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3,158,484
**LIGHT-SENSITIVE COLLOID SILVER HALIDE
 PHOTOGRAPHIC ELEMENTS**

Jozef Frans Willems, Wilrijk-Antwerp, Robrecht Julius Thiers, Brasschaat-Antwerp, and Joseph Louis De Munnck, Beveren-Waas, Belgium, assignors to Gevaert Photo-Producten N.V. Mortsel-Antwerp, Belgium, a Belgian company

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The present invention relates to a process for improving the quality of photographic materials, and more particularly to a process for enhancing the developability and general light-sensitivity of silver halide emulsion layers.

It is known that the general sensitivity of photographic emulsions which can be optimally sensitized throughout the whole range of the spectrum by means of the so-called chemical sensitizers, such as sulphur sensitizers, can be still further increased if polyglycols are added to these photographic elements (U.S. Patent Nos. 2,240,472 and 2,432,549).

It is also known that the same increase of sensitivity can be obtained by working up in the photographic material alkylene oxide polymers obtained by polymerizing alkylene oxide in the presence of hexitol ring dehydration products, aliphatic alcohols, aliphatic acids, amines, amides and phenols (U.S. Patent Nos. 2,400,532, 2,784,091 and 2,716,062).

It is further known that these polyglycols and alkylene oxide polymers should possess a molecular weight of at least 400 and in order to obtain a noticeable effect it is in practice necessary to use compounds which possess 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 wherein the chemical sensitizers increase the inherent sensitivity and those wherein the cyanine dyes increase the spectral absorption, it appears that the final sensitivity of the silver halide emulsion layers wherein these compounds are incorporated is higher since these compounds exert a favorable influence on the development of these silver halide layers by means of the usual developers. These compounds can thus be considered as development accelerators.

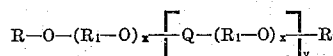
It is, however, also known that these compounds, irrespective of the fact that they can be used as a component in more sensitive silver halide layers, make these layers less suitable for storage and specially for storage at elevated temperatures and relative humidities, since these compounds considerably increase fog. It was further found that these compounds, when added to a photographic element for obtaining more sensitive silver halide emulsion layers, impair the image-tone of the developed silver obtained and give rise to brown and reddish-brown images.

It has now been found that the developability of the light-sensitive emulsions can be favorably influenced by adding to at least one emulsion layer or other layer comprised by the photographic element, compounds which are obtained by polycondensation of low-molecular alkylene oxide derivatives, showing no action on themselves, with functional linking agents.

On applying this new method, it was found that with these new compounds higher sensitivities can be obtained than with the known polyoxyalkylene compounds and also that these new compounds give rise to less fog on storage. Furthermore when using these new compounds, the image-tone of the developed silver remains unaltered.

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These new compounds correspond to the following general formula:



wherein:

R₁ represents an alkylene group of from about 2 to about 3 carbon atoms including ethylene, propylene and isopropylene;

x and y each represent a positive integer equal to or higher than 2 and preferably less than about 35;

Q is a member of the group consisting of

(1) A $\begin{matrix} \text{—CHO—} \\ | \\ R_2 \end{matrix}$ group, wherein R₂ represents a hydrogen atom

or an alkyl group containing from about 1 to about 4 carbon atoms;

(2) A $\begin{matrix} \text{C—R}_3\text{—C—O—} \\ || \quad || \\ \text{O} \quad \text{O} \end{matrix}$ group, wherein R₃ represents a bivalent

aliphatic hydrocarbon radical of from about 2 to 20 carbon atoms which radical may be interrupted by a hetero atom, or an aromatic or heterocyclic radical including

(3) A $\begin{matrix} \text{C—NH—R}_4\text{—NH—C—O—} \\ || \quad || \\ \text{O} \quad \text{O} \end{matrix}$ group, wherein R₄ represents

a group as described for R₃;

(4) A $\begin{matrix} \text{—P—O—} \\ | \\ \text{O R}_5 \end{matrix}$ group wherein R₅ has the same significance as R₂;

(5) A $\begin{matrix} \text{O} \\ || \\ \text{—P—O—} \\ | \\ \text{O R}_5 \end{matrix}$ group wherein R₅ has the same significance as R₂;

and

(6) A $\text{—CH}_2\text{—CHOH—R}_6\text{—CHOH—CH}_2\text{—O—}$ group wherein R₆ represents a chemical bound or a bivalent organic radical.

