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(54) **Silver halide photographic material.**

(57) A silver halide photographic material having formed on one of its surfaces at least one silver halide emulsion layer and a nonsensitive hydrophilic colloidal layer forming the outermost layer is disclosed. Said nonsensitive hydrophilic colloidal layer contains substantially spherical fine organic particles having an average size of 1.5 to 2.5 microns and such a size distribution that the frequency of particles smaller than 4 microns is at least 95%.

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SILVER HALIDE PHOTOGRAPHIC MATERIAL

BACKGROUND OF THE INVENTION

1. Field of the Invention:

The present invention relates to a silver halide photographic material, and more particularly, to a silver halide photographic material having improved surface properties.

2. Description of the Prior Art:

Silver halide photographic materials generally consist of a support having formed on one of its surfaces a certain number of photosensitive and non-sensitive layers superimposed in a certain order. At least one silver halide emulsion layer is present as the photosensitive layer, and the outermost layer consists of a nonsensitive hydrophilic colloidal layer containing as a binder a hydrophilic colloid typified by gelatin. When these silver halide photographic materials are wound, rewound or transported in the course of their manufacture or service (e.g. picture-taking, development, printing and projection of motion pictures), the contact or friction of the photographic materials between themselves or other objects will cause scratches or abrasions on the surface of the photographic materials or reduce their drivability within the camera or projector. In particular, silver halides are sensitive not only to light but also to pressure, and any surface

defects will cause pressure fog or desensitization which eventually leads to an irreparable damage to the photographic image obtained. In order to avoid these defects, methods have been proposed for improving the physical properties of a silver halide photographic material by either increasing the resistance of a photographic layer to abrasion or reducing the sliding friction of the surface of the photographic material. These methods aim at making the photographic material adequately resistant to abrasions and improving its drivability in cameras or projectors.

According to one method for reducing the sliding friction at the surface of the photographic material, a high-boiling organic solvent, solid paraffin or whale oil is dispersed in a hydrophilic colloid used in the outermost layer. This method effectively attains the intended object. However, in a hot and humid atmosphere, the high-boiling organic solvent or other additives in the hydrophilic colloid come to the surface and increase the adhesiveness or stickiness of the photographic material. If such "bleeding" photographic materials come into contact with each other or with other objects, they easily stick to each other to cause "blocking". There is another defect with the use of a high-boiling organic solvent. The stability of the organic solvent in a dispersion of the hydrophilic colloid depends on the viscosity of the dispersion or the concentration of a surface active

agent, so it is difficult to prepare a stable colloidal dispersion.

U.S. Patent No. 3,121,060 shows the use of ester compounds for reducing the dynamic friction of silver halide photographic materials. However, the ester compounds have poor dispersibility and the preparation of a homogeneous and stable dispersion of fine particles is difficult. The dispersed particles easily aggregate to form clumps which are undesirable from a viewpoint of easy application of the dispersion when making the outermost layer.

The ester compounds shown in Japanese Patent Application (OPI) No. 14163/76 (the symbol OPI as used herein means an unexamined published Japanese patent application are also effective in reducing the sliding friction, but they cause an undesired side effect in that a photosensitive film material containing them are devitrified upon development.

Because of this complexity of factors that are associated with the efforts toward improving the surface properties of silver halide photographic materials, none of the methods so far proposed have proved completely satisfactory in all aspects of the photographic materials ranging from their manufacture through processing to image viewing.

SUMMARY OF THE INVENTION

Therefore, the primary object of the present invention is to provide a silver halide photographic material having its surface properties, particularly slip properties, improved without sacrificing other properties such as resistance to blocking and devitrification.

This object of the present invention can be accomplished by a silver halide photographic material having formed on one of its surfaces at least one silver halide emulsion layer and a non-sensitive hydrophilic colloidal layer forming the outermost layer, said non-sensitive hydrophilic colloidal layer containing substantially spherical fine organic particles having an average size of 1.5 to 2.5 microns and such a size distribution that the frequency of particles smaller than 4 microns is at least 95%.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The silver halide photographic material of the present invention is characterized by the following two aspects: 1) a non-sensitive hydrophilic colloidal layer is formed one surface of a support as the outermost layer; and 2) this non-sensitive hydrophilic colloidal layer has incorporated therein substantially spherical fine organic particles having an average size of 1.5 to 2.5 microns and such a size distribution that the frequency of particles

smaller than 4 microns is at least 95% (such particles are hereunder simply referred to as the fine organic particles or grains of the present invention).

