This invention relates to photographic emulsions in which mercury compounds are employed and to processes of making such emulsions.

One object of the invention is to provide a photographic emulsion, based upon the use of salts of mercury, which will function properly as a developing-out emulsion, and will have greatly improved properties because of the use or presence therein of materials, the sensitizing properties of which, in such emulsions, we have discovered. Another object of our invention is to provide emulsions of the above mentioned type in which the light-sensitiveness of the well known so called gaslight emulsions. By the term light-sensitiveness, we include the ability of the emulsion to give the earliest visible impression or image with the minimum exposure, or its ability to give density after a given exposure or both, the usual photographic fluid treatments being used in preparing such impression or image of density. Another object of the invention is to provide improved processes for making such improved emulsions. Other objects will hereinafter appear.

The usual light-sensitive emulsions employed in the photographic art comprise a colloid, such as gelatin, gum arabic, collodion, or the like, in which are dispersed minute particles of light-sensitive silver salts, such as the bromide, chloride and iodide. When attempts have been made to prepare corresponding emulsions, by using salts of mercury instead of salts of silver, the resulting products have possessed only slight light-sensitiveness. A latent image has been detectable and developable only after prolonged exposure. Their sensitiveness has been markedly inferior to that of gaslight emulsions.

We have found that such colloid-mercury-compound emulsions can be remarkably improved, especially as regards their light-sensitiveness, by having incorporated therein one or more related chemical compounds. Broadly speaking, each compound of the series contains a divalent atom of the sulfur group (a sulfur atom in one series, a selenium atom in another series, a tellurium atom in still another series) 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, but not necessarily, a carbon atom. Said another group of atoms preferably is one which induces a chemical affinity toward the mercury salt.

For some of the preferred examples of our invention, we select from the above series the following subspecies—thiocarbamids, selenocarbamids, and tellurocarbamids. As the corresponding carbamids are likewise usable in preferred examples of our invention and are readily changed into said carbamids, it will be understood that the corresponding carbamids are included hereinafter when said carbamids are claimed. These subspecies of carbamids and carbamids include many compounds containing one or more substituent radicals, such as alkyl, aryl, acyl, alkyl-oxy, aryl-oxy, etc. groups. Thus, for example, allylthiourea (thiosinamine) containing an allyl radical in place of one of the hydrogen atoms of thiourea, is especially useful in practicing our invention. So are allyl isothiocyanate, allyl isoselenocyanate, allyl selenourea, and the corresponding tellurium compounds.

Not only can each compound of our series of light-sensitizers be used alone to improve an emulsion (or colloid for an emulsion) but two or more of such compounds may be used together to obtain their mutual or cumulative effects.

It is a common characteristic of the compounds which we use, that said double bonded atom of the sulfur group is chemically held in the molecule with intermediate firmness. Consequently said double bonded sulfur-group atoms in our compounds correspond roughly in the firmness with which they are held to the firmness with which the sulfur atoms are held in the so-called potential mercaptans, although there is, of course, some range of difference in the firmness with which said double-bonded atoms
are held in the different compounds of our series. We attribute the sensitizing action of our compounds to their forming in the emulsion grains small, mostly ultramicroscopic, nuclei which include mercury combined with either sulfur, or selenium, or tellurium, such as silver sulfid, silver selenid, and silver tellurid. The intermediate firmness with which said double-bonded atoms are held in our compounds facilitates this scattered formation or reaction without reacting on the whole of each grain. Since this deduction is not indispensable to the practical use of our invention, we do not wish to be limited to it except as defined in the claims.

We have also found that the best proportions of sensitizing compounds, relative to the rest of the emulsion, are very small. While these proportions are variable, the amount of sensitizing compound is usually less than 1/1000 of the weight of the other ingredients of the emulsion. Of course, the amount for any particular emulsion is readily adjusted by test so as to obtain the maximum sensitivity, compatible with the production of a good image and freedom from fog and other defects. The proportion of sensitizing compound which accomplishes this purpose is determined about as readily, for example, as the proportion of sulfur permissible in steel for a particular purpose. It will vary with the proportion of gelatin or other colloid to the mercury compound, with the specific nature of the individual mercury compound or compounds which are employed, with the type of emulsion as regards grain size characteristics and alkanility and so forth.

