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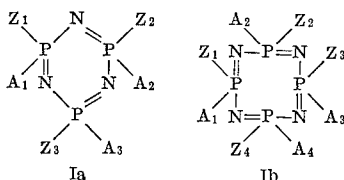
3,552,968

PHOTOGRAPHIC DEVELOPMENT PROCESS
Jozef Frans Willems, Wilrijk, Belgium, assignor to
Gevaert-Agfa N.V., Mortsel, Belgium, a Belgian company
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Claims priority, application Great Britain, Aug. 19, 1966,
37,178/66
Int. Cl. G03c 5/30, 1/48, 1/02
U.S. Cl. 96—66.3

5 Claims

ABSTRACT OF THE DISCLOSURE

A photographic light-sensitive material comprising a silver halide emulsion layer containing a compound corresponding to one of the following structural Formulae Ia or Ib:

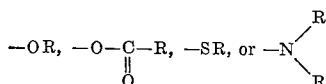


wherein:

each of A₁, A₂, A₃, A₄, Z₁, Z₂, Z₃, and Z₄ stands for a chlorine atom or a polyoxyalkylene group of the formula —(OR₁)_n—X, at least one of the groups A₁, A₂, A₃, A₄, Z₁, Z₂, Z₃, or Z₄ being the group —(OR₁)_n—X wherein n represents an integer of at least 5, the



group representing repeating units entirely consisting of ethylene oxide units or a mixture of ethylene oxide units and propylene oxide units, and X being a terminal group that is unreactive with respect to an active halogen atom of an acid halide compound and is selected from the group consisting of



wherein R is an alkyl, an aryl, a cycloalkyl, or a heterocyclic radical, said radicals having unreactive with respect to said active halogen atom

is described. The silver halide emulsion has a high developing activation in combination with a very low fog production.

This invention relates to an improved photographic material and more especially to silver halide emulsion layers having a better developability and an increased general light-sensitivity.

It is known to further increase the general sensitivity of photographic emulsions, which have already obtained an optimal sensitivity with the so-called chemical sensitizers, e.g. the sulphur sensitizers, by adding polyglycols to the photographic elements (see British patent specifications 548,019 and 600,058).

It is also known that such an additional increase of sensitivity may be obtained when incorporating into the photographic material alkylene oxide polymers prepared by the polymerization of alkylene oxide in the presence of dehydration products of hexitol rings, aliphatic alcohols, aliphatic acids, amines, amides and phenols (see British patent specifications 592,676, 748,745 and 748,750).

Further, it is known that these polyglycols and alkylene oxide polymers must have a molecular weight of at least 400 and that it is practically necessary to use compounds

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having a molecular weight from 1,500 to 2,000 and more to obtain a substantial effect.

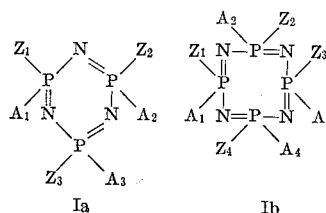
Contrarily to the other known methods to increase the sensitivity of silver halide emulsions, e.g. the methods according to which the inherent sensitivity is increased by chemical sensitizers, and the methods according to which the spectral absorption is increased by cyanine dyestuffs, it has been observed that the final sensitivity of the silver halide emulsion layers containing the above described compounds is higher, since these compounds have a favorable influence upon the development of these silver halide emulsion layers in the conventional developers. Thus these compounds may be considered as developing accelerators.

However, it is also known, that these compounds may be used as ingredients in more sensitive silver halide emulsion layers, but they impair the keeping quality of these layers, particularly at high temperatures and elevated degrees of relative humidity, since they induce a substantial increase of fog. It has been also observed that the incorporation of these compounds into the photographic material in order to prepare more sensitive silver halide emulsion layers impaired the image tone of the developed silver, thereby forming brown and red-brown images.

These disadvantages can be reduced, even practically oxyacid of phosphorus. For such type of condensation products containing in their structure ester groups of an oxyacid of phosphorus. For each type of condensation products reference is made to the United Kingdom patent specifications 945,340 and 1,015,023, the German patent specification 1,182,523 and the French patent specification 1,396,860.

