

UNITED STATES PATENT OFFICE

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PHOTOGRAPHIC LIGHT-SENSITIVE MATERIAL AND PROCESS FOR MAKING SAME

No Drawing.

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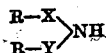
This invention relates to photographic light-sensitive materials and to processes of making such materials.

In the manufacture of photographic emulsions it is known that the colloidal material used contains minute quantities of biochemical origin that have a sulfiding or sulfiding and reducing action on the silver halides. These materials have been described in the United States Patent, No. 1,600,736, Punnett, September 21, 1926, and a process is therein given for separating these bodies from the colloidal material. Compounds are likewise added to photographic emulsions to extend the light-sensitivity far into the red end of the spectrum.

Photographic emulsions, if prepared with added, and often when they contain only the native sensitizing bodies, have a tendency to fog the light-sensitive materials contained therein. The more powerful the sensitizer, the greater is the tendency to fog. While such fogging action is associated with the speed of the inception of the latent image, nevertheless, apparent fog must be avoided with its attendant loss in the commercial value of the product.

The object of the present invention is to provide a series of compounds for the purpose of stabilizing light-sensitive materials and thereby correcting the hereinabove described tendencies without markedly retarding the sensitivity of the light-sensitive materials. Other objects will hereinafter appear.

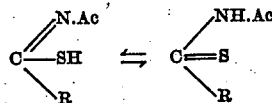
We have now found a class of anti-sensitizing or fog-inhibiting compounds which are effective in the production of light sensitive emulsions and in the preparation of colloidal intermediates for the manufacture of such emulsions. This new class of substances may be indicated by the following formula:



In this formula R stands for any organic radical not containing a double bonded nitrogen. X and Y can be the same or different activating electro-negative radicals, comprising as, for example, sulphur (:SR), carbon (:CR), or imid nitrogen (:NR).

The photographic sensitivity of silver halide emulsions is largely conditioned by the formation in the halide grain of very small specks of silver sulphide, silver or both, or analogous bodies. We have found that the production of chemical fog, which is otherwise known as inherent emulsion fog, is probably due to these nuclei becoming excessively large, whereby spontaneous reducibility is brought about.

Sheppard & Hudson in Photographic Journal vol. 67, p 359 (1927) have shown in the thioanilides a class of bodies of the general formula:



which have either sensitizing or anti-sensitizing and fog-inhibiting properties according as they react to form silver sulphide or combine with the silver bromide to form a stable non-reducible body.

While the theory of sensitivity restraint and fog inhibition is not essential to the practical application of our discovery, it exhibits the reasoning by which we were led to it.

Proceeding from these conceptions, we have sought for substances which could combine with the silver halide and particularly at the boundary of a growing silver sulphide or other sensitizing speck.

For example, in the structure given above if X and Y are substituted by CH₂ groupings, there results a compound which is only weakly active in its fog inhibiting or stabilizing action. The substitution of oxygen for H₂ attached to one of the carbon atoms, or, in other words, the substitution of CO for X and CH₂ for Y, somewhat increases the effectiveness of the substance. A more powerful body results when the carbonyl group is substituted for both X and Y. An example of this type of substance is diacetamide, phthalimide, the pyrrol and pyrrol derivatives such as succinimide. A powerful fog inhibitor or stabilizer is also obtained if carbonyl be substituted for X and a sulfonyl be substituted for Y. In this case we

have sulfo-amides and their derivatives, such for example as saccharin.

There are other configurations of the imid group which are also active in respect of this inhibitory action on the fogging of silver halides. If imid nitrogen replaces the X while CH, imid nitrogen, or carbonyl, replaces the Y in our above configuration, we have a series of compounds which show this activity. The pyrazolone ring, pyrazole ring, the pyrazolodone ring, and the osotriazole ring are examples of this class of substances.

In order to thoroughly and uniformly incorporate the non-fogging agent into the emulsion it is usually necessary to dissolve the material in a suitable solvent such as water or alcohol, or acetone. Other solvents or mixtures of them, of course, may be used that are compatible with the emulsion but we have found the above solvents to be most desirable.

The proportions in which these compounds are incorporated in the emulsions, or in the colloids for the emulsions, are important. Too much of them will often desensitize the emulsion. The maximum proportions which can be used practically vary slightly with the particular sensitizing compound which is selected, with the ratio of gelatin to silver halide in the emulsion, with the type of emulsion as regards grain size and alkalinity, with the amount of natural sensitizer also present in the gelatin when the latter is manufactured, with the particular silver or halides employed, or with the fog standards which are set by the emulsion manufacture. The optimum proportion is readily obtained by routine test.

With gelatino silver halide developing-out emulsions, it is generally advantageous to add from .01 to 10 grams of the restraining substance per 1,000 grams of gelatine. Where gelatine is used in more than one operation, as for example in small amounts for precipitation, or in larger amounts at later meltings, these gelatins may be differentially treated with the restraining bodies as will be understood by those skilled in the art.

Our present fog-inhibiting compounds are effective in all kinds of emulsions ordinarily met with, such as orthochromatic, panchromatic, X-ray, as well as the ordinary non-color sensitized ones. They can be added without or with sensitizing dyes or before or after them. Alternatively, the fog inhibiting agent may be used as a solution for treating the finished photographic material.

