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PREVENTION OF STATIC IN LIGHT-SENSITIVE PHOTOGRAPHIC MATERIALS USING BIS-AMINIMIDE COMPOUNDS

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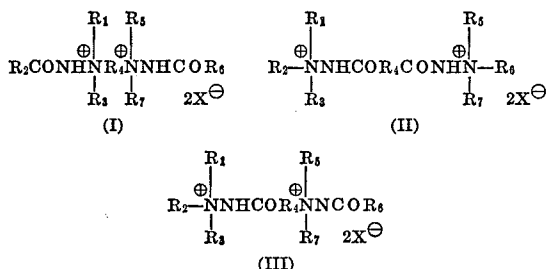
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5 Claims

ABSTRACT OF THE DISCLOSURE

Antistatic agents for use in light-sensitive silver halide photographic materials comprise bis-acyl hydrazinium salts having the formula



wherein R₁, R₃, R₅ and R₇ are individually a lower alkyl group; R₂ and R₆ are individually an alkyl, aralkyl or aryl group or a hetero ring; R₄ is a divalent group; and X is an anion residue.

This invention relates to new bis-acylhydrazinium compounds. More particularly, this invention relates to a light-sensitive silver halide photographic material comprising a bis-acylhydrazinium salt of the general formula shown later.

A principal object of the present invention is to provide a light-sensitive silver halide photographic material less subject to problems caused by static.

Another object of the invention is to provide a light-sensitive radiographic material having improved color tone and a light-sensitive color photographic material having excellent resolution and graininess.

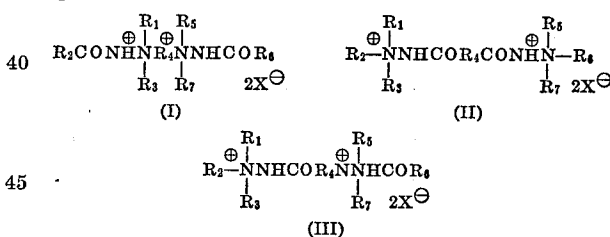
When developed, a light-sensitive silver halide photographic material frequently forms branch-like or fluffy linear spots on the surface thereof. These linear spots are so-called static marks, and it is considered that the formation of such marks is ascribable to the fact that the surface of the light-sensitive material is statically charged due to friction and this static charge is discharged to excite the light-sensitive material. Problems derived from such static charge are not limited merely to the formation of static marks but bring about the adhesion of dust onto the surface of the light-sensitive material. Such static troubles are necessarily brought about at substantially all stages where light-sensitive materials undergo friction, e.g. at stages where photographic emulsions are coated on supports, and the resulting film sheets are cut and packed in boxes, or the sheet films are taken out of the boxes and subjected to photographing, and particularly cinefilms which are subjected to photographing or handled before development. The static troubles are

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brought about also at the time when light-sensitive materials are released. That is, a light-sensitive material, which has been coated with a photographic emulsion and dried, is rolled up, in general, and when this rolled film is successively released in order to subject the film to the subsequent step, a static charge is generated between the surface and the back of the film at the moment when the film is released from the roll. Further, when a light-sensitive photographic printing paper is subjected to ferrotype drying, a static charge is generated between the surface of the film and the metal surface at the time when the printing paper is taken up, to cause the phenomenon that it cannot be superposed immediately on another one.

For the prevention of such static problems, a moisture-absorptive material is frequently incorporated into a certain layer of the light-sensitive material. This procedure, however, is effective only when the humidity is relatively high and is ineffective during dry periods when static problems are brought about frequently. Further, when the humidity is excessively high, the light-sensitive material incorporated with the moisture-absorptive material becomes sticky on the film surface. In addition to such moisture-absorptive material, a considerable number of compounds have been known as antistatic agents. For application to light-sensitive photographic materials, however, they are required to satisfy such conditions as not to have any detrimental effect on the photographic properties of the light-sensitive material such as sensitivity, gradation, fog, storability, etc. Accordingly, it is extremely difficult to find excellent antistatic agents applicable to light-sensitive silver halide photographic materials.