It has now been found that a high developing activation in combination with a very low fog production can be obtained by the use in working contact with a light-sensitive silver halide emulsion layer of a cyclic phosphonitrile trimer or tetramer derivative wherein at least one of the phosphorus atoms is linked to a polyoxyalkylene oxide chain forming part of a terminally monoblocked polyoxyalkylene oxide polymer or a cyclic phosphonitrile trimer or tetramer derivative wherein trimer and/or tetramer phosphonitrile nuclei are linked together through their phosphorus atoms by means of a bivalent radical containing oxyalkylene units.

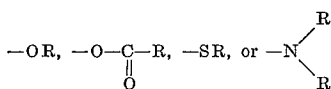
Preferred representatives of the first type of phosphonitrile trimer and tetramer derivatives fall within the scope of the following structural Formulae Ia and Ib



wherein:

each of A₁, A₂, A₃ and A₄ represents a chlorine atom at least one of them, however, being a polyoxyalkylene residue of the formula —(OR₁)_n—X, wherein n represents a positive integer of at least 5, preferably from 5 to 35, and the —(OR₁)— repeating units are entirely consisting of ethylene oxide units or consisting of a mixture of ethylene oxide and propylene oxide units, the ratio of said units being preferably chosen in such a way that water-soluble products are obtained, and X represents a terminal group that is unreactive in respect of an active halogen atom of an acid halide compound e.g.

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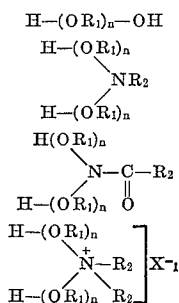


wherein R represents an alkyl, aryl, cycloalkyl or heterocyclic radical, including said radicals substituted with groups that are unreactive in respect of said halogen atom; and

each of Z₁, Z₂, Z₃ and Z₄ represents a chlorine atom or a radical as described for A₁.

Representatives of the second type are condensation polymers, which can be obtained by the reaction of a phosphonitrile chloride trimer or tetramer with a compound containing polyoxyalkylene units and having at least two reactive groups for a chlorine atom of a phosphonitrile chloride.

Examples of such compounds having two such reactive groups can be represented by the following structural formulae:



wherein:

the $-(\text{OR}_1)-$ units are entirely consisting of ethylene oxide units or of a mixture of ethylene oxide and propylene oxide units, the ratio of said units being preferably chosen in such a way that water-soluble products are obtained;

R₂ represents an alkyl radical or an aralkyl radical, X⁻¹ represents an acid radical, and n is an integer of at least 5, preferably between 5 and 35.

Specific polyoxyalkylene diols according to the general formulae above are mentioned, e.g. in the United Kingdom patent specification 1,015,023 and French patent specification 1,447,262. Some of these diols are commercially available, for example under the trade name Pluronic L 31, which is a water-soluble mixed-condensation product of ethylene oxide and propylene oxide, with an average molecular weight of 1,100, manufactured by Wyandotte Chemicals Corporation, Wyandotte, Mich., U.S.A.

The condensation reaction is preferably carried out in an inert solvent for the reaction compounds, e.g. benzene or dioxane and in the presence of a basic compound, e.g. piperidine, triethylamine, sodium metal and the like. The chloride salts formed during the condensation reaction with said basic compound are filtered off at the end of the reaction and the formed phosphonitrile-polyoxyalkylene derivative separated by evaporating the solvent.

Although it is possible, depending upon whether a phosphonitrile chloride trimer or tetramer is used, to introduce six or eight polyoxyalkylene residues or repeating units, the reaction conditions are rather severe and in order to avoid the application of a rather long reaction time and too high reaction temperatures it is desirable that only half of the chlorine atoms are substituted by the radicals containing oxyalkylene units. Moreover, it has been found that condensation compounds that still contain chlorine atoms produce less fog on storage of the photographic silver halide emulsion layers.