R is a member of the group consisting of

(1) A hydrogen atom;

(2) A $\begin{matrix} R_2 \\ | \\ \text{—CHOH—} \end{matrix}$ group where Q represents a $\begin{matrix} \text{H} \\ | \\ \text{—C—O—} \\ | \\ R_2 \end{matrix}$ group;

(3) A $\begin{matrix} \text{C—R}_4\text{—C—OH—} \\ || \quad || \\ \text{O} \quad \text{O} \end{matrix}$ group where Q represents a

$\begin{matrix} \text{—C—R}_4\text{—C—O—} \\ || \quad || \\ \text{O} \quad \text{O} \end{matrix}$ group;

(4) A $\begin{matrix} \text{C—NH—R}_5\text{—NH}_2\text{—} \\ || \\ \text{O} \end{matrix}$ group where Q represents a

$\begin{matrix} \text{—C—NH—R}_5\text{—NH—C—O—} \\ || \quad || \\ \text{O} \quad \text{O} \end{matrix}$ group;

(5) A $\begin{matrix} \text{O R}_2 \\ | \\ \text{—P—} \\ | \\ \text{O R}_2 \end{matrix}$ group where Q represents a $\begin{matrix} \text{—P—O—} \\ | \\ \text{O R}_2 \end{matrix}$ group;

(6) A $\begin{matrix} \text{O} & \text{O R}_2 \\ || & | \\ \text{—P—} & \text{—P—} \\ | & | \\ \text{O R}_2 & \text{O R}_2 \end{matrix}$ group where Q represents a $\begin{matrix} \text{O} \\ || \\ \text{—P—O—} \\ | \\ \text{O R}_2 \end{matrix}$ group;

(7) A $\text{—CH}_2\text{—CHOH—R}_6\text{—CH—CH}_2\text{—}$ group where Q

represents a $\text{—CH}_2\text{—CHOH—R}_6\text{—CHOH—CH}_2\text{—O—}$ group.

The polyoxyalkylene compounds which are especially suitable include the linear polyoxyalkylene oxides, polypropylene oxides and mixtures thereof having an average molecular weight of at least 200 and preferably not exceeding 500.

Illustrative alkyl phosphites include the dialkyl phosphites exemplified by dimethyl phosphite, diethyl phos-

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phite, di-n-propyl phosphite, di-isopropyl phosphite, di-n-butyl phosphite and mixtures thereof, such as methyl ethyl phosphite. The trialkyl phosphites can also be employed with particularly good results being obtained from triethyl phosphite.

The epoxy compounds suitable for use in the instant invention include 1,2 di(2',3'-epoxypropoxy)ethane, 1,4 bis-(2',3'-epoxypropoxy)butane and similar epoxides including those more fully described in British patent specification No. 793,915. The polyepoxy compounds provide particularly good results.

The illustrative aliphatic aldehydes include formaldehyde, acetaldehyde, isobutyraldehyde, and isopropionaldehyde.

The carboxylic acids and anhydrides which can be used in the instant invention include maleic, succinic, phthalic, adipic, sebacic and diglycolic.

The ratio of the two reagents used in the condensation may vary within wide limits and depends upon the desired properties which are intended to be ascribed to the condensation product. The ratios, however, must be judiciously selected so that water soluble condensation products are obtained. Suitable ratios are, for example, 1 mol of polyoxyalkylene compound and 1 mol of phosphonic acid ester or phosphoric acid ester; 1 mol of polyoxyalkylene compound and 0.5 mol of polyepoxide compound; 1 mol of polyoxyalkylene compound and 1 mol of aldehyde and 1 mol polyglycol per mol of acid or acid anhydride. However, it is to be noted that depending on the reagents selected, the ratios may vary over a relatively wide range so long as the condensate remains water soluble. Thus, operable ratios of polyoxyalkylene compounds to the second reagent vary from about 1:5 to 5:1. The selection of the proper ratio is within the ability of one skilled in the art in view of the instant teaching.