We made extensive studies on antistatic agents having no detrimental effect on light-sensitive silver halide photographic materials to find that compounds of the General Formula I, II or III shown below are excellent antistatic agents.



wherein R₁, R₃, R₅ and R₇ are individually a lower alkyl group; R₂ and R₆ are individually an alkyl, aralkyl or aryl group or a hetero ring; R₄ is a divalent group; and X is an anion residue.

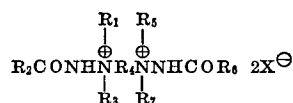
When any of the above-mentioned compounds is incorporated into at least one of the silver halide emulsion layer, sub layer, inter layer, filter layer, antihalation layer, protective layer and backing layer which are constitutive elements of a light-sensitive silver halide photographic material, it is possible to obtain a light-sensitive silver halide photographic material which is extremely less subject to static problems. The incorporation of said compound not only does not have any detrimental effect on the sensitivity, gradation, fog and the like properties of the light-sensitive material but also displays, depending on the kind of light-sensitive material, such favorable effects as to inhibit the fog and enhance the storability of the light-sensitive material. Further, when the compound is applied to a light-sensitive radiographic

material, there is attained the effect, in addition to the prevention of antistatic troubles, that the color tone of the developed silver image can be made bluish black, and when the compound is applied to an internal color photographic emulsion, the dispersibility of the coupler

is enhanced to make it possible to obtain a color photographic material having excellent resolution and graininess.

Typical examples of certain bis-acylhydrazinium salts having the aforesaid general formulas are as follows:

