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[54] **PHOTOGRAPHIC SILVER HALIDE
LIGHT-SENSITIVE ELEMENT WITH
GELATIN SUBBING LAYER**

[72] Inventors: **Fumihiko Nishio; Nobuo Tsuji; Teppei Ikeda; Hideo Kawaguchi**, all of Kanagawa, Japan

[73] Assignee: **Fuji Photo Film Co., Ltd.**, Kanagawa, Japan

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[51] Int. Cl.....**G03c 1/80**

[58] Field of Search**96/87, 87 A**

[56]

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Primary Examiner—Ronald H. Smith

Attorney—Sughrue, Rothwell, Mion, Zinn & Macpeak

[57]

ABSTRACT

A photographic element having a subbing layer comprising at least one member selected from the group consisting of (1) a glycidyl methacrylate homopolymer, (2) a glycidyl acrylate homopolymer, (3) a copolymer of glycidyl methacrylate and a copolymerizable vinyl compound, (4) a copolymer of glycidyl acrylate and a copolymerizable vinyl compound which prevents sticking of the photographic element is disclosed.

8 Claims, No Drawings

PHOTOGRAPHIC SILVER HALIDE LIGHT-SENSITIVE ELEMENT WITH GELATIN SUBBING LAYER

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a photographic silver halide element having a subbing layer, in particular, wherein sticking is prevented. The term "sticking" as used herein means the phenomenon that occurs when a subbing layer is brought into contact with another layer or surface and removed, the contacted surface is contaminated with contact marks and, in extreme cases, the subbing layer or support surface is stripped off or scratched.

2. Prior Art

In making a photographic silver halide element (hereinafter referred to as "photographic element"), a hydrophobic film used as a support, is coated with a hydrophilic silver halide emulsion layer on one side and with a back layer on the opposite side. In this case, adhesion of the surface of the support with the silver halide emulsion layer or back layer is strengthened by use of a subbing layer or substratum therebetween. Since this subbing layer is generally hydrophilic, sticking often occurs between the subbing layers coated on both surfaces of the support, between the subbing layer and a silver halide emulsion layer coated on another surface, or between the subbing layer and a back layer coated on another surface, during the steps of making a photographic element, as for example, winding up in the form of a roll or sticking in the form of a sheet. Furthermore, sticking often occurs between the subbing layer and a spindle when the subbing layer is brought into contact with the heated spindle during the making step.

Previous attempts to prevent sticking by incorporating water or organic solvent-insoluble fine particles, such as starch, barium sulfate, silica gel or titanium oxide, in a protective layer, a subbing layer or a back layer of a photographic element to mat the surface have been unsatisfactory and, in particular, have been accompanied by difficulty in dispersing such material in a coating solution to be applied to a subbing layer of a photographic element. For example, if a coating solution containing such material is allowed to stand for a long time, the material settles through aggregation. If the solution has the low viscosity of the coating solution used for a subbing layer of a photographic element, the dispersion is so unstable that the material added for matting the surface settles. Therefore, production of a stable dispersion for subbing is extremely difficult.

It is an object of this invention to provide a subbing composition for a photographic element, which is capable of resisting storage for a long time.

It is another object of the invention to provide a subbing layer of a photographic element, which is sufficiently protected from sticking.

DESCRIPTION OF THE INVENTION

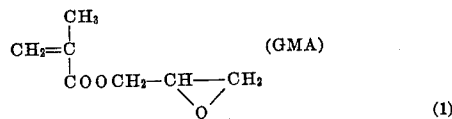
The above-mentioned objects can be accomplished by incorporating a homopolymer of glycidyl methacrylate, hereinafter referred to as GMA, a homopolymer of glycidyl acrylate, hereinafter referred to as GA, or a copolymer of a vinyl monomer with GMA or GA into a subbing layer of a photographic element.

The subbing layer of this invention containing a homopolymer of GMA or GA or copolymer of vinyl monomer with GMA or GA minimizes the effects of sticking. Although not desiring to be bound by theory, it is believed that sticking is minimized due to the fact that the fine particles of polymer mat the surface of the film and the gelatin hardening action of the glycidyl group of the polymer decreases the hygroscopic characteristics of the subbing layer.

