

[54] **PROCESS FOR THE MANUFACTURE OF SILVER HALIDE PHOTOGRAPHIC EMULSION CONTAINING IRIIDIUM AND RHODIUM**

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[22] Filed: **July 1, 1974**

[21] Appl. No.: **485,035**

Related U.S. Application Data

[63] Continuation of Ser. No. 259,127, June 2, 1972, abandoned.

[30] Foreign Application Priority Data

June 2, 1971 Japan..... 46-38383

[52] U.S. Cl..... **96/95; 96/108**

[51] Int. Cl..... **G03c 1/28; G03c 1/06**

[58] **Field of Search**..... 96/108, 95

[56] References Cited

UNITED STATES PATENTS

2,717,833	9/1955	Wark	96/108
2,956,882	10/1960	Herold	96/108
3,317,322	5/1967	Porter et al.	96/108
3,531,289	9/1970	Wood	96/108
3,672,901	6/1972	Ohkubo et al.	96/108

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[57] ABSTRACT

A process for the manufacture of a silver halide emulsion for the flash exposure in which a rhodium and an iridium compound are added to the emulsion during emulsion preparation or on the first ripening of the emulsion is disclosed.

21 Claims, No Drawings

PROCESS FOR THE MANUFACTURE OF SILVER HALIDE PHOTOGRAPHIC EMULSION CONTAINING IRIIDIUM AND RHODIUM

This is a continuation of application Ser. No. 259,127, filed June 2, 1972 now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a process for the manufacture of a silver halide photographic emulsion.

2. Description of the Prior Art

In photocomposition and facsimile, the sensitive material is exposed imagewise to a light of a high illumination for a very short time (about 10^{-2} - 10^{-6} sec) and the material should have such characteristics that a high contrast image can be formed by conventional development by means of activator. Hitherto, for the formation of a high contrast image, a water soluble rhodium compound has been added during the emulsification of silver halide emulsion in the preparation of the sensitive material. However, when a rhodium compound is added to an emulsion of high sensitivity, above all, a silver halide emulsion prepared using the ammonia method, the sensitivity is elevated within the short time after the exposure of the sensitive material. This is called as "latent image sensitization." In the practical use of these sensitive materials, the periods of time between exposure to development are different and, therefore, the sensitivity of the initial portion of sensitive material in the form of a roll is different from that of the final portion thereof. When even the final portion is developed completely in the development of such a sensitive material, the development of areas other than the image area in the initial portion proceeds rapidly resulting in, for example, an unclearness of letters or a different densities in the letters. An object of this invention is to provide a process for the manufacture of a silver halide photographic emulsion through which a high contrast image can be formed and which provides only a slight latent image sensitization even by subjecting to a flash exposure of high illumination and short time.

SUMMARY OF THE INVENTION

After much research to solve the problems as described above, we have reached to the following invention. Namely, this invention relates to a process for the manufacture of a silver halide photographic emulsion for the flash exposure characterized by adding a rhodium compound and an iridium compound during the emulsification or the first ripening of the emulsion.

DETAILED DESCRIPTION OF THE INVENTION

As the photographic emulsions which are manufactured according to this invention, those to which this invention are particularly, applicable, as was described above, are those silver halide emulsions prepared by the ammonia method. The invention is also applicable in general to suspensions in which a single or combined hydrophilic colloid substances, (e.g., natural or synthetic organic colloids) such as gelatin, gelatin derivatives such as those set forth in Japanese application Ser. No. 75325/71 (e.g., reaction products of gelatin and an aromatic or aliphatic acid anhydride; of gelatin and a compound having a halogen atom; of gelatin and an isocyanate compound; of gelatin and an N-

acryvinylsulphonamide (e.g., phthalic gelatin, acetyl gelatin, maleic gelatin, carboxy methyl gelatin, benzenesulfonic gelatin, trimellitic gelatin, benzoic gelatin, sulfophthalic gelatin, succinic gelatin, etc.), polyvinyl alcohol, carboxy methyl cellulose, maleic anhydride-phthalic acid copolymer and the like are used as the protective colloid and in which microscopic particles of a silver halide such as silver bromide, chlorobromide or their mixtures with silver iodide are contained in the form of a dispersion in the emulsion. These photographic emulsions are manufactured in general through the first ripening (physical ripening) and the second ripening (chemical ripening) after the so-called "emulsion process" in which particles of silver halide are formed in the aqueous solution of gelatin.