When applying mild reaction conditions as illustrated

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hereinafter the reaction between phosphonitrile chloride trimer or tetramer and an excess of polyethylene glycol can result in a condensation product having unit with either three or four chlorine atoms respectively.

The following preparations illustrate the production of compounds suitable for use according to the present invention.

PREPARATION 1

Reaction of monomethoxy-polyethylene glycol (average molecular weight 750) with phosphonitrile dichloride (trimer).

To a solution of 225 g. (0.3 mole) of methoxypolyethylene glycol (average molecular weight 750) in 400 ccs. of benzene are added at room temperature: a solution of 34.8 g. (0.1 mole) of phosphonitrile dichloride (trimer) in 200 ccs. of benzene and a solution 30.3 g. (0.3 mole) of triethylamine in 100 ccs. of benzene. This mixture is stored at room temperature for 24 days. After this storing period 39 g. of triethylammonium chloride is formed. The precipitate of triethylammonium chloride is filtered by suction and the benzene filtrate is concentrated by evaporation. The condensation product obtained is water-soluble. Yield: 253 g.

PREPARATION 2

Reaction of the condensation product of 20 moles of ethylene oxide and 1 mole of cetyl alcohol with phosphonitrile dichloride (trimer).

To a solution of 168.3 g. (0.15 mole) of the condensation product of 20 moles of ethylene oxide and 1 mole of cetyl alcohol in 400 ccs. of benzene are added at room temperature: a solution of 17.4 g. (0.05 mole) of phosphonitrile dichloride (trimer) in 100 ccs. of benzene and a solution of 15.15 g. (0.15 mole) of triethylamine in 100 ccs. of benzene. This mixture is stored for 21 days at room temperature. After this storing period 19.3 g. of triethylammonium chloride have formed. The precipitate consisting of the said chloride is filtered by suction and the benzene filtrate is concentrated by evaporation. The condensation product obtained is water-soluble. Yield: 178 g.

PREPARATION 3

Reaction of a water-soluble mixed condensation product of ethylene oxide and propylene oxide (average molecular weight 1,100) with phosphonitrile dichloride (trimer).

To a solution of 79 g. (0.075 mole) of the said mixed condensation product in 300 ccs. of benzene are added at room temperature: a solution of 17.4 g. (0.05 mole) of phosphonitrile dichloride (trimer) in 100 ccs. of benzene and a solution of 15.15 g. (0.15 mole) of triethylamine in 75 ccs. of benzene. This mixture is stored for 21 days at room temperature. After this storing period 19.5 g. of triethylammonium chloride have formed. The precipitate of triethylammonium chloride is filtered by suction and the benzene filtrate is concentrated by evaporation. The condensation product obtained is soluble in water/ethanol (80/20). Yield: 95 g.

PREPARATION 4

Condensation product of polyethylene glycol (average molecular weight: 1,000) with phosphonitrile dichloride (trimer).

To a solution of 150 g. (0.15 mole) of polyethylene glycol (average molecular weight: 1,000) in 500 ccs. of benzene are added at room temperature: a solution of 34.8 g. (0.1 mole) of phosphonitrile dichloride (trimer) in 200 ccs. benzene and a solution of 30.3 g. (0.3 mole) of triethylamine in 75 ccs. of benzene. This mixture is stored for 25 days at room temperature. After this storing period 39 g. of triethylammonium chloride have formed. The precipitate consisting of the said chloride is filtered by suction and the benzene filtrate is concentrated

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by evaporation. The condensation product obtained is soluble in water. Yield: 168 g.

PREPARATION 5

Condensation product of polyethylene glycol (average molecular weight: 2,000) with phosphonitrile dichloride (trimer).

To a solution of 150 g. (0.075 mole) of polyethylene glycol (average molecular weight: 2,000) in 600 ccs. of benzene are added at room temperature: a solution of 17.4 g. (0.05 mole) of phosphonitrile dichloride (trimer) in 100 ccs. of benzene and a solution of 15.15 g. (0.15 mole) of triethylamine in 75 ccs. of benzene. This mixture is stored for 27 days at room temperature. After this storing period 19 g. of triethylammonium chloride have formed. The precipitate consisting of the said chloride is filtered by suction and the benzene filtrate is concentrated by evaporation. The condensation product obtained is soluble in water. Yield: 157 g.