It has been known to incorporate organic or inorganic fine particles in the outermost layer of a silver halide photographic material. However, in the prior art, the fine particles are used primarily for the purpose of reducing the stickiness of the surface of the photographic material by matting or increasing the surface roughness. So, when a coating solution is prepared from a dispersion of the fine particles, it often occurs that aggregates form to make the formation of a uniform coating impossible. Furthermore, the aggregates reduce the slip properties of the photographic material and may cause other side effects such as impaired transparency and image quality. However, the silver halide photographic material of the present invention is clearly distinguished from the prior art technique by the two features shown above. More specifically, the silver halide photographic material of the present invention has its surface properties, in particular slip properties, improved and is capable of effectively preventing the occurrence of scratches or abrasions that may lead to pressure fog or desensitization without sacrificing other desired properties such as transparency and resistance to blocking.

The fine organic particles of the present invention are either high-molecular weight compounds in a sub-

stantially spherical form that are synthesized by suspension polymerization or those which have been converted to a substantially spherical form by spray drying or other suitable methods. These high-molecular weight compounds include polymethyl methacrylate, cellulose acetate propionate, polystyrene, benzoquanamine-formaldehyde condensate, as well as alkali-soluble foraminous polymers made of acrylic acid and methyl acrylate. Illustrative monomers that can be synthesized to high-molecular weight compounds by suspension polymerization include styrene and styrene derivatives such as alkylstyrenes (e.g. o-methylstyrene, m-methylstyrene, p-methylstyrene, p-ethylstyrene, 2,4-dimethylstyrene, p-butylstyrene, p-tertiary-butylstyrene, p-hexylstyrene, p-octylstyrene, p-nonylstyrene, p-decylstyrene and p-dodecylstyrene), alkoxystyrenes (e.g. p-methoxystyrene), arylstyrenes (e.g. p-phenylstyrene) and halogenated styrenes (e.g. p-chlorostyrene and 3,4-dichlorostyrene); olefins such as ethylene, propylene, butylene and isobutylene; vinyl halides such as vinyl chloride, vinylidene chloride, vinyl bromide and vinyl fluoride; vinyl esters such as vinyl acetate, vinyl propionate, vinyl benzoate and vinyl butyrate; acrylate esters such as methyl acrylate, ethyl acrylate, butyl acrylate, isobutyl acrylate, propyl acrylate, octyl acrylate, dodecyl acrylate, 2-ethylhexyl acrylate, phenyl acrylate and methyl α-chloroacrylate; methacrylate esters such as methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate, isobutyl methacrylate, octyl methacrylate, dodecyl methacrylate, 2-ethylhexyl

methacrylate, stearyl methacrylate, phenyl methacrylate, dimethylaminoethyl methacrylate and diethylaminoethyl methacrylate; acrylic acid or methacrylic acid derivatives such as acrylonitrile, methacrylonitrile and acrylamide; vinyl ethers such as vinylmethyl ether, vinylethyl ether and vinylisobutyl ether; vinyl ketones such as vinyl methyl ketone, vinyl hexyl ketone and methylisopropenyl ketone; N-vinyl compounds such as N-vinylpyrrole, N-vinylcarbazole, N-vinylindole and N-vinylpyrrolidone; as well as vinylnaphthalene. These monomers may be synthesized to homopolymers or copolymers. For the purpose of the present invention, polymethyl methacrylate is particularly preferred.

The average size of the fine organic particles of the present invention is generally determined on the basis of a size distribution curve as obtained by size-frequency analysis of these grains. Specifically, the light transmission method depending on liquid sedimentation is used. The size-frequency of the fine organic particles is generally determined on the basis of a size-frequency curve as also obtained by size-frequency analysis of these grains. The size-frequency curve is also obtained by a known method of measurement of particle size in the fine particle art, but, specifically the light transmission method depending on the fine organic particles is used. The way of obtaining the size-frequency curve is described in detail in, for example, "A Method of Measurement of Particle Grain Size" compiled by the Society for Research in Particle Engineering, published by Yoken-Do (1965). The size distribution such that the frequency of grains smaller than 4 microns is at least 95% means that the cumulative frequency of grains smaller than 4 microns

is at least 95% in number of the whole grains present.

According to the present invention, the organic fine grains have an average size of 1.5 to 2.5 microns. If their average size is less than 1.5 microns, the silver halide photographic material of the present invention is not given high blocking resistance. If their average size exceeds 2.5 microns, the resulting photographic material has an improved resistance to blocking but then its transparency and compatibility with writing instruments are impaired. According to the present invention, the organic fine grains are also required to have such a size distribution that the frequency of grains smaller than 4 microns is at least 95%, but it is particularly preferred that these grains are substantially free of coarse particles.