GENERAL FORMULA I

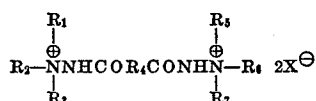


Compound	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	R ₇	X [⊖]
1.....	CH ₃	CH ₃	CH ₃	$\begin{array}{c} \text{OH} \\ \\ \text{CH}_2\text{CHCH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CHCH}_2 \\ \qquad \qquad \qquad \\ \text{CH}_2\text{Cl} \end{array}$	CH ₃	CH ₃	CH ₃	Cl
2.....	CH ₃	C ₁₅ H ₃₁	CH ₃	CH ₂ CH ₂ CH ₂ CH ₂	CH ₃	C ₁₅ H ₃₁	CH ₃	I
3.....	CH ₃	C ₁₁ H ₂₃	C ₂ H ₅	$\begin{array}{c} \text{OH} \qquad \qquad \text{OH} \\ \qquad \qquad \\ \text{CH}_2\text{CH} \text{---} \text{C}_6\text{H}_4 \text{---} \text{CHCH}_2 \end{array}$	CH ₃	C ₁₁ H ₂₃	C ₂ H ₅	Cl
4.....	CH ₃	C ₁₅ H ₃₁	CH ₃	$\begin{array}{c} \text{OH} \\ \\ \text{CH}_2\text{CHCH}_2\text{OCH}_2\text{CH}_2 \end{array}$	CH ₃	C ₁₅ H ₃₁	CH ₃	I
5.....	CH ₃	C ₁₅ H ₃₁	CH ₃	$\text{---CH}_2\text{---C}_6\text{H}_4\text{---CH}_2$	CH ₃	C ₁₅ H ₃₁	CH ₃	BF ₄
6.....	CH ₃	$\text{Cl---C}_6\text{H}_4\text{---}$	CH ₃	CH ₂ CH ₂ CH ₂ CH ₂	CH ₃	$\text{---C}_6\text{H}_4\text{---Cl}$	CH ₃	Cl
7.....	CH ₃	$\text{C}_6\text{H}_4\text{---}$	CH ₃	$\text{CH}_2\text{---C}_6\text{H}_4\text{---CH}_2$	CH ₃	$\text{---C}_6\text{H}_4\text{---}$	CH ₃	Cl
8.....	CH ₃	CCl ₃	CH ₃	$\begin{array}{c} \text{OH} \qquad \qquad \text{OH} \\ \qquad \qquad \\ \text{CH}_2\text{CHCH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CHCH}_2 \end{array}$	CH ₃	CCl ₃	CH ₃	Cl
9.....	CH ₃	$\text{C}_6\text{H}_4\text{---CH}_2$	CH ₃	$\begin{array}{c} \text{OH} \qquad \qquad \text{OH} \\ \qquad \qquad \\ \text{CH}_2\text{CHCH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CHCH}_2 \end{array}$	CH ₃	$\text{CH}_2\text{---C}_6\text{H}_5$	CH ₃	Br
10.....	CH ₃	$\text{C}_5\text{H}_4\text{N---}$	CH ₃	$\begin{array}{c} \text{OH} \qquad \qquad \text{OH} \\ \qquad \qquad \\ \text{CH}_2\text{CHCH}_2\text{O---C}_6\text{H}_4\text{---OCH}_2\text{CHCH}_2 \end{array}$	CH ₃	$\text{---C}_5\text{H}_4\text{N---}$	CH ₃	Cl
11.....	CH ₃	C ₁₁ H ₂₃	CH ₃	$\begin{array}{c} \text{OH} \\ \\ \text{CH}_2\text{---C}_6\text{H}_4\text{---OCH}_2\text{CHCH}_2 \end{array}$	CH ₃	$\text{---C}_6\text{H}_4\text{---CH}_2$	CH ₃	Cl
12.....	CH ₃	$\text{C}_5\text{H}_4\text{N---}$	CH ₃	$\begin{array}{c} \text{OH} \\ \\ \text{CH}_2\text{CHCH}_2\text{OCH}_2\text{CH}_2 \end{array}$	CH ₃	$\text{CH}_2\text{---C}_6\text{H}_5$	C ₂ H ₅	Br
13.....	CH ₃	$\text{C}_4\text{H}_3\text{O---}$	CH ₃	$\begin{array}{c} \text{OH} \qquad \text{CH}_3 \qquad \text{OH} \\ \qquad \qquad \\ \text{CH}_2\text{CHCH}_2\text{OCH}_2\text{CH}(\text{OCH}_3)\text{CH}_2\text{CHCH}_2 \end{array}$	CH ₃	$\text{---C}_4\text{H}_3\text{O---}$	CH ₃	ClO ₄
14.....	CH ₃	C ₁₁ H ₂₃	CH ₃	$\begin{array}{c} \text{OH} \qquad \qquad \text{OH} \\ \qquad \qquad \\ \text{CH}_2\text{CHCH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CHCH}_2 \end{array}$	CH ₃	$\text{---C}_6\text{H}_4\text{---}$	CH ₃	Cl

Elementary analysis

Compound	Calculated					Found				
	C	H	N	Halogen	B	C	H	N	Halogen	B
1.....	41.95	7.60	10.30	19.56	-----	41.76	7.82	10.15	19.41	-----
2.....	52.97	9.34	6.18	27.98	-----	52.86	9.25	6.36	28.05	-----
3.....	64.23	10.24	7.49	9.48	-----	64.15	10.32	7.61	9.30	-----
4.....	51.67	9.10	5.88	26.64	-----	51.60	9.15	6.01	26.32	-----
5.....	60.41	9.68	6.41	17.38	2.47	60.21	9.72	6.31	17.25	2.50
6.....	50.39	5.77	10.69	27.05	-----	50.45	5.81	10.70	27.25	-----
7.....	62.02	6.41	11.13	14.08	-----	62.21	6.25	11.31	14.25	-----
8.....	29.20	4.60	8.51	43.10	-----	29.36	4.51	8.51	43.20	-----
9.....	48.56	6.40	8.09	23.08	-----	48.25	6.66	8.25	23.05	-----
10.....	51.91	6.37	15.97	11.79	-----	51.81	6.38	14.05	11.99	-----
11.....	62.27	8.61	8.54	10.81	-----	62.50	8.31	8.46	10.95	-----
12.....	45.48	6.14	11.53	26.31	-----	45.49	6.25	11.66	26.41	-----
13.....	59.60	5.49	8.03	10.17	-----	59.56	5.72	8.05	10.56	-----
14.....	56.95	8.94	8.57	10.85	-----	56.49	9.25	8.41	10.86	-----