PREPARATION 6

Condensation product of polyethylene glycol (average molecular weight: 1,000) with phosphonitrile dichloride (tetramer).

To a solution of 50 g. (0.05 mole) of polyethylene glycol (average molecular weight: 1,000) in 170 ccs. of benzene are added at room temperature: a solution of 11.6 g. (0.025 mole) of phosphonitrile dichloride (tetramer) in 70 ccs. of benzene and a solution of 10.1 g. (0.1 mole) of triethylamine in 40 ccs. of benzene. The solution is stored for 27 days at room temperature. After this storing period 13 g. of triethylammonium chloride have formed. The precipitate consisting of said chloride is filtered by suction and the benzene filtrate is concentrated by evaporation. The condensation product obtained is soluble in water. Yield: 57 g.

When saying that the new compounds according to the present invention are used in working contact with the silver halide emulsion layer it is meant that they must be present during the development in the emulsion layer and this is realized either by incorporating them therein before exposure or by diffusion from an adjacent water-permeable layer or developing composition.

Preferably, the developing activators used in the present invention are added directly to the silver halide emulsion. However, they may be also added to a hydrophilic colloid layer adjacent to said emulsion layer. The addition of these compounds may be eventually effected in the form of an aqueous solution or of a mixture of water and an organic solvent which does not impair the photographic properties of the light-sensitive material.

The emulsion layer may occasionally be treated with a solution of the development activators instead of incorporating said solution into the emulsion ready for coating.

The developing activators used in the present invention may be incorporated at different steps of the emulsion preparation. For instance they may be added as a separate addition or in admixture with one or several other ingredients used for the initial precipitation of the silver halide grains, during the physical or chemical ripening process or in any other step before coating the emulsion. However, they are preferably added to the emulsion after its chemical ripening and just before coating.

The optimum amount added to the emulsion depends upon the selected compound, the nature of the colloidal binding agent for the silver halide present in the emulsion. Generally, the developing activators used in the present invention are added in an amount of 30 mg. to 6 g. per mole of silver halide.

In order to increase the light-sensitivity of a silver halide emulsion layer of a photographic material the developing activators used in the present invention can be incorporated in the silver halide emulsion layer in combination

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with small amounts of a sulphur containing compound, such as allyl isothiocyanate, allyl thiourea and sodium thiosulphate, small amounts of reduction sensitizers, such as the tin compounds described in the Belgian patent specifications 493,464 and 568,687 and the iminoamino-methane sulphinic acid compounds described in the British patent specification 789,823, or small amounts of precious metal compounds, such as of gold, platinum, palladium, iridium, ruthenium and rhodium. Of course, the sensitizing effect of the compounds initially present in the gelatin may be very advantageously completed by the new developing activators.

In combination with the developing activators used in the present invention, stabilizers may also be used, e.g. mercury compounds, and the compounds mentioned in the prior art and claimed in the Belgian patent specifications 571,916 and 571,917, and compounds of the oxytriazolopyrimidine type, e.g. 5-methyl-7-hydroxy-s-triazolo-[1,5-a]-pyrimidine.

It is also usual to sensitize and/or to stabilize silver halide emulsions by incorporating cadmium salts or by processing these emulsions in the presence of cadmium salts. 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-alkylene pyridinium salts, alkylquinolinium 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. Further, other ingredients such as fog inhibiting agents, colour couplers, developing substances, hardeners and wetting agents, may also be added in a known manner to the emulsion, without impairing it in any way.

