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DEVELOPMENT ACCELERATORS FOR SILVER HALIDE EMULSION LAYERS

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U.S. Cl. 96—66.3 4 Claims

ABSTRACT OF THE DISCLOSURE

Process for producing a photographic silver image by development of exposed light-sensitive silver halide in the presence of compound influencing the sensitometric characteristics of a light-sensitive silver halide emulsion by an increase of the speed and/or the gradation.

This invention relates to a process for producing a photographic silver image by development of exposed light-sensitive silver halide in the presence of compounds influencing the sensitometric characteristics of a light-sensitive silver halide emulsion by an increase of the speed and/or the gradation. The present invention also relates to photographic materials and developing baths containing said compounds and to a class of said compounds.

It is known that the general sensitivity of photographic emulsions, which can already be sensitised optimally throughout the whole range of the spectrum by means of the so-called chemical sensitizers, such as sulphur sensitizers, can be increased yet if amines or some polyamines such as diethylenetriamine, triethylenetetramine, etc. are added to these photographic elements. (U.S. patent specification No. 734,474 filed Nov. 6, 1953 by Kodak.)

Such substances, however, cause an increase of the free silver ion concentration of the emulsion and greatly diminish its stability.

It is also known that an increase of sensitivity can be obtained by incorporating into the photographic material polyethylene glycols, alkylene oxide, polymers obtained by polymerising alkylene oxide in the presence of hexitol ring dehydration products, aliphatic alcohols, aliphatic acids, amines, amides, and phenols (U.K. patent specifications Nos. 548,019 filed Mar. 19, 1941 by Kodak, 600,058 filed Jan. 10, 1946 and 592,676 filed Apr. 20, 1945 both by E. I. du Pont de Nemours, 758,745 filed Jan. 6, 1954 by Raduner & Co., A. G. and 748,750 filed June 28, 1954 by Kodak).

It is further known that these polyglycols and alkylene oxide polymers should possess a molecular weight of at least 400. In order to obtain a noticeable effect, it is in practice necessary to use compounds having a molecular weight of 1500 to 2000 and more.

Contrary to the other known methods for increasing the sensitivity of silver halide emulsions such as those in which the chemical sensitizers increase the inherent sensitivity and those in which the cyanine dyes increase the spectral absorption, it appears that the final sensitivity of the silver halide emulsion layers in which these compounds are incorporated is higher since these compounds exert a favourable influence on the development of these silver halide layers by means of the usual developers. Consequently these compounds can be considered as development accelerators.

It is also known, however, that a noticeable increase in sensitivity is only obtained with these compounds when developing in rather slow working developers of the fine grain developer type used in the development of continuous tone images. In fast acting p-N-methyl-amino-phenol - hydroquinone or 1 - phenyl - 3-pyrazolidinone-hydro-quinone developers their development accelerating action manifests itself only by a very moderate increase of the speed of the developed photographic material.

TABLE I

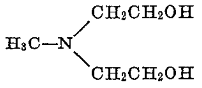
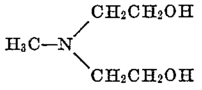
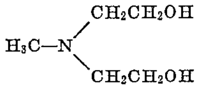
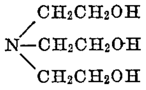
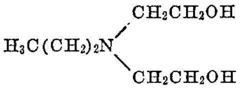
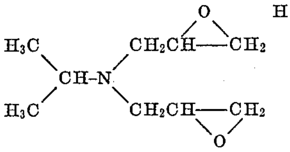
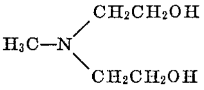
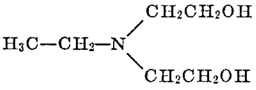
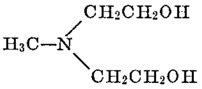
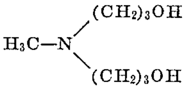
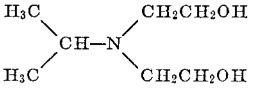
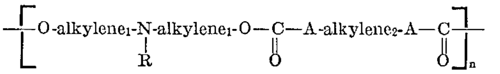
	Used bis-ω-hydroxy-alkylene amines or 2,3:2′,3′-diepoxy-N-alkyldipropylamines	Used dicarboxylic acid or derivative thereof	Reaction time, hr.	Reaction temp., °C.	Remarks
Compound 1		$HOOC(CH_2)_2COOH$	20	110–50	Distil off azeotropically the formed water in toluene. Water-soluble.
		$C_2H_5OOC(CH_2)_2COOC_2H_5$	8	145–200	Distil off ethanol. Water-soluble.
Compound 2		$HOOCCH_2OCH_2COOH$	6	150–5	Distil off azeotropically the formed water in anisol. Water-soluble.
Compound 3		$HOOC(CH_2)_4COOH$	7	200–220	The formed water distils over. Soluble in water in the hydroxychloride form.
Compound 4		HOOC—CH=CH-COOH	3	135–40	Distil off the formed water in xylene. Water-soluble.
Compound 5		$HOOC(CH_2)_4COOH$	8	180–230	The formed water distils over. Soluble in water in tolusulphonate form.
Compound 6		$HOOC(CH_2)_4COOH$	3	100–120	Viscous gel; soluble in water in the tolusulphonate form.

