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N-YLIDE COMPOUNDS AS ANTISTATIC AGENTS IN PHOTOGRAPHY

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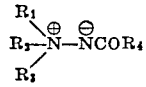
U.S. Cl. 96—50 5 Claims

ABSTRACT OF THE DISCLOSURE

A new use, as an antistatic agent for light-sensitive silver halide photographic material, of an N-ylide represented by the general formula



wherein R_1, R_2 and R_3 are individually an alkyl group, an aralkyl group or a group derived from any of said groups, and R_4 is an alkyl group, an aryl group or a hetero ring.

This invention relates to a light-sensitive silver halide photographic material characterized by containing in at least one of the layers constituting the photographic material an N-ylide represented by the general formula shown hereinafter.

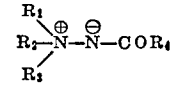
A principal object of the present invention is to provide a light-sensitive silver halide photographic material having fewer drawbacks due to electrostatic charge.

Another object of the invention is to provide a light-sensitive material resulting in an improved tone of developed silver image and a light-sensitive color photographic material which is excellent in image resolution and graininess.

When a light-sensitive silver halide photographic material is developed, undesired images in the form of branched lines and fluffs are frequently observed. These undesired images are the so-called static marks. It is believed that the formation of such static marks is ascribable to the fact that the surface of light-sensitive material is electrostatically charged due to friction and this electrostatic charge is discharged to excite the light-sensitive material. Such electrostatic charge results not only in the formation of static marks but also in the adhesion of dust onto the surface of light-sensitive material. Such electrostatic effects are unavoidably brought about every time light-sensitive materials undergo friction and is seen in almost all stages of production and handling of light-sensitive materials, e.g. in such film production stages as the coating of emulsions and the cutting and packaging of films, and in such film handling stages as the withdrawal of films from boxes, the taking of pictures by use of films, particularly those for movies, and the handling of films before development. Further, such electrostatic trouble is sometimes brought about also in the case of releasing light-sensitive materials. For example, in releasing in succession a light-sensitive material, which has been rolled up, in general, after completion of coating and drying operations, in order to transfer the light-sensitive material to the subsequent step, or in unrolling in succession a rolled photographic paper in order to subject the photographic paper to printing operation, a static charge is generated between the surface and the reverse side of the peeled or unrolled light-sensitive material when the material is peeled from the roll portion. Further, in removing a photographic paper, which has been subjected to ferrotype drying, there is also generated an electrostatic charge between the drying surface (metal) and the surface of the photographic paper at the moment of separation, so that the paper can not be stacked at once.

In order to overcome such static trouble, a process is used by which hygroscopic materials are incorporated into the layers constituting light-sensitive materials. This process, however, is effective only when humidity is relatively high and is ineffective at dry times when the static trouble most frequently takes place. Further, if the humidity is excessively high, the above-mentioned process brings about troubles in the mutual adhesion between gelatinous layers of separate light-sensitive materials. In addition to the above-mentioned hygroscopic materials, there are a considerable number of compounds which are known as antistatic agents. However, antistatic agents are required to be such that they should not have any detrimental effects on such photographic properties of light-sensitive materials as sensitivity, gradation, fog, stability, etc. Therefore it is extremely difficult to find excellent antistatic agents applicable to light-sensitive silver halide photographic materials.

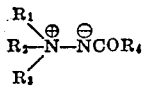
As a result of extensive studies on excellent antistatic agents which have no detrimental effects on light-sensitive silver halide photographic materials, it has been found that a compound represented by the general formula

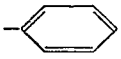
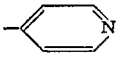
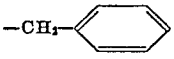
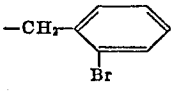


wherein R_1, R_2 and R_3 are individually an alkyl group, an aralkyl group or a group derived from any of said groups, and R_4 is an alkyl group, an aryl group or a hetero ring, is an excellent antistatic agent.