GENERAL FORMULA II

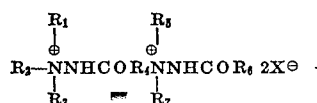


Compound	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	R ₇	X [⊖]
15.....	CH ₃		C ₂ H ₅		CH ₃		C ₂ H ₅	Cl
16.....	CH ₃		CH ₃		CH ₃		CH ₃	Br
17.....	CH ₃		CH ₃		CH ₃		CH ₃	Cl
18.....	CH ₃	CH ₃	CH ₃		CH ₃	CH ₃	CH ₃	Cl
19.....	CH ₃		CH ₃		CH ₃		CH ₃	Cl
20.....	CH ₃	C ₆ H ₁₁	CH ₃		CH ₃	C ₆ H ₁₁	CH ₃	ClO ₄
21.....	CH ₃		CH ₃		CH ₃		CH ₃	Cl
22.....	CH ₃		CH ₃		CH ₃		CH ₃	I
23.....	CH ₃		CH ₃		CH ₃		CH ₃	BF ₄
24.....	CH ₃		CH ₃		CH ₃	CH ₃	CH ₃	Cl
25.....	CH ₃	CH ₃	CH ₃		CH ₃		CH ₃	Cl
26.....	CH ₃		CH ₃		CH ₃		CH ₃	Br

Elementary analysis

Compound	Calculated					Found				
	C	H	N	Halogen	B	C	H	N	Halogen	B
15.....	59.73	9.47	7.74	9.80	-----	59.66	9.82	7.75	9.95	-----
16.....	58.71	8.14	5.95	10.99	-----	59.00	8.01	6.02	17.15	-----
17.....	59.73	9.47	7.74	9.80	-----	59.61	9.86	7.78	10.11	-----
18.....	49.60	9.37	14.46	18.30	-----	49.25	9.61	14.48	18.20	-----
19.....	52.18	6.20	10.14	25.68	-----	52.20	6.40	10.31	25.70	-----
20.....	44.67	6.82	9.47	11.99	-----	44.81	6.83	9.56	12.11	-----
21.....	46.08	7.46	7.68	9.72	-----	46.31	7.26	7.81	9.95	-----
22.....	50.04	8.30	6.95	25.18	-----	50.15	8.15	7.21	25.61	-----
23.....	49.47	6.04	7.69	20.87	2.97	49.56	6.68	7.31	20.66	2.56
24.....	56.81	8.44	10.20	12.90	-----	56.41	8.42	10.15	12.90	-----
25.....	48.93	7.07	12.68	24.07	-----	49.15	7.05	12.75	24.15	-----
26.....	53.03	8.35	7.73	22.05	-----	53.06	8.41	7.79	23.15	-----

GENERAL FORMULA III



Compound	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	R ₇	X [⊖]
27.....	CH ₃		CH ₃		CH ₃	C ₁₁ H ₂₃	CH ₃	Cl
28.....	CH ₃		C ₂ H ₅		CH ₃	C ₁₁ H ₂₁	CH ₃	Br
29.....	CH ₃		CH ₃	-CH ₂ CH ₂ -	CH ₃		CH ₃	I
30.....	CH ₃		CH ₃	-CH ₂ CH ₂ -	CH ₃		CH ₃	BF ₄
31.....	CH ₃		CH ₃	-CH ₂ CH ₂ -	CH ₃		CH ₃	ClO ₄

Compound	Elementary analysis									
	Calculated					Found				
	C	H	N	Halogen	B	C	H	N	Halogen	B
27.....	60.45	9.51	8.81	11.15	-----	60.46	9.61	8.72	11.41	-----
28.....	60.51	8.83	6.14	17.51	-----	60.61	8.91	6.25	17.61	-----
29.....	40.38	4.93	8.56	38.79	-----	40.41	5.01	8.96	38.59	-----
30.....	47.25	7.64	8.16	22.15	3.15	47.25	7.68	8.21	22.41	3.28
31.....	39.21	5.85	10.16	12.86	-----	39.61	5.91	10.26	12.85	-----

