

UNITED STATES PATENT OFFICE.

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PHOTOGRAPHIC EMULSION AND MATERIAL AND PROCESS USED IN THE PREPARATION THEREOF.

No Drawing.

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This invention relates to photographic emulsions, and to materials and processes used in preparing the same.

One object of the invention is to provide photographic emulsions, especially developing-out ones, having new or improved properties because of the use or presence therein of materials, the sensitizing properties of which we have discovered. Still another object of our invention is to provide processes in which such materials are used to improve photographic emulsions, especially developing-out ones, as regards light-sensitiveness, by which term we include their ability to give the earliest visible impression or image with the minimum exposure or their ability to give density after a given exposure or both, the usual photographic fluid treatments being used in preparing such impression or image or density.

A further object of the invention is to provide colloid products, such for instance, as gelatins, the usefulness of which for forming light sensitive photographic emulsions, especially developing-out emulsions, is greatly increased and controlled by our said sensitizing materials incorporated therewith. Another object of the invention is to provide processes for preparing said colloid products or intermediates.

Other objects are,—to increase the sensitiveness of photographic emulsions, especially developing-out emulsions, while wholly or partially dispensing with expensive or long and uncertain so-called ripening methods; to enable the use of a type of gelatin having desirable physical qualities in making such a photographic emulsion of greater light-sensitiveness than that normally obtainable with said gelatin; to obtain more stable emulsions through the purity of the ingredients; to increase the light-sensitiveness of photographic emulsions, particularly developing-out ones, the grain characteristics of which have already been determined; to increase the general light-sensitiveness of such photographic emulsions throughout the spectral ranges to which they are normally sensitive; to make such photographic emulsions of standard light-sensitive characteristics with gelatins

which normally do not produce emulsions having such characteristics; to make, as intermediates in the manufacture of photographic emulsions, gelatins of standard light-sensitiveness giving power out of gelatins which do not normally have the power of giving such standard sensitiveness to emulsions, such as developing-out ones, made from them. Further objects will hereinafter appear.

In United States Patent No. 1,574,944, March 2nd, 1926. S. E. Sheppard photographic light-sensitive material and process of making the same, there is disclosed the remarkable sensitizing properties of certain compounds, when employed in the proper proportions in photographic emulsions, especially developing-out ones, and when employed in gelatin or other colloids for use in making such emulsions. Each member of these series of compounds contains a divalent atom of the sulfur group (a sulfur atom, or a selenium atom, or a tellurium atom), which is joined by a double bond to a single metalloid atom (not one bond to one atom and the other bond to a different atom) to which at least another group of atoms is attached. The metalloid atom to which the atom of sulfur, selenium, or tellurium is joined by a double bond is in many instances a carbon atom. These substances include thiocarbamids, selenocarbamids and tellurocarbamids. The corresponding carbimids are also usable. Various organic groups can be substituted in such carbamids and carbimids.

Examples of such substances are; thio-sinamine (allyl thiourea), allyl isothiocyanate, phenyl isothiocyanate, phenyl thiourea, thiocarbamide, thiourea, thiosemicarbazide, sodium thiosulfate, (but not sulfate or sulfite) di-otolyl thiourea, seleno-mustard-oil (allyl isoselenocyanate), potassium selenocyanide, allyl selenourea, thioacetamid, thioformamid, thiobarbituric acid, telluro-mustard-oil (allyl isotellurocyanate) potassium tellurocyanide, allyl tellurourea. It is preferable to use these compounds in substantially pure or "C.P." form; but impurities, which are harmless to the emulsion and are not bulky, can be tolerated. The selenocyanide and

tellurocyanide are used in higher proportions than the other listed compounds.

We have found that these substances may be usefully supplemented by reducing agents. These reducing agents are of such a nature, and are used in such proportions, that if they were present alone in a developing-out emulsion, they would produce a slight fogging action and would not usefully increase the sensitivity. When, however, these reducing agents are incorporated with the sensitizing materials mentioned above, they assist the latter in creating or increasing the sensitivity of the emulsion. When incorporated with the sensitizing substances in gelatin, they usefully assist in reinforcing or increasing the power of the gelatin to give sensitive emulsions.

There are numerous kinds of reducers which may be used as auxiliaries to the sensitizers, which latter are not reducers of the silver salts in the emulsion in the ordinary sense. Typical reducers are the alkaline salts of arsenious acid, alkaline hyposulfites, alkaline hypophosphites hydroxylamine and substituted hydroxylamine, aldehydes, such as formaldehyde. Of course, this list is merely illustrative and not limited.

The amount of reducing substance to be combined with the sensitizing substance may vary with the type and treatment of the emulsion, just as the amount of the sensitizing agent varies when used alone. But in general the quantities of reducer which are permissible in conjunction with the sensitizing substance are of the same order of magnitude as the latter. Preferably we use equimolecular parts of sensitizer and reducer. In any event, the amount of reducer is such that the fog in the final emulsion is below the manufacturing tolerance.

