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SILVER HALIDE EMULSIONS WITH INCREASED SENSITIVITY

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4 Claims. (Cl. 96—107)

The invention relates to a method of increasing the sensitivity of photographic silver halide emulsions.

Numerous compounds are known which can be used as additives to the emulsion or developer to increase the sensitivity of a photographic layer. Many different terms are used for substances that have this effect, e.g., chemical sensitizers or activators. The best known class of substances in this field are polyalkylene oxides, in particular polyethylene oxides and water-soluble onium compounds such as quaternary ammonium, phosphonium and sulphonium salts or combinations thereof or derivatives of thiourea, for example, thiouranium salts.

The maximum sensitivities obtained in silver halide emulsions by the addition of the above mentioned compounds presupposes that the silver halide emulsions have been activated by treatment with noble metal salts, especially gold salts.

The most commonly used combination for gold sensitization consists of gold-(III)-salts and thiocyanate or thiosulphate, although the solutions of thiocyanate are not very stable and those of thiosulphate are difficult to prepare. Reaction kinetic investigations, e.g., by Protass, Bjirrum and Kirschner (Z. Wiss. Angew. Phot. Kine 1, 455 (1956)), on gold complexes with thiocyanate ions admit of the assumption that sensitization is caused by a controlled, slow decomposition of the Au-(I)-complexes in which the thiocyanate ions participate. The mechanism of this sensitization process is not certain since many reaction components are involved, such as metallic gold, Au-(I), Au-(III) and thiocyanate ions, dithiocyanogen and additional sulphur degradation products including thiosulphate and gelatine.

Moreover, a considerable excess of thiocyanate ions is required to stabilize the gold-(I) complex and obtain maximum sensitivity of the silver halide emulsions.

This method thus has numerous disadvantages. A considerable amount of the gold-(III)-salts is bound by the gelatin, partly by absorption and partly by complex formation; another amount is reduced to metallic gold and lost for chemical sensitization. In addition the large excess of thiocyanate impairs the stability of the latent image after exposure.

It has now been found that a combined noble metal ripening and reduction ripening of silver halide emulsions can be obtained without the above mentioned disadvantages if the after-ripening is performed with salts of noble metals of group VIII of the periodic system of the elements, having an atomic weight greater than 100 and preferably with salts of gold in the presence of aliphatic hydroxycarboxylic acids having up to 10 carbon atoms or their salts, preferably in the presence of polyhydroxycarboxylic acids of the following general formula:



In this formula, X represents hydrogen, metal ions preferably alkali metal cations or ammonium ions in which the hydrogen may be substituted and n is an integer between 0 and 8, preferably 0 and 5.

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Examples of suitable compounds are:

- | | |
|----------|---|
| (I) | COONa
$ \text{CH}_2\text{OH}$ |
| 5 (II) | COONa
$ \text{CHOH}$
$ \text{CH}_2\text{OH}$ |
| 10 (III) | COOK
$ \text{(CHOH)}_4$
$ \text{CH}_2\text{OH}$ |
| (IV) | COONa
$ \text{(CHOH)}_4$
$ \text{CH}_2\text{OH}$ |
| 15 (V) | COONa
$ \text{CHOH}$
$ \text{CH}_3$ |

Such compounds are known per se and have been described in the literature, e.g., by E. Fischer, A., 270, 72 and 92; Philippe, A. ch. (8) 26, 314; Hudson, Hartley, and Purves, J.A.C.S., 56 (1934), 1248—1249.

The nature of the cation of the salts of the aliphatic hydroxycarboxylic acids is not critical and may be varied as desired. Suitable cations are, for example, those of sodium, potassium, ammonium and the like.

The invention can be used for all photographic silver halide emulsions. The silver halide may be silver chloride, bromide or iodide or mixtures thereof, but iodobromide emulsions are preferred. These emulsions may be further chemically sensitized, for example, with sulfur compounds, polyalkylene oxides, water-soluble onium compounds or combinations of polyethylene oxides and onium compounds. In addition, they may be optically sensitized, e.g., by methine cyanine, merocyanine, rhodacyanine dyes or the like.

Organic mercapto compounds, quaternary benzthiazoles, triazoles, tetraazaindolizines and the like may be added as stabilizers.

A further advantage of the process according to the invention is that the sensitized emulsions can be used for the production of black-and-white photographic material or color photographic material; in the latter case, hydrophobic or hydrophilic color couplers can be incorporated.

The noble metal salts and the aliphatic hydroxycarboxylic acids of the present invention can be added to the emulsion at any stage of the preparation of the emulsion either before or during the after-ripening. Aliphatic hydroxycarboxylic acids or their salts may be added in solution or in solid form before, during or after the addition of the noble metal salt. Alternatively, a mixture of a solution of the noble metal salt, for example, gold-(III)-chloride and a solution of an aliphatic hydroxy carboxylic acid or their salts can be added to the emulsions. The compounds are used in concentrations of 0.1 g. to 5 g. per 1 kg. emulsion, preferably about 0.1 to 0.5 g./kg. The optimum quantity to be added depends on the reduction capacity of the aliphatic hydroxy carboxylic acid or their salts and on the type of emulsion. It can easily be determined by a few tests.

The effect of the process according to the invention is demonstrated in the examples given below.

