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3,666,475

## PHOTOGRAPHIC MATERIALS

David Ramsay Douglas, Ilford, England, assignor to  
Ilford Limited, Ilford, Essex, England

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2 Claims

### ABSTRACT OF THE DISCLOSURE

A photographic gelatino silver chlorobromide emulsion containing from 0.2 to 3 grams, per gram mole of silver in the emulsion, of a polyethylene oxide which has terminal end groups selected from the class consisting of hydrogen and halogen atoms, carboxyl, amino and carbamoyl groups, higher fatty alcohol residues, saturated higher fatty acid residues and alkyl phenol residues, and from 0.5 to 15 grams of water-soluble hydrolysed polyvinyl acetate having a molecular weight from 5000 to 30,000 and whose residual acetate content is at least 35%.

This application is a continuation-in-part of application No. 575,518, filed Aug. 29, 1966, now abandoned.

This invention relates to photographic light-sensitive materials, and more particularly to photographic materials intended for use in recording half-tone dot images or line images and which carry a gelatin silver halide emulsion of very high contrast characteristics, and which are designed to be developed in formaldehyde-containing low-sulphite hydroquinone developers as well as developers of the more usual types, and which exhibit in the former class of developers the phenomenon known as infectious development.

Emulsions of the foregoing type (which are herein referred to as "lith" emulsions) may be developed satisfactorily over a considerable range of development times, other development conditions being held constant. The effective "speed" of the lith emulsions increases as the development time is increased, and accordingly it is a valuable property of such materials that by controlling development time it is possible to control the effective emulsion speed.

It is, however, desirable with such lith materials that the effective speed should not increase at too high a rate as development proceeds, e.g., during the first 2 to 3 minutes, since otherwise control of the image by inspection becomes very difficult.

It is, however, important in such lith materials that the contrast of the resulting images should remain high over as large a range of development times as possible and it is known to achieve this by the addition of polyethylene oxide compounds to the photographic emulsion so that normal formaldehyde/bisulphite/hydroquinone developer solutions can be used. However, the addition of polyethylene oxide compounds to lith emulsions has led to high fog on development.

It is the object of the present invention to provide a photographic lith type emulsion which comprises a polyethylene oxide compound which shows reduced fog on development.

According to the present invention there is provided a photographic gelatino silver chlorobromide emulsion consisting essentially of per gram mole of silver in the emulsion, from 0.02–3 g. of a polyethylene oxide which has terminal end groups selected from the class consisting of hydrogen and halogen atoms, carboxyl, amino, and carbamoyl groups and higher fatty alcohol residues, satu-

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rated higher fatty acid residues and alkyl phenol residues and from 0.5 to 15 g. of water-soluble hydrolysed polyvinyl acetate having a molecular weight from 5,000 to 30,000 and whose residual acetate content is at least 35%.

The water solubility of the hydrolysed polyvinyl acetates depends on their residual acetate content, determined on a weight basis, and their viscosity characteristics (which in turn depends on their molecular weight). The hydrolysed polyvinyl acetates for use in the present invention must have a molecular weight of at most 30,000 (which means that they are of lower viscosity type) and should be so hydrolysed that they have a residual polyvinyl acetate content of at least 35%. Typical of such products is that commercially known as Gelvatol 40/10 referred to in Example I (Emulsion III) which has molecular weight 10,000 and residual acetate 40% and which is freely soluble in cold water.

It is preferred that the molecular weight of the polyethylene oxide or the polyethylene oxide modified by having at least terminal group substituted by a halogen atom or a carboxyl, amino or carbamoyl group should be between 1,000 and 15,000.

It is preferred that the molecular weight of the polyethylene oxide modified by having at least one fatty or alkyl phenol terminal group should be between 100 and 15,000. Examples of higher alcohols which form ethers with polyethylene oxide are cetyl alcohol and oleyl alcohol. Examples of alkyl phenols which form ethers with polyethylene oxide are isooctylphenol and nonylphenol. Examples of saturated higher fatty acids which form esters with polyethylene oxide are lauric acid and stearic acid.

The preferred chlorobromide emulsions for use in the present invention have a chloro-bromide ratio of from 1.5–15 chloride to 1 bromide.

The addition of either or both of the polyethylene oxide and of the water-soluble polyvinyl acetate can be made prior to or after the process of chemical sensitisation.