In gelatino-silver-halid developing-out emulsions, we employ approximately 10 grains or less of active sensitizing compound, such as thiosinamine, for example, in 130 pounds of emulsion (the latter being computed as the weight of its non-aqueous ingredients in the dry state). This amounts to less than about 10 grains in 100 pounds of gelatin, computed as dry gelatin when the sensitizer is added to the gelatin before the latter is used in making the emulsion. The amount of reducer is, therefore, generally less than 10 grains in 130 pounds of emulsion or less than 10 grains in 100 pounds of gelatin. We have found 2 to 3 grains of sensitizing compound, such as thiosinamine, for instance, and 2 to 3 grains of a reducer, such as sodium hyposulfite for instance, to 100 pounds of gelatin (computed as dry) or 130 pounds of emulsion (computed as dry) is within the useful limits and generally excellent,—for example, with alkaline developing-out gelatino-silver-halid emulsions. Of course, smaller amounts of sensitizer and re-

ducer are employed when less sensitizing effects are desired; but it is important not to exceed the upper or fogging limits, as indicated above. It is to be noted that we use the term hyposulfite in its correct scientific sense and not as misapplied to sodium thiosulfate, as is sometimes done in the photographic literature.

The amounts of the sensitizer and reducer which are used together in the emulsion are so small that the addition of them does not appreciably dilute the emulsion or the emulsion-forming colloid; nor does it affect their physical properties. This enables us to select gelatins, for instance, because of their physical properties like setting ability, melting points and viscosity, without regard to whether they can be made into sufficiently light-sensitive emulsions; and any deficiency in sensitizing power can be made up by incorporating a proper, but very small quantity, of the sensitizer with the reducer. Such additions do not effect the grain-size characteristics, which are thus susceptible of independent control.

The effect of using these sensitizers in conjunction with reducers of the type indicated above, is to produce "chemical" sensitization, instead of an "optical" one. In other words the effect is unlike that of sensitizing dyes, the sensitiveness being increased throughout the normal spectral range of the emulsion instead of at only those spectral points corresponding to the spectral absorption of the sensitizing compound and reducer. But, of course, we can use the sensitizers in conjunction with our reducers in increasing the general light-sensitiveness of orthochromatic, panchromatic, X-ray and special emulsions, as well as the ordinary ones.

We may use the sensitizers in conjunction with our reducers in many ways, the uses of this combination being similar to those enumerated for the sensitizers alone in the above cited application. Broadly they may be incorporated in emulsions or in colloids for emulsions or in both. They may be added at different stages of emulsion manufacture, even when the latter is otherwise ready for coating.

The following example illustrates how light-sensitive photographic emulsions of the developing-out type may be prepared and improved by the aid of our combination of sensitizer and reducer. Of course, our invention is not restricted to this illustration except as indicated in the claims. The emulsion forming operations hereinafter described are along the lines of known practice, as described in the literature of the art.

The two following solutions are made up, the parts being by weight:

A. 900 parts of silver nitrate in 9,200 parts of water.

B. 690 parts of potassium bromide and 50 parts of potassium iodide in 6,100 parts of water along with 300 parts of gelatin.

In mixing B, the halid salts are first dissolved, the water and the gelatin then added to the salt solution. Solution B is then warmed, say to 140° F. or 150° F. for example; and the silver nitrate solution A is gradually added to it with constant stirring. It is preferable to warm solution A before adding it to B, say to 150° F. or 160° F. for instance. When solution A has been thoroughly incorporated in solution B, there are then added 43 parts of strong ammonia previously dissolved in 900 parts of water. The emulsion formed by these operations is allowed to stand for a short time, say 15 minutes to a half hour for example. Then 1050 parts of gelatin are dissolved in it with thorough mixing. The emulsion is next cooled, such as by keeping in a cool space, until it sets to a firm jelly. The latter is broken up, as by shredding, for instance, and thoroughly washed to remove soluble salts, such as potassium nitrate and any excess potassium halids. The wash water is, of course, cool enough not to melt the pieces of emulsion jelly. The washed emulsion is next remelted to 100° F. and 1050 parts of water soaked gelatin are thoroughly mixed into it, the temperature then being raised, say between 120° F. and 150° F., for instance, for a short time, say a few minutes. It is then cooled and set. It is an example of the ammonia or alkaline type of developing-out emulsion.

Our sensitizing compounds and reducers may be incorporated together or sequentially in the emulsion or its ingredients at different stages of the above described process. They are most conveniently handled by dissolving them in a solvent which is inert with respect to the emulsion and simply acts as a vehicle to help in spreading the sensitizer and reducer throughout the emulsion.

The different gelatins sold for photographic emulsion-making may be used in the example given above, hard ones being very useful. The temperatures given are, of course, readjusted if the particular gelatin employed has melting and setting points which deviate considerably from the usual ones, this adjustment being a matter of routine control.

Instead of employing gelatins which give emulsions of useful but lower sensitiveness even before the addition of our sensitizer and reducer, we may use practically inert gelatin. This may be prepared, for example, by treating active photographic gelatins with oxidizing agents. Dilute aqueous solutions of a peroxide, such as sodium peroxide (say from 5 to 10% by weight) may be intimately mixed into the gelatin and then

washed when the oxidation has occurred. Such an inert gelatin, when made into an emulsion by the above described process, produces little, if any, useful sensitiveness. But when our combination of a sensitizing compound and reducing compound is added, either to the emulsion, or to the gelatin before it is made into an emulsion, highly sensitive developing-out emulsions are produced.

