigment of both 15 parts by weight of anatase-form titanium oxide (IV)(average particle size $0.2\mu\text{m}$) surface-treated with alumina and silica, and 10 parts by weight of calcium carbonate (average particle size $0.6\mu\text{m}$), instead of titanium oxide for Sample 1.

Each of Samples No.2, No.3 and No.4 was exposed and developed, and its characteristics were determined in the same manner as for Sample No.1. The results are shown in Table 1.

Table 1

Sample No.	Support thick., μm	Transmission factor for whole visible light, %	White- ness, %	Glossi- ness, %	Resolving power, %
Inv.1	180	5	92	92	72
Inv.2	180	7	95	92	70
Ref.3	180	5	93	90	63
Ref.4	180	10	85	82	55

It proves from Table 1 that the reflective photographic material of the invention is considerably better in resolving power as well as whiteness and glossiness of the resulting photographic image compared with reference though the opacity is excellent in both invention and reference samples. In addition, no aging changes of the photographic image possibly due to the permeation of residual processing solution from the cut edges of the support film were observed at all.

Example 2

A composition of 100 parts by weight of PET resin with an intrinsic viscosity of 0.74 (phenol/tetrachloroethane [60/40 wt/wt], 20°C), 8 parts by weight of barium sulfate having an average particle size of 0.6 μm and 17 parts by weight of rutile-form titanium oxide (IV) surface-treated with alumina and having an average particle size of 0.2 μm , was melted and kneaded and extruded from a slit die onto a rotating quenching

drum to make an amorphous sheet 1.1mm thick.

The amorphous sheet thus obtained was trebled longitudinally at 90°C and then was stretched laterally at 110°C and further was heat-set at 220°C to make a film for the support of the invention for photographic use.

The thickness of the support film for photographic use thus obtained was 125 μ m. In order to evaluate the opacity of the sample, a digital turbidimeter Model T-2600DA (Tokyo Denshoku Co., Ltd.) was used for the measurement of the transmission factor for whole visible light. The results are shown in Table 2.

Aforesaid support film for photographic use, after the corona discharging treatment therefor, was subcoated and then was coated on the same side of subcoating with a gelatinsilver halide photographic emulsion used commonly for color photographic paper so as to form an emulsion layer 15 μ m thick after drying. Sample No.5 of reflective photographic material was thus prepared.

Sample No.5 of reflective photographic material obtained in the way described above was evaluated in the same manner as for Example 1. The results are shown in Table 2.

Table 2

Sample No.	Support thick., μm	Transmission factor for whole visible light, %	White- ness, %	Glossi- ness, %	Resolving power, %
Inv.5	125	8	92	95	67

WHAT IS CLAIMED IS:

1. A photographic material characterized by that photosensitive emulsion layers are applied on at least one side of a support film of thermoplastic resin essentially comprised of polyester resin that contains white pigment containing 90% by weight or more of surface-treated titanium oxide having an average particle size of $0.1\mu\text{m}$ to $0.5\mu\text{m}$ and having substantially no particles whose size is $50\mu\text{m}$ or more.
2. The photographic material according to claim 1, wherein the thickness of said support film of thermoplastic resin is $50\mu\text{m} \sim 300\mu\text{m}$ and the transmission factor for whole visible light is 20% or less.
3. The photographic material according to claim 2, wherein said polyester resin is polyethylene terephthalate.
4. The photographic material according to claim 3, wherein the intrinsic viscosity of said polyethylene terephthalate at a temperature of 20°C of phenol/tetrachloroethane (60/40 ratio by weight) is $0.4 \sim 1.0$.
5. The photographic material according to claim 2, wherein said surface-treated titanium oxide is titanium oxide surface-treated with at least one selected from the group of an

oxygen bond- or hydroxyl group bond-carrying aluminum compound or silicon compound, metallic soaps, surfactants, coupling agents and polyhydric alcohol.

6. The photographic material according to claim 5, wherein said surface-treated titanium oxide is further surface-treated with at least one of those selected from metallic soap, surfactant, coupling agent and polyhydric alcohol.

7. The photographic material according to claim 2, wherein titanium oxide is rutile-form and/or anatase-form titanium oxide (IV).

8. The photographic material according to claim 2, wherein the content of white pigment is 10 ~ 15 parts by weight against 100 parts by weight of thermoplastic resin.

9. The photographic material according to claim 2, wherein thermoplastic resins consist of polyester resin.

10. The photographic material according to claim 2, wherein a white pigment consists of surface-treated titanium oxide.