The following example will serve to illustrate the invention:

### EXAMPLE I

Emulsion I.—A gelatin silver chlorobromide emulsion containing 31 mole percent of silver bromide, having a grain size of 0.2 $\mu$ , was sulphur sensitized, stabilized and treated with an orthochromatic sensitizing dye. The emulsion was then coated on film.

Emulsion II.—A similar emulsion was treated in the same manner except that 0.17 gr. polyethylene oxide (Carbowax 6000) was added prior to coating.

Emulsion III.—An emulsion similar to that described above but with the addition of 0.85 gr. Gelvatol 40/10 per gram mole silver was prepared. Gelvatol 40/10 is a water-soluble polyvinyl acetate which is manufactured by Shawinigan Ltd., and has a molecular weight 10,000 and contains 40% residual acetate. Polyethylene oxide (Carbowax 6000) 0.03 gr. was also added prior to coating.

All coated emulsions were exposed behind an optical wedge in the usual manner. The exposed coatings were then developed in a developer made from the following solutions:

#### Solution A:

Sodium sulphite—120 gr.

Hydroquinone—45 gr.

Boric acid—15 gr.

Potassium bromide—3.15 gr.

Water to make 1,500 ml.

## Solution B:

Paraformaldehyde—15 gr.  
Potassium metabisulphite—5.25 gr.  
Sodium sulphite—1.05 gr.  
Water to make 500 ml.

The developer is made by mixing 3 parts of solution A with one part of solution B immediately before use.

It will be seen from the results of the test coatings set out below that the use of polyethylene oxide and a water-soluble polyvinyl acetate in combination requires reduced quantities of the polyethylene oxide. The improved dot and line image quality is directly related to the higher contrast achieved.

TABLE I

Emulsion	Development time in mins. <sup>1</sup>	Relative log speed	Contrast (γ)	Incubation fog
I.....	2	2.30	6	0.05
	2½	2.52	8	0.15
	3	2.70	9	
	4	2.99	7	
	5	3.13	7	
II.....	2	2.05	9	0.05
	2½	2.20	10	1.79
	3	2.45	8	
	4	2.61	12	
	5	2.70	14	
III.....	2	2.15	8	0.05
	2½	2.40	10	0.69
	3	2.64	8	
	4	2.88	13	
	5	2.94	10	

<sup>1</sup> In formaldehyde/hydroquinone based developer.

TABLE II

Polyethylene oxide compound, per gram mole silver	Gelvatol 40/10, per gram mole silver, gr.	Development time in minutes <sup>1</sup>	Relative log speed S1.0	Contrast (γ)	Incubation fog	Description of polyethylene oxide
0.....	0	2	2.51	7.4	0.06	Control.
		2½	2.75	9.4		
		3	2.90	10.4		
		4	2.93	9.8		
		5	3.04	6.2		
0.05 gr. Carbowax 6000.....	0	2	2.50	6	0.04	Carbowax 6000. Unbranched polyethylene oxide chain M.W.≈6000.
		2½	2.70	9		
		3	2.87	11		
		4	2.97	7.4		
		5				
0.05 gr. Carbowax 6000.....	1.65	2	2.04	9.2	0.04	0.14
		2½	2.19	11		
		3	2.31	15.2		
		4	2.50	15.2		
		5	2.68	16		
0.05 gr. Carbowax 6000.....	6.6	2	1.84	9	0.05	0.21
		2½	2.05	9.4		
		3	2.19	18		
		4	2.36	24		
		5	2.59	18.2		
0.27 Carbowax 6000.....	0	2	2.27	6	0.04	0.70
		2½	2.44	8.4		
		3	2.62	12.6		
		4	2.74	22		
		5	2.92	17.4		
0.165 Texofo A 60.....	0	2	2.33	5.2	0.04	Cetyl/oleyl ether on polyethylene oxide chain (60 ethylene oxide units).
		2½	2.56	6.6		
		3	2.75	8.2		
		4	2.99	7.2		
		5	3.05	7.0		
0.165.....	1.65	2	1.97	6.6	0.05	0.28
		2½	2.14	10.8		
		3	2.27	14		
		4	2.47	18		
		5	2.67	14		
0.165 Texofo A 60.....	6.6	2	1.68	5.2	0.05	0.30
		2½	1.91	7.0		
		3	2.08	9.4		
		4	2.29	18		
		5	2.39	20		
0.66 Texofo A 60.....	0	2	1.92	6.0	0.05	1.44
		2½	2.18	8.6		
		3	2.40	9.0		
		4	2.64	17		
		5	2.99	10.4		
0.165 gr. Texofo F 60.....	0	2	2.45	4.8	0.04	Alkyl phenol ether on polyethylene oxide (60 ethylene oxide units).
		2½	2.66	4.8		
		3	2.78	10.0		
		4	2.95	7.6		
		5	3.03	6.8		