In the present invention, the fine organic grains are generally incorporated in the non-sensitive hydrophilic colloidal layer in an amount ranging from 10 to 500 mg, preferably 20 to 200 mg, per square meter of the final silver halide photographic material.

The silver halide photographic material of the present invention has formed on one surface of a support at least one silver halide emulsion layer and a non-sensitive hydrophilic colloidal layer forming the outermost layer. Aside from these requirements, there is no upper limit for the maximum number of the silver halide emulsion layers and the non-sensitive layers that may be included

in the present invention. Furthermore, these photographic layers may be arranged in any order. A typical example is a silver halide photographic material having formed on one surface of a support at least one unit of photosensitive silver halide emulsion layers having different degrees of photosensitivity to substantially the same color. This unit of sensitive layers has sensitivity to blue, green or red light, and even a multi-layer silver halide color photographic material capable of general color reproduction is included in the category of the silver halide photographic material of the present invention. A multi-layer silver halide color photographic material generally consists of a support coated with a sequence of red-, green- and blue-sensitive layers, the red-sensitive layer being the closest to the support. This order may be reversed or modified in various ways. Units of photosensitive layers may optionally be interposed with nonsensitive hydrophilic colloidal layers such as filter layers or intermediate layers. In each unit, the photosensitive silver halide emulsion layers are typically arranged in such a manner that a layer having the highest sensitivity is disposed the farthest from the support and the sensitivity decreases gradually toward the support. A nonsensitive hydrophilic colloidal layer may be disposed between each photosensitive silver-halide emulsion layer.

According to the present invention, a non-sensitive

hydrophilic colloidal layer is formed on one surface of a support as the outermost layer. This is usually a non-sensitive surface protective layer and has incorporated therein a hydrophilic colloid as a binder. The thickness of this non-sensitive hydrophilic colloidal layer generally ranges from 0.1 to 3 microns, perferably from 0.3 to 1 microns. Gelatin is preferred as the hydrophilic colloid. Any of the gelatins that are conventionally used in the art may be used and they include lime-treated gelatin, acid-treated gelatin, enzyme-treated gelatin, as well as gelatin derivatives and modified gelatins. These gelatins may be replaced by proteins such as colloidal albumin and casein, cellulose compounds such as carboxymethyl cellulose and hydroxyethyl cellulose, polyvinyl alcohol, poly-N-vinyl pyrrolidone, polyacrylic acid copolymer, polyacrylamide, as well as derivatives or partial hydrolyzates thereof. These colloids may be used in combination with themselves.

The fine organic grains according to the present invention may be incorporated in the non-sensitive hydrophilic colloidal layer in a conventional manner. For example, a solution containing gelatin and a surface active agent is mixed with the fine organic grains and the mixture is homogenized to form a uniform dispersion.

The non-sensitive hydrophilic colloidal layer according to the present invention may contain an organic fluorocompound in order to provide a further improved

blocking resistance. Suitable organic fluorocompounds include linear or cyclic compounds having at least three fluorine atoms and at least three carbon atoms, and any types of compounds, i.e. cationic, nonionic, anionic or betaine, may be used with advantage. Particularly preferred compounds are anionic organic fluorine-containing surfactants. The organic fluorocompound is used in an amount ranging from 0.1 to 500 mg, preferably from 1 to 200 mg, per square meter of the non-sensitive hydrophilic colloidal layer in which said compound is incorporated.

The non-sensitive hydrophilic colloidal layer forming the outermost layer in the present invention may further contain dispersed colloidal silver. The layer may also contain substantially undeveloped, fine grains of silver halide as shown in U.S. Patents Nos. 3,050,391, 3,140,179 and 3,523,022. The layer may further contain a lipophilic additive such as UV absorber.

The non-sensitive hydrophilic colloidal layer used in the present invention may be processed by any of the known hardeners, which include ketone compounds such as diacetyl and dichloropentanedione; compounds having a reactive halogen such as bis(2-chloroethylurea), 2-hydroxy-4,6-dichloro-1,3,5-triazine, and those shown in U.S. Patents Nos.3,635,718, 3,232,763, 2,732,316, 2,586,168, 3,103,437, 3,117,280, 2,983,611, 2,725,294, 2,725,295, 3,100,704, 3,091,537, 3,321,313 and 3,543,292, as well

as British Patent No. 994,869.

