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2,950,970

## COLOR DEVELOPERS CONTAINING POLY-ETHYLENE GLYCOLS

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1 Claim. (Cl. 96—55)

This invention relates to photography and particularly to accelerators for color developing solutions.

Multilayer reversal color films of the type described in Mannes, Godowsky and Wilder U.S. Patent 2,252,718 are developed first in a black-and-white developer, then re-exposed through separation filters and color developed to form a subtractive dye image in each of the emulsion layers. There are two important problems in connection with the first color development step, that is, the cyan development of the red-sensitive emulsion layer. First, the desired maximum cyan density must be obtained in the exposed regions with a minimum of cyan fog in the unexposed areas (i.e., cyan development in the green-sensitive or blue-sensitive layers which have not been re-exposed). Any attempt to increase cyan D-max. such as by prolonged cyan development is usually accompanied by an increase in cyan fog. Second, all of the exposed silver halide grains from the first re-exposure must be completely reduced before subsequent magenta and yellow development in order to avoid magenta or yellow contamination of the cyan layer.

It is therefore an object of the present invention to provide a method and means for accelerating reversal color development. A further object is to provide a color development giving dye images of increased maximum density or D-max. A still further object is to provide a method for increasing the density of color developed dye images. Other objects will appear from the following description of our invention.

These objects are accomplished by incorporating in the color developer used to develop an exposed silver halide emulsion, especially an emulsion of a multilayer photographic element, a non-ionic or ionic polyethylene glycol as described hereinafter.

In the process of Mannes, Godowsky and Wilder U.S. Patent 2,252,718 a multilayer element is employed having red-sensitive, green-sensitive and blue-sensitive emulsion layers superimposed in that order on a support. The emulsions do not contain color couplers but there is a yellow filter layer between the blue-sensitive and green-sensitive emulsion layers. After exposure in the usual way, the film is developed in an ordinary black-and-white developer. It is then exposed through the base to light passing through a red filter to re-expose only the red-sensitive layer, and this layer is developed to a cyan positive dye image in a primary aromatic amino developing solution containing a cyan-forming coupler. The remaining two emulsion layers are then successively exposed or rendered developable and developed in appropriate color-forming developers, yellow for the blue-sensitive emulsion and magenta for the green-sensitive emulsion. This produces positive dye images in each of the emulsion layers. All of the developed silver is then removed in a bleach which does not affect the dye images.

We have found that the maximum density of the dye images, especially the cyan dye image, may be increased in this process by incorporating a non-ionic or ionic

2

polyethylene glycol in the color developing solution and that this increase in dye density is not accompanied by an increase in color fog. Emulsions may be used containing polyethylene glycols to obtain a speed increase independently of the dye density increase obtained by adding the polyethylene glycols to the color developers.

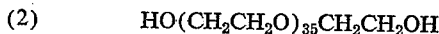
The polyethylene glycols used in the developing solution are polymers derived from ethylene oxide. The preparation of these compounds is described in Ellis, "The Chemistry of Synthetic Resins" (1935), pages 990 to 994. The polymers which we employ should have a molecular weight of at least 600 since the lower molecular weight polymers do not show any appreciable accelerating effect.

The following compounds are useful according to our invention; these being illustrative only:

### NON-IONIC



Polyethylene glycol—M.W. about 600



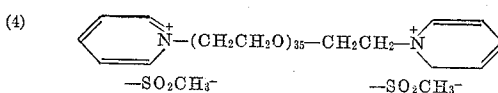
Polyethylene glycol—M.W. about 1500

(A useful polyethylene glycol is Carbowax 1540, a product of Carbide and Carbon Chemicals Corporation, which has the formula  $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2\text{OH}$  where  $n$  has an average value of 35. This polyethylene glycol is believed to be a mixture of compounds, and has an average molecular weight of 1300 to 1600, a specific gravity of 1.15, a freezing point of 43 to 46° C., a viscosity at 210° F. of 25 to 32 centistokes, a Cleveland Open Cup flash point of 510° F., and is 70% by weight soluble in water at 20° C.)

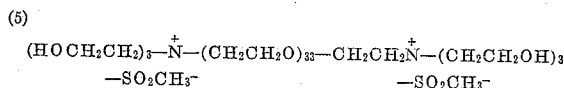


Polyethylene glycol—M.W. about 4000

### CATIONIC

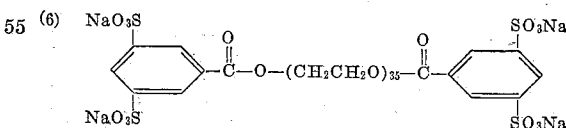


45 Polyethoxyethyl-bis-pyridinium methane sulfonate (derived from polyethylene oxide of molecular weight 1540)

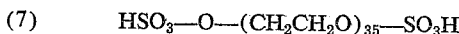


50 Polyethoxyethyl-bis-tri(β-hydroxyethyl)-ammonium methane sulfonate

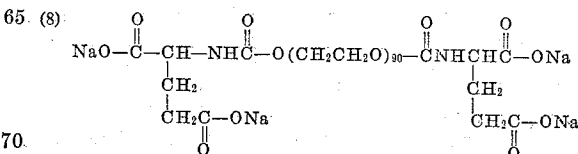
### ANIONIC



60 Polyethoxyethyl-bis(3,5-disulfobenzoate) (tetra sodium salt)



Polyethoxyethyl-bis-sulfuric acid



70 Polyethoxyethyl-bis-carboglutamic acid (sodium salt)

The polyethylene glycols listed above may be prepared as follows:

Compounds 1, 2 and 3 are prepared as described in Ellis supra, page 990.

Compounds 4 to 6 and 8 are prepared as follows:

#### COMPOUND 4

To 400 ml. of dry pyridine contained in a one-liter flask equipped with stirrer, thermometer, and dropping funnel was added 154 g. (0.1 mole) of Carbowax 1540. The solution was chilled to 0° C. and 24 g. (0.20 mole +5 percent excess) of methane sulfonyl chloride was slowly added through the dropping funnel so that the temperature never rose above 5° C. After stirring the slurry for two hours, the solution was allowed to warm up to room temperature while stirring an additional three hours. The slurry was acidified with 1:1 hydrochloric acid at 20° C., and the solution saturated with sodium chloride. The ester was extracted four times with 500-ml. portions of hot benzene. Concentration of the benzene extracts yielded 102 g. (59 percent) of a light yellow viscous oil which turned to a semi-solid upon standing, Carbowax 1540- $\alpha,\omega$ -bis(methanesulfonate) (the yield can be improved by extracting the ester continuously in a liquid-liquid extractor from the weakly acidic solution).

Fifty milliliters of dry pyridine and 44.4 g. (0.025 mole) of Carbowax 1540 -  $\alpha,\omega$  - bis(methanesulfonate), were heated gently on the steam bath for three hours at 90° C. An exothermic reaction occurred in the beginning of the reaction. The excess pyridine was removed completely on the steam bath under vacuum, leaving a tan semi-solid, Carbowax 1540- $\alpha,\omega$ -bis-(pyridinium methanesulfonate).

#### COMPOUND 5

Sixteen and six-tenths grams (0.01 mole) of Carbowax 1540- $\alpha,\omega$ -bis(methanesulfonate), and 3.8 g. (0.02 mole) of triethanolamine were added together. The two layers were heated to 120–130° C. with vigorous stirring for one hour. A clear, uniform, pale yellow oil was obtained weighing 18.5 g. (91 percent) which solidified upon cooling. The product gave a clear foaming solution when dissolved in water.

#### COMPOUND 6

In a flask equipped with a drying tube and sealed stirrer, 77 parts of Carbowax 1540 were dissolved in 250 parts of dry benzene. The temperature was adjusted to 10° C. with a cooling bath, and 27.4 parts of 3,5-disulfonyl chloride chlorobenzene were added. The reaction was allowed to warm to room temperature in an hour; during this time the complete solution resulted. Heat was applied and reflux was maintained for 4 to 5 hours, after which the solvent and evolved hydrochloric acid were removed by distillation at reduced pressure.

With water jet cooling, 65 parts of distilled water were added from a dropping funnel, care being taken not to exceed 25° C. A solution of 32 parts of sodium hydroxide in 80 parts of distilled water was added at 5–15° C. in small portions. Stirring was continued for an hour. The mixture was diluted to a total weight of 539 parts for a 20 percent aqueous solution and was gravity filtered before use.

#### COMPOUND 8

A mixture of 151 g. of Carbowax 4000 and 15 g. of dimethyl isocyanatoglutarate was heated at 70° C. for 20 hours, protected from atmospheric moisture. The resulting product was treated gradually with 6 g. of sodium hydroxide in 15 ml. of water. The mixture was heated at 60–70° C. for 3 hours, water being added occasionally to maintain the product in a fluid state. It was finally diluted with water to a total weight of 332 g. The resulting solution contained an estimated 166 g. of

solid. The water can be removed from the product to yield a pale yellow solid.

Compound 7 is prepared as described in Carroll, Elins, Graham and Wilson application Serial No. 627,136.

Our invention will now be illustrated by reference to the following specific examples:

#### Example 1

A high-speed gelatino-silver bromiodide emulsion containing 0.24 mole of silver halide per liter was digested with a sulfur compound such as disclosed in Sheppard U.S. Patent 1,574,944 and potassium chloroaurate and optically sensitized to red light. To a portion of this emulsion there was added 0.66 gram per gram mole of silver halide of the condensation product of one mole of oleyl alcohol with approximately 25 moles of ethylene oxide (polyethylene glycol oleyl ether). These emulsions were separately coated on film base and were exposed on an Eastman type 1b sensitometer and developed for 3 minutes at 70° F. in a developer of the following formula:

	Grams
N-methyl-p-aminophenol sulfate	0.6
Hydroquinone	20
Sodium sulfite (desiccated)	50
Sodium bromide	6.88
Sodium thiocyanate	6
Sodium hydroxide	20
Potassium iodide	0.003
Water to 1 liter.	