Owing to their property of promoting the developability, the new compounds may be very efficiently used to increase the X-ray sensitivity and the general light-sensitivity of orthochromatic, panchromatic and all special emulsions as well as the conventional non-spectral sensitized emulsions. They may be added separately or in combination with optically sensitizing dyestuffs. In the latter case, the addition must be effected before or after the addition of the optically sensitizing dyestuffs. In addition, they may be very advantageously used in the most various emulsions since they lead to an outstanding sensitivity increase in the negative as well as in the positive emulsion types.

The new compounds can be applied, with particularly good results, for the development of light-sensitive materials suitable for use in the graphic art, on account of the very contrasting development obtained when these compounds are added either to the formaldehyde bisulphite-hydroquinone developer or to the light-sensitive emulsion layer. Further, it has been found that in the latter light-sensitive materials these compounds improve the quality of the developed dot screen prints (dot sharpness) and reduce the number of "peppers."

When using the development accelerating compounds in the developing bath they are normally incorporated therein in amounts ranging from 0.1 g. to 10 g. per liter. If necessary, these compounds can also be added in amounts exceeding that range. Preferably they are used in the photographic material as well as in the developing bath in water-soluble form.

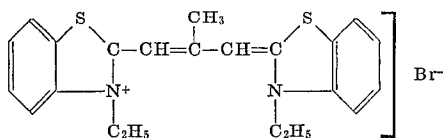
The following examples illustrate the present invention without, however, limiting it thereto.

Example 1

A washed negative gelatin silver bromiodide 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 silver iodide, is ripened at 45°C . The emulsion ready for coating contains per kg.

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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 I. The control emulsion and the emulsion portions containing a development accelerator 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—1000 ccs.

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

TABLE I

Added compound	Amount of compound per kg. of emulsion	Sensitometric results		
		Fog	Gamma	Speed
Monomethoxypolyethylene glycol with average mol. weight of 750.	300 mg.	0.10	0.60	105
	1 g.	0.09	0.64	74
Compound of preparation 1	300 mg.	0.12	0.67	78
	1 g.	0.10	0.75	62
Condensation product of 20 mole of ethylene oxide and 1 mole of cetyl alcohol.	300 mg.	0.12	0.90	64
	1 g.	0.10	0.76	68
	1 g.	0.11	0.75	70
Compound of preparation 2	300 mg.	0.10	0.84	63
	1 g.	0.08	0.88	65
Mixture condensation product of ethylene oxide (80 moles percent) and propylene oxide (20 moles percent) (average mol. weight of the condensation product-1,100).	300 mg.	0.09	0.65	78
	1 g.	0.09	0.53	83
Compound of preparation 3	300 mg.	0.08	0.74	68
	1 g.	0.08	0.72	69

Example 2

An emulsion as described in Example 1 is used, which emulsion, however, is divided in aliquot portions and respectively added thereto the compounds mentioned in Table II. The test strips, after an incubation of 36 hours in an atmosphere of 57° C. and 34% relative humidity and after having been exposed, were developed for 5 min. at 20° C. in a 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 litre.

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In Table II, the obtained fog values are listed.

TABLE II

Compound added	Amount of compound added per kg. of emulsion	Fog
Methoxypolyethylene glycol with average molecular weight of 750.	300 mg.	0.34
Compound of preparation 1	300 mg.	0.19
	1 g.	0.19
Condensation product of 20 moles of ethylene oxide and 1 mole of cetyl alcohol.	300 mg.	1.09
	1 g.	0.18
Compound of preparation 2	300 mg.	0.20
	1 g.	0.19
Mixture condensation product of ethylene oxide and propylene oxide (average mol. weight of 1100).	300 mg.	0.20
	1 g.	0.11
Compound of preparation	300 mg.	0.12
	1 g.	0.12

Example 3

After the addition of the hereafter indicated amounts of developing accelerators to the silver halide emulsion as described in Example 1 and a processing identical to that of Example 1, the following sensitometric results are obtained:

TABLE III

Compound added	Amount of compound per kg. of emulsion, g.	Sensitometric results		
		Fog	Gamma	Speed
Compound of preparation 4	1	0.08	0.49	148
Compound of preparation 5	1	0.10	0.57	112
	1	0.10	0.61	110