When forming the non-sensitive hydrophilic colloidal layer, one or more surfactants may be employed for various purposes such as facilitating the coating application, emulsification, sensitization, improving the photographic characteristics, and preventing static buildup or blocking of photographic materials. The surfactants that can be used in the present invention are classified into natural surfactants such as saponin; nonionic surfactants such as alkylene oxides, glycerins and glycidols; cationic surfactants such as higher alkylamines, quaternary ammonium salts, pyridine and other hetero compounds, phosphonium and sulfonium compounds; anionic surfactants containing acidic groups such as carboxylic acid, sulfonic acid, phosphoric acid, sulfate ester and phosphate ester groups; and amphoteric surfactants such as amino acids, aminosulfonic acids, and sulfate or phosphate esters of amino alcohols. Several of the compounds that can be used as surfactants are shown in various prior art references: U.S. Patents Nos. 2,271,623, 2,240,472, 2,288,226, 2,739,891, 3,068,101, 3,158,484, 3,201,253, 3,210,191, 3,294,540, 3,441,413, 3,442,654, 3,475,174, 3,545,974, German Patent Application (OLS) No. 1,942,665, and British Patents Nos. 1,077,317 and 1,198,450.

The non-sensitive hydrophilic colloidal layer according to the present invention may contain other various photographic additives depending on specific needs.

The silver halide photographic material of the present invention has at least one silver halide emulsion layer formed on a support. Any known techniques may be used for the silver halide emulsion layers, support and optional non-sensitive layers such as anti-halation layer, filter layer, intermediate layer, and subbing layer.

The silver halides that are incorporated in the silver halide emulsion layers of the photographic material of the present invention have silver halide grains dispersed in the hydrophilic colloid. Suitable silver halides are silver bromide, silver chlorobromide, silver iodobromide and silver chloroiodobromide. These silver halides may be prepared by various methods such as the ammoniacal method, neutral method, acid method, as well as the conversion method and double-jet method described in British Patent No. 635,841 and U.S. Patent No. 3,622,318.

These silver halide grains may be dispersed in hydrophilic colloids which are the same as those employed for forming the non-sensitive hydrophilic colloidal layer. The silver halide emulsions shown above may be chemically sensitized by known techniques. They may be optionally subjected to spectral sensitization or supersensitization by cyanine dyes such as cyanine, merocyanine and carbocyanine used either alone or in combination with themselves or with styryl dyes.

Various compounds may be incorporated in the photographic emulsions in order to prevent a sensitivity drop

or fog from occurring during the manufacture, storage or processing of the photographic material. For this purpose, a great number of compounds are known and they include 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene, 3-methylbenzothiazole, 1-phenyl-5-mercaptotetrazole, as well as many heterocyclic compounds, mercury containing compounds, mercapto compounds and metal salts.

If the silver halide photographic material of the present invention is a multi-layer color photographic material capable of general color reproduction, it may use the following yellow, magenta and cyan couplers. Conventionally, open-chain ketomethylene compounds are used as yellow couplers, and among them, benzoylacetanilide and pivaloylacetanilide types are extensively used. Two-equivalent type compounds may also be used wherein the carbon atom at a coupling site is substituted by a split-off group that can be eliminated upon coupling reaction. Typical yellow couplers are shown in U.S. Patents Nos. 2,875,057, 3,265,506, 3,664,841, 3,408,194, 3,447,928, 3,277,155, 3,415,652, Japanese Patent Publication No. 13576/74, and Japanese Patent Applications (OPI) Nos. 29432/73, 66834/73, 10736/74, 122335/74, 28834/75 and 132926/75.

Suitable magenta couplers include pyrazolone, pyrazolotriazole, pyrazolinobenzimidazole and indazolone compounds. Typical magenta couplers of pyrazolone type are shown in

U.S. Patents Nos. 2,600,788, 3,062,653, 3,127,269, 3,311,476, 3,419,391, 3,519,429, 3,558,318, 3,684,514, 3,888,680, Japanese Patent Applications (OPI) Nos. 29639/74, 111631/74, 129538/74, 13041/75, 105820/76, Japanese Patent Applications Nos. 134470/75 and 156327/75. Typical magenta couplers of pyrazolotriazole type are shown in British Patent No. 1,247,493 and Belgian Patent No. 792,525. Typical magenta couplers of pyrazolinobenzimidazole type are shown in U.S. Patent No. 3,061,432, German Patent No. 2,156,111 and Japanese Patent Publication No. 60479/71. Typical magenta couplers of indazolone type are shown in Belgian Patent No. 769,116.

