CHEMICAL SENSITIZATION OF PHOTOGRAPHIC SILVER HALIDE EMULSIONS WITH MAGNESIUM METAL POWDER

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This invention relates to photography, and more particularly, to the manufacture of photographic silver halide emulsions which have been chemically sensitized by treatment with magnesium metal.

It is known that the sensitivity of photographic silver halide emulsions can be increased by a number of different methods, other than by optical or spectral sensitization which results in a speed increase in a given region of the spectrum, as contrasted with a sensitivity increase in the region of the spectrum to which the silver halide emulsion already has inherent sensitivity. One of the more common methods of sensitizing emulsions is with a labile sulfur compound, this form of sensitization being known as sulfur sensitization. Still a different type of sensitization is by treatment with a gold compound, or some other noble metal. Still another form of sensitization is known as reduction sensitization, wherein the silver halide emulsion is treated with a reducing compound, such as stannous chloride or thiourea dioxide, for example. Other types of sensitization are also known as hereinafter explained.

We have found a novel method of increasing the sensitivity of photographic silver halide emulsions by treating the liquid emulsions with magnesium metal. The magnesium metal can be added to the emulsions in the form of a finely-divided powder, preferably having a particle size within the range of about 50 to 400 microns. The amount of magnesium metal added can be varied, depending upon the presence or absence of other sensitization, silver halide content, inherent sensitivity of the emulsion, etc. In general, we have found that from about 0.5 to 10.0 grams of magnesium per mole of silver halide is adequate to accomplish the results desired. Prior to coating, the emulsion should generally be filtered, for example, through glass wool or some other inert material, to remove excess magnesium metal.

The photographic emulsions used in practicing our invention are of the developing-out type.

The emulsions can be chemically sensitized, e.g., by digestion with naturally active gelatin, or sulfur compounds can be added such as those described in Sheppard U.S. Patent 1,574,944, issued March 2, 1926, Sheppard et al. U.S. Patent 1,623,499, issued April 5, 1927, and Sheppard et al. U.S. Patent 2,410,689, issued November 5, 1946.

The emulsions can also be treated with salts of the noble metals such as ruthenium, rhodium, palladium, iridium, and platinum. Representative compounds are ammonium chloropalladate, potassium chloroplatinate, and sodium chloropalladate, which are used for sensitizing in amounts below that which produces any substantial fog inhibition, as described in Trivelli and Trivelli U.S. Patent 2,448,060, issued August 31, 1944, and as antifogants in higher amounts, as described in Trivelli and Smith U.S. Patents 2,566,245, issued August 28, 1951 and 2,566,263, issued August 28, 1951.

The emulsions can also be chemically sensitized with gold salts as described in Weilker et al. U.S. Patent 2,399,083, issued April 23, 1946, and Damschroder et al. U.S. Patent 2,642,361, issued June 16, 1953. Suitable compounds are potassium chloraurate, potassium aurithiocyanoate, potassium chloroaurate, auric trichloride and 2-anrosulfobenzothiazole methochloride.

The emulsions can also be optically sensitized with cyanine and merocyanine dyes, such as those described in Brooker U.S. Patents 1,846,301, issued February 23, 1932; 1,846,302, issued February 23, 1932, etc.


The addenda which we have described may be used in various kinds of photographic emulsions. In addition to being useful in X-ray and other nonoptically sensitized emulsions they may also be used in orthochromatic, panchromatic, and infrared sensitive emulsions. They may be added to the emulsion before or after any sensitizing dyes which are used. Various silver salts may be used as the sensitive salt, such as silver bromide, silver iodide, silver chloride, or "mixed" silver halides, such as silver chlorobromide or silver bromoiodide. The agents may be used in emulsions intended for color photography, for example, emulsions containing color-forming couplers, or emulsions to be developed by solutions containing couplers or other color-generating materials, emulsions of the mixed-package type, such as described in Godowsky U.S. Patent 2,688,794, issued January 4, 1952, or emulsions of the mixed-grain type, such as described in Carroll and Hanson U.S. Patent 2,592,243, issued April 8, 1952. These agents can also be used in emulsions which form latent images predominantly on the surface of the silver halide crystal or in emulsions which form latent...
images predominantly inside the silver halide crystals, such as those described in Davey and Knott U.S. Patent 2,592,250, issued April 8, 1952.