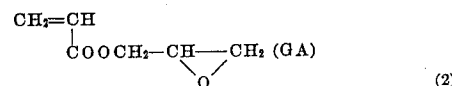
The subbing composition containing a homopolymer of GMA or GA or a copolymer of vinyl monomer with GMA or GA is so stable, unlike dispersions containing known matting agents, that no aggregation or settling of grains occurs even on

standing for a long period of time. Furthermore, the foregoing components of the subbing layer for the photographic element according to this invention have no adverse influence on the adhesion of the silver halide emulsion layer or back layer to a support. Not only is this an essential role of a subbing layer, but also this results in a further strengthening of the adhesion through the gelatin hardening action of the glycidyl group present in the foregoing polymer.

The polymer to be incorporated in a subbing layer of a photographic element according to this invention is a homopolymer of GMA represented by the following formula (1):



or a homopolymer of GA represented by the following formula (2):



or a copolymer of GMA or GA with a vinyl monomer. The copolymer may be a terpolymer containing two or more vinyl monomers.

The vinyl monomer to be copolymerized with GMA or GA is a monomer which will substantially copolymerize with GMA or GA, which will not react with the glycidyl group during emulsion polymerization and which will effect emulsion polymerization even though extremely soluble in water. Suitable vinyl monomers are, for example, alkyl acrylates, said alkyl group having from one to four carbon atoms; alkyl methacrylates, said alkyl group having from one to four carbon atoms; other substituted alkyl acrylates; acrylamide derivatives; methacrylamide derivatives; vinyl halides such as vinyl chloride; vinylidene halides, such as vinylidene chloride; vinylpyrrolidone; other N-vinylamides; vinylpyridines; styrene; styrene derivatives such as α -methyl styrene; butadiene; isoprene; acrylonitrile; methacrylonitrile, and the like.

The proportion of GMA or GA in the copolymer of GMA or GA with the vinyl monomer is preferably 3 mol percent or more. When it is less than 3 mol percent, sticking is not prevented.

The aqueous polymer dispersion of this invention is prepared by emulsion-polymerizing the monomer in an anionic surface agent, such as lauryl alcohol sulfate, sodium alkylbenzenesulfonate and sodium, 1,3-p-nonylphenoxy-5,8,11-trioxatridecane-1-sulfonate. The emulsion polymerization can be carried out in any conventional manner. For example, an aqueous polymer dispersion can be obtained by adding to deaerated distilled water the monomer in a proportion of from 10 to 60 percent by weight, a suitable amount of the anionic surface active agent as a dispersing agent and a water-soluble polymerization initiator such as potassium persulfate and, if necessary, polymerization additives, stirring the mixture vigorously and then heating the mixture at from 50° to 90° C. for several hours.

The grain size of the polymer in the aqueous polymer dispersion of the invention can be controlled by the conditions of the emulsion polymerization as in the conventional manner, for example, by controlling the amount of the surface active agent as the dispersing agent, the stirring condition, the reaction time and the reaction temperature. The grain size is preferably within a range of from 0.05 to 1 micron.

The amount of the aqueous polymer dispersion of the invention applied to the subbing layer preferably ranges from 4

mg./m.² to 200 mg./m.² based on the weight of the polymer. When the amount is less than the above, the sticking preventing effect is small. When the amount is more than the above, the adhesion of a subbing layer to an emulsion layer or back layer tends to deteriorate. When the subbing layer or layers have been dried, an ordinary gelatin silver halide emulsion is coated thereon and dried.

To eliminate any tendency to curl, the other subbed surface is overcoated with a gelatin composition which contains no silver halide, but which can contain, if desired, antistatic agents, filter dyes, antihalation agents, and the like.

The photographic elements produced as above described are characterized by firm adherence of the layers to one another and to the hydrophobic film support without sticking, and shows excellent dimensional stability under testing, use and storage conditions.

A silver halide photographic emulsion layer, an antihalation layer, a backing layer and the like, which are coated on the subbed film support, are not specifically limited to those described, so long as the subbing layer mentioned above is employed.

The silver halide photographic emulsion can contain a silver chloride emulsion, a silver bromide emulsion, a silver chlorobromide emulsion, a silver bromiodide emulsion, a silver chlorobromiodide emulsion, and the like. The photographic elements, of course, can have multiple silver halide emulsion layers.