The condensation products according to the instant invention can be prepared by mixing the reagents while heating at temperatures from slightly above ambient to above about 240° C. while stirring. The selection of the proper temperature depends upon the reagent chosen and upon the desired rate of reaction. As a rough rule of thumb, the rate for a given reaction is doubled for each 10° rise in temperature. If desired, a suitable catalyst may be employed. It may be desirable at times to terminate the reaction by heating under reduced pressure.

More specifically, the compounds can be prepared:

- (1) By polyacetalizing polyoxyalkylenes by means of an aliphatic aldehyde;
- (2) By heating at about 200° C. polyoxyalkylenes with carboxylic anhydride such as maleic anhydride, succinic anhydride and phthalic anhydride or with dibasic carboxylic acids such as for example adipic acid, maleic acid, sebacic acid and diglycolic acid;
- (3) By heating polyoxyalkylenes with diisocyanates;
- (4) By heating polyoxyalkylene compounds with dialkyl phosphites described more completely in the British patent specification No. 796,466; and
- (5) By heating polyoxyalkylene compounds with a polyepoxide.

The following preparations will demonstrate illustrative condensation products employed in the instant invention.

PREPARATION 1

A solution of 20 g. of polyglycol (average molecular weight: 400), 4.5 g. of paraformaldehyde and 3 drops of concentrated sulphuric acid in 25 cm.³ of toluene is boiled for 2 days. The toluene is then distilled off under reduced pressure. The residue is dissolved in chloroform and filtered. After evaporation of the chloroform, 16 g. of a viscous product are obtained.

PREPARATION 2

A solution of 25 g. of polyglycol (average molecular weight: 1000), 2.25 g. of paraformaldehyde and 3 drops of concentrated sulphuric acid in 30 cm.³ of toluene is

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boiled for 2 days. Before filtering, another 50 cm.³ of toluene are added. The toluene is then distilled off under reduced pressure. The residue is dissolved in chloroform and filtered. After evaporation of the chloroform the remaining powder is washed with ether whereby 13 g. of a white powder are obtained.

PREPARATION 3

50 g. of polyglycol (average molecular weight: 1000), and 4.9 g. of maleic anhydride are heated together under nitrogen atmosphere for 3 hours at 200 to 230° C. The reaction product obtained is washed with a mixture consisting of 4 parts of ether and one part of benzene. 30 g. of a light-brown solid substance soluble in water and alcohols are obtained.

PREPARATION 4

30 g. of polyglycol (average molecular weight: 300) and 4.9 g. of maleic anhydride are heated together under nitrogen atmosphere for 1 hour at 200° C. The reaction product obtained is washed with a mixture consisting of 3 parts of ether and 4 parts of benzene. After drying under vacuum, 17 g. of a viscous yellow oil are obtained.

PREPARATION 5

50 g. of polyglycol (average molecular weight: 1000) and 10 g. of sebacic acid are heated together under nitrogen atmosphere for 7 hours at 210° C., whereby water vapor evolves. On cooling, 52 g. of a resinous product which is quite soluble in water are obtained.

PREPARATION 6

50 g. of polyglycol (average molecular weight: 1000) are dissolved in anhydrous acetone to which 4.2 g. of hexamethylene diisocyanate are added. The reaction mixture is boiled for 7 hours whereafter the solvent is removed under reduced pressure. 52 g. of a white solid powder which is soluble in water are obtained.

PREPARATION 7

30 g. of polyglycol (average molecular weight: 600), 6.7 g. of diglycolic acid and 3 g. of paratoluene sulphonic acid are heated under inlet of nitrogen for 1 hour at normal pressure and next for 5 hours at 2 mm. Hg. at 200° C. After cooling, a viscous oil which is quite soluble in water is obtained.