Suitable cyan couplers are phenolic and naphtholic couplers. These cyan couplers are shown in, for example, U.S. Patents Nos. 2,423,730, 2,474,293, 2,801,171, 2,895,826, 3,476,563, 3,737,316, 3,758,308, 3,839,044, Japanese Patent Applications (OPI) Nos. 37425 /72, 10135/75, 25228/75, 112038/75, 117422/75 and 130441/75.

Colored magenta couplers and colored cyan couplers may also be used in the present invention with advantage. "DIR" compounds may also be incorporated in the silver halide emulsion layers. The latter may further incorporate any suitable photographic additives such as agents to prevent dye discoloration and stain.

Preferred examples of the support on which the nonsensitive hydrophilic colloidal layers, silver halide emulsion layers and other nonsensitive layers are formed

include cellulose ester films such as nitrocellulose and acetyl cellulose; polyester films such as polyethylene terephthalate; polyvinyl acetal, polyvinyl chloride, polystyrene and polycarbonate films; baryta paper and polyethylene-coated paper.

The coating method for forming the nonsensitive hydrophilic colloidal layer, the silver halide emulsion layers and other photosensitive layers must be properly determined in order to ensure uniform quality and high process efficiency. Suitable coating methods are dip coating, double-roll coating, air knife coating, extrusion coating and curtain coating. The extrusion coating and curtain coating are particularly useful because either method permits the simultaneous formation of two or more layers. The coating speed may be selected at any value, but for ensuring high process efficiency, a speed not lower than 30 m/min is preferred. The hardener and other components which are so highly reactive that they form a gel if they remain long in the coating solution are preferably mixed in a static mixer with the coating solution just before the latter is applied to the support.

The photographic material of the present invention has many applications such as black-and-white photography, X-ray photography, printing, microphotography, recording with electron beams, IR recording and color photography.

In order to form an image, the silver halide photographic material of the present invention is first exposed

and subsequently developed by any of the known methods. Preferred color developers for use in the present invention contain aromatic primary amine compounds as the olor developing agent. Typical color developing agents are p-phenylenediamine compounds such as diethyl-p-phenylenediamine hydrochloride, monomethyl-p-phenylenediamine hydrochloride, dimethyl-p-phenylenediamine hydrochloride, 2-amino-5-diethylaminotoluene hydrochloride, 2-amino-5-(N-ethyl-N-dodecylamino)-toluene, 2-amino-5-(N-ethyl-N-ß-methanesulfonamidoethyl)-aminotoluene sulfate, 4-(N-ethyl-N-ß-methanesulfornamidoethylamino)-aniline, 4-(N-ethyl-N-ß-hydroxyethylamino)aniline, and 2-amino-5-(N-ethyl-N-ß-methoxyethyl)aminotoluene.

After the development, the developed silver and silver halide are removed by a sequence of conventional steps including bleaching, fixing (the two steps may be combined into a single step of bleach-fixing), rinsing and drying.

The silver halide photographic material of the present invention has its surface properties, especially slip properties, improved without sacrificing other desired properties such as transparency and blocking resistance. Therefore, scratches or abrasions due to contact or friction are less likely to occur on the surface of the photographic material in the course of its manufacture of service, and an image free from such defects as pressure fog and desensitization can be produced.

The present invention is now described in greater detail by reference to the following examples, to which the embodiments of the invention are by no means limited.

EXAMPLE 1

Twenty samples of a blue-sensitive silver iodobromide emulsion (with 7 mol% of silver iodide) were prepared from a mixture of 300 g of gelatin, 2.5×10^{-2} mol of a yellow coupler or α-pivaloyl-α-(1-benzyl-2,4-dioxy-imidazoline-3-yl-2-chloro-5-{γ-(2,4-tertamylphenoxy)-butylamido}acetanilide, and a hardener or 1,2-bis(vinylsulfonyl)ethane. The respective amounts are based on one mol of the silver halide. Twenty samples of a coating solution for the protective layer were also prepared from the formulation indicated below.