According to this invention, a rhodium and an iridium compound are added in the preparation of the photographic emulsion, during the emulsification or the first ripening thereof. Examples of suitable rhodium compounds are the simple salts such as rhodium di- or tri- halide (e.g., chloride, bromide), or the octahedral complex salts such as alkali metal (e.g., sodium, potassium) or ammonium hexahalogenorhodate (e.g., hexachlororhodate, hexabromorhodate) etc.; and suitable iridium compounds are the simple salts such as iridium tri- or tetra halide (e.g., chloride, bromide) the octahedral complex salts such as alkali metal (e.g., sodium, potassium) or ammonium hexahalogenoiridate (e.g., hexachloroiridate (III), hexachloroiridate (IV), hexabromoiridate (III), hexabromoiridate (IV), and the octahedral complex acids such as hexahalogenoiridic (III) acid, hexahalogenoiridic (IV) acid. These compounds are preferably water soluble and the amount thereof added to the emulsion is preferably at a level of from 10^{-8} to 10^{-6} mol/mol of silver halide. The range of the above described amount is the most effective for an object of the present invention and the upper limit means the saturation of this effect; there is also an effect even outside of the range.

The rhodium or iridium compound is added during the emulsification or first ripening in the preparation of the emulsion.

Namely, both the rhodium and the iridium compound are added during the emulsification or first ripening or the rhodium compound is added during the emulsification and the iridium compound during the first ripening or vice versa. The rhodium or iridium compound can also be added during both steps.

After the first ripening and the washing with water, a chemical sensitizer such as a sulfur compound (See Mees *The Theory of the Photographic Process*, 3rd Ed. P. 114, (1966) U.S. Pat. Nos. 1,574,944, 2,278,947, 2,440,206, 3,189,458, etc.) or a gold compound (See Mees, supra, P. 113, U.S. Pat. Nos. 2,540,085, 2,597,859, 2,597,915, etc.) is added in a conventional manner to the photographic emulsion to be prepared. After the second ripening spectral sensitizers such as cyanines, stabilizers (See Mees, supra, P. 344) and antifoggants (See U.S. Pat. Nos. 2,384,393, 2,708,162, 2,403,927, etc.), surface active agents (See U.S. Pat. No. 3,415,649), such as saponine, polyethylene oxide, sodium 3-p-nonyl phenoxy-propan-1-sulfonate, and lauryl alcohol sulfate ester, film hardeners such as formaldehyde, mucochloric acid (See Mees, supra, pp. 55 - 60) and the like are added. One useful class of cyanines is the methine cyanine dyes. The term "cyanine" as used herein includes the simple cyanine dyes, the merocyanine dyes, the trinuclear merocyanine dyes

and their higher homologs, e.g., the carboecyanine, the dicarboecyanine and the tricarboecyanine dyes. As is well known, cyanine dyes feature the amidinium ion chromophore system. In cyanine dyes, each nitrogen atom of the amidinium ion system is contained in a heterocyclic ring (See Mees, supra, PP. 201 - 2). The preparation is then coated on a support. If desired, the main developer can be contained in the silver halide emulsion layer or another layer of the sensitive material. As the support paper (coated with Baryta), films of polyethylene terephthalate, cellulose ester or polystyrene, metal plate etc. can be used. The use of these supports is not critical.

The sensitive material of silver halide photographic emulsion obtained according to this invention is characterized in that the image obtained by flash exposure (high illumination and short time) and conventional development (See U.S. Pat. No. 3,043,698, Mee, supra, PP 51 - 58) or the development by means of an activator such as sodium hydroxide (See C.E.K. Mees, *The Theory of the Photographic Process*, Rev., Ch. 14) is very hard and that only a slight latent image sensitization results in the elapse of a considerably long period of time between exposure and development.

This invention will be illustrated more fully by reference to the following examples.

