United States Patent Office

3,582,340

Patented June 1, 1971

3,582,340

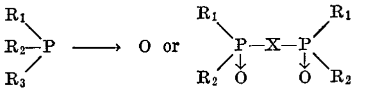
PROCESS FOR THE ANTISTATIC TREATMENT OF LIGHT-SENSITIVE SILVER HALIDE PHOTOGRAPHIC MATERIALS WITH PHOSPHINE OXIDE

Yoshimi Kuwabara, Tokyo, Sadao Sugita, Hanno-shi, and Kenichi Koda and Kunihiro Fujiwara, Tokyo, Japan, assignors to Konishiroku Photo Industry Co., Ltd.

No Drawing. Filed July 2, 1968, Ser. No. 741,883
Claims priority, application Japan, July 7, 1967, 42/43,325
Int. Cl. G03c *1/78*
U.S. Cl. 96—87A 2 Claims

ABSTRACT OF THE DISCLOSURE

A phosphine oxide having the general formula



wherein R_1, R_2 and R_3 are individually an alkyl, aryl or aralkyl group and X is an alkylene group, is incorporated into a light sensitive silver halide photographic material to impart thereto an antistatic effect.

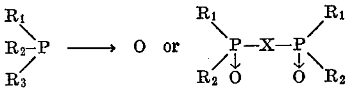
This invention relates to a process for the antistatic treatment of light-sensitive silver halide photographic materials, characterized by using phosphine oxides.

When a light-sensitive silver halide photographic material has been developed, there are some cases where spots in the form of branches or fluffs are found therein. These spots are so-called static marks, and are said to be derived from such phenomenon that the surface of the light-sensitive material has been electrostatically charged due to mechanical abrasion and the electrostatic charge has been discharged to excite the light-sensitive material. Such undesirable static 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 drawbacks due to static charge unavoidably takes place in substantially all the steps of production and handling of light-sensitive materials where the materials undergo abrasion. For example, said drawbacks are brought about in such production steps as the step for coating of emulsion, the steps of cutting and packaging light-sensitive materials, and the like steps; in the case of taking sheet films from a box; in the case of taking pictures, particularly in filming; or in the case of handling of light-sensitive materials before development. Such drawbacks due to static charge are sometimes brought about also in the case of releasing of light-sensitive materials, in addition to the case of abrasion. That is, after emulsion-coating and drying, a light-sensitive material is rolled up, in general, and is then successively unrolled in order to transfer the material to subsequent step, or a rolled printing paper is successively released to be subjected to printing. In this case, static charge due to frictional electricity is generated between the surface and the back side of the light-sensitive material at the moment when it is released from the rolled portion. Further, when a printing paper is subjected to ferrotype drying and is then taken out, static charge due to frictional electricity is generated as well between the metal surface and the surface of light-

sensitive material to cause such a phenomenon that the superposing of the printing paper cannot be effected immediately.

As a procedure for preventing such drawbacks due to static charge, a hygroscopic material is frequently incorporated into the constitutive elements of a light-sensitive material. This procedure, however, is effective only in the case where humidity is relatively high, and is ineffective at a dry time when static charge is frequently discharged. Further, in case humidity is excessively high, said procedure accompanies such drawback as the mutual adhesion of film surfaces of light-sensitive material. In addition to said hygroscopic material, there are a considerable number of compounds which have been known as antistatic agents. However, in application of antistatic agents to light-sensitive photographic materials, it is a required condition that they should not have any detrimental effect on photographic characteristics of the light-sensitive materials, such as speed, gradation, fog, stability, and the like. It is therefore extremely difficult to find excellent antistatic agents applicable to light-sensitive silver halide photographic materials.

As the result of various studies on excellent antistatic agents having no detrimental effect on light-sensitive silver halide photographic materials, the present inventors have found that compounds represented by the general formula



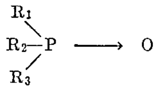
wherein R_1, R_2 and R_3 individually represent an alkyl, aryl or aralkyl group; and X represents an alkylene group, are excellent antistatic agents.

When the above-mentioned compounds are incorporated into at least one layer of silver halide emulsion layer, subbing layer, inter layer, filter layer, anti-halation layer, protective layer and backing layer, it is possible to obtain light-sensitive silver halide photographic materials which are markedly less in drawbacks due to static charge. Further, the incorporation of the aforesaid compounds gives no detrimental effect to the characteristics of light-sensitive photographic material, such as speed, gradation, fog, and the like.

