

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 U. S. Patent No. 1,600,736, Punnett, September 21, 1926, and a process is therein given for separating these bodies from the colloidal material. Sensitizing dyes are likewise added to photographic emulsions to extend the light sensitivity of the emulsion 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.

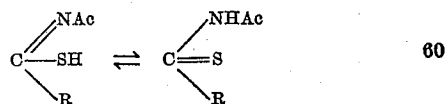
The object of the present invention is to provide a series of compounds for the purpose of stabilizing light-sensitive materials and thereby correcting the hereinabove described tendencies without markedly retarding the sensitivity of the light sensitive materials. Other objects will hereinafter appear.

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 class includes the substituted carbamides, the acid amides, the aryl acid amides, the allyl acid amides, the cyclic carbamides, and the alpha amide hydrazides.

The photographic sensitivity of silver halide emulsions is largely conditioned by the formation in the halide grain of very small specks of silver sulfide, silver or both, or analogous bodies. We have found that the production of chemical fog, which is other-

wise known as inherent emulsion fog, is probably due to these nuclei becoming excessively large, whereby spontaneous reducibility, is brought about.

S. E. Sheppard and H. Hudson in Photographic Journal vol. 67, p 359, (1927) have shown in the thioanalides, a class of bodies of the general formula



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

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

Proceeding from these conceptions, we have found a general class of substances which combine with the silver halide and particularly at the boundary of a growing silver sulfide or other sensitizing speck which may be called derivatives of the amid of carbonic acid or carbamides. We have found, as described above, that the organic substances which may be classified as the substituted carbamides, have this desirable characteristic. For example, this is shown by n-methyl carbamide, 1 methyl 2 ethyl carbamide, 1 methyl 2 phenyl carbamide, 1:2 diphenyl carbamide, 1 allyl 2 phenyl carbamide, nitrocarbamide, and carbamyl chloride. We have likewise found that the acid amides are useful for this purpose. For example, the propionamide and the methyl acetamide and cyanoacetamid. Of the aryl acid amides, benzamide, benzanilide, n-ethyl benzamide, acetanilide and phenyl acetanilide illustrate classes of substances which impart this desirable quality. Examples of the allyl acid amides are acrylamide and 1 allyl 2 phenyl carbamide. The cyclic carbamides, methylene carbamide, ethylidene carbamide and malonyl carbamide, as well as the closely allied equivalents, have proven suitable. The amide hydrazides may also be classed

with the above. An example of this class of substances is benzol hydrazine.

It will, of course, be understood that the equivalents of the above listed carbamides which necessarily includes the other members of the alkyl, aryl, allyl, acyl, alkyloxy, aryloxy, alkylene, or other radicals, some of which are illustrated in the above examples, may be substituted for the hydrogen or imid nitrogen in the original nucleus. The electro negative radicals such as NO_2 , the halogens, SO_2 , CN , which have a tendency to increase the effectiveness of the compound may replace one of the amid groups in the carbamide or one of the hydrogen atoms therein or any of the possible substitutions or replacements made which are known by those skilled in the art. It is necessary, however, that the compound used be soluble in water, or alcohol, or acetone. The uniform incorporation of small amount of insoluble compounds is very difficult and generally undesirable. The substitutions may be made without in any way departing from the invention except as restricted by the appended claims.

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 manufacturer. The optimum proportion may readily be obtained by routine test.

With the gelatino-silver-halide developing-out emulsions, it is generally advantageous to add from 1/100 to 10 grams of the restraining substance per 1,000 grams of gelatin. Where gelatin is used in more than one operation, as for example, in small amounts for precipitation, or in larger amounts at later meltings, these gelatines may be differentially treated, 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 ortho-chromatic, pan-chromatic, X-ray, as well as the ordinary non-color sensitizing 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 U. S. Patent of S. E.

Sheppard No. 1,574,944, March 2, 1926. For example, a mixed silver bromide and iodine emulsion in gelatine 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 the stabilizing compounds 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 gelatine, they, nevertheless, have utility with emulsions made in other colloids as 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 chloride, 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 recognized 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 selected from the group of carbamides including the substituted carbamides, cyclic carbamides, acid amides, substituted acid amides and alpha amide hydrazides.

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 selected from the group of carbamides including the substituted carbamides, cyclic carbamides, acid amides, substituted acid amides and alpha amide hydrazides, said compound being soluble in a water miscible solvent.

3. In the process of preparing a developing-out colloid 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 selected from the group of carbamides including the substituted carbamides, cyclic carbamides, acid amides, substituted acid amides and alpha amide hydrazides.

4. In the process of preparing a developing-out colloid silver salt emulsion, stabiliz-

ing 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 selected from the group of carbamides including the substituted carbamides, cyclic carbamides, acide amides, substituted acid amides and alpha amide hydrazides, said compound being soluble in a water miscible solvent.

5. In the process of preparing a developing-out gelatino-silver halide emulsion, mixing with the gelatin a stabilizing compound, said compound being selected from the group of carbamides including the substituted carbamides, cyclic carbamides, acid amides, substituted acid amides and alpha amide hydrazides, and thereafter incorporating the mixture with other ingredients of the emulsion.

6. The process of making an intermediate for use in the preparation of photographic emulsions which comprises incorporating therein a stabilizing compound, said compound being selected from the group of carbamides including the substituted carbamides, cyclic carbamides, acid amides, substituted acid amides and alpha amide hydrazides, said compound being soluble in a water miscible solvent.

7. The process of making an intermediate for use in the preparation of photographic emulsions which comprises incorporating therein in gelatin from .001 to 1% by weight, of a stabilizing compound, said compound being selected from the group of carbamides including the substituted carbamides, cyclic carbamides, acid amides, substituted acid amides and alpha amide hydrazides.

8. A photographic emulsion comprising a colloid, with particles of photographic silver salts suspended therein, said colloid containing acetanilide.

9. A photographic emulsion comprising gelatin, with particles of photographic silver salts suspended therein, said gelatin containing from 1/100 to 10 parts of acetanilide for every 1,000 parts of gelatin.

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

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