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[54] **PHOTOGRAPHIC ELEMENT COMPRISING AN OPAQUE BACKCOAT**

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[51] **Int. Cl.**[2] **G03C 1/84**

[58] **Field of Search** ..... 96/84 M, 87 A, 84 R

[56] **References Cited**

UNITED STATES PATENTS

1,434,453	11/1922	Seel	96/87 A
2,386,627	10/1945	Nadean et al.	96/87 A
2,791,504	5/1957	Plambeck	96/84 R
3,060,025	10/1962	Burg et al.	96/84 R
3,269,252	8/1966	DeKeyser et al.	96/84 R
3,511,660	5/1970	Stevens et al.	96/84 R
3,758,376	9/1973	Beckner et al.	96/84 R
3,793,029	2/1974	Parker	96/84 R
3,832,218	8/1974	Seto	96/84 R

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[57] **ABSTRACT**

A backing or antihalation layer for a photosensitive element containing carbon black additionally contains a salt of a heavy metal. The heavy metal inhibits fog formation in the silver halide emulsion of the photosensitive element.

7 Claims, No Drawings

PHOTOGRAPHIC ELEMENT COMPRISING AN OPAQUE BACKCOAT

BACKGROUND OF THE INVENTION

Photosensitive elements often have light-absorbing layers coated on one side of the silver halide emulsion layer to avoid exposure of an underlying film unit, or as an antihalation layer. For convenience, the light-absorbing layers will be referred to as backing layers. These backing layers may be applied directly to one side of the emulsion or on the reverse side of a support which carries the emulsion. Even though a support separates the emulsion from the backing layer, there can still be contact because in a roll of film some portion of the emulsion will contact the backing. With stacked film units, there is usually front-to-back contact.

The backing layers may be opaque or only sufficiently light-absorbing as to prevent the above-mentioned exposure of the emulsion layer or underlying film units or, as in the case of antihalation layers, sufficiently light absorptive to avoid undesirable reflections from the film base or from interfaces between the emulsion layer and other layers, which, if not avoided, cause additional diffused exposure of the silver halide emulsions.

The above-described light-absorbing qualities of the backing layer may be provided by dyes, pigments or silver. Silver is relatively expensive because of the amount necessary and usually two or three dyes are required in backing layers to provide the desired degree of light absorption.

One of the most commonly used and effective light-absorbing materials is carbon black. However, it is well known that the presence of carbon black in a layer of a film unit adversely effects the silver halide emulsion layer. Specifically, an appreciable fog level is noted, as a function of time on stored film units employing carbon black as a component of the backing layer. Fading of the latent image has also been reported as an effect attributable to the carbon black.

A novel backing layer has now been found which is not susceptible to the deficiencies of the prior art.

SUMMARY OF THE INVENTION

The present invention is directed to a photosensitive element comprising at least one silver halide emulsion layer and a backing layer containing carbon black and a salt of a heavy metal. Preferably, water-soluble salts are employed.

DETAILED DESCRIPTION OF THE INVENTION

It has now been found that water-soluble heavy metal salts capable of forming relatively insoluble sulfides disposed in carbon black-containing layers of film units inhibit fog formation in the silver halide layer to a significant degree. Specifically, water-soluble salts of silver, copper (cupric), platinum, palladium, zinc, cadmium, lead, iron (ferrous and ferric) and bismuth provide the above-described enhanced stability.

It has been found that the cation is the active species in the present invention and, therefore, substantially any anion may be employed so long as it will not deleteriously react with other components of the carbon black layer or interfere with the proper photographic employment of the film unit.

Suitable anions include, but are not limited to, nitrate, fluoride, sulfate, perrhenate, bromide, chloride and acetate. The salt may be added to the carbon black mix prior to coating the layer or may be formed in situ.

While not intending to be bound by theory, it is believed that sulfur or a sulfur-containing compound is associated with the carbon black that results in the fogging of the silver halide during storage. The fact that the silver halide and the carbon black layer are not necessarily in direct, physical contact for fogging to occur indicates that the vapor phase may be involved. It is believed that the presence of the heavy metal salt reacts with the sulfur or sulfur-containing compound, forming an insoluble sulfide thereby rendering it unavailable for contamination of the silver halide.

The concentration of the heavy metal salt varies with the particular salt and with the particular type of carbon black employed. Unexpectedly, appreciable effects have been noted at relatively low levels. Levels ranging from 100 to 10,000 ppm (based on total solids of coating mix) and more have been employed.

It is also believed that it may not be necessary that the heavy metal salt be distributed throughout the entire carbon black coating to be effective. Surprisingly, a significant decrease in fog has been noted in silver halide emulsions in areas of the emulsions not in contact with the compositions of the present invention but surrounding it.

The novel compositions of the present invention were evaluated in the following manner.

The following master batch was prepared:

Elvanol 70-05[1]	25 g.
Elvanol T-25[2]	75 g.
Carbon black	50 g.
GAF S-630[3]	37 g.
Voranol RN-485[4]	21 g.