EXAMPLE I

The following liquid compositions (I) - (IV) were prepared:

(I)	Water	500 cc
	Gelatin	20 g
	Aqueous Ammonia (2.5%)	30 g
(II)	Water	500 cc
	Silver Nitrate	100 g
(III)	Potassium Bromide	21 g

	Sodium Chloride	34 g
	Aq. Ammonium Hexachlororodate (corresponding to 10^{-7} mols of rhodium compound per mol of silver halide formed)	3.5 cc
	Aq. Potassium Hexachloroiridate (IV) (corresponding to 10^{-7} mols of iridium compound)	3.0 cc
(IV)	Water	500 cc
	Gelatin	200 g
	Water	200 cc

The prepared liquid composition (I) was kept at 50°C. both liquid (II) and (III) were added thereto at the same time with stirring, the liquid (IV) was then added thereto after ripening at 50°C for 20 min. and aged for 30 min. while keeping at 50°C. The resulting photographic emulsion was cooled to solidify, cut finely and washed for 1 hr in a water stream. After washing with water, it was dissolved again, a slight

amount of potassium chloroaurate as chemical sensitizer was added, ripened at approximately 50°C for 80 min, a dye sensitizer (cyanine dye), stabilizer (tetrazindene compound), film hardener (formaldehyde) and surface active agent (Saponin) were added and the mixture coated on Baryta paper. The resulting sensitive material was designated as Sample 1.

Sample 2 (free from potassium hexachloroiridate (III) in the liquid (III)). Sample 3 (free from ammonium hexachlororhodate) and Sample 4 (free from both compounds) were prepared as controls in the same manner.

These samples were subjected to "EGG 10^{-6} second xenon flash exposure" (refer to "Industrial Manual", published by EGG Co., Ltd.) using a Mark 6 sensitometer, 2-, 20-, 40- and 60-minute-elapsed time period between the exposure and development were formed in each sample, developed with a liquid developer of D-72 formulation, stopped, fixed and washed with water in a conventional manner.

D-72 Formulation

"Elon"	3.1 g
Sodium Sulfite (anhyd.)	45.0 g
Hydroquinone	12.0 g
Sodium Carbonate (anhyd.)	67.5 g
Potassium Bromide	1.9 g
Water to make	1 l

The relative sensitivity and gradation (r) of the resulting images were determined where the sensitivity of the portion developed 2 minutes after the exposure at D (density) = 0.1, where the sensitivity is shown as $1/E \times 10^{-4}$ (E : the exposure amount at $D = 0.1$), was rated as 100. The results obtained are shown in Table 1.

Table 1

Sample	Time Period Between Exposure and Development						
	2 min.		20 min.		40 min.		60 min.
1	100		105		105		105
2	100	2.6	120	2.62	140	2.62	150
(control)							
3	100	1.8	103	1.85	105	1.87	105
(control)							
4	100	1.2	102	1.20	102	1.22	103
(control)							
		0.9		0.90		0.90	0.90

In the table, the values shown on the left side of the column are the sensitivity and those on the right side of the column are the $\bar{r}$ value.

From the results as shown in Table 1, it is found that the use of ammonium hexachlororhodate to give a high contrast as in Sample 2 provides an emphasized latent image sensitization and that the combination of the ammonium hexachlororhodate compound with potassium hexachloroiridate prevents the latent image sensitization with a large effect in comparison with the single use of the compound as in Sample 2 and 3, resulting in a high contrast photographic image.

EXAMPLE 2

The following liquid compositions (I) - (IV) were prepared:

(I)	Gelatin	10 g
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-continued

	Water	500 cc
(II)	Silver Nitrate	100 g
	Aqueous Ammonia (25%)	100 cc
	Water	500 cc
(III)	Potassium Bromide	70 g
	Potassium Iodide	2 g
	Aq. Potassium Hexachlororhodate (corresponding to 10^{-7} mols of iridium compound (same iridium compound as used in Example 3 but at 3.00 cc level) per mol of silver halide formed)	3.0 cc
	Aq. Potassium hexachloroiridate (III) (corresponding to 10^{-7} mols of iridium compound)	3.5 cc
(IV)	Gelatin	200 g
	Water	300 cc

The prepared liquid composition (I) was kept at 45°C., the liquid (III) was added with stirring, the liquid (II) was then added, ripened for 7 min and sulfuric acid was added to neutralize. Thereafter, the liquid (IV) was added, cooled to solidify, cut finely and washed for 1 hr in a water stream. The solid mass washed with water was then warmed to dissolve again, a conventional sulfur and gold sensitizer were added, ripened at 60°C for 1 hr, the dye sensitizer, stabilizer, film hardener and surface active agent as described in Example 1 were added to the resulting emulsion, which was then coated on Baryta paper. The resulting sensitive material was designated as Sample 5.