In consequence of the very small proportions of our sensitizing compounds which are employed in the mercury emulsions, the addition of them does not harmfully dilute the emulsion; nor does it affect the physical properties of the latter. Thus the use of our compounds provides a dependable way for controlling the properties of the colloid-mercury-compound emulsions. The sensitizing compounds can be added without any colloid, such as gelatin, and are, therefore, independent thereof. Moreover, the grain size characteristics of the emulsion are not affected by the additions of our compounds, they being independently controlled by the emulsion maker.

Illustrative examples of the compounds comprised within our series are thiosamine, (allyl thiourea); allyl isothiocyanate, phenyl isothiocyanate, phenyl thiourea, thioctabnilide, thiourea thiosemicarbazide, sodium thiosulfate, (but not sulfate or sulfite) di-tetyl thiourea, seleno-mustard-oil (allyl isoelenocyanate), 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 “P. F.” 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.

Just as silver halids, —silver chloride, silver bromide and silver iodide, are used singly or in mixture in the usual photographic emulsions, so we prefer to use one or more mercury halids. We have found that an emulsion of mercuric iodide has excellent properties and we shall now describe the preparation of such an emulsion by way of example; but it will be understood that the invention is not limited to the employment of mercury iodide, or to the other details thus given, except as indicated in the appended claims.

In 6,000 parts of water we dissolve 800 parts of gelatin. We also dissolve 200 parts of mercuric chloride, HgCl₂, in 1,000 parts of water. This amount of mercuric chloride is dissolved in the water by any of the known expedients, such as by heating to about 80° C. These solutions are then mixed, and any coagulum which may form, is redissolved by continual stirring at about 60° C. A solution of 240 parts of potassium iodide, KI, is prepared in 760 parts of water. Into this are stirred about 20 parts of a 20% aqueous chrom alum solution. This solution containing the potassium iodide and alum is then stirred into the solution containing gelatin and mercuric chloride. We prefer to carefully stir the solutions as they are being added, and use a temperature of 65° C.

After the ingredients have been added to each other gradually, or step by step, with agitation, the emulsion is allowed to set, being cooled in any suitable manner, say by being brought under the influence of ice, or placed in a refrigerating chamber. After being set, the emulsion is shredded and washed for two hours or more. This removes the soluble salts formed by the reaction and is carried out in the same way that potassium bromide is washed out from gelatino-silver-bromide emulsions during manufacture. After thorough washing and draining the emulsion is melted up.

We next incorporate the sensitizier into the emulsion. The latter is heated to 50° C., and to each 4000 volumes of it are added 200 volumes of a solution of thiosamine, this solution being made up with a strength of one part of thiosamine in 100 of water. Of course, the ingredients are thoroughly intermixed.

While the increase in sensitiveness is not absolutely dependent upon a heating operation, nevertheless we have found it highly
advantageous to provide a ripening or digestion step. For example, when the sensitizer is added to the emulsion, as hereinabove described, the mixture is brought to a temperature of 80° C. and maintained at that temperature for 15 minutes. The temperature may vary considerably above and below that amount. We have found useful results to be obtained over a range of from 60° C. to 100° C., and this is not a restrictive range. This brings about an especially effective action of the sensitizer on the emulsion, giving remarkable increase in speed as well as good density in the images or deposits formed in the emulsion. In these respects the emulsion is brought within the range of the well known gaslight emulsions.

It will be understood that the ripened emulsion is spread upon paper, film, glass or any other suitable or desirable support in the customary manner. While the time and temperature of the ripening or digestion operation may be varied considerably, we prefer to conduct it in such a way that only relatively small amounts of red tetragonal mercuric iodide are present.

