

[54] SILVER HALIDE PHOTOGRAPHIC
ELEMENTS CONTAINING REMOVABLE
ANTIHALATION LAYER

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[51] Int. Cl. G03c 1/84

[58] Field of Search 96/84, 78

[56] References Cited

UNITED STATES PATENTS

3,488,708 1/1970 Smith 96/84

3,660,153	5/1972	Seto	96/84
3,617,286	11/1971	Kameyama et al.	96/84
2,221,873	11/1940	Knoefel	96/85
2,856,283	10/1958	Yackel et al.	96/64
3,545,972	12/1970	D'Cruz	117/138.8 A

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[57] ABSTRACT

A silver halide photographic element which comprises a polyester support bearing on one surface thereof an antihalation layer which includes a continuous, compatible, solid mixture of anionic polymers including one polymer having a melting point below about 30° C, finely divided conductive carbon, and a particulate phase of a hard, water-insoluble wax.

10 Claims, No Drawings

SILVER HALIDE PHOTOGRAPHIC ELEMENTS CONTAINING REMOVABLE ANTIHALATION LAYER

The present invention relates to the field of silver halide photography, and more particularly relates to silver halide photographic elements which include removable, electrically conductive antihalation layers.

Antihalation layers have long been employed in photography to reduce or eliminate the light-scattering which may occur when light from an imaging source strikes a photographic element and is reflected from an interface therein. Antihalation layers ordinarily are disposed between a light-sensitive layer and the supporting film or on the rear surface of the supporting film, and contain a light-absorber to absorb light which would otherwise be reflected or scattered throughout the photosensitive layer. Such light absorbers have included manganese dioxide, carbon black, various dye-stuffs, and the like.

It has been found that rapid winding and unwinding of photographic film elements may produce static charges, particularly when film elements utilizing extremely non-conductive film backings such as polyester are employed. Discharge of such static charges during winding or unwinding may cause undesirable fogging of silver halide photographic films. It is important, therefore, that a layer of a photographic film element, such as an antihalation layer, be provided with means to drain away accumulated electric charges so as to avoid such problems, e.g., the layer may be made electrically conductive. In addition, an antihalation layer disposed on the backside of a photographic film element must be resistant to scratching and marring which may be caused by the rigors of winding and unwinding of photographic film.

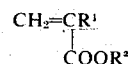
The resistance of an antihalation layer to scratching and marring can be improved by increasing the adhesion of the layer to the supporting substrate, and by increasing the slipperiness, or lubricity, of the layer. Further, it is desirable that antihalation layers be capable of being easily removed from supporting substrates, e.g., by treatment with alkaline photographic processing solutions.

Acceptable adhesion of an antihalation layer to polyester (polyethylene terephthalate) photographic substrates has been difficult to attain. One method for obtaining adhesion employs adhesion-promoting additives such as resorcinol (U.S. Pat. No. 3,201,249). Antihalation layers in general are described in U.S. Pat. Nos. 3,545,972 and 2,976,168. In general, however, increasing the adhesion of a given antihalation layer to a polyester substrate tends to decrease the ease with which the antihalation layer can be removed from the substrate. Further, it has been found necessary to provide photographic films employing a polyester substrate with a greater degree of conductivity than had been necessary with, for example, cellulose triacetate-based photographic film, since polyester-based films are far more apt to develop a lingering static charge during manipulation thereof.

It is accordingly an object of the invention to provide a photographic element having on one surface thereof an antihalation layer which is scratch and mar resistant, is easily removable during photographic processing, and is electrically conductive.

Briefly, the present invention relates to a photographic film element which includes a polyester film support bearing on one surface thereof, as an outer layer, an antihalation layer having a resistivity ("surface" resistivity) of less than 50 megohms/square. The layer comprises:

- a. a continuous phase of a compatible, solid mixture of normally water-insoluble anionic polymers, at least one species thereof being a copolymer of an acrylate monomer of the formula



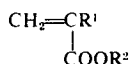
- wherein R¹ and R² are lower alkyl groups and an acid which is acrylic acid or a lower alkyl acrylic acid, said species having a melting point below about 30° C;
 - b. finely divided conductive carbon; and
 - c. a particulate phase of a hard, water-insoluble wax.
- The carbon and the wax are laterally uniformly distributed in the antihalation layer relative to one surface thereof.