Example 1

To a highly sensitive iodobromide gelatin emulsion with 4 mol percent of silver iodide containing silver halide equivalent to 50 g. silver per liter are added an aqueous solution of 35 to 40 mg. KBr per liter and sulfur compounds in order to effect chemical ripening. Thereafter

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the emulsion is divided into three samples A, B and C before after-ripening.

Sample A is a standard sample. Before after-ripening, the following mixture is added per liter of emulsion to sample B:

1 ml. of an 0.08% gold-III-chloride solution, and
3 ml. of a 10% aqueous solution of compound IV.

To sample C is added per liter of emulsion also prior to after-ripening the following mixture:

2 ml. of an 0.08% gold-III-chloride solution, and
3 ml. of a 10% aqueous solution of compound IV.

The three samples are after-ripened at a temperature about 50° C. until a maximum sensitivity at pAg⁺²⁰ of up to 30 mv. has been reached. Thereafter a wetting agent and a stabilizer, e.g., of the azaindolizine type is added and the emulsion applied to a sheet-like cellulose acetate support.

The three samples are exposed to light and developed in a usual p-methylaminophenol hydroquinone developer for 10 minutes at 20° C.

The results are given in Table 1:

TABLE 1

	Increase in sensitivity	Fogging	Gamma
Sample A-----	0	0.19	0.55
Sample B-----	(1)	0.25	0.55
Sample C-----	(1)	0.11	0.45

¹+2° DIN.

Concerning the figures giving the sensitivity, it should be pointed out that an increase in sensitivity of 3° corresponds to an increase by one shutter stop.

Example 2

A highly sensitive iodo silver bromide emulsion as described in Example 1 is divided into three samples A, B, C.

Sample A is a standard sample.

To sample B is added per liter of emulsion a mixture of 3 mol. of a 10% aqueous solution of compound I and 1 ml. of a 0.08% gold-III-chloride solution.

To sample C is added per liter of emulsion a mixture of 3 ml. of a 10% aqueous solution of compound I and 2 ml. of a 0.08% gold-III-chloride solution.

The three samples are after-ripened as described in Example 1 and applied to a sheet-like support of polyethyleneterephthalate. The resulting light sensitive photographic material is developed in the same way.

TABLE 2

	Increase in sensitivity	Fogging	Gamma
Sample A-----	0	0.19	0.55
Sample B-----	(1)	0.17	0.50
Sample C-----	(2)	0.12	0.45

¹+2° DIN.

²+1.5° DIN.

It will be clear to those skilled in this art that the practice of the invention lends itself readily to a number of useful modifications in method, material etc. For example, the noble metal salts are not limited to the previously mentioned, because it is possible to use any suitable salt which is soluble in water or lower alcohols. Such compounds are: gold halides, such as auric chloride,

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or complex gold halides, such as potassium chloroaurate (KAuCl₄) and sodium chloroaurate (NaAuCl₄). However, gold compounds, such as auric sulfate, are practically as useful as the gold halides. Aurous, as well as auric compounds can be used. Complex gold salts, such as alkali metal aurous thiosulfates, alkali metal aurous sulfites (e.g., sodium or potassium aurous thiosulfate and sodium or potassium aurous thiosulfite). Potassium chloroaurite, potassium bromoaurite, potassium iodoaurite, or the corresponding sodium, calcium, strontium, cadmium or gallium salts can also be used. Pyridinotrichloro-gold, ethylenediamine - bis - trichloro - gold, diethyl - monobromogold and diethyl gold acetone and gold complexes with sulfur compounds such as are commonly present in gelatin, e.g., the gold thiosinamine complexes, can also be used.

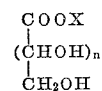
Suitable salts of noble metals of the VIII group are ammonium or potassium, chloropalladate, ammonium, sodium and potassium chloroplatinate, ammonium potassium and sodium bromoplatinate, ammonium chlororhodate, ammonium chlororuthenate, ammonium chloroiridate, ammonium, potassium and sodium chloroplatinite, ammonium, potassium and sodium chloropalladite, etc.

The after-ripening of the emulsion with the noble metal salt and the o-hydroxybenzylamine compounds is performed at an appropriate temperature particularly between 30 and 60° C. During after-ripening the pH of the emulsion is advantageously adjusted to the acid side of neutrality preferably between 5 and 7. Maintenance of the emulsion on the acid side of neutrality during coating of the emulsion is also preferred.

The noble metal salts are employed in an amount below that which produces a substantial fog. In practicing the present invention, a quantity of the noble metal salt is employed, equivalent to between 0.1 and 50 mg. of the noble metal per mol of silver halide in the emulsion. The noble metal compounds are preferably incorporated in the emulsions in the form of their solutions in a suitable solvent such as water, methyl alcohol, ethyl alcohol or the like.

We claim:

1. Method of increasing the sensitivity of silver halide emulsions, characterized in that the after-ripening is performed with noble metal salts and water-soluble aliphatic hydroxycarboxylic acids having up to 10 carbon atoms of the following formula:



where X is hydrogen, a metal ion or an ammonium ion and n represents 0-8.

2. Process according to claim 1, characterized in that gold salts are used as noble metal salts.

3. Process according to claim 1, characterized in that the emulsion additionally contains as chemical sensitizers sulphur compounds, onium compounds and polyalkylene oxides.

4. Process according to claim 1, characterized in that tetraazaindolizine stabilizers are added to the emulsion.

No references cited.

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