Among the acylhydrazinium salts of the aforesaid general formulas, the acylhydrazinium halides are obtained according to the methods disclosed in W. H. Berry & P. Brocklehurst: "The Journal of Chemical Society," 2264 (1964); R. L. Hinman & M. C. Flores: "Journal of Organic Chemistry," 24 660 (1959); and U.S. Pat. 3,064,051. Alternatively, the acylhydrazinium salts are prepared by treating ylides, which are obtained according to the methods disclosed in the above-mentioned references and R. C. Alagel: "Journal of Organic Chemistry," 33 1374 (1968), with hydrochloric acid, hydrobromic acid, hydriodic acid or perchloric acid according to an ordinary procedure. Further, the acylhydrazinium fluoroborates are obtained by treating acylhydrazides with trialkyloxonium fluoborates in either or by treating acylhydrazinium chlorides with sodium borofluoride.

A typical procedure for synthesis of the present compound is set forth below with reference to a synthesis example.

SYNTHESIS EXAMPLE

Synthesis of the exemplified Compound 2

7.75 grams of 1,4-iodobutane and 17.9 g. of N,N-dimethyl-N'-hexadecanoyl-hydrazine were dissolved in 20 ml. of dioxane, and the resulting solution was reacted at 73° C. for 48 hours. After completion of the reaction, the liquid reaction mixture was concentrated, and the concentrate was dissolved in 20 ml. of methanol. To the resulting solution was added 300 ml. of ether to precipitate white crystals, which were then recovered by filtration and repeatedly recrystallized from a methanol-ether mixed solvent to obtain crystals of bis-acylhydrazinium iodide (2) M.P. 109-110° C., yield 90.2%.

Elementary analysis.—Found (percent): C, 52.86; H, 9.25; N, 6.36; I, 28.05. Calculated (percent): C, 52.97; H, 9.34; N, 6.18; I, 27.98 (for C₄₀H₈₄N₄O₂I₂).

For incorporation of any of the compounds having the aforesaid general formulas into the silver halide emulsion layer, sub layer, inter layer, filter layer, antihalation layer, protective layer or backing layer of a light-sensitive silver halide photographic material, the compound in the form of a solution in a suitable solvent such as water or an alcohol may be incorporated into said

layer or spray-coated on the surface of the light-sensitive material, or the light-sensitive material may be dipped in said solution. Further, the compound of the present invention may be incorporated into a developing solution, stopping solution, fixing solution, water drop-preventing solution or the like treating bath. In incorporating the compound into any of the layers constituting a light-sensitive material, the amount of the compound is about 0.1 mg. to 1 g. per m.² of the light-sensitive material, though the amount varies depending on the nature of the compound and of the layer to which the compound is to be incorporated.

The compounds of the present invention are usable as well for static charge prevention of cellulose ester, polyester, polystyrene, polycarbonate, polyethylene, polypropylene and the like synthetic resin films, moldings and fibers.

The following examples illustrate the invention.

EXAMPLE 1

Each of the exemplified compounds 2, 5, 10, 14, 17, 22, 26 and 28 was dissolved in ethyl alcohol to form a 1% solution. This solution was spray-coated on the surface of a high sensitivity roentgen film and then dried to prepare a sample. On the other hand, the said high speed roentgen film was dipped in the above-mentioned solution for 1 minute to prepare another sample. For comparison, a control sample was prepared in the same manner as above, except that the above-mentioned treatment was effected by use of only an ethanol solution. The thus prepared samples and an untreated roentgen film were allowed to stand for 24 hours under conditions of RH 30% and 25° C., rubbed on the surfaces with nylon and polyester cloths, and then developed, without exposure, according to an ordinary procedure by use of a radiographic developing solution. Subsequently, the developed samples were individually subjected to Sakura Densitometer (a product of Konishiroku Photo Industry Co., Ltd.) to measure the average values of blackened density. The samples were further measured for the amount of developed silver according to X-ray analysis and, at the same time, for specific surface resistivity. The results obtained were as set forth in Table 1.