Protective layer

Binder: gelatin

Matting agent: see Table 1

Coating aid: sodium di-2-ethylhexylsulfosuccinate

Hardener: 1,2-bis(vinylsulfonyl)ethane

The respective silver halide emulsions and coating solutions for the protective layer were applied to subbed triacetyl cellulose film bases simultaneously in a superimposed fashion by the slide hopper method at a coating speed of 50 m/min. The silver halide emulsion layers overlied the protective layers. The webs were

dried to a thickness of 6.8 μ and the resulting samples of silver halide photographic material were numbered 1 to 20 (silver content = 5.6 mg/m^2). The respective samples were tested for their slip properyies, blocking resistance and transparency by the methods indicated below. Thereafter, the samples were exposed to white light in a sensitometer (Model KS-1 of Konishiroku Photo Industry Co., Ltd.) according to the method specified in the JIS, processed with the solutions shown in connection with the description of the procedures of transparency testing, and checked for their sensitometric characteristics. The results of the three tests and sensitometric analysis are shown in Table 1. The sensitivity is shown in Table 1 in terms of relative values, with that of comparative sample (No. 10) taken as 100.

Testing methods:

1. Slip properties

a) Dynamic friction coefficient of each sample was measured in accordance with the method shown in ASTM D-1814. Before the measurement, the sample had its moisture content conditioned by being held at 23°C for 24 hours both at 55% r.h. and 80% r.h. The values shown in Table 1 are indicative of the coefficient of dynamic friction against a backing paper for roll film.

b) The abrasion causing load was measured by scratching the surface of each film with a stylus (head: 0.1 mm^{ϕ})

that was given varying loads until a first abrasion developed.

2. Blocking resistance

A pair of test pieces (5 cm x 5 cm) cut from each sample were held at 23°C and 80% r.h. for 24 hours. Then, the two test pieces were superimposed so that the respective protective layers are in a face-to-face relationship. The superimposed test pieces were pressed at a load of 800 g and held in a hot and humid atmosphere (40°C x 80% r.h.) for 24 hours. Thereafter, the load was removed and the test pieces were peeled from each other. The blocking resistance of each sample was evaluated by the area where two test pieces adhered to each other. The indices of rating were as follows.

Rating	Blocking area (%)
A:	0 - 20
B:	21 - 40
C:	41 - 60
D:	61 - 80
E:	81 or more

3. Transparency

A set of unexposed samples No. 1 to No. 20 were processed according to the following schedule and dried. The turbidities of the color images on the respective samples were measured with a nephelometer of Nippon Seimitsu Kogyo K.K.

Processing steps (38°C)	Time
Color development	3 min. 15 sec.
Bleaching	6 min. 30 sec.
Water rinsing	3 min. 15 sec.
Fixing	6 min. 30 sec.
Water rinsing	3 min. 15 sec.
Stabilization	1 min. 30 sec.

The respective processing solutions had the following compositions.

Color developer:

4-amino-3-methyl-N-ethyl-N-(ß-hydroxy-ethyl)aniline sulfate	4.75 g
Anhydrous sodium sulfite	4.25 g
Hydroxylamine hemisulfate	2.0 g
Anhydrous potassium carbonate	37.5 g
Sodium bromide	1.3 g
Trisodium nitrilotriacetate (monohydrate)	2.5 g
Potassium hydroxide	1.0 g
Water to make	1,000 ml
pH	10.0

Bleaching solution:

Ethylenediaminetetraacetic acid iron (III) ammonium salt	100.0 g
Diammonium ethylenediaminetetraacetate	10.0 g
Ammonium bromide	150.0 g
Glacial acetic acid	10.0 g
Water to make	1,000 ml
pH	6.0

Fixing solution:

Ammonium thiosulfate (50% aqueous sol.)	162 ml
Anhydrous sodium sulfite	12.4 ml
Water to make	1,000 ml
pH	6.5

Stabilizing solution:

Formalin (37% aqueous sol.)	5.0 ml
Konidax (product of Konishiroku Photo Industry Co., Ltd.)	7.5 ml
Water to make	1,000 ml

Table 1

	Sample	Matting agent				Friction coefficient		Abrasion resistance (g)	Trans-parency (ppm)	Blocking resist-ance	Sensitometric characteristics	
		Compound name	Amount (mg/m^2)	Average grain size (μ)	Frequency of grains smaller than 4μ(%)*	23°C x 55% r.h.	23°C x 80% r.h.				Sens-itivity	Fog
Samples of the present invention	1	Polymethyl-methacrylate	65	1.63	99	0.26	0.34	195	22	A	102	0.15
	2	do.	130	1.63	99	0.25	0.32	230	30	A	100	0.15
	3	do.	65	2.10	98	0.24	0.35	190	20	B	101	0.15
	4	do.	130	2.10	98	0.24	0.32	235	31	A	101	0.14
	5	do.	65	2.41	98	0.23	0.33	195	23	A	100	0.15
	6	do.	130	2.41	98	0.24	0.31	235	32	A	99	0.14
	7	Benzoguanamine-formaldehyde condensate	65	1.64	99	0.24	0.31	235	23	A	101	0.15
	8		130	1.64	99	0.23	0.28	230	31	A	99	0.15
	9	do.	130	2.31	96	0.24	0.29	235	33	A	99	0.15