When the above-mentioned compound is incorporated into at least one of the silver halide emulsion, subbing, inter, filter, anti-halation, protective and backing layers which constitute a light-sensitive silver halide photographic material, it is possible to obtain a light-sensitive silver halide photographic material markedly improved with respect to static trouble. The above-mentioned compound not only has no detrimental effects on such characteristics of a light-sensitive photographic material as speed, gradation, fog, and so forth but also displays, depending on the kind of light-sensitive material, such desirable effects as to inhibit fog and to enhance stability. Further, when the compound is applied to a light-sensitive black-and-white photographic material, there is attained, in addition to the prevention of electrostatic trouble, such advantage that the color tone of the developed silver image can be made bluish black and, when it is applied to a color photographic emulsion, having a color former incorporated therein, the dispersibility of the color former is improved to make it possible to obtain a light-sensitive color photographic material which is excellent in image resolution and graininess.

Typical examples of the N-ylide represented by the aforesaid general formula are as shown hereinafter.



	R_1	R_2	R_3	R_4	Elementary analysis Calculated C	H	N	Found C	H	N
I	CH_3	CH_3	CH_3	C_9H_{19}	68.37	12.36	12.27	66.85	12.55	11.88
II	CH_3	CH_3	CH_3	$C_{11}H_{23}$	70.26	12.58	10.93	69.72	12.76	10.61
III	CH_3	CH_3	CH_3	$C_{15}H_{31}$	73.01	12.90	8.96	72.12	12.79	8.20
IV	CH_3	CH_3	CH_3		67.38	7.92	15.72	66.80	8.19	16.00
V	CH_3	CH_3	CH_3		60.31	7.31	23.45	59.92	7.22	24.11
VI	CH_3	CH_3	C_2H_5	$C_{15}H_{31}$	73.56	12.96	8.58	72.78	12.76	8.34
VII	CH_3	CH_3	$C_{12}H_{25}$	CH_3	71.05	12.67	10.36	70.06	12.45	10.15
VIII	CH_3	CH_3		$C_{15}H_{31}$	77.26	11.41	7.21	76.77	11.37	7.06
IX	CH_3	CH_3		C_9H_{11}	55.05	7.08	8.56	54.60	7.28	8.11
X	CH_3	C_2H_5	C_2H_5	$C_{11}H_{23}$	71.77	12.76	9.85	70.98	12.53	9.13
XI	C_2H_5	C_2H_5	C_2H_5	$C_{13}H_{31}$	74.51	13.08	7.90	73.66	12.85	7.28
XII	CH_3	CH_3	C_8H_{17}	C_7H_{15}—	74.42	12.83	9.39	72.55	12.85	9.42
XIII	CH_3	CH_3	CH_3CHCH_2— (OH)	$C_{11}H_{23}$—	67.94	12.07	9.32	68.02	12.33	9.38
XIV	CH_3	CH_3	$C_6H_{13}CHCH_2$— (OH)	$C_{11}H_{23}$—	71.29	12.51	7.56	17.31	12.50	7.66

The N-ylide compounds of the aforesaid general formula can be prepared according to any of the processes disclosed W. H. Berry & P. Brocklehurst in Journal of the Chemical Society, 2264 (1964); R. H. Hinman in Journal of Organic Chemistry, 24 660 (1969); and R. C. Slagel in Journal of Organic Chemistry, 33 1374 (1968).

The preparation of a typical compound is set forth below with reference to a synthesis example.

Synthesis example

Synthesis of N-trimethylamine hexadecanimide [Exemplification (III)]

A solution of 10 g. of N-dimethyl-N'-hexadecanoyl hydrazine in 40 ml. of methyl iodide was refluxed for 22 hours. After completion of the reaction, excess methyl iodide was removed by distillation under reduced pressure, and the residue was recrystallized from methanol to obtain 14.2 g. of N-trimethyl-N'-hexadecanoyl hydrazinium iodate, yield 96.3%, M.P. 142–143° C.

Elementary analysis.—Calculated (for $C_{19}H_{41}ON_2I$) (percent): C, 51.81; H, 9.38; N, 6.36. Found (percent): C, 52.20; H, 9.55; N, 6.65.