According to this invention, an aqueous dispersion of a homopolymer of GMA or a homopolymer of GA or a copolymer of GMA or GA with a vinyl monomer can be added to a coating solution for subbing as used in the prior art, as it is. The thus added solution is coated onto a hydrophobic film support to obtain a subbing layer having a sufficient sticking preventing effect. Suitable hydrophobic film supports are supports of cellulose derivatives such as cellulose triacetate, cellulose diacetate, cellulose acetate butyrate and cellulose acetate propionate, polyethylene terephthalate, polycarbonate, polyvinyl chloride, or polystyrene.

The subbing composition contains an aqueous gelatin solution, a solvent, such as acetone, methylene chloride, ethylene chloride, trichloroacetate or phenol, to swell the hydrophobic film support, and a water-soluble organic solvent, such as acetone or methanol. The solvent used to swell the hydrophobic film support and water-soluble organic solvent can be the same. These compounds are well known in the prior art of subbing compositions, and therefore, are not to be considered as limiting. Other compounds can, if desired, be added to the composition.

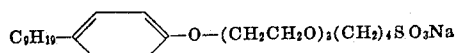
The following examples are given in order to illustrate the invention. They are not to be considered as limiting the scope of the invention. All parts are to be taken as parts by weight.

PREPARATION EXAMPLE 1

800 parts of deaerated distilled water, 120 parts of GMA, purified by distillation, and 180 parts of butyl methacrylate were added to a closed-type, glass-lined reactor equipped with a temperature regulator, a stirrer, a reflux condenser, a heater and a gas inlet and purged with nitrogen gas. 5.0 parts of sodium laurylbenzenesulfonate, as a dispersing agent, was then added thereto and the reaction mixture was stirred vigorously at 500–800 r.p.m. for emulsification. Then, 0.15 part of ammonium persulfate and 0.05 part of sodium acid sulfite, as polymerization initiators, were added thereto and heated with stirring at 90°–100° C. After 6 hours, the polymerization was completed. The grain size of the solid polymer in the thus resulting aqueous dispersion of copolymer of GMA and butyl methacrylate was about 0.1–0.3 micron, measured using an electron microscope.

PREPARATION EXAMPLE 2

Using the same apparatus as used in Preparation Example 1, 1,754 parts of distilled water, 80 parts of GMA, 106 parts of butyl methacrylate, 9.3 parts of



as a dispersing agent, and 0.5 part of potassium persulfate as a polymerization initiator were processed in a manner similar to that mentioned in Preparation Example 1 to obtain an aqueous polymer dispersion having a GMA to butyl methacrylate copolymerization ratio of 4 to 6 by mol. The grain size of the solid polymer in the thus resulting aqueous dispersion was 0.1–0.2 micron.

PREPARATION EXAMPLE 3

Using the same apparatus as was used in Preparation Example 1, the procedure of Preparation Example 1 was repeated with the exception that 80 parts of GA and 100 parts of styrene as the monomers were used, thus obtaining a stable aqueous copolymer dispersion having a grain size of 0.1–0.3 micron.

In the following Examples, estimating the sticking preventing effect of the subbing layer was carried out as follows. Samples were cut to a size of 35 mm.×35 mm. The coated surfaces were faced toward each other, and a 2 kg. weight was placed on the samples. The samples were allowed to stand for a day and night in a thermostat at a temperature of 30° C. and at a relative humidity of 80 percent. Thereafter, the ratio of the area suffering sticking to the whole area was measured.

EXAMPLE 1

Both surfaces of a polyethylene terephthalate film support of 100 microns in thickness and 30 cm. in width biaxially stretched and heat fixed were radiated at 100° C. in the air using a mercury lamp of quartz of 1 kw. for 2 minutes and directly coated with a subbing solution, followed by drying at 120° C. for 3 minutes. The following composition was used as the subbing solution. Comparison of sticking was carried out in cases in which 0, 0.5, 1.0 and 1.5 parts of the aqueous dispersion of the copolymer of GMA and butyl methacrylate, prepared by the procedure of Preparation Example 1 (Copolymerization ratio:GMA:butyl methacrylate=6:4) were added.