TABLE 1

Sample No.	Antistatic agent	Spray coating			Dip coating		
		Average density measured by densitometer	Amount of developed silver (mg./100 cm. ²)	Specific surface resistivity (Ω)	Average density measured by densitometer	Amount of developed silver (mg./100 cm. ²)	Specific surface resistivity (Ω)
1.....	Non-treatment.....	1.55	45.5	10 ¹⁴	1.45	42.2	10 ¹⁴
2.....	Ethanol solution containing no antistatic agent.....	1.52	40.1	10 ¹⁴	1.28	40.0	10 ¹⁴
3.....	Exemplified Compound 2.....	0.05	1.6	10 ¹²	0.05	2.9	10 ¹²
4.....	Exemplified Compound 5.....	0.08	2.8	10 ¹²	0.11	3.7	10 ¹²
5.....	Exemplified Compound 10.....	0.06	2.1	10 ¹²	0.09	3.1	10 ¹²
6.....	Exemplified Compound 14.....	0.09	3.0	10 ¹²	0.13	4.0	10 ¹²
7.....	Exemplified Compound 17.....	0.10	3.4	10 ¹²	0.12	3.9	10 ¹²
8.....	Exemplified Compound 22.....	0.05	1.8	10 ¹¹	0.08	2.8	10 ¹²
9.....	Exemplified Compound 28.....	0.07	2.2	10 ¹²	0.09	3.3	10 ¹²
10.....	Exemplified Compound 28.....	0.06	2.0	10 ¹²	0.08	2.9	10 ¹²

As is clear from Table 1, the sample treated with the solution containing no exemplified compound and the untreated sample were high in average density value and large in amount of developed silver, and showed a considerable increase in fog due to formation of static marks, whereas no formation of static marks was observed in the samples according to the present invention (Samples 3 to 10).

On the other hand, these samples were exposed to light, developed at 20° C. for 4 minutes and 30 seconds with a strongly alkaline roentgen film developer containing 1-phenyl-3-pyrazolidone hydroquinone (PQ) as developing agent, and then measured in speed and fog. Further, the samples were subjected to sensitometry after incubation for 3 days in a thermostat chamber kept at 55° C. and under conditions of 50° C. and R.H. 80%. The results obtained were as set forth in Table 2.

temperature and humidity, the samples according to the present invention (Samples 3 to 10) were not deteriorated at all in speed, gradation and fog. In addition, the color tone of the developed silver changed to bluish black to give favorable results.

EXAMPLE 2

Each of the exemplified compounds 2, 4, 6, 12, 15, 20, 25 and 30 was dissolved in a 4% solution of sodium decylisooamyl succinate-2-sulfonate so that the concentration of the compound was 2%, and 2 cc. of the resulting solution was added to 1 liter of a 2% gelatin solution to be used as a protective layer. Subsequently, the solution was coated as a protective layer on a high speed roentgen film and then dried. Samples prepared in the above manner and a sample having a protective layer containing no exemplified

TABLE 2

Sample No.	Spray coating			Dip coating							
	Relative speed	Relative gamma	Fog	Relative speed	Relative gamma	Fog	After incubation at 55° C. for 3 days		After incubation at 50° C. and R.H. 80% for 3 days		Fog
							Relative speed	Fog	Relative speed	Fog	
1.....	100	1.0	0.14	100	1.0	0.16	100	0.22	100	0.22	
2.....	98	1.0	0.12	99	0.98	0.15	98	0.23	87	0.20	
3.....	103	1.0	0.14	105	0.99	0.17	99	0.23	96	0.21	
4.....	104	0.98	0.15	108	1.0	0.16	99	0.24	95	0.19	
5.....	101	1.0	0.13	103	1.0	0.15	100	0.24	100	0.20	
6.....	100	1.1	0.14	101	1.1	0.16	100	0.24	101	0.21	
7.....	100	1.1	0.14	100	1.0	0.17	100	0.25	98	0.20	
8.....	99	1.0	0.12	98	1.0	0.13	102	0.23	97	0.18	
9.....	100	1.0	0.14	99	1.0	0.16	100	0.27	100	0.19	
10.....	102	0.99	0.14	100	1.0	0.15	100	0.26	100	0.21	

From Table 2, it is understood that even when incubated not only at normal temperature but also at high

compound were subjected to the same tests as in Example 1 to obtain the results as set forth in Table 3.