TABLE II

	Used N-alkyl-bis-	Used diisocyanate	Reaction time, hr.	Reaction temp., ° C.	Remarks
Compound 7		$OCN(CH_2)_6NCO$	3 dioxane	100	Add the dioxane solution dropwise to ether. Filter the solid product by suction. Soluble in water in the tolusulphonate form.
Compound 8		$OCN(CH_2)_6NCO$	do	100	Add the dioxane solution dropwise to ether. Filter the solid product by suction. Soluble in water in the tolusulphonate form.
Compound 9		$OCN(CH_2)_2OOC(CH_2)_2COO(CH_2)_2NCO$	do	100	Distill off the dioxane. Soluble in water in the tolusulphonate form.
Compound 10		$OCN—(CH_2)_6NCO$	3½ dioxane	100	Distill off the dioxane. Soluble in water in the acetate form.
Compound 11		$OCN(CH_2)_6NCO$	do	100	Distill off the dioxane. Soluble in alcohol/water (20/80).

It has been found now that polymeric compounds containing N-alkyl-bis-alkylene-amino groups, and obtained by polycondensation of a N-alkyl-bis-ω-hydroxyalkylene-amine with a dicarboxylic acid or derivative thereof e.g. an ester, acid chloride, or anhydride or with an organic diisocyanate, are very suitable for substantially increasing the developability and also the sensitivity of photographic silver halide emulsions on development in slow as well as in fast acting developers.

Polycondensation products, which have proved to be very suitable in that respect, contain recurring units, which can be represented by:



$$-\left[\text{O-alkylene}_1\text{-}\underset{\displaystyle R}{\underset{|}{N}}\text{-alkylene}_1\text{-O}-\underset{\displaystyle O}{\underset{\|}{C}}-\text{A-alkylene}_2\text{-A}-\underset{\displaystyle O}{\underset{\|}{C}}\right]_n-$$

wherein:

R represents an alkyl group of 1 to 5 carbon atoms e.g. methyl, eythl, propyl, isopropyl, or a substituted alkyl group e.g. 2-hydroxyethyl, or an aralkyl group,

both alkylene$_1$ or alkylene$_2$ are alkylene groups containing from 2 to 10 carbon atoms, including alkylene groups substituted e.g. with a hydroxyl group and/or the carbon chain of which is interrupted by (a) hetero-atom(s) such as oxygen, sulphur, or a substituted nitrogen atom,

n is a positive integer of at least 3, and

A represents a chemical bond or a —NH—group.

The compounds according to the invention in which A represents a chemical bond can be prepared by condensing a N-alkyl-bis-ω-hydroxy-alkyleneamine with a dicarboxylic acid or derivative of a dicarboxylic acid such as an ester, an acid chloride, or the anhydride.

The condensations with the dicarboxylic acids are carried out with elimination of water either as such or by azeotropic distillation e.g. in toluene, anisol, or tetraline. The condensation with an ester of a dicarboxylic acid is performed in such condition that the alcohol from which the ester is prepared, is distilled off continuously during the polycondensation reaction.

All techniques sufficiently known from the polyester chemistry can be applied in the preparation of these compounds. Care should be taken, however, that the obtained condensation products are soluble in water either in the basic form or in the salt form.