PREPARATION 8

20 g. of polyglycol (average molecular weight: 1000), 2.68 g. of diglycolic acid and 2 mg. of paratoluene sulphonic acid are heated for 1½ hours at normal pressure and for 5 hours at 2 mm. Hg. at 200° C. After cooling, a viscous oil which is quite soluble in water is obtained.

PREPARATION 9

A solution of 30 g. of polyglycol (average molecular weight: 300) and 14.8 g. of phthalic anhydride are heated at 210° C. for 6 hours under nitrogen atmosphere. After cooling, a very viscous oil is obtained.

PREPARATION 10

A solution of 20 g. of polyglycol (average molecular weight: 1000) and 3 g. of phthalic anhydride are heated at 210° C. for 6 hours under nitrogen atmosphere. After cooling, a resin is obtained.

PREPARATION 11

22.5 g. (0.075 mol) of polyglycol (average molecular weight: 300) dissolved in 75 cm.³ of tetrahydrofurane are dried over sulphate and at 60-65° C. This solution is dropwise added within a period of 5 hours to a suspension of 16.3 g. (0.075 mol) of pyromellitic dianhydride in 80 cm.³ of tetrahydrofurane. The solution obtained is filtered over Norit and under vacuum evaporated on the waterbath. The residue obtained is a viscous oil which is washed with benzene and ether. Yield: 26 g. of oil.

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PREPARATION 12

50 g. (0.05 mol) of polyglycol (average molecular weight: 1000) dissolved in 125 cm.³ of tetrahydrofuran are dried over sodium sulphate and at 60–65° C. this solution is dropwise added within a period of 5 hours to a suspension of 10.9 g. (0.05 mol) of pyromellitic dianhydride in 75 cm.³ of tetrahydrofuran. The solution obtained is filtered over Norit and under vacuum evaporated on the water bath. The residue obtained is an oil which is washed with ether. Yield: 30 g. of end product.

PREPARATION 13

A mixture of 60 g. of polyethylene glycol (average molecular weight: 300) and 27.6 g. of diethyl phosphite, is gradually heated on the oil-bath under nitrogen atmosphere and in the presence of a trace of magnesium for 4 hours at 200° C., whereby 14 cm.³ of ethanol are distilled over. Then the reaction mixture is heated under reduced pressure for 4 hours at 200° C. The reaction product is obtained in the form of a very viscous oil which is quite water-soluble.

PREPARATION 14

A mixture of 100 g. of polyethylene glycol (average molecular weight: 1000) and 13.8 g. of diethyl phosphite is gradually heated on the oil-bath under nitrogen atmosphere in the presence of a trace of magnesium at 200° C. for 3 hours whereby ca. 10 cm.³ of ethanol are distilled over. Then the reaction mixture is heated under reduced pressure for 4 hours at 200° C. The reaction product is obtained in the form of a quite water-soluble wax.

PREPARATION 15

A mixture of 100 g. of polyethylene glycol (average molecular weight: 1000) and 18.2 g. triethyl phosphate is gradually heated on the oil-bath under nitrogen atmosphere and in the presence of a trace of magnesium for 3 hours at 200° C., whereby ca. 12 cm.³ of ethanol are distilled over. Then the reaction mixture is heated under reduced pressure for 4 hours at 200° C. The reaction product is obtained in the form of a quite water-soluble wax.

PREPARATION 16

To 30 g. of polyethylene glycol (average molecular weight: 300) heated under nitrogen atmosphere at 90° C., 1.25 g. of 50% aqueous potassium hydroxide is gradually added while stirring. After further heating of the reaction mixture for 45 minutes, 8.7 g. of 1,2-di(2',3'-epoxypropoxy)-ethane are quickly added. Then the mixture is heated for 90 minutes at 100° C. and finally neutralized with ½ g. of 85% aqueous phosphoric acid. The reaction product is obtained in the form of a very viscous oil which is quite water-soluble.