The relationship between the continuous polymer phase, the finely divided carbon and the particulate wax phase is such that the outer-most surface of the antihalation layer includes both wax particles and finely divided carbon. Movement of a hard object across the surface under pressure appears to cause the wax particles to deform and coalesce across the surface of the antihalation layer, thus providing lubricity for improved scratch resistance. Lubricity may also be obtained through the use of anionic, nonionic or amphoteric emulsifiers. The finely divided carbon particles on the surface of the antihalation layer provide electrical access through the outer surface of this layer. The anionic nature of the continuous polymer phase permits the polymer mixture to be water-solubilized but not dissolved to any appreciable extent when treated with common alkaline photographic developing solutions. The thus-solubilized continuous polymer phase may then be dissolved in water, resulting in complete removal of the antihalation layer during processing but without contamination of the developer solution.

The continuous polymer phase employs a compatible, solid mixture or normally water-insoluble anionic polymers. As used herein, an anionic polymer is a water-insoluble polymer which is capable of forming a salt in aqueous media with a suitable cation such as a sodium ion. The sodium salts of anionic polymers are water-soluble. The ability of a candidate water-insoluble polymer to form a water-soluble sodium salt may easily be tested by adding a small quantity, e.g., 0.5 grams, of a candidate polymer to 50 ml. of a water solution containing 85 grams of anhydrous sodium sulfite per liter, followed by dilution of the resulting solution with a 10-fold excess of water. The polymer, if anionic, will be dissolved in the latter solution. Most preferred are those anionic polymers which, in the above test, do not dissolve in the initial 50 ml. of aqueous sodium sulfite solution. In practice, it has been found that immersion of photographic elements of the invention into alkali metal-containing, aqueous alkaline photographic developer baths solubilizes the anionic polymers of the antihalation layers thereof (due to formation of the alkali metal salt of the polymers), but ordinarily does not itself cause dissolution of the polymers. Upon subsequent washing with water, the alkali metal

salts of the polymers are dissolved, and the antihalation layer is thus easily removed.

The anionic polymers employed in antihalation layers of photographic elements of the present invention preferably are acrylate polymers and most preferably are copolymers of acrylate monomers of the formula



wherein R^1 is hydrogen or lower alkyl and R^2 is lower alkyl group, and acrylic acid or lower alkyl acrylic acid (e.g., methacrylic acid, etc.). As used herein, "lower alkyl" refers to alkyl groups having no more than about two carbon atoms. Such polymers are known to the art, and the ratio of the acid monomer to the acrylate monomer is chosen so that the resulting polymer is anionic, as defined above. The antihalation layers of the present invention may employ two or more anionic polymers, and these polymers are chosen so that they form, when mixed, a solid, compatible (non-phase-separating) mixture. At least one anionic polymer species of the mixture is a relatively low molecular weight copolymer of an acrylate monomer of the above formula and acrylic or a lower alkyl acrylic acid, which copolymer exhibits a melting point below about 30° C. This polymer species is believed to contribute to the excellent adhesion between antihalation layers of the invention and polyester substrates. It is further believed that this polymeric species tends to plasticize to some extent the other anionic polymer or polymers, thereby contributing flexibility to antihalation layers of the invention. Although the amount of low molecular weight anionic polymer species may vary widely depending upon the nature of the other polymeric species employed, from about 2 to about 30 percent by weight of this low molecular weight polymeric species (based upon the total anionic polymer weight) is preferred.