If the above-mentioned compounds are increased in hydrophobic properties by extending the chain lengths of, for example, alkyl groups of R_1, R_2 and R_3 in the aforesaid general formulas, the compounds are deteriorated in water solubility, with the result that the incorporation thereof into the constitutive elements of light-sensitive materials becomes difficult. This difficulty, however, can be overcome by the combination use of an excellent anionic surface active agent. This combination use is not only effective for the solubilization of the present compounds but also gives the following advantages:

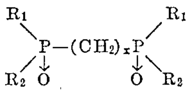
That is, the use of anionic surface active agents makes favorable the spreadability of photographic emulsions, in general, but disadvantageously increases the drawbacks due to static charge. Accordingly, it is impossible to select the kind of said agents only from the standpoint of spreadability. However, when said agents are used in combination with the present compounds, the question of drawbacks due to static charge is solved, with the result that in the selection of anionic surface active agents, it becomes possible to give priority to the spreadability thereof.

Examples of phosphine oxides having the aforesaid general formulas are as follows:

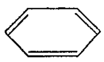
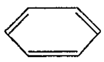


$$\overset{R_1}{\underset{R_3}{R_2{-}P}} \longrightarrow O$$

Compound No.	R_1	R_2	R_3	B.P. (° C./ mm. Hg)	M.P. (° C.)
I	CH_3	CH_3	CH_3	----------------	140~1
II	C_2H_5	C_2H_5	C_2H_5	83~5/3	--------
III	C_3H_7	C_3H_7	C_3H_7	260~5	38
IV	C_4H_9	C_4H_9	C_4H_9	153~4/7	53~4
V	C_8H_{17}	C_8H_{17}	C_8H_{17}	200/0.1	51~2
VI	i-C_5H_{11}	i-C_5H_{11}	i-C_5H_{11}	325~330	606~5
VII	CH_3	C_6H_{13}	C_6H_{13}	182~3/6	42~3
VIII	C_4H_9	C_4H_9	—CH_2	215/5	63
IX			$C_{12}H_{25}$	----------------	65~6



$$\overset{R_1}{\underset{R_2}{}}\underset{\downarrow\atop O}{P}-(CH_2)_x\underset{\downarrow\atop O}{P}\overset{R_1}{\underset{R_2}{}}$$

Compound No.	R_1	R_2	X	B.P. (° C./ mm. Hg)	M.P. (° C.)
X	CH_3	CH_3	1	----------------	132~4
XI	CH_3	CH_3	4	219~22/0.35	205
XII	CH_3	CH_3	5	249~52/1.3	167~8
XIII	CH_3	CH_3	6	217/0.35	179~80
XIV	C_2H_5	C_2H_5	4	181~2/0.25	111~2
XV	C_4H_9	C_4H_9	3	----------------	128~9
XVI	Same	Same	4	270~1/2	116~8
XVII	do	do	5	259/0.75	106~7
XVIII	do	do	6	279~81/0.9	110~1
XIX	do	do	1	218~223/0.2	33~35
XX			1	----------------	181~2
XXI	Same	Same	2	----------------	276~8
XXII	do	do	4	290~1/1.6	154~5
XXIII	do	do	5	326~7/0.27	119~20
XXIV	do	do	6	292~4/0.20	196~8

The phosphine oxides represented by the above-mentioned general formulas are synthesized, in general, either by reacting phosphorus hemitetraiodide with an alkyl iodide and then treating the reactor mixture with concentrated nitric acid, or by reacting phosphorus oxychloride, or a substituted phosphorus oxychloride in which the chlorine has been substituted by other substituent, with a Grignard reagent. The process for the synthesis thereof is disclosed in such literature as E. S. Levchenko, Y. V. Piren, A. B. Kilsanov: Zhurnal Obshchei Khimii, 30 1976–81 (1960), or G. M. Kosolapoff, R. F. Struck: Journal of the Chemical Society, 1959, 3950–2.

In incorporating the compounds having the aforesaid general formulas into the silver halide emulsion layer, subbing layer, inter layer, filter layer, antihalation layer, protective layer and backing layer, the compounds may be used in the form of solutions in suitable solvents such as water or alcohols. Alternatively, said solutions may be sprayed onto the surface of light-sensitive photographic materials, or light-sensitive materials may be immersed in said solutions. In the case of compounds poor in water solubility, they may be incorporated after dissolving in solutions of suitable surface active agents less in influence on photographic emulsions, such as for example, anionic surface active agents, as mentioned before. Alternatively, they may be incorporated, into emulsions, in the form of dispersions formed by dissolving the compounds in suitable solvents such as dibutyl phthalate and the like, forming the solutions into colloidal solutions by means of a colloid mill or of ultrasonic waves, and dispersing the colloidal solutions into water. Further, the compounds of the present invention give favorable results even when incorporated into such treating solutions as developer, stopper, fixing solution and thickener, particularly into the thickener. The amounts of the present compounds to be incorporated into said layers vary depending on the kinds of compounds and of layers, but are preferably within the range of from about 0.1 mg. to about 1 g. per square meter of light-sensitive materials.

The following examples illustrate the present invention.