These may also be used in emulsions intended for use in diffusion transfer processes which utilize the undeveloped silver halide in the nonimage areas of the negative to form a positive by dissolving the undeveloped silver halide and precipitating it on a receiving layer in close proximity to the original silver halide emulsion layer. Such processes are described in Rott U.S. Patent 2,352,014, issued June 20, 1944, and Land U.S. Patents 2,584,029, issued January 29, 1952; 2,698,236, issued December 28, 1954 and 2,543,181, issued February 27, 1951; and Yackel et al. U.S. Patent 3,020,155, issued February 6, 1962. They may also be used in color transfer processes which utilize the diffusion transfer of an image-wise distribution of developer, coupler or dye, from a light-sensitive layer to a second layer, while the two layers are in close proximity to one another. Color processes of this type are described in Land U.S. Patents 2,559,643, issued July 10, 1951 and 2,618,798, issued January 4, 1955; Land and Rogers Belgian Patents 554,933 and 554,934, granted August 12, 1957; International Polaroid Belgian Patents 554,212, granted July 6, 1957 and 554-935, granted August 12, 1957; Yutzy U.S. Patent 2,756,142, granted July 24, 1956 and Whitmore and Mader U.S. patent application Serial No. 734,141, filed May 9, 1958 (now abandoned). They may also be used in emulsions intended for use in a monobath process such as described in Haist et al. U.S. Patent 2,875,048, issued February 24, 1959, and in web-type processes, such as the one described in Tregillus et al. U.S. patent application Serial No. 835,473, filed August 24, 1959, now U.S. Patent No. 3,179,517.

In general, our photographic emulsions can employ any of the conventional silver halide dispersing agents, such as gelatin, albumin, hydrolyzed polyvinyl acetate, hydrolyzed cellulose ester, etc.

The magnesium metal used in our invention can be added at various stages during the preparation of the emulsion, but we have found that particularly useful results can be obtained when the magnesium metal is added shortly before coating and after conventional finishing operations, which are designed to produce optimum sensitivity in the emulsion. The emulsion is then advantageously filtered as described above and coated in the conventional manner.

The following examples will serve to illustrate more fully the manner of practicing our invention.

**Example 1**

To 317 g. (0.1 mole) of a fine-grain gelatino-silver bromoiodide emulsion which had been sensitized with a gold compound as described in U.S. Patent 2,399,983, and sulfur sensitized as described in U.S. Patent 1,574,944 was added 0.10 g. of powdered magnesium metal having an average particle size of about 0.2 microns. The gelatin content of the emulsion was 24.5 grams, and it was stirred to insure distribution of the powdered magnesium throughout the emulsion. The emulsion was then filtered through ordinary glass wool, coated on conventional cellulose acetate film support and dried. The coated film was then exposed in the conventional manner on an Eastman type T6 sensitometer (intensity scale) and processed for 5 minutes in an MQ developer having the following composition:

- Water, about 125° F. (50° C.) .......................... 500 g.
- N-methyl-p-aminophenol sulfone.......................... 2.5 grams
- Sodium sulfite, desiccated.............................. 30.0 g.
- Hydroquinone ......................................... 2.5 g.
- Sodium metaborate ....................................... 10.0 g.
- Potassium bromide ....................................... 0.5 g.
- Water to make 1.0 liter.

The film was then fixed, washed and dried in the usual manner. A similar coating was prepared without treatment with magnesium metal and coated and processed as described above. Increased speed was exhibited by the treated emulsion in comparison to the untreated.

Some chemical fog is produced by the strong chemical action of the powdered magnesium and it has been found that this fog can be materially reduced by incorporating an antifoggant into the emulsion prior to treatment with the magnesium metal. One of the more useful antifoggants for this purpose is 4-hydroxy-6-methyl-1,3,5,7-tetrazaindene.

**Example 2**

A medium-speed gelatino-silver bromoiodide emulsion which had been sulfur- and gold-sensitized as described in Example 1 was treated with magnesium metal as described in that example, except that the emulsions were held for 30 minutes at 40° C. prior to filtration. The following tabulation shows the effect of varying concentrations of magnesium powder, as well as the beneficial effects produced by the tetrazaindene antifoggant used in Example 1. The tabulation further shows that no antifoggant is necessary when small amounts of magnesium powder are employed, but that significant improvement is produced at higher concentrations.