Subbing Solution

Gelatin	1 part
Water	2 part
Monochloroacetic Acid	2 part
Phenol	5 part
Methanol	35 part
Methylene Chloride	57 part

The results of the subbed film relative to the prevention of sticking are as follows:

No.	Amount of Aqueous Copolymer Dispersion (part)	Area Suffering Sticking (%)
1	0	25
2	0.5	10
3	1.0	0
4	1.5	0

As is evident from the results shown above, sticking is prevented remarkably when the aqueous dispersion of the copolymer of GMA and butyl acrylate is added.

EXAMPLE 2

Both surfaces of a polyethylene terephthalate film support of 75 microns in thickness and 31 cm. in width, biaxially stretched and heat fixed, was radiated with ultraviolet light at

80° C. for 1 minute in the air using a mercury lamp of quartz of 1 kw. and directly coated with a subbing solution having the following composition to which each of various aqueous dispersions of a copolymer of GMA and butyl acrylate, differing in the copolymerization ratio, had been added, followed by drying at 120° C. for 2 minutes.

Subbing Solutions

Gelatin	1 part
Water	2 part
Trichloroacetic Acid	2 part
Methanol	40 part
Methylene Chloride	43 part
Phenol	6 part
Tetrachloroethane	6 part
Copolymer Aqueous Dispersion	2 part
(polymer solid = about 9%)	

The results relative to the prevention of sticking are as follows:

No.	Molar Copolymerization Ratio (GMA/Butyl Methacrylate)	Area Suffering Sticking (%)
1	100/0	3
2	40/60	0
3	5/95	0
4	0/100	20

As can be seen from the results given above, the homopolymer of butyl methacrylate has not sticking preventing effect but the homopolymer or copolymer of GMA prevents sticking remarkably.

EXAMPLE 3

A cellulose triacetate film having a width of 31 cm. and a thickness of 100 microns was coated with a subbing solution having the following composition to which an aqueous dispersion of copolymer of GA and styrene (copolymerization ratio by mol:GA:styrene=4:6) had been added, and then dried at 100° C. for 2 minutes.

Subbing Solution

Gelatin	1 part
Water	2 part
Acetic Acid	1 part

Methanol	60 part
Acetone	30 part
Copolymer Aqueous Dispersion	1.0 part
(polymer solid about 20%)	

With the resulting subbed film, no sticking occurred between the subbing layer and the emulsion layer or the back layer.

What is claimed is:

1. A photographic element comprising a hydrophobic film support having on at least one surface thereof a subbing layer containing gelatin and at least one member selected from the group consisting of particles of (1) of glycidyl methacrylate homopolymer, (2) a glycidyl acrylate homopolymer, (3) a copolymer of glycidyl methacrylate and a copolymerizable vinyl compound, and (4) a copolymer of glycidyl acrylate and a copolymerizable vinyl compound, and having a light-sensitive silver halide emulsion layer coated over at least one of said subbing layer.

2. The photographic element as claimed in claim 1 wherein said copolymerizable vinyl compound is a member selected from the group consisting of acrylic acid; methacrylic acid; alkyl acrylate, said alkyl group having from one to four carbon atoms; alkyl methacrylate, said alkyl group having from one to four carbon atoms; acrylamide; methacrylamide; vinyl chloride vinylidene chloride; N-vinylamide; styrene; alpha-methyl styrene; acrylonitrile; and methacrylonitrile.

3. The photographic element as claimed in claim 1 wherein said copolymer is a member selected from the group consisting of a glycidyl methacrylate-butyl methacrylate copolymer and a glycidyl acrylate-styrene copolymer.

4. The photographic element as claimed in claim 1 wherein said hydrophobic film support is a cellulose derivative selected from the group consisting of cellulose triacetate, cellulose diacetate cellulose acetate butylate, and cellulose acetate propionate.

5. The photographic element as claimed in claim 1 wherein said hydrophobic film support is a synthetic resin film selected from the group consisting of polyethylene terephthalate, polycarbonate, polyvinylchloride and polystyrene.

6. The photographic element as claimed in claim 1 wherein said copolymer contains more than 3 mol percent of glycidyl methacrylate or glycidyl acrylate and less than 97 mol percent of the vinyl compound.

7. The photographic element as claimed in claim 1, wherein said subbing layer is applied as an aqueous dispersion.

8. The photographic element as claimed in claim 1, wherein said particles have a particle size ranging from 0.05 to 1 micron.

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