(Cont'd)

Table 1 (Cont'd)

	Sample	Matting agent			Friction coefficient		Abrasion resistance (g)	Transparency (ppm)	Blocking resistance	Sensitometric characteristics	
		Compound name	Amount (mg/m2)	Average grain size (μ)	Frequency of grains smaller than 4μ(%)*	23°C x 55% r.h.	23°C x 80% r.h.				Sensitivity	Fog
Comparative Samples	10	Polymethylmethacrylate	65	1.32	98	0.29	0.53	190	24	B	100	0.16
	11	do.	130	1.32	98	0.28	0.48	225	32	A	97	0.15
	12	do.	65	2.43	85	0.29	0.45	185	22	B	101	0.16
	13	do.	130	2.43	85	0.29	0.41	230	31	A	100	0.15
	14	do.	65	3.41	75	0.28	0.43	185	24	A	99	0.16
	15	do.	130	3.41	75	0.29	0.40	235	32	A	97	0.14
	16	do.	130	3.43	97	0.27	0.41	235	34	B	96	0.15
	17	Benzoguanamine-formaldehyde condensate	130	2.36	88	0.28	0.38	230	33	A	98	0.15
	18	do.	130	3.44	83	0.28	0.36	235	32	A	97	0.15
	19	SiO_2	65	3.5	67	0.38	0.39	185	35	E	100	0.15
	20	SiO_2	130	3.5	67	0.37	0.38	210	49	C	98	0.15

* Measured with automatic grain size-distribution analyzer CAPA-500 (manufactured by Horiba, Ltd., Japan).

As shown in Table 1, given the same amount of matting agent for unit area, sample Nos. 1 to 9 using the fine organic grains having the average size and size frequency defined in the present invention had significantly improved slip properties over comparative sample Nos. 10 to 20 without sacrificing the transparency, blocking resistance and sensitometric characteristics. In both the unprocessed and processed samples of the present invention, the fine organic grains remained uniformly dispersed without forming aggregates.

EXAMPLE 2

A subbed triacetyl cellulose film base was coated with the following layers, the first layer being the closest to the base.

First layer:

Anti-halation layer containing black colloidal silver (dry thickness: 1 μ).

Second layer:

Red-sensitive silver iodobromide emulsion layer (dry thickness: 6 μ, with 8 mol% silver bromide) containing, per mol of silver halide, 6.8×10^{-2} mol of a cyan coupler or 1-hydroxy-N-{γ(-2,4-di-tertamylphenoxy)-butyl}-2-naphthamide, 1.7×10^{-2} mol of a colored coupler or 1-hydroxy-N-{δ-(2,4-di-tert-amylphenoxy)-butyl}-4-(2-ethoxycarbonylphenylazo)-2-naphthamide, and

4×10^{-3} mol of a DIR compound or 2-(1-phenyl-5-tetrazolylthio)-4-(2,4-di-tertamylphenoxyacetamido)-1-indanone.

Third layer:

Green-sensitive (low sensitivity) silver iodobromide emulsion layer (dry thickness: 3.5 μ, with 8 mol% silver iodide) containing, per mol of silver halide, 5.8×10^{-2} mol of a magenta coupler or 1-(2,4,6-trichloro)-phenyl-3-{3-(2,4-di-tert-amylphenoxy)acetamido}benzamido-5-pyrazolone, 1.7×10^{-2} mol of a colored coupler or 1-(2,4,6-trichlorophenyl)-3-{3-(octadecenylsuccinimido)-2-chloro}anilido-4-(γ-naphthylazo)-5-pyrazolone and 7×10^{-3} mol of a DIR compound or 2- (1-phenyl-5-tetrazolylthio)-4-(2,4-di-tertamylphenoxyacetamido)-1-indanone.

Fourth layer:

Green-sensitive (high sensitivity) silver iodobromide emulsion layer (dry thickness: 2.5 μ, with 6 mol% silver iodide) containing, per mol of silver halide, 1.1×10^{-2}, 5×10^{-3} and 2×10^{-2} mol, respectively, of a magenta coupler, colored coupler and DIR compound which were the same as those used in the third layer.