TABLE 3

Sample No.	Antistatic agent	Photographic properties									
		Antistatic property			Immediately after preparation						
		Average density measured by densitometer	Amount of developed silver (mg./100 cm. ²)	Fog	Relative speed	Relative gamma	Fog	After incubation at 55° C. for 3 days		After incubation at 50° C. and R.H. 80% for 3 days	
								Relative speed	Fog	Relative speed	Fog
11.....	Protective layer containing no antistatic agent.....	1.58	39.8		100	1.00	0.14	100	0.18	100	0.17
12.....	Exemplified Compound 2.....	0.17	6.2		101	1.00	0.13	100	0.18	100	0.17
13.....	Exemplified Compound 4.....	0.15	4.9		103	0.98	0.14	98	0.20	99	0.16
14.....	Exemplified Compound 6.....	0.13	4.1		100	1.0	0.14	100	0.18	100	0.18
15.....	Exemplified Compound 12.....	0.18	5.9		100	1.0	0.11	100	0.16	102	0.16
16.....	Exemplified Compound 15.....	0.16	5.1		100	1.0	0.13	100	0.16	100	0.17
17.....	Exemplified Compound 20.....	0.18	6.0		101	0.99	0.14	99	0.20	99	0.18
18.....	Exemplified Compound 22.....	0.17	5.7		100	1.0	0.12	102	0.18	103	0.18
19.....	Exemplified Compound 30.....	0.15	5.0		99	1.08	0.13	101	0.19	105	0.16

As is clear from Table 3, it is understood that the samples according to the present invention (Samples 12 to 19) could be prevented from the formation of static marks without being deteriorated in photographic properties.

EXAMPLE 3

To 1 liter of a green-sensitive high speed color photographic silver iodobromide emulsion was added 10 cc. of a 5% methanol solution of each of the exemplified compounds 1, 3, 9, 13, 17, 24 and 30. To the emulsion was further added a solution of 20 g. of an internal color photographic magenta coupler 1-(4'-phenoxy-3'-sulphophenyl) - 3 - heptadecyl - 5 - pyrazolone in a 1 N caustic soda solution which had been adjusted to pH 6.8 by addition of citric acid. Subsequently, the emulsion was coated on a cellulose triacetate film base and then dried. Samples obtained in the above manner and a sample, which had not been incorporated with any exemplified compound, were subjected to the same tests as in Example 1. The results obtained were as set forth in Table 4. Provided that in this example, the average density value was measured by using a green filter as a light source of the densitometer, and the development was effected according to a conventional procedure using diethyl p-phenylenediamine as the developing agent.

TABLE 4

Sample No.	Antistatic agent	Antistatic property		Photographic properties				
		Average density measured by densitometer	Specific surface resistivity (Ω)	Immediately after preparation			After incubation at 50° C. for 3 days	
				Relative speed	Relative gamma	Fog	Relative speed	Fog
20	None	0.96	10 ¹²	100	1.00	0.13	100	0.18
21	Exemplified Compound 1	0.18	10 ¹¹	101	1.05	0.14	102	0.18
22	Exemplified Compound 3	0.16	10 ¹¹	108	0.98	0.13	99	0.20
23	Exemplified Compound 9	0.12	10 ¹⁰	105	0.98	0.14	100	0.18
24	Exemplified Compound 13	0.16	10 ¹¹	100	1.00	0.13	101	0.18
25	Exemplified Compound 17	0.18	10 ¹¹	103	0.99	0.13	100	0.18
26	Exemplified Compound 24	0.11	10 ¹⁰	100	1.02	0.12	102	0.17
27	Exemplified Compound 30	0.17	10 ¹¹	106	1.00	0.14	99	0.18

From Table 4, it is clear that by addition of the exemplified compounds to the emulsion, the samples according to the present invention were inhibited from formation of static marks and improved in dispersibility of the formed dyes without any detrimental effect on photographic properties.