The hard wax which is utilized in the invention may be any of the water-insoluble hard waxes known to the art such as carnauba wax, candelilla wax, Japan wax, montan wax, beeswax, and the like. Carnauba wax is especially preferred because of its hardness. Waxes utilized in the invention preferably have a melting point below about 100° C and above room temperature. The most preferred waxes (e.g., carnauba wax) have melting points between about 80° C and 100° C so that the antihalation layers may be dried at elevated temperatures without melting of the wax constituent, as will be further described below. The purpose of the wax is to impart lubricity to the antihalation coatings and accordingly any hard, water-insoluble wax may be utilized. The wax is present in antihalation layers of the invention as a particulate phase (as distinguished from a continuous film of wax). The particulate nature of the wax permits the carbon particles to come into contact and provide conductive paths through this layer. Hence, "particulate phase" of wax refers to a wax phase which is sufficiently discontinuous as to permit the presence of continuous carbon electrical paths therethrough. The wax particles themselves may touch each other, and a small amount of coalescence between particles may be permitted without interrupting the continuous carbon electrical pathways. The quantity of wax which is incorporated in an antihalation layer of the invention may vary widely, and it is required only

that enough wax be utilized to provide lubricity and hence scratch resistance to the surface of the layer.

The lubricity (and concurrent scratch and mar resistance) of antihalation layers of the present invention may be further improved by the presence in such layers of anionic, nonionic, or amphoteric wax emulsifiers known to the art. Such emulsifiers include a hydrocarbyl (e.g., alkyl) group of from about 10 to about 18 carbon atoms and a water solubilizing polar group such as $-\text{COOK}$, $-\text{SO}_3\text{K}$, $-(\text{CH}_2\text{CH}_2\text{O})_{10}-\text{H}$, $-\text{OPO}_2\text{Na}_2$, etc. Exemplary of anionic wax emulsifiers are sodium lauryl sulfate, ammonium stearate, etc. Nonionic wax emulsifiers include $\text{C}_{17}\text{H}_{35}\text{CO}_2(\text{C}_2\text{H}_4\text{O})_{14}\text{H}$, $\text{C}_{12}\text{H}_{25}\text{N}[(\text{C}_2\text{H}_4\text{O})_5\text{H}]_2$, etc.; and amphoteric wax emulsifiers include $\text{C}_{12}\text{H}_{25}\text{N}(\text{CH}_3)_2(\text{CH}_2)_2\text{SO}_3$, $\text{C}_{18}\text{H}_{37}\text{N}(\text{CH}_2\text{CH}_2\text{CO}_2\text{Na})_2$, etc. Such emulsifiers may desirably be employed during formation of the relatively stable emulsion which in turn is coated upon a polyester substrate and dried to form antihalation layers of the invention, as will be more particularly described below. Although the amount of emulsifier may vary widely depending upon the various emulsion ingredients, best results from the standpoint of lubricity have been obtained when the emulsifier constituent of the emulsion (and hence of the final antihalation layer) is from about 1.0 percent to about 10 percent on a solids basis. The particulate wax phase described above and the thus-described emulsifier impart excellent lubricity to antihalation layers of the invention.

The conductive carbon constituent provides antihalation layers of the invention with an electrical resistivity of less than 50 megohms/square (preferably less than 10 megohms/square and most preferably less than 1 megohm/square.) Many types and sizes of finely divided carbon are known to the art. It is believed that the formation of conductive paths through the antihalation layers is dependent upon particle-to-particle contact in the finely divided carbon phase. It has been found that carbon particles of the type characterized by highly irregular, fiber-like shapes provide far greater conductivity than do particles which are more regular and compact in nature. Examples of carbon particles of this type are "Vulcan XC-72" and "Vulcan C" (products of the Cabot Corporation) and acetylene black (e.g., from Shawinigan Products Corp). In general, surface resistivity values for antihalation layers of the invention are less than 50 megohms per square, and preferably are less than about 10 megohms per square. Most preferred antihalation layers of the invention have exhibited surface resistivity values of less than 1 megohm per square. The relative amount of carbon which is required in antihalation layers of the invention may vary widely depending upon the relative amounts of wax and polymer phases and upon the nature of the carbon particles.