Similarly, with the use of the liquid (III) free from either potassium hexachloroiridate (III) or potassium hexachlororhodate as well as free from both of the compounds, three emulsions were prepared, from which Sample 6, 7 and 8 each was formulated.

From these Samples 5 - 8, images were formed as in Example 1, from which the relative sensitivity and gradation ($\bar{F}$) were determined. The results obtained are shown in Table 2.

Table 2

Sample	Time Period Between Exposure and Development							
	2 min.		20 min.		40 min.		60 min.	
5	100		103		105		105	
6	100	2.40		2.42		2.45		2.45
(control)			130		150		160	
7	100	1.60		1.65		1.70		1.70
(control)			102		104		104	
8	100	1.10		1.10		1.15		1.20
(control)			102		102		102	
		0.80		0.80		0.80		0.82

In Table 2, the values have the same meanings as in Table 1.

As can be seen from the results shown in Table 2, for Sample 6 in which only potassium hexachlororhodate was used, a very hard image was obtained compared with Sample 8 free from the compounds but, due to the latent image sensitization, the longer time from exposure to development provided the higher sensitivity. However, Sample 7 containing only potassium hexachloroiridate (III) could not give a great contrast al-

though the latent image sensitization was a slight. For Sample 5 according to this invention, in which both compounds were used, the latent image sensitization was prevented and an image of so much increased contrast, which could not be expected from the contrast of Sample 6 and 7, could be obtained.

EXAMPLE 3

The following liquid compositions (I) - (IV) were prepared:

(I)	Gelatin	15 g
	Aqueous Ammonia (25%)	20 cc
	Water	500 cc
(II)	Silver Nitrate	100 g
	Water	500 cc
(III)	Potassium Bromide	70 g
	Potassium Iodide	1 g
	Aq. Ammonium Hexachlororhodate (corresponding to 10^{-7} mols of rhodium compound per mol of silver halide formed)	3.5 cc
	Aq. Potassium Hexachloroiridate (III) (corresponding to 10^{-7} mols of iridium compound)	
	Water	500 cc
(IV)	Gelatin	200 g
	Water	300 cc

The prepared liquid composition (I) was kept at 45°C, the liquid (III) was added with stirring and the liquid (II) was added additionally. The mixture was ripened at 45°C for 15 min, a suitable amount of sulfuric acid was added to neutralize, the liquid (IV) was added and the entire amount was cooled to solidify. The resulting mass was cut finely, washed with water for 1 hr in a water stream, dissolved again, a conventional sulfur and gold sensitizer were added and ripened at 60°C for 1 hr. The resulting emulsion was coated on a Baryta paper, on which a gelatin layer containing 1 g/m² of hy-

droquinone was applied, to form a sensitive material (Sample 9).

Similarly, Sample 10 (free from potassium hexachloroiridate (III), in the liquid (III), Sample 11 (free from ammonium hexachlororhodate and Sample 12 (free from both compounds) were prepared as controls.

For these Samples 9 to 12, images were formed as in Example 1, from which the relative sensitivity and gradation were determined. The results obtained are shown in Table 3.

Table 3

Sample	Time Period Between Exposure and Development							
	2 min.		20 min.		40 min.		60 min.	
9	100		104		105		105	
10	100	3.0		3.10		3.10		
(control)			140		150		160	

Table 3-continued

Sample	Time Period Between Exposure and Development							
	2 min.		20 min.		40 min.		60 min.	
11 (control)	100	1.8	103	1.85	105	1.90	105	1.90
12 (control)	100	1.2	100	1.20	100	1.22	98	1.22
		0.9		0.9		0.9		0.9

In Table 3, the values have the same meaning as in Table 1.

From the results shown in Table 3, the same conclusion as in the preceding examples was obtained.