<table>
<thead>
<tr>
<th>Coating number</th>
<th>Mg. Powder (g./Ag mole)</th>
<th>Antifoggant (g./Ag mole)</th>
<th>Relative speed</th>
<th>Gamma</th>
<th>Fog</th>
</tr>
</thead>
<tbody>
<tr>
<td>a. ..................</td>
<td>Control</td>
<td>100</td>
<td>2.80</td>
<td>0.16</td>
<td></td>
</tr>
<tr>
<td>b. ..................</td>
<td>0.1</td>
<td>0.0</td>
<td>110</td>
<td>2.20</td>
<td>0.39</td>
</tr>
<tr>
<td>c. ..................</td>
<td>1.0</td>
<td>0.0</td>
<td>181</td>
<td>2.22</td>
<td>0.32</td>
</tr>
<tr>
<td>d. ..................</td>
<td>0.1</td>
<td>4.0</td>
<td>115</td>
<td>2.10</td>
<td>0.10</td>
</tr>
<tr>
<td>e. ..................</td>
<td>1.0</td>
<td>4.0</td>
<td>169</td>
<td>2.30</td>
<td>0.16</td>
</tr>
</tbody>
</table>

**Example 3**

The following example illustrates that the advantageous effects of the magnesium powder cannot be obtained when other metal powders are used (even though the metal powder does not have recognized deleterious effects, as in the case of metal contaminants, such as copper). In this example, magnesium is compared with aluminum as a treating agent.

In exactly the manner described in Example 2, a medium-speed gelatino-silver bromoiodide emulsion was treated with aluminum powder, and a separate aliquot portion was treated with magnesium powder. The following results were obtained:

<table>
<thead>
<tr>
<th>Coating number</th>
<th>Addenda</th>
<th>Relative speed</th>
<th>Gamma</th>
<th>Fog</th>
</tr>
</thead>
<tbody>
<tr>
<td>a. ..................</td>
<td>Control</td>
<td>100</td>
<td>2.46</td>
<td>0.18</td>
</tr>
<tr>
<td>b. ..................</td>
<td>Aluminum powder (0.1)</td>
<td>102</td>
<td>2.28</td>
<td>0.38</td>
</tr>
<tr>
<td>c. ..................</td>
<td>Magnesium powder (0.1)</td>
<td>174</td>
<td>2.14</td>
<td>0.45</td>
</tr>
</tbody>
</table>

The sensitization provided by the magnesium powder of our invention can be effected, as shown in the above examples, by merely mixing the magnesium powder intimately with the silver halide emulsion. The time of contact between the magnesium powder and the emulsion can be varied considerably, depending upon temperature, size of silver halide grains, silver-collodio ratio, etc. In general, it is necessary to mix the emulsion and the powder together only for a minute or two before removing the unreacted powder by filtration or other suitable means. If desired, the emulsion can be slightly warmed to diminish the contact time, although there is ordinarily no advantage in warming the emulsion. In general, we have found that the mixing can be performed quite effectively at ambient or room temperatures.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.
3,282,700

as described hereinabove and as defined in the appended claims.

We claim:

1. A photographic silver halide emulsion which has been chemically sensitized by incorporating therein magnesium metal powder, followed by filtration to remove unreacted magnesium particles.

2. A photographic silver halide developing-out emulsion which has been chemically sensitized with a gold sensitizer and sulfur sensitized, said emulsion having been treated by incorporating therein magnesium powder, followed by filtration to remove unreacted magnesium particles.

3. A photographic gelatino-silver bromoiodide emulsion which has been chemically sensitized with a gold sensitizer and sulfur sensitized, said emulsion having been treated by incorporating therein magnesium powder, followed by filtration to remove unreacted magnesium particles.

4. A photographic silver halide which has been chemically sensitized by incorporating therein magnesium metal powder having a particle size between about 50 and 400 microns, followed by filtration to remove unreacted magnesium particles.

5. A photographic silver halide developing-out emulsion which has been chemically sensitized by incorporating therein magnesium metal powder having an average particle size between 50 and 400 microns, the amount of said magnesium powder varying between about 0.5 and 10 grams per mole of silver halide, followed by filtration to remove unreacted magnesium particles.

6. A method of chemically sensitizing photographic silver halide emulsion comprising adding to an aqueous suspension of said emulsion a small amount of magnesium metal powder, intimately admixing said powdered magnesium metal with said emulsion, followed by filtration to remove substantially all unreacted magnesium powdered particles.

7. A photographic silver halide emulsion which has been chemically sensitized by the incorporation of powdered magnesium, said emulsion being substantially free of unreacted powdered magnesium.

References Cited by the Examiner

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2,642,361 6/1953 Damschroder et al. 96—108
3,189,454 9/1965 Luckey et al. 96—66

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