Our present stabilizing substances may be in general incorporated in the emulsions or in the colloids for the emulsions in the same way as those set forth in United States Patent No. 1,574,944, March 2, 1926. For example, a mixed silver bromide and iodide

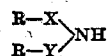
emulsion in gelatin may be prepared as set forth in said patent, page 3. After the emulsion is prepared, it may be melted and the proper amount of stabilizing compound thoroughly mixed into it. This mixing is conveniently effected by dissolving the stabilizing substance in a suitable solvent or mixture of them, and then stirring such solution into the emulsion.

While our novel sensitizing compounds are preferably used with gelatin, they, nevertheless, have utility with emulsions made in other colloids or agar agar, albumins, gums like gum arabic and cellulose derivatives. Our compounds likewise have utility in emulsions in which different kinds of silver salts are present such as silver bromide, silver iodide, silver chlorides, or mixtures of any of these with one or more of the others.

Various changes may be made, therefore, in the method of compounding our stabilizing materials with the colloids for the photographic emulsion and known equivalents may be used therefor without in any way departing from our invention or sacrificing any of the advantages derived therefrom.

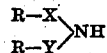
Having thus described our invention, what we claim as new and desire to secure by Letters Patent is:

1. A photographic emulsion comprising a colloid, particles of photographic silver salts suspended therein, and an added compound therein which stabilizes the emulsion and on which at least part of the light sensitiveness depends, said compound being of the type



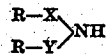
in which R is a nitrogen free organic radical and X and Y are selected from activating electro-negative radicals.

2. A photographic emulsion comprising a colloid, particles of photographic silver salts suspended therein, and an added compound therein which stabilizes the emulsion and on which at least part of the light sensitiveness depends, said compound being of the type



in which R is a nitrogen free organic radical and X and Y are selected from activating electro-negative radicals, said compound being soluble in a water miscible solvent.

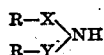
3. A photographic emulsion comprising a colloid, particles of photographic silver salts suspended therein, and an added compound therein which stabilizes the emulsion and on which at least part of the light sensitiveness depends, said compound being of the type



in which R is a nitrogen free organic radical and X and Y are selected from the group comprising the activating electro-negative

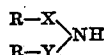
radicals containing sulfur, carbon, and imide nitrogen.

4. A photographic emulsion comprising a colloid, particles of photographic silver salts suspended therein, and an added compound therein which stabilizes the emulsion and on which at least part of the light sensitiveness depends, said compound being of the type



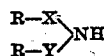
in which R is a nitrogen free organic radical and X and Y are selected from the group comprising the activating electro negative radicals containing sulfur, carbon, and imide nitrogen, said compound being soluble in a water miscible solvent.

5. A photographic emulsion comprising a colloid, particles of photographic silver salts suspended therein, and an added compound therein which stabilizes the emulsion and on which at least part of the light sensitiveness depends, said compound being of the type



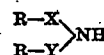
in which R is a nitrogen free organic radical and X and Y are selected from the group of carbonyl, sulfuryl and imide nitrogen, said compound being soluble in a water miscible solvent.

6. A photographic emulsion comprising a colloid, particles of photographic silver salts suspended therein, and an added compound therein which stabilizes the emulsion and on which at least part of the light sensitiveness depends, said compound being of the type



in which R is a nitrogen free organic radical and X and Y comprise activating electro-negative radicals, said compound forming a closed ring and soluble in a water miscible solvent

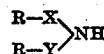
7. In the process of preparing a developing-out colloid sensitive silver salt emulsion, stabilizing the light sensitiveness thereof by incorporating a stabilizing compound therein in an amount corresponding to .001 to 1% by weight, of the gelatin present, said compound being of the type



in which R is a nitrogen free organic radical and X and Y comprise activating electro-negative radicals.

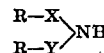
8. In the process of preparing a developing-out colloid sensitive silver salt emulsion, stabilizing the light sensitiveness thereof by incorporating a stabilizing compound therein in an amount corresponding to .001 to 1% by weight, of the gelatin

present, said compound being of the type



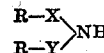
in which R is a nitrogen free organic radical and X and Y comprise activating electro-negative radicals, said compound being soluble in a water miscible solvent.

9. In the process of preparing a developing-out colloid sensitive silver salt emulsion, stabilizing the light sensitiveness thereof by incorporating a stabilizing compound therein in an amount corresponding to .001 to 1% by weight, of the gelatin present, said compound being of the type



in which R is a nitrogen free organic radical and X and Y are selected from the group of electro-negative radicals comprising carbonyl, sulfuryl and imide nitrogen.

10. The process of making an intermediate for use in the preparation of photographic emulsions which comprises incorporating in the gelatin .001 to 1% by weight thereof of a stabilizing compound, said compound being of the type



in which R is a nitrogen free organic radical and X and Y comprise activating electro-negative radicals.

11. A photographic emulsion comprising a colloid, particles of photographic silver salts suspended therein, and an added compound therein which stabilizes the emulsion, said compound being selected from the group of heterocyclic compounds containing nitrogen in the ring and consisting of those compounds containing a pyrazolone ring, a pyrazole ring, a pyrazolodone ring or an osotriazole ring.

Signed at Rochester, New York this 19th day of February, 1929.

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