While the invention has been described in detail and in terms of specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

What is claimed is:

1. In a negative-working silver halide photographic emulsion comprising an unfogged silver halide emulsion of silver halide particles dispersed in an aqueous emulsion of a hydrophilic colloid, the improvement comprising a combination of a rhodium compound and an iridium compound which have been added to said emulsion during the precipitation of the silver halide particles in an amount sufficient to produce a high contrast image with a minimum of latent image sensitization.

2. The emulsion of claim 1, wherein said silver halide is silver bromide, silver chlorobromide, silver bromoiodide or silver chlorobromoiodide.

3. The emulsion of claim 1, wherein said aqueous emulsion contains ammonia.

4. The emulsion of claim 1, wherein said hydrophilic colloid is a natural organic colloid or a synthetic organic polymer.

5. The emulsion of claim 4, wherein said hydrophilic colloid is gelatin, a gelatin derivative, polyvinyl alcohol, carboxy methyl cellulose, or maleic anhydride-phthalic acid copolymer.

6. The emulsion of claim 5, wherein said hydrophilic colloid material is gelatin, phthalic gelatin, maleic gelatin, carboxy methyl gelatin, or trimellitic gelatin.

7. The emulsion of claim 1, wherein said rhodium compound is a simple salt or an octahedral complex salt of alkali metal or ammonium and wherein said iridium compound is a simple salt, an octahedral complex acid or an alkali metal or ammonium salt thereof.

8. The emulsion of claim 7, wherein said rhodium compound is rhodium dihalide, rhodium trihalide, or alkali metal or ammonium hexahalogeno rhodate and wherein said iridium compound is iridium trihalide, iridium tetrahalide, hexahalogenoiridic (III) acid, hexahalogenoiridic (IV) acid, or the salts of said acids.

9. The emulsion of claim 1, wherein both the rhodium compound and the iridium compound are water-soluble.

10. The emulsion of claim 1, wherein said iridium compound and said rhodium compound are each present

at a level of 10^{-8} to 10^{-6} mol per mol of silver halide.

11. The emulsion of claim 1 wherein said combination consists essentially of said rhodium compound and said iridium compound.

12. In a process for the manufacture of a negative-working silver halide photographic emulsion having an improved property for a flash exposure comprising preparing an unfogged silver halide emulsion of silver halide particles dispersed in an aqueous emulsion of a hydrophilic colloid including two ripening steps, said emulsion being unfogged because reducing agents are not added during the second ripening step, the improvement comprising:

adding a combination of a rhodium compound and an iridium compound to said emulsion during the precipitation of the silver halide particles in an amount sufficient to produce a high contrast image with a minimum of latent image sensitization.

13. The process of claim 12, wherein said silver halide is silver bromoiodide, silver chlorobromide, or silver chlorobromoiodide.

14. The process of claim 12, wherein said aqueous emulsion contains ammonia.

15. The process of claim 12, wherein said hydrophilic colloid is a natural organic colloid or a synthetic organic polymer.

16. The process of claim 15, wherein said hydrophilic colloid is gelatin, a gelatin derivative, polyvinyl alcohol, carboxy methyl cellulose, or maleic anhydride-phthalic acid copolymer.

17. The process of claim 16, wherein said hydrophilic colloid material is gelatin, phthalic gelatin, maleic gelatin, carboxy methyl gelatin, or trimellitic gelatin.

18. The process of claim 12, wherein said rhodium compound is a simple salt or an octahedral complex salt of alkali metal or ammonium and wherein said iridium compound is a simple salt, an octahedral complex acid or an alkali metal or ammonium salt thereof.

19. The process of claim 18, wherein said rhodium compound is rhodium dihalide, rhodium trihalide, or alkali metal or ammonium hexahalogeno rhodate and wherein said iridium compound is iridium trihalide, iridium tetrahalide, hexahalogenoiridic (III) acid, hexahalogenoiridic (IV) acid, or the salts of said acids.

20. The process of claim 12, wherein both the rhodium compound and the iridium compound are water-soluble.

21. The process of claim 12, wherein said iridium compound and said rhodium compound are each present at a level of 10^{-8} to 10^{-6} mol per mol of silver halide.

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