Antihalation layers of the invention may be prepared by coating onto a film element support a coating fluid which comprises a normally water-insoluble anionic polymer in aqueous alkaline solution, the fluid further having dispersed therein finely divided conductive carbon as described above and a hard, water-insoluble wax. The resulting wet coating is then dried, for example, by a current of warm air. The maximum drying temperature is of course dependent to some extent upon the melting point of the hard wax which is employed. It has been found that drying temperatures of 80° C may be employed when carnauba wax is utilized

as the wax constituent. The coating fluid may be prepared by a method which comprises the steps of

- a. stirring into a molten solution of a hard, water-insoluble wax an anionic, non-ionic, or amphoteric surfactant and water heated to a temperature above the melting point of the wax to form an aqueous dispersion, and
- b. adding said aqueous wax dispersion to a solution of a normally water-insoluble anionic polymer, the sodium salt of which polymer is water soluble, the solution having dispersed therein finely divided conductive carbon.

In preparing the coating fluid of the invention, it has been found desirable to first prepare the water-insoluble hard wax aqueous dispersion. This may be accomplished by first melting the wax in a suitable container and, under agitation, adding a small amount of an anionic emulsifier such as sodium lauryl sulfate (Maprofix 563, a product of Onyx Oil and Chemical Company), Richonol A.M. (ammonium lauryl sulfate, a product of The Richardson Company) to the molten wax. Thereafter, a quantity of water which has been heated to a temperature above the melting point of the wax is slowly added to the molten wax with vigorous agitation and results in a fine dispersion of wax particles in the water.

A second dispersion of finely divided carbon in an aqueous alkaline solution may be prepared by dry blending together (e.g., in a ball mill) finely divided carbon, a dispersing agent (preferably an anionic dispersing agent) and, if desired, a protective colloid which is preferably an alkali-soluble polymer such as acrylamide or an anionic polymer. To the resulting blend is then added an ammoniacal water solution to provide, with further agitation, an aqueous carbon dispersion.

A third separate solution is prepared by dissolving an anionic polymer mixture in water which has been made alkaline by addition of a base such as ammonium hydroxide. Thereafter, the polymer solution, the carbon dispersion and the wax dispersion are combined with vigorous stirring. Viscosity regulators and the like may be added if desired. A viscosity regulator which has been found especially useful is an acrylic latex emulsion (Acrysol ASE-60—a product of Rohm and Haas Company).

The resulting coating fluid may then be coated onto the surface of a polyester film support and dried in a warm current of air. The reverse surface of the supporting film may then be provided with the desired photographic emulsion layers (e.g., silver halide) of the types and by the methods known to the art.

This invention will be further understood by reference to the following illustrative example:

EXAMPLE 1

To 35 g. of molten carnauba wax (Grade 1-yellow) is added, with stirring, 5.4 g. of Maprofix 563 emulsifier (sodium lauryl sulfate, a product of Onyx Oil and Chemical Company). To the resulting mixture of gradually added, with vigorous stirring, 59.6 g. of boiling water. This wax emulsion is stored until used as described below.

A dispersion of carbon in water is prepared as follows: Carbon black (Shawinigan acetylene black, Shawinigan Products Corp., 50 g.), polyacrylamide (Cyanamer P250—a product of American Cyanamid Co., 5

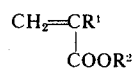
g.) and the sodium salt of condensed naphthalene sulfonic acid (Tamol SN, a product of Rohm and Haas Co., 10 g.) are combined and blended together in a small ball mill for 10 minutes. To the resulting blend is then added 264 g. of deionized water and 4 g. of ammonium hydroxide. The resulting mixture is blended in the ball mill for an additional 24 hours to provide a smooth aqueous carbon dispersion.