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 a photographically sensitive salt of mercury suspended therein, and an added compound wherein upon which at least part of the light-sensitivity of the emulsion depends, said 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, the proportion of said compound being substantially independent of the proportion of said colloid.

2. A photographic developing-out emulsion comprising a colloid, particles of mercury iodide suspended therein, and an added compound wherein upon which at least part of the light-sensitivity of the emulsion depends, said compound containing a divalent atom of the sulfur group directly joined by a double bond to a single carbon atom to which at least another group of atoms is attached, the proportion of said compound being substantially independent of the proportion of said colloid.

3. A photographic developing-out emulsion comprising gelatin, particles of a photographically sensitive salt of mercury suspended therein, a compound wherein upon which at least part of the light-sensitivity of the emulsion depends, said compound containing an atom of the sulfur group joined to a single metalloid atom, to which at least another atom or group of atoms is attached, the presence of said last named group affecting said chemical affinity, the proportion of said compound being substantially independent of the proportion of said gelatin.

4. A photographic developing-out emulsion comprising gelatin, particles of mercury iodide suspended therein, and an added compound wherein upon which at least part of the light-sensitivity of the emulsion depends, said compound containing a divalent atom of the sulfur group directly joined by a double bond to a single carbon atom to which at least another atom or group of atoms is attached, the proportion of said compound being substantially independent of the proportion of said gelatin.

5. A photographic developing-out emulsion having a speed within the speed range of gaslight emulsions comprising gelatin, particles of mercury iodide suspended therein, and an added sensitizer containing thiocarbamid upon which at least part of the light-sensitivity of the emulsion depends, the proportion of said thiocarbamid being substantially independent of the proportion of said gelatin.

6. A photographic developing-out emulsion having a speed within the speed range of gaslight paper emulsions comprising gelatin, particles of mercury iodide suspended therein, and thiosinamine added therein upon which at least part of the light-sensitivity of the emulsion depends, the proportion of said thiosinamine being substantially independent of the proportion of said gelatin.

7. A photographic developing-out gelatino-mercury-salt emulsion having a speed within the speed range of gaslight emulsions, comprising a mixture of the constituents of a gelatino-mercury-salt emulsion of lower light-sensitivity, and an added sensitizing compound upon which depends the difference between said lower and said higher light-sensitivity, said 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, the proportion of said compound being substantially independent of the proportion of gelatin.

8. A photographic developing-out gelatino-mercury-iodide emulsion having a speed within the speed range of gaslight emulsions, comprising a mixture of the constituents of a gelatino-mercury-iodide emulsion of lower light-sensitivity, and an added sensitizing compound upon which depends the difference between said lower and said high light-sensitivity, said compound containing a divalent atom of the sulfur group directly joined by a double bond to a single carbon atom to which at least another group of atoms is attached, the proportion of said compound being substantially independent of the proportion of the gelatin.
9. In the process of preparing a developing-out colloid-sensitive-mercury-salt emulsion, increasing the light-sensitiveness thereof by incorporating with the other constituents thereof an independent sensitizing compound, said 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.

10. In the process of preparing a developing-out colloid-sensitive-mercury-emulsion having a speed within the speed range of gas-light emulsions, increasing the light-sensitiveness thereof by incorporating with the other constituents thereof an independent sensitizing compound, said compound containing a divalent atom of the sulfur group directly joined by a double bond to a single carbon atom to which at least another group of atoms is attached.

11. In the process of preparing a developing-out gelatino-mercury-iodide emulsion, increasing the light-sensitiveness thereof by incorporating with the other constituents thereof an independent thiocarbamid.

12. In the process of preparing a developing-out colloid-sensitive-mercury-salt emulsion, increasing the light-sensitiveness thereof by incorporating with the other constituents thereof an independent sensitizing compound, and ripening the emulsion by heating the same.

Signed at Rochester, New York this 28th day of October 1925.

SAMUEL E. SHEPPARD.
JAMES H. HUDSON.