1. A fully hydrolyzed but water-soluble polyvinyl alcohol sold by E. I. DuPont de Nemours, Inc., Wilmington, Delaware.

2. A medium molecular weight, fully hydrolyzed polyvinyl alcohol sold by E. I. DuPont de Nemours, Inc., Wilmington, Delaware.

3. A polyvinylpyrrolidone/vinyl acetate copolymer sold by GAF Corp., New York, New York.

4. A polyether polyol sold by the Dow Chemical Company, Midland, Michigan.

A water solution of the polyvinyl alcohol and polyvinylpyrrolidone/vinyl acetate copolymer was prepared to which the carbon black was added as an aqueous dispersion. Enough water was used to provide 14.0 percent total solids.

The various salts to be tested were prepared as 1.0 percent solutions in water. In some cases, the mixture contained both dissolved and undissolved material but was treated as if it were all in solution when aliquots are taken.

The carbon black mixes containing the salt additives were coated on an unsubbed polyester film base using a 6.0 mil fixed clearance bar. These coatings were then dried for 3 minutes at 194° F. and then conditioned for 24 hours at 75° F. and 45 percent R.H. before testing.

Pieces 2 × 3¾ inches were cut from the test coatings and interleaved in film packs between a photographic emulsion coated on dye back base; i.e., base with only a dye antihalation layer on the back side and an opaque top layer. The test pieces were placed with the test back coat in contact with the emulsion. The test packs were sealed in polyethylene/foil pouches and stored in

an oven at 120° F. for 5 days after which they are allowed to equilibrate to room conditions. The packs are then processed as black spreads (unexposed) with fresh processing composition and receiving sheets suitable for silver diffusion transfer processing, and the antihalation layer was removed from the negatives. The negatives are then examined by transmitted light for evidence of chemical fog in the area in contact with the test back coat and also in the surrounding area. Each sample was given a visual rating on a scale of 0 to 10 with 0 indicating no fog and 10 indicating complete fog. A control was designated as having a rating of 5.

The effects of the heavy metal salts are tabulated below.

TABLE 1

Cation	Anion	Formula	K_{sp} of Sulfide	RELATIVE CONTAMINATION RATING 100 ppm	500	1,000	5,000	10,000
SILVER	Nitrate	$AgNO_3$	10^{-51}	2	2	0	0	0
	Fluoride	AgF	"			0		0
	Sulfate	Ag_2SO_4	"			0		0
	Perrhenate	$AgReO_4$	"			0		0
COPPER	Sulfate Nitrate Chloride	$CuSO_4 \cdot 5H_2O$	10^{-38}	6	2	1	0	0
PLATINUM	Chloride	K_2PtCl_4	1					0
PALLADIUM	Chloride	K_2PdCl_4	1					0
ZINC	Acetate	$Zn(OAc)_2 \cdot 2H_2O$	10^{-24}	5	5	5	2	0
CADMIUM	Acetate	$Cd(OAc)_2 \cdot 2H_2O$	10^{-28}	5	5	3	2	2
LEAD	Sub-Acetate		10^{-29}	4	4	4	3	2
BISMUTH	Nitrate	$Bl(NO_3)_3 \cdot 5H_2O$	10^{-72}					2
IRON	Chloride	$FeCl_2 \cdot 4H_2O$	10^{-19}			0		
	Nitrate	$Fe(NO_3)_3 \cdot 9H_2O$	d			0		

1 - listed in the literature as forming an insoluble sulfide.
d - listed in the literature as forming a sulfide which decomposes in water.

From the foregoing it will be seen that the fog level of the negative was significantly reduced from the control level of 5 and, in many instances, totally eliminated.

As stated above, the novel compositions are particularly useful as light-absorbing layers and antihalation layers. For example, the novel compositions are particularly useful as the removable backing layer in the film units disclosed and claimed in copending application Ser. No. 239,582, filed Mar. 20, 1972.

It should be understood, however, that the novel compositions are suitable for use wherever a light-absorbing layer is desired, for example, as an opaque backing for a receiving layer, mask, dark slide film package and the like.

What is claimed is:

1. A photographic element which includes at least one silver halide emulsion layer and which also includes a layer containing carbon black and a water-soluble salt of a heavy metal capable of forming a relatively insoluble sulfide.

2. A product as defined in claim **1** wherein said metal is selected from the group consisting of silver, copper, platinum, palladium, zinc, cadmium, lead, iron and bismuth.

3. A product as defined in claim **2** which includes a support carrying said carbon black layer on a first side and said silver halide emulsion layer on said second side.

4. A product as defined in claim **1** wherein said heavy metal salt is silver nitrate.

5. A product as defined in claim **1** wherein said heavy metal salt is present at a level of at least 100 ppm based on the weight of said carbon black layer.

6. A product as defined in claim **1** wherein said carbon black layer includes a polymeric binder.

7. A product as defined in claim **6** wherein said polymeric binder includes polyvinyl alcohol.

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