To 645.8 g. of deionized water is added 32.5 g. of a 30 percent ammoniacal solution of a solid anionic copolymer of ethyl acrylate and acrylic acid having 525 percent by weight of carboxyl groups (Carboset Resin No. 514, a product of B. F. Goodrich Chemical Company); 7.5 g. of a 50 percent ammoniacal solution of a similar anionic copolymer sold under the trade name Carboset Resin No. 515, a low molecular weight (about 7,000) liquid copolymer of ethyl acrylate and acrylic acid (B. F. Goodrich Chemical Company) and 195 g. of a 10 percent ammoniacal solution of a similar anionic, solid acrylate copolymer sold under the trade name Carboset Resin No. 525 by the same company. The resulting solution is added to 86.5 g. of the carbon dispersion as prepared above over a 20 minute period with vigorous stirring. The pH of the resulting dispersion is adjusted to 10.0 with ammonium hydroxide and 15.2 g. of a 10 percent solution of sodium lauryl sulfate and 8.6 g. of the wax emulsion prepared as above with gentle stirring. To the resulting dispersion is then added 8.9 g. of a 28 percent solids acrylic latex emulsion as a viscosity regulator (Acrysol ASE-60, a product of Rohm and Haas Company). The resulting dispersion is filtered and is then coated upon the surface of a 2.5 mil polyester film to a wet thickness of about 3.0 mils. The coated film is dried in a forced air oven at a temperature of 82° C. The reverse side of the polyester film may then be coated with a silver halide emulsion to form a photographic film element. It is found that the dried antihalation layer has a surface resistivity of less than 1 megohm per square and is capable of resisting scratching by thumbnail pressure.

I claim:

1. A silver halide photographic film element which includes a polyester support bearing on one surface thereof, as an outer layer, an antihalation layer having a resistivity of less than 50 megohms/square, said layer comprising

- a. a continuous phase of a compatible, solid mixture of normally water insoluble anionic polymers, at least one species thereof being a copolymer of an acrylate monomer having the formula



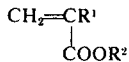
wherein R¹ and R² are lower alkyl, and acrylic or lower alkyl acrylic acid, said species having a melting point below about 30° C;

- b. finely divided conductive carbon; and
- c. a particulate phase of a hard, water-insoluble wax.

2. The photographic element of claim 1 wherein said at least one species is the copolymer of ethyl acrylate and acrylic acid.

3. The photographic element of claim 1 wherein said mixture of anionic polymers comprises a compatible, solid mixture of two or more of said anionic polymers, each derived from an acrylate monomer of the formula

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wherein R¹ and R² are lower alkyl, and acrylic or lower alkyl acrylic acid.

4. The photographic element of claim 1 wherein said antihalation layer includes at least one anionic, non-ionic or amphoteric emulsifier having a hydrocarbyl group of from about 10 to about 18 carbon atoms.

5. The photographic element of claim 4 wherein said emulsifier is employed in said antihalation layer in an amount of from 1.0 to about 10 percent by weight of solids thereof.

6. The photographic element of claim 1 wherein sufficient of said conductive carbon is employed in said antihalation layer to impart to said layer a surface resistivity of not greater than 1.0 megohm/square.

7. The photographic element of claim 1 wherein said wax is carnauba wax.

8. The photographic element of claim 1 wherein said

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emulsifier is sodium lauryl sulfate.

9. A silver halide photographic film element which includes a bare polyester support bearing on one surface thereof, as an outer layer, an antihalation layer having a resistivity of less than 50 megohms/square, said layer comprising

a. a continuous phase of a compatible, solid mixture of normally water insoluble anionic polymers, at least one species thereof being a copolymer of ethyl acrylate and acrylic acid having a melting point below about 30° C;

b. finely divided conductive carbon; and

c. a particulate phase of a hard, water-insoluble wax.

10. The photographic element of claim 9 wherein said antihalation layer includes at least one anionic, non-ionic or amphoteric emulsifier having a hydrocarbyl group of from about 10 to about 18 carbon atoms.

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