11 g. of this hydrazinium iodate was suspended in 30 ml. of water, and to the suspension was added with stirring a solution of 1.5 g. of sodium hydroxide in 10 ml. of water. Subsequently, the liquid was heated over a water bath at 50–60° C. for 20 minutes. After cooling, the liquid was extracted 3 times with 60 ml., 30 ml. and 30 ml. of chloroform in this order, and the chloroform layer was washed with an aqueous saturated sodium chloride solution and then dehydrated with anhydrous sodium sulfate. After separating the anhydrous sodium sulfate by filtration, the chloroform was removed by distillation under reduced pressure, and the resulting crystals were recrystallized from petroleum benzine to obtain 73 g. of N-trimethylamine hexadecanimide, yield 93.5%, M.P. 71.5–73° C.

Elementary analysis.—Calculated (for $C_{19}H_{40}ON_2$) (percent): C, 73.01; H, 12.90; N, 8.96. Found (percent): C, 72.12; H, 12.79; N, 8.20.

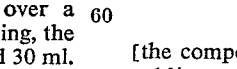
For the incorporation into any of the layers constituting a light-sensitive silver halide photographic material, the compound of the aforesaid general formula may be brought into the form of a solution in a suitable solvent such as water or an alcohol, or the solution may be sprayed onto the surface of the light-sensitive material. Alternatively, the light-sensitive material may be immersed in the solution of the compound. Further, the compound of the present invention may be added to a treating bath of developing solution, stopping solution, fixing solution, water drop-preventing solution or the like. The amount of the compound to be incorporated into the layer of a light-sensitive material is about 0.1 mg. to 1 g. per $m.^2$ of the light-sensitive material, though the amount varies depending on the kinds of the compound and of the layer.

The compounds of the present invention are applicable also for the static prevention of films, fibers and molded articles of cellulose esters, polyesters, polystyrenes polycarbonates, polyethylenes, polypropylenes and the like synthetic resins.

The present invention is illustrated in further detail below with reference to examples.

EXAMPLE 1

The compound of the formula

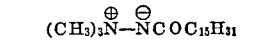


[the compound of exemplification (II)] was formed into a 1% aqueous solution. This solution was sprayed onto the surface of a high speed X-ray film so that the amount of the compound became 10 mg. per $m.^2$ of the film, and then the film was dried to prepare a sample. The same X-ray film as above was immersed for 1 minute in the above-mentioned solution and then dried to prepare another sample. On the other hand, two control samples were prepared in the same manner as above, except that the above-mentioned N-ylide compound was not used. The thus prepared 4 kinds of samples were allowed to stand for 24 hours under conditions of a relative humidity of 30% and a temperature of 25° C. Thereafter, the samples were abraded on the surfaces with nylon and

polyester cloths and then subjected, without exposure, to ordinary development using a developing solution. As the result, considerably marked generation of static marks was observed on both of the control films, whereas no generation of static marks was observed on the films treated with the solution of the N-ylide compound (i.e. the light-sensitive materials of the present invention). On the other hand, these 4 kinds of films were subjected to sensitometry according to the method specified in JIS K–7609 whereby the light-sensitive silver halide photographic materials of the present invention gave such favorable results that not only no change was observed in speed, gradation and fog, but also the developed silver image tone changed to bluish black. Further, these films were developed after storing them for 3 days in a thermostat at 55° C., and under the conditions of a temperature of 50° C. and a relative humidity of 80%, respectively. In this case also, the light-sensitive silver halide photographic materials of the present invention gave desirable results.

EXAMPLE 2

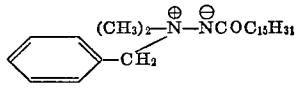
The compound of the formula



[the compound of exemplification (III)] was prepared in a 2% aqueous solution. To this solution was added 5 cc. per liter of said solution of an 8% aqueous gelatine solution used as protective layer. Further, 2 cc. of a 5% saponine solution was added as a coating aid. The mixed solution thus formed was coated as a protective layer onto a high speed X-ray film, followed by drying. The resulting light-sensitive material was subjected, together with a light-sensitive material in which the above-mentioned compound had not been incorporated into the protective layer, to the same tests as in Example 1 to obtain the same results as in Example 1.