EXAMPLE 4

To a 5% aqueous gelatin solution containing an anti-halation dye was added 2 cc. of a 2% aqueous solution of each of the exemplified compounds 4, 10, 17 and 30. The resulting solution was charged with 3 cc. of a 5% saponin solution and then coated on a triacetate film base. On the opposite side of this film base was coated a high speed photographic emulsion for negative, and a protective layer was formed on the resulting emulsion layer by application of a gelatin solution containing 300 mg. per liter of said solution of the above-mentioned exemplified compound. Samples prepared in the above manner were subjected to the same tests as in Example 1 to obtain the results as set forth in Table 5.

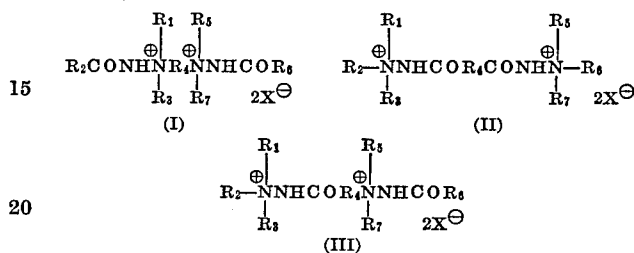
TABLE 5

Sample No.	Antistatic agent	Antistatic property		Photographic properties				
		Average density measured by densitometer	Amount of developed silver (mg./100 cm. ²)	Immediately after preparation			After incubation at 50° C. for 3 days	
				Relative speed	Relative gamma	Fog	Relative speed	Fog
28	None	1.48	46.5	100	1.00	0.13	100	0.23
29	Exemplified Compound 4	0.10	3.6	102	1.00	0.12	100	0.21
30	Exemplified Compound 10	0.08	2.6	100	0.98	0.13	103	0.20
31	Exemplified Compound 17	0.08	2.4	109	1.02	0.12	102	0.22
32	Exemplified Compound 30	0.11	3.7	102	0.99	0.14	100	0.23

As is clear from Table 5, the samples according to the present invention (Samples 29 to 32) were inhibited from formation of static marks and were not deteriorated in photographic properties.

5 What we claim is:

1. A method for the prevention of static in a light-sensitive silver halide photographic material comprising a support and at least one photographic layer coated on said support, said method comprising treating said photographic material with a bis-aminimide compound of the formula



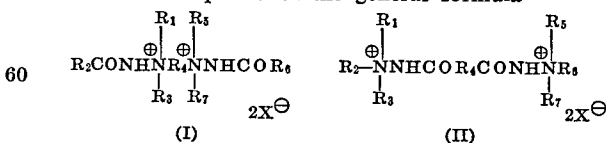
wherein R₁, R₃, R₅ and R₇ are individually a lower alkyl group; R₂ and R₆ are individually an alkyl, aralkyl or aryl group or a hetero ring; R₄ is a divalent group; and X is an anion residue.

2. A method as claimed in claim 1, wherein the bis-aminimide compound is incorporated into at least one of the photographic layers constituting said light-sensitive silver halide photographic material.

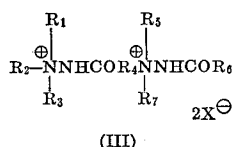
3. A method as claimed in claim 1, wherein the light-sensitive silver halide photographic material is treated with a photographic treating bath containing the bis-aminimide compound and being one member selected from the group consisting of a developing bath, a stopping bath and a fixing bath.

4. A method as claimed in claim 1, wherein the light-sensitive silver halide photographic material is sprayed with a solution of the bis-aminimide compound.

5. A light-sensitive silver halide photographic material which comprises a support and coated thereon photographic layers at least one of which contains a bis-aminimide compound of the general formula



13



(III)

wherein R₁, R₃, R₅ and R₇ are individually a lower alkyl group; R₂ and R₆ are individually an alkyl, aralkyl or aryl group or a hetero ring; R₄ is a divalent group; and X is an anion residue.

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RONALD H. SMITH, Primary Examiner

U.S. Cl. X.R.

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