When adding our combination of reducer and sensitizer they may be mixed with a little ethyl alcohol as a vehicle to enable their ready admixture with the other ingredients. One very useful way of employing our combination is to form a highly concentrated emulsion of silver halid in inert gelatin. When the proper grain sizes and other characteristics have been established, we may then stir into the emulsion gelatin containing our mixed sensitizing agents and reducing agents.

In the examples given above, the steps of treating with ammonia and warming of the emulsion may be, one or both, omitted. Our combination acts to increase the light-sensitiveness independent of such ripening steps. But we prefer to use them because the effect of either or both of them is to give a stronger initial sensitized condition which is multiplied or increased by using our sensitizing and reducing compounds. Moreover, it is desirable to have sufficient ammonia, or equivalent alkali present to form slightly alkaline emulsions.

In place of the colloids mentioned above, other colloids used in photographic emulsions may be employed. Moreover, the principle of the invention is applicable to silver chloride, as well as to silver bromide and silver iodide and to mixtures of any two or more of them.

While the theory of operation of our invention is not vital to the successful use of it, nevertheless, the following explanation of the action appears to be what takes place. First there is formed a complex of silver halid and the sensitizer, such as a thiocarbamid. Next there is an interaction of silver halid and the sensitizer, such as thiocarbamid, to form small specks of silver sulfide in the silver halid grains. Of course, where selenium or tellurium sensitizing compounds are used, there are correspondingly formed specks of silver selenide or telluride. Mixtures of these substances form corresponding mixed effects. These specks act as nuclei of silver deposition. These nuclei then become enlarged by the addition of metallic silver atoms from the reduction of silver halid by the small amount of cooperating reducer. This nucleating action prevents the slight fog which would be present if the reducer were used alone.

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 salt suspended therein, and added sensitizing and reducing compounds upon which at least part of the light-sensitiveness of the emulsion depends, the sensitizing compound containing a divalent atom of the sulfur group directly joined by a double bond to a single metalloid atom, to which at least another group of atoms is attached.

2. A photographic developing-out gelatino-silver-halid emulsion of the alkaline type of relatively high light-sensitiveness, comprising a mixture of the constituents of a gelatino-silver halid emulsion of lower light-sensitiveness, and an added sensitizing compound and an added reducing compound, the difference between said lower and said high light-sensitiveness depending upon said last two named compounds.

3. A photographic emulsion comprising a colloid, particles of photographic silver salt suspended therein and coating sensitizing and reducing substances upon which at least part of the light-sensitiveness of the emulsion depends, the amount of said coating substances being less than the order of 10 grains per 130 pounds of emulsion and insufficient to cause immediate fogging tendency.

4. In the process of preparing a developing-out colloid-sensitive-silver-salt emulsion, increasing the light-sensitiveness thereof by incorporating with the other constituents thereof an independent sensitizing compound and a coating reducing compound.

5. In the process of preparing a developing-out colloid-silver-salt emulsion of the alkaline type of relatively high light-sensitiveness, combining constituents of a colloid-sensitive silver-salt emulsion of lower light-sensitiveness with sufficient coating sensitizing and reducing compounds to effect high light-sensitiveness, the sensitizing compound containing a divalent atom of the sulfur group directly joined by a double bond to a single metalloid atom to which at least another group of atoms is attached.

6. In the process of preparing a developing-out gelatino-silver-halid emulsion, increasing the light-sensitiveness thereof by incorporating with the other constituents thereof an independent thiocarbamid and an independent reducing compound.

7. In the process of preparing a developing-out colloid-sensitive-silver-salt emulsion, increasing the light-sensitiveness thereof by incorporating with the other constituents thereof an independent sensitizing compound and a reducing compound, the amount of said last two named compounds being less than the order of 10 grains per 130 pounds of emulsion and being insufficient to cause immediate fogging tendency.

8. The process of preparing photographic gelatino-silver-halid emulsions, which comprises substantially freeing gelatin from any sensitizing compounds originated therein, mixing a sensitizing compound and a reducing compound therein, and preparing a sensitive photographic emulsion from said mixture.

9. An intermediate for use in making photographic emulsions, comprising an emulsion-forming colloid having incorporated therein an independent sensitizing compound and coating reducing compound.

10. The process of making an intermediate for use in the preparation of photographic emulsions, which comprises incorporating in an emulsion-forming colloid an independent sensitizing compound containing a divalent atom of the sulfur group directly joined by a double bond to a single metalloid atom to which at least another group of atoms is attached, and also incorporating therein a reducing compound.

11. The process of making an intermediate for use in the preparation of photographic gelatino-silver-halid emulsions, which comprises substantially freeing gelatin from sensitizing compounds and incorporating therein coating sensitizing compounds and reducing compounds.

Signed at Rochester, New York, this 11th day of June, 1925.

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