Fifth layer:

Gelatin layer (dry thickness: 1 μ) containing yellow colloidal silver and 2,5-di-tert-octylhydroquinone.

Sixth layer:

Blue-sensitive silver iodobromide emulsion layer

(dry thickness: 6 μ, with 7 mol% silver iodide) containing, per mol of silver halide, 350 g of gelatin, 3×10^{-1} mol of a yellow coupler or α-pivaloyl-α-(1-benzyl-2-phenyl-3,5-dioxotriazolidine-4-yl)-5'-{α-(2,4-di-tert-amylphenoxy)butylamido}-2'-chloroacetanilide and a hardener or 1,2-bis(vinylsulfonyl)ethane.

On the sixth layer, protective layers having the basic formulation indicated below were formed so as to provide sample Nos. 21 to 25 of silver halide color photographic material.

Protective layer:
Binder: gelatin
Matting agent: see Table 2.
Coating aid: sodium di-2-ethylhexylsulfosuccinate
UV absorber: dispersion of Tinuvin PS 320 and 326
Hardener: 1,2-bis(vinylsulfonyl)ethane
Dry thickness: 0.8 μ

The respective samples were dried and tested for their slip properties, blocking resistance and transparency as in Example 1. Thereafter, the samples were exposed to white light in a sensitometer (Model KS-1 of Konishiroku Photo Industry Co., Ltd.), processed with the same solutions as used in Example 1, and subsequently evaluated for their sensitometric characteristics sensitivity and fog). The results of the tests and sensitometric analysis are shown in Table 2. The sensitivity and fog having the same meanings as in Example 1

were measured for the three different dyes, blue (B), green (G) and red (R).

As is clear from Table 2, sample Nos. 21 to 23 of the present invention had high blocking resistance and transparency and yet exhibited better slip properties than comparative sample Nos. 24 and 25. The improvement in the slip properties of the samples of the present invention was more marked in a humid atmosphere than in a relatively dry atmosphere. No adverse effects on the photographic characteristics accompanied the improvement in the slip properties. The improved slip properties were not lost even after the photographic materials of the present invention were subjected to photographic processing. In both the unprocessed and processed films, the fine organic grains according to the present invention were uniformly dispersed and formed no visible aggregates.

Table 2

	Sample	Matting agent: Compound name	Amount (mg/m^2)	Average grain size (μ)	Frequency of grains smaller than 4μ(%)	Friction coefficient: 23°C x 50% r.h.	23°C x 80% r.h.	Abrasion resistance (g)	Transparency (ppm)	Blocking resistance	Sensitivity: B	G	R	Fog: B	G	R
Sample of the present invention	21	Polymethyl-methacrylate	130	1.63	99	0.24	0.33	235	30	A	100	99	100	100	100	99
	22	do.	130	2.41	98	0.25	0.32	230	33	A	99	100	100	100	100	100
	23	Benzo-guanamine-formaldehyde condensate	130	2.31	96	0.24	0.30	235	32	A	100	99	99	99	99	100
Comparative samples	24	Polymethyl-methacrylate	130	2.43	85	0.29	0.38	225	34	B	99	101	99	99	100	100
	25	SiO_2	130	3.5	67	0.30	0.45	215	48	C	100	100	100	100	100	100

WHAT IS CLAIMED IS:

1. A silver halide photographic material having formed on one of its surfaces at least one silver halide emulsion layer and a nonsensitive hydrophilic colloidal layer forming the outermost layer, said nonsensitive hydrophilic colloidal layer containing substantially spherical fine organic particles having an average size of 1.5 to 2.5 microns and such a size distribution that the frequency of particles smaller than 4 microns is at least 95%.

2. A silver halide photographic material according to Claim 1, wherein said organic particles are comprised of particles of a high-molecular weight compound selected from the group consisting of polymethyl methacrylate, cellulose acetate propionate, polystyrene and benzoguanamine-formaldehyde condensates.

3. A silver halide photographic material according to Claim 2, wherein said organic particles are comprised of particles of a polymethyl methacrylate compound.

4. A silver halide photographic material according to Claim 1, wherein said colloidal layer contains said organic particles in an amount of 10 to 500 mg per square meter.

5. A silver halide photographic material according to Claim 4, wherein the content of said organic particles is 20 to 200 mg per square meter.

6. A silver halide photographic material according to Claim 1, wherein said colloidal layer further contains an organic fluoro compound.