Example 4

The following sensitometric results are obtained as described in Example 1, but after having developed the samples for 7 minutes at 20° C., in a solution having the following composition:

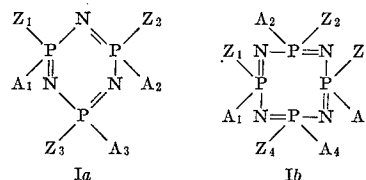
Monomethyl-p-aminophenol sulphate—4.5 g.
 Sodium sulphite (anhydrous)—90 g.
 Sodium chloride—30 g.
 Boric acid till pH 7.8
 Water to—1000 ccs.

TABLE IV

Compound added	Amount of compound per kg. of emulsion, g.	Sensitometric results		
		Fog	Gamma	Speed
Compound of preparation 4	1	0.08	0.31	181
Compound of preparation 5	1	0.12	0.41	132
	1	0.11	0.41	130

What we claim is:

1. A photographic light-sensitive material which comprises a silver halide emulsion layer containing a compound corresponding to one of the following structural Formulae Ia or Ib:

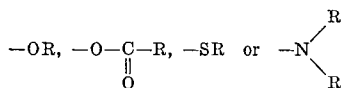


wherein:

each of A₁, A₂, A₃, A₄, Z₁, Z₂, Z₃, and Z₄ stands for a chlorine atom or a polyoxyalkylene group of the formula —(OR₁)_n—X, at least one of the groups A₁, A₂, A₃, A₄, Z₁, Z₂, Z₃, or Z₄ being the group —(OR₁)_n—X wherein n represents an integer of from about 5 to 35, the —(OR₁)— group representing repeating units entirely consisting of ethylene oxide units or a mixture of ethylene oxide units and propylene oxide units, and X being a terminal group

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that is unreactive with respect to an active halogen atom of an acid halide compound and is selected from the group consisting of



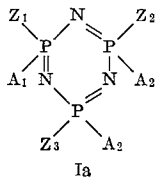
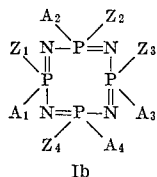
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wherein:

R is an alkyl, an aryl, a cycloalkyl or a heterocyclic radical, said radicals being unreactive with respect to said active halogen atom.

2. A photographic light-sensitive material according to claim 1 wherein said compound is incorporated in the silver halide emulsion layer in an amount of 30 mg. to 6 g. per mole of silver halide.

3. A process for producing photographic images comprising the steps of image-wise exposing a photographic material containing a light-sensitive silver halide emulsion layer to electromagnetic radiation creating a latent silver image and developing said image by selectively reducing the silver halide to metallic silver in the presence of a development accelerating compound corresponding to one of the following structural Formula Ia or Ib:



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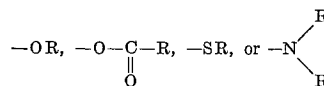
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wherein:

each of A₁, A₂, A₃, A₄, Z₁, Z₂, Z₃, and Z₄ stands for a chlorine atom or a polyoxyalkylene group of the formula $-(\text{OR}_1)_n-\text{X}$, at least one of the groups A₁, A₂, A₃, A₄, Z₁, Z₂, Z₃, or Z₄ being the group $-(\text{OR}_1)_n-\text{X}$ wherein n represents an integer of

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from about 5 to 35, the $-(\text{OR}_1)-$ group representing repeating units entirely consisting of ethylene oxide units or a mixture of ethylene oxide units and propylene oxide units, and X being a terminal group that is unreactive in respect of an active halogen atom of an acid halide compound and is selected from the group consisting of



wherein:

R is an alkyl, an aryl, a cycloalkyl or a heterocyclic radical, said radicals being unreactive with respect to said active halogen atom.

4. A process according to claim 3 wherein the development accelerator is present in the photographic material before its exposure and comes in effective contact with the silver halide during the development.

5. A process according to claim 3 wherein the development accelerator is present in the developing solution.

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DAVID KLEIN, Primary Examiner

U.S. Cl. X.R.

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