EXAMPLE 1

The compound V was dissolved in water containing sodium dodecylbenzenesulfonate to form a 1% solution. The solution was sprayed onto the surface of a high speed X-ray film, and was then dried. On the other hand, the same X-ray films were immersed for 1 minute individually in the above-mentioned solution, and in a 1% sodium dodecylbenzenesulfonate solution, and were then dried. These 3 treated films and an untreated X-ray film were allowed to stand for 24 hours under the conditions of a relative humidity of 30% and a temperature of 25° C. Therefore, the surfaces of said films were abraded with nylon and polyester cloths, and then the films were developed, without exposure, according to an ordinary procedure using a developing solution for X-ray films. In the film treated with the solution containing no compound V and in the untreated film, the generation of considerably marked static marks was observed, whereas in the films treated with the solution containing the compound V, no generation of static marks was observed.

On the other hand, the films treated with the solution containing the compound V were subjected to sensitometry according to JIS procedure, but no influence on the films in speed, gradation and fog due to treatment with the solution containing the compound V was observed at all. Further, these films were stored for 3 days both in a thermostat at 55° C., and under the conditions of a temperature of 50° C. and a relative humidity of 80%, and were then subjected as well to sensitometry according to JIS procedure. In this case also, it was found that the compound V gave no influence to the films.

EXAMPLE 2

The compound XIX was dissolved in a 4% solution of sodium decyl-isoamyl sulfosuccinate so that the concentration thereof became 2%. This solution was poured into a 2% gelatine solution, which was to be employed as a protective layer, in an amount of 20 cc. per liter of said gelatine solution. The mixed solution was applied as a protective layer onto the surface of a high speed X-ray film and was then dried. The resulting light-sensitive material was subjected to entirely the same test as in Example 1 together with the said X-ray film having the protective layer which had not been incorporated with the compound XIX, whereby the same results as in Example 1 were obtained.

EXAMPLE 3

10 cc. of a 5% methanol solution of the compound VIII was added to 1 l. of a green-sensitive silver iodobromide color-photographic emulsion. To the mixture was added a solution prepared by dissolving in a 1 N

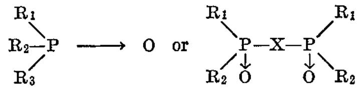
caustic soda solution 20 g. of the magenta coupler, 1-(4′-phenoxy-3′-sulfophenyl)-3 - heptadecyl - 5 - pyrazolone, and then adjusting the resulting solution to pH 6.8 by means of citric acid. The thus obtained emulsion was applied onto a cellulose triacetate base and was then dried. The resulting film was subjected to entirely the same test as in Example 1 together with a sample film to which the compound VIII had not been added. Provided that, in the above case, the films were developed according to an ordinary procedure by use of a color developer composed mainly of diethyl-p-phenylenediamine, and were then subjected to the after-treatment. As the result, the generation of static marks was completely inhibited by incorporation of the compound VIII, but said compound gave no influence to photographic characteristics of the film, i.e. speed, gradation and fog. Further, in the heat resistance test of the film also, the compound VIII gave no detrimental effect.

EXAMPLE 4

2 cc. of a 2% aqueous solution of the compound VI was added to a 5% aqueous gelatine solution containing an antihalation dye. To the mixed solution, 3 cc. of a 5% saponin solution was further added, and the mixture was applied onto the surface of a triacetate base and was then dried. Onto the reverse side of the base, a high speed photographic negative emulsion was applied, and as the protective layer thereon was applied a layer, into which 300 mg. per liter of the gelatine solution of the above-mentioned compound had been incorporated in the same manner as in Example 2. The resulting light-sensitive material was subjected to entirely the same test as in Example 1 to find that by addition of the compound VI, the generation of static marks was inhibited, and the compound gave no infiuence to the speed, gradation, fog and stability of the photographic emulsion.

What is claimed is:

1. A photographic composition comprising a light sensitive silver halide photographic material and a phosphine oxide having the general formula



$$R_1R_2R_3P \longrightarrow O \quad \text{or} \quad (R_1)(R_2)\underset{\downarrow \atop O}{P}-X-\underset{\downarrow \atop O}{P}(R_1)(R_2)$$

wherein R_1, R_2 and R_3 individually represent an alkyl, aryl or aralkyl group and X is an alkylene group.

2. A developer containing the phosphine oxide of claim **1.**

References Cited

UNITED STATES PATENTS

2,420,610	12/1945	Meeller	96—87A
2,968,554	1/1961	Land	96—66
3,385,704	5/1968	Grabhöfer et al.	96—66
3,377,292	4/1969	Halvorson	252—301.3
3,422,079	1/1969	Welch et al.	260—80

NORMAN G. TORCHIN, Primary Examiner

J. L. GOODROW, Assistant Examiner

U.S. Cl. X.R.

96—66