EXAMPLE 3

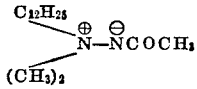
30 cc. of a 3% methanol solution of the compound of the formula



[the compound of exemplification (VIII)] was added to one liter of a green light-sensitive high speed silver iodobromide color photographic emulsion. To this emulsion was added a solution of 15 g. of 1-(4-carboxyphenyl)-3-(4-palmitoylaminobenzoylamino)-5-pyrazolone (magenta coupler) in a 1 N caustic soda solution, and the emulsion was adjusted to pH 6.8 by addition of citric acid. The thus prepared emulsion was coated onto a cellulose triacetate base, followed by drying, to obtain a light-sensitive silver halide photographic material. This light-sensitive material was subjected, together with a control prepared in the same manner as above except that the above-mentioned N-ylide compound was not added, to entirely the same tests as in Example 1. Provided that in the above case, the processing was effected in such a manner that each sample was subjected to ordinary color development using a color developing solution containing diethyl-p-phenylenediamine as a main ingredient and then to water-washing, bleaching, water-washing, fixing, water-washing and drying. As the result, it was observed that the light-sensitive material of the present invention had been completely inhibited from generation of static marks and, in addition, had been enhanced in dispersibility of the coupler.

EXAMPLE 4

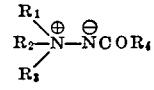
10 g. of the cyan coupler 1-hydroxy-N-[γ-(2,4-diamylphenoxy)propyl]-2-naphthamide was dissolved at an elevated temperature in a mixed liquid comprising 10 g. of dibutyl phthalate and 30 g. of ethyl acetate. Subsequently, the liquid was charged into 100 cc. of 10% gelatine in the presence of 40 cc. of a 1% solution of dodecylbenzenesulfonic acid, and then the mixture was dispersed by means of a ultrasonic disperser to form a suspension. This suspension was added to one liter of a red light-sensitive high speed silver iodobromide color photographic emulsion, which was then coated onto a polyester film base, followed by drying, to prepare a light-sensitive material. On the other hand, another light-sensitive material was prepared by repeating the above operation, except that to one liter of the emulsion was added 50 cc. of a 2% methanol solution of the compound of the formula



[the compound of exemplification (VII)]. These two light-sensitive materials were subjected to entirely the same tests as in Example 1 to find that in the case of the light-sensitive material prepared by use of the compound of exemplification (VII), not only the generation of static marks had been completely inhibited but also the coupler had been increased in dispersibility and the developed dye image had been improved in transparency. In the tests, the treatments were carried out according to ordinary color negative treatments.

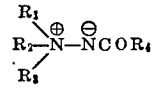
What we claim is:

1. A light-sensitive silver halide photographic material comprising a plurality of layers and in at least one of the layers an N-ylide represented by the general formula



wherein R_1, R_2 and R_3 are individually an alkyl group, and aralkyl group or a group derived from any of said groups, and R_4 is an alkyl group, an aryl group or a hetero ring.

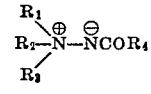
2. A process for the antistatic treatment of a light-sensitive silver halide photographic material, comprising treating said photographic material with an aqueous or organic solvent solution containing an ylide represented by the general formula



wherein R_1, R_2 and R_3 are individually an alkyl group, an aralkyl group or a group derived from any of said groups, and R_4 is an alkyl group, an aryl group or a hetero ring.

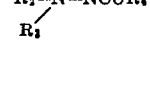
3. A process for the antistatic treatment of a light-sensitive silver halide photographic material as claimed in claim **2**, wherein said solution further contains a surface active agent.

4. A developing solution for light-sensitive silver halide photographic materials, comprising an N-ylide represented by the general formula



wherein R_1, R_2 and R_3 are individually an alkyl group, an aralkyl group or a group derived from any of said groups, and R_4 is an alkyl group, an aryl group or a hetero ring.

5. A new use as an antistatic agent for light-sensitive silver halide photographic material, of an N-ylide represented by the general formula



wherein R_1, R_2 and R_3 are individually an alkyl group, an aralkyl group or a group derived from any of said groups, and R_4 is an alkyl group, an aryl group or a hetero ring.

References Cited

UNITED STATES PATENTS

3,113,026	12/1963	Sprung	96—190
3,549,369	12/1970	Koda	96—94

FOREIGN PATENTS

864,874	4/1961	Great Britain	96—87

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96—61, 66, 87 A, 114.2