After a two-minute wash in water, the films were flashed for 10 seconds with a No. 2 Reflector Photoflood 5 feet away. The portions of the films were then developed for from 3 to 5 minutes at 80° F. in a cyan developer of the following composition and also in this same developer to which 1 gram per liter of several of the polyethylene glycols had been added:

2-amino-5-diethylamino toluene HCl	gram	0.6
Sulfuric acid	cc	1.5
Sodium sulfite (desiccated)	grams	5
Sodium hexametaphosphate	do	0.5
Sodium carbonate, monohydrate	do	15
Sodium bromide	do	0.25
Potassium iodide	do	0.002
2,4-dichloro - 5 - (p-tolylsulfonamido)- $\alpha$ -naphthol	grams	1.2
Sodium hydroxide	do	0.3
Water to 1 liter.		

After a ten-minute water wash, films were bleached for two minutes in a solution having the following composition:

	Grams
Potassium ferricyanide	100
Potassium bromide	10
Borax	7.5
Boric acid	5
Water to 1 liter.	

After a further water rinse, the films were then fixed for two minutes in a solution of the following composition:

Sodium thiosulfate $\cdot 5H_2O$	grams	240
Sodium sulfite (desiccated)	do	15
Acetic acid (28% solution)	cc	48
Boric acid	grams	7.5
Potassium alum	do	15
Water to 1 liter.		

A second set of film strips was processed in exactly the same manner except that the flash re-exposure was omitted.

The maximum cyan dye density and the cyan fog were

then read through a complementary color filter and each of the samples and the results tabulated as follows:

Developer with Compound No.	Emulsion without PEG		Emulsion contain- ing PEG	
	Cyan D-max.	Cyan Fog	Cyan D-max.	Cyan Fog
None.....	2.25	.16	2.25	.22
1.....	2.45	.15	2.75	.23
2.....	3.00	.17	3.05	.22
3.....	3.00	.21	2.50	.22
4.....	3.20	.15	3.25	.23
7.....	2.70	.15	3.25	.22

#### Example 2

Coatings were made and processed as in Example 1 except that a magenta developer was used instead of the cyan developer, and Carbowax 1540 was the only compound tested in this developer. The results for maximum magenta density and magenta fog when read through a complementary color filter are tabulated below. The magenta developer had the following composition:

	Grams
2-amino-5-diethylamino toluene HCl .....	1.5
Sodium sulfite (desiccated) .....	5
Sodium hexametaphosphate .....	0.5
Sodium carbonate, monohydrate .....	20
Sodium bromide .....	0.22
Potassium iodide .....	0.002
6-nitrobenzimidazole nitrate .....	0.01
Sodium hydroxide .....	1.7
2-cyanoacetyl coumarone .....	0.5
Water to 1 liter.	

The results are shown in the following table:

Developer Addenda	Emulsion without PEG		Emulsion contain- ing PEG	
	Magenta D-max.	Magenta Fog	Magenta D-max.	Magenta Fog
None.....	1.30	0.77	1.30	0.61
Carbowax 1540 (1 g./l.).....	1.60	.62	1.60	.60

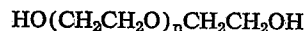
#### Example 3

The effect of the polyethylene glycols in a p-phenylene diamine developer containing a yellow coupler was also investigated. Development acceleration was noted with no increase in maximum color density but with shorter development time required for producing equal maximum densities. With the emulsion coating of Examples 1 and 2 containing the polyethylene glycol oleyl ether a maximum density of 1.45 at fog of 0.65 was attained after five minutes in the color developer containing  $\omega$ -benzoyl-acet-(p-toluene sulfonamido)anilide as the yellow coupler. These same values were attained with the developer containing the polyethylene glycol after only four minutes development.

It will be understood that the above examples are illustrative only and that our invention is to be taken as limited only by the scope of the appended claims.

We claim:

A photographic color developer capable of producing dye images of increased dye density with no increase of color fog upon color development of a silver halide emulsion, comprising a developing solution separate from said emulsion, containing an alkylamino paraphenylenediamine color developer, a coupler compound capable of coupling with the oxidation product of said developer to form a dye upon photographic development, and a polyethyleneglycol selected from the group consisting of (1) polyethylene glycols having the formula



where  $n$  is from 14 to 85, (2) polyethoxyethyl-bis-pyridinium methane sulfonate, and (3) polyethoxyethyl-bis-sulfuric acid.

#### References Cited in the file of this patent

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