See footnotes at end of table.

For the incubation test samples of coated emulsion were developed in a phenidone/hydroquinone based developer. The first column represents the fog level after 7 days normal shelf storage and the second column represents the fog level after 7 days incubation at 69% relative humidity at 125° F.

## EXAMPLE II

The emulsion used was Emulsion I of Example I. To this emulsions was added the amounts of the polyethylene oxide compounds and the water-soluble polyvinyl acetate shown in Table II, all the compounds were added to the emulsion prior to coating.

All the coated emulsions were exposed behind an optical wedge in the usual manner. The exposed coatings were then developed in the same developer as used in Example I. The incubation test was carried out in a similar manner to Example I.

It will be seen from the results set out below that the use of the polyethylene oxide compound and water-soluble polyvinyl acetate together requires reduced quantities of the polyethylene oxide to obtain the high contrast required and that when a relatively large quantity of the polyethylene oxide compound is used alone a considerable increase in incubation fog results.

TABLE II—Continued

Polyethylene oxide compound, per gram mole silver	Gelvatol 40/10, per gram mole silver, gr.	Development time in minutes †	Relative log speed S1.0	Contrast (γ)	Incubation fog	Description of polyethylene oxide
0.165 g. Texofo F 60.....	1.65	2 2½ 3 4 5	1.96 2.19 2.29 2.48 2.72	8.6 10.0 14 18 18	0.05	0.08
0.165 g. Texofo F 60.....	6.6	2 2½ 3 4 5	1.79 1.97 2.13 2.32 2.55	6 9.2 10.2 22 16.2	0.06	0.20
0.66 gr.....	0	2 2½ 3 4 5	1.86 2.17 2.32 2.56 2.84	6.0 9.2 13 19 10.4	0.04	0.76
0.33 gr Texofo E 23.....	0	2 2½ 3 4 5	2.46 2.71 2.86 3.03 3.07	6.6 10 11.6 8.8 9.6	0.06	2.14 Saturated fatty acid ester on polyethylene oxide (23 ethylene oxide units).
0.33 gr. Texofo E 23.....	1.65	2 2½ 3 4 5	2.09 2.29 2.44 2.61 2.80	7.2 10.0 11.4 12.0 8.0	0.05	1.35
0.33 gr. Texofo E 23.....	6.6	2 2½ 3 4 5	1.98 2.13 2.24 2.42 2.69	7.2 10.4 11.4 13.0 10.4	0.05	0.44
1.33 gr. Texofo E 23.....	0	2 2½ 3 4 5	2.13 2.26 2.42 2.60 2.85	7.0 9.0 12.4 16.0 14.0	0.05	3.49

† In formaldehyde/hydroquinone based developer.

I claim as my invention:

1. A photographic gelatino silver chlorobromide emulsion having a chlorobromide ratio of from 1.5–15 chlorine to 1 bromine and consisting essentially of per gram mole of silver in the emulsion from 0.02–3 g. of a polyethylene oxide or polyethylene oxide condensation product as a sensitizer having a molecular weight of 1,000 to 15,000 and from 0.5 to 15 g. of water-soluble hydrolyzed polyvinyl acetate having a molecular weight from 5,000 to 30,000 and whose residual acetate content is at least 35%.

2. A photographic gelatino silver chlorobromide emulsion according to claim 1 wherein the polyethylene oxide condensation product has terminal end groups selected from the class consisting of halogen atoms, carboxyl, amino, carbamoyl group and higher fatty acid residues,

35 saturated higher fatty acid residues and alkyl phenol residues.

## References Cited

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NORMAN G. TORCHIN, Primary Examiner

45 R. E. FICHTER, Assistant Examiner

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