In general, both reagents are made to react in equimolar ratio, though an excess of one of them is not harmful in most cases.

Very suitable dicarboxylic acids and derivatives thereof are succinic acid and succinates, diglycollic acid and diglycollates, adipic acid and adipates, maleates and maleic anhydride etc.

Particularly suitable N-alkyl-bis-ω-hydroxyalkylene-amines are N-alkyl-diethanolamines such as methyl-, ethyl-, propyl-, isopropyl-, and butyl-diethanolamine, N-alkyldipropanoliamines such as N-methyl-dipropanolamine, triethanolamine, triisopropanolamine, N-α-methylbenzyl-diethanolamine etc.

By way of illustration some typical preparations of compounds according to the present invention are stated in Table 1. Compounds according to the present invention in which A represents a chemical bond and in which alkylene$_1$ is substituted by a hydroxyl group, can be prepared by condensing a 2,3:2′,3′-diepoxy-N-alkyl-di-propylamine with a dicarboxylic acid (e.g. the compound 6 from the Table I).

Compounds according to the invention in which A represents a —NH-group can be prepared by condensing a N-alkyl-bis-ω-hydroxyalkleneamine with adiisoyanate. The above - mentioned N - alkyl-bis-ω-hydroxyalkyleneamines are also particularly suited therefor. Very suitable diisocyanates are aliphatic diisocyanates e.g. hexamethylene diisocyanates. Aliphatic diisocyanates in which the alkylene chain is interrupted by a hetero atom e.g. bis(2-isocyanatoethyl) succinate can also be used for preparation of polyurethans suited for use according to the present invention. Generally, the polycondensations are performed in an inert solvent such as benzene, dioxane etc. Uusually the reaction is continued for some hours at the boiling temperature of the solvent. The polycondensation product is separated either by precipitation with a solvent in which the polycondensation product is insoluble e.g. diethyl ether, or by evaporation of the solvent. By way of illustration some typical preparations are stated in table II.

The development accelerators used according to the present invention can be added as a base or in the salt form to the coating composition of a silver halide emulsion and/or can be incorporated into a water-permeable layer, which applied under or on top of the emulsion layer forms a water-permeable system with the silver halide emulsion layer and thus can come into effective contact with the silver halide.

The development accelerators can be incorporated into the coated emulsion layer either by treating the emulsion layer with an aqueous solution of these development accelerators or by coating this layer with a water-permeable layer containing the development accelerators, or also by bringing the development accelerators from a water-permeable layer lying under the emulsion layer and comprising said development accelerators into effective contact with the silver halide.

The water-soluble development accelerators can be added to the light-sensitive silver halide emulsion during different preparation steps of the light-sensitive material. For instance they can be incorporated therein as a separate addition either mixed with one or more ingredients, which are used in the preparation of the silver halide grains during the physical or chemical ripening process or another moment preceding the application of the emulsion.

The development accelerators are preferably added to the silver halide emulsion composition after the chemical ripening process and just before coating the emulsion.

The development accelerators are preferably added in dissolved form in water or in an aqueous mixture of water and water-miscible organic solvents that do not impair the photographic properties of the light-sensitive silver halide emulsion. When the condensation products are not sufficiently soluble in water in their base form they are converted into the salt form by neutralisation e.g. with an acid such as sulphuric acid, hydrochloric acid, p-toluenesulphonic acid, and acetic acid.

The optimum amount of development accelerator added to the silver halide emulsion depends on the very compound, on the nature of the colloid binding agent for the silver halide grains, and on the amount and the kind of the silver halide in the emulsion. In general, however, the development accelerators are added to the light-sensitive material in amounts ranging from 100 mg. to 10 g. per mole of silver halide. In the developing bath they are normally used in amounts ranging from 0.1 to 10 g. per liter. If necessary, these compounds can also be added in amounts exceeding these limits.

The step of increasing the sensitivity according to the present invention can be combined with a method known as chemical sensitization, in which together with the above-mentioned development accelerators usual amounts of chemical sensitizers are added to the silver halide emulsion, e.g., sulphur-containing compounds such as allyl isothiocyanate, allylthiourea, or sodium thiosulphate, reducing compounds such as the tin compounds described 1950 by Gevaert Photo-Producten, N.V., and 568,687 filed June 18, 1958 by Gevaert Photo-Producten N.V., the iminoaminomethane sulphinic acid compounds described in the British patent specification 789,823 filed Apr. 29, 1955 by Gevaert Photo-Producten N.V. or noble metal compounds such as gold, platinum, palladium, iridium, ruthenium, and rhodium compounds. As a matter of fact, the sensitizing action of the development accelerators used in the present invention comes in addition to the sensitzing action of the sensitizing compounds originally present in gelatin.

The development accelerators applied in the present invention can also be used in combination with stabilizers and fog-inhibiting compounds for the silver halide emulsion, for instance with mercury compounds or organic sulphur-containing compounds that form an insoluble silver salt with silver ions, preferably heterocyclic nitrogen-containing thione compounds such as benzothiazolin-2-thione and 1-phenyltetrazolin-5-thione, the compounds described in the Belgain patent specifications 571,916 and 571,917 both filed Oct. 10, 1958 by Gevaert Photo-Producten N.V., and compounds of the oxytriazolopyrimidine type, e.g. 5-methyl-7-hydroxy-s-triazolo[1,5-a]pyrimidine. The combination with sensitizing and stabilizing cadmium salts in the light-sensitive material as well as in the developing bath can also be applied.

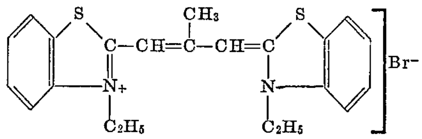
Other compounds, which sensitize the photographic emulsion by development acceleration, such as organic onium compounds and polyonium compounds, preferably of the ammonium or sulphonium type, e.g. quaternary tetraalkylammonium salts, alkylpyridinium salts, bis-alkylenepyridinium salts, alkylquinoline salts, and trialkylsulphonium salts can be used together with the development-accelerators according to the invention in the developing solution as well as in the light-sensitive material. Other ingredients, such as colour couplers, developing substances, hardening agents, and wetting agents can also be added to the emulsions in the ordinary way.

The development of low-sensitive as well as of high-sensitive, of fine-grain as well as of coarse-grain silver halide emulsions is accelerated by the action of the above-mentioned development accelerators. These products can be applied for accelerating the development of X-ray emulsions as well as of the most different spectrally or non-spectrally sensitized emulsions. They can be incorporated into the photographic emulsion either with or without optical sensitizers and can be used for increasing the sensitivity of negative emulsions as well as of positive emulsions.

The following examples illustrate the invention.

EXAMPLE 1

A washed negative gelatin silver bromoiodide emulsion (average grain size of the silver halide: 0.8μ), the silver halide of which consists of 94.5 mole percent of silver bromide and 5.5 mole percent of silver iodide, is ripened at 45° C. The emulsion ready for coating contains per kg. 50 g. of silver halide, 75 g. of gelatin, 30 mg. of optical sensitizer with the following structural formula:



50 mg. of 5-methyl-7-hydroxy-s-triazolo[1,5-a]pyrimidine as a stabilizer, and 500 mg. of saponine as a wetting agent.

This emulsion is divided into several aliquot portions and to the separate portions is added one of the development accelerators as mentioned in the following Table 1. These emulsion portions are separately applied to a cellulose triacetate support and dried. All test strips are then exposed in the same conditions through a grey wedge and developed for 7 min. at 20° C. in a fine-grain developer of the following composition:

Water—800 ccs.
Monomethyl-p-aminophenol sulphate—2 g.
Hydroquinone—5 g.
Anhydrous sodium sulphite—100 g.
Borax—10 g.
Boric acid—5 g.
Potassium bromide—0.5 g.
Water to 1,000 ccs.

The speed is represented by exposure values. A decrease in exposure value of −30 means a doubling in sensitivity.

TABLE 1

Added compound	Amount of compound per kg. of emulsion	Sensitometric results		
		Fog.	Gamma	Rel. speed
		0.06	0.60	104
Compound No. 1	100 mg	0.05	0.61	90
	1 g	0.06	0.64	84
Compound No. 2	100 mg	0.05	0.60	88
	1 g	0.06	0.61	95
Compound No. 3	1 g	0.08	0.64	75
Compound No. 5	1 g	0.07	0.67	96
Compound No. 7	100 mg	0.07	0.65	80
	1 g	0.15	0.61	72
Compound No. 8	50 mg	0.07	0.60	98
	1 g	0.08	0.71	91
Compound No. 9	100 mg	0.06	0.70	87
	1 g	0.06	0.71	82

EXAMPLE 2

An emulsion as described in Example 1 is used, which emulsion, however, is divided in aliquot portions respectively containing the compounds mentioned in Table 2. The test strips, after having been exposed were developed for 5 min. at 20° C. in a classical fast acting p-N-methyl-aminophenol-hydroquinone developer of the following composition:

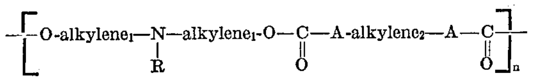
Water—800 ccs.
Monomethyl-p-aminophenol sulphate—2 g.
Hydroquinone—5 g.
Anhydrous sodium sulphite—25 g.
Crystalline sodium carbonate—40 g.
Potassium bromide—1 g.
Water to 1 l.

TABLE 2

Added compound	Amount of compound added per kg. of emulsion	Sensitometric Results		
		Fog	Gamma	Rel. speed
		0.08	0.73	79
Polyethyleneglycol (average molecular weight: approximately 6000).	100 mg	0.13	0.81	78
$C_{12}H_{23}O(CH_2CH_2O)_{23}H$	300 mg	0.10	0.86	75
Compound No. 5	300 mg	0.11	0.74	64
Compound No. 8	300 mg	0.10	0.78	66

We claim:

1. Process for developing photographic materials containing light-sensitive silver halide which comprises the step of developing said materials in the presence of a polymeric compound, containing the following structural units or these units in salt form:



$$\left[-\text{O-alkylene}_1-\underset{R}{\underset{|}{N}}-\text{alkylene}_1\text{-O}-\underset{O}{\underset{\|}{C}}-\text{A-alkylene}_2-A-\underset{O}{\underset{\|}{C}}-\right]_n$$

wherein:

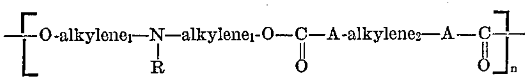
R represents an alkyl group of 1 to 5 carbon atoms, an aralkyl group, or a hydroxy-substituted alkyl group, both alkylene$_1$ and alkylene$_2$ are alkylene chains containing from 2 to 10 carbon atoms, including substituted alkylene chains and such chains interrupted by (a) heteroatom(s),

n is a positive integer of at least 3, and

A represents a chemical bond or a —NH-group.

2. Process for developing photographic materials containing light-sensitive silver halide which comprises the step of developing said materials in the presence of a water-soluble polymeric compound in basic or salt form and which is obtained in basic form by allowing to react a N-alkyl-bis-ω-hydroxylkyleneamine with a dicarboxylic acid or derivative thereof or with an organic diisocyanate.

3. A photographic light-sensitive silver halide material containing a polymeric compound containing the following structural units or these units in salt form:



$$\left[-\text{O-alkylene}_1-\underset{R}{\underset{|}{N}}-\text{alkylene}_1\text{-O}-\underset{O}{\underset{\|}{C}}-\text{A-alkylene}_2-A-\underset{O}{\underset{\|}{C}}-\right]_n$$

wherein:

R represents an alkyl group of: 1 to 5 carbon atoms, an aralkyl group, or a hydroxy-substituted alkyl group, both alkylene$_1$ and alkylene$_2$ are alkylene chains containing from 2 to 10 carbon atoms, including substituted alkylene chains and such chains interrupted by (a) heteroatom(s),

n is a positive integer of at least 3, and

A represents a chemical bond or a —NH-group.

4. A photographic light-sensitive silver halide material according to claim 3 containing said polymeric compound in an amount ranging from 100 mg. to 10 g. per mole of silver halide.

References Cited

UNITED STATES PATENTS

3,129,100	4/1964	Grabhöfer et al.	96—66.3
3,307,948	3/1967	Julius Thiers et al.	96—66.3

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U.S. Cl. X.R.

96—95, 114; 260—77.5