PREPARATION 17

To 100 g. of polyethylene glycol (average molecular weight: 1000) heated under nitrogen atmosphere at 90° C., 1.25 g. of 50% aqueous potassium hydroxide is slowly added. After further heating of the reaction mixture for 45 minutes whereby the temperature rises to 100° C., 8.7 g. of 1,2-bis(2',3'-epoxypropoxy)-ethane are quickly added. Then the mixture is heated for 90 minutes at 100° C. and finally neutralized by means of 0.5 g. of 85% aqueous phosphoric acid. The reaction product is obtained in the form of a water-soluble wax.

PREPARATION 18

To 200 g. of polyethylene glycol (average molecular weight: 1000) heated under nitrogen atmosphere at 90° C., 2.5 g. of 50% aqueous potassium hydroxide are slowly added while stirring. After further heating of

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the reaction mixture for 45 minutes whereby the temperature rises to 100° C., 20.1 g. of 1,4-bis(2',3'-epoxypropoxy)-butane are slowly added. Then the mixture is heated for 75 minutes at 100° C. and finally neutralized with 1 g. of 85% aqueous phosphoric acid. 208 g. of a reaction product are obtained in the form of a water-soluble wax.

The compounds according to the invention may be added to the emulsions or brought into intimate contact with silver halide emulsion layers by dissolving them in water or in an aqueous mixture of organic solvents which do not have a deleterious effect on silver halide emulsions and by adding the solution obtained to an emulsion or applying it to an emulsion layer as a coating composition.

The compounds can be introduced into the emulsion at various stages during its preparation; for example, they may be incorporated as a separate addition, or mixed with one or more of the other ingredients used at the initial precipitation of the silver halide grains, during the physical or chemical ripening process, or at some other point prior to coating the emulsion. Preferably, they are added after the chemical ripening and just before coating the emulsion.

The optimum amount of the compound to be added to the emulsion depends on the particular compound chosen, the nature of the colloid binding agent for the silver halide grains and the amount and kind of silver halide in the emulsion. In general, however, the compounds according to the invention are added in a quantity of 50 mg. to 7 gm. per mol silver halide. If necessary, however, still other quantities of these compounds can be added which fall outside these limits.

The process of the present invention can be combined with a method for increasing the sensitivity of the photographic material by incorporating therein 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 Belgian specifications Nos. 493,464 and 568,687, the imino-aminomethane sulphinic acid compounds described in British specification No. 789,823 or small amounts of noble metal compounds such as of gold, platinum, palladium, iridium, ruthenium and rhodium. As a matter of fact, the new process is advantageously superimposed on the sensitizing action of compounds originally present in gelatin.

By application of the method according to our present invention stabilizing agents such as, for example, mercury compounds and the compounds claimed and referred to in the statement of prior art of Belgian specifications Nos. 571,916 and 571,917 may be added to the emulsion. It is also usual to sensitize and/or to stabilize silver halide emulsions by incorporating therein cadmium salts or by carrying out their processing in the presence of cadmium salts. Still other ingredients such as antifogging agents, color couplers, developing substances, hardening and wetting agents, can moreover and without deleteriously affecting the emulsion, be added thereto in a manner known to those skilled in the art.

As a result of their property of conferring a better developability, the new compounds are effective in increasing the X-ray sensitivity and the general light-sensitivity of orthochromatic, panchromatic, and all special emulsions, as well as of the ordinary non-spectrally sensitized ones. Thus, they can be added without or with optical sensitizing dyes and in the latter case before or after them. They are also useful with a variety of emulsions, since the production of pronounced speed is increased in either negative or positive types of emulsions.

Having described the invention in general terms, the following examples will more clearly illustrate the instant invention. However, the examples are not to be construed as limiting the inventive concept.

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Example 1

A washed coarsely grained gelatino silver iodo-bromide negative type of emulsion (average grain size 0.8μ) wherein the silver halide consists of 94.5 mol percent silver bromide and 5.5 mol percent silver iodide is ripened at 45°C . After addition of a panchromatic sensitizing dye and other usual ingredients the emulsion is coated onto a suitable support (sample 1). Further samples were prepared by adding prior to coating to the same emulsion and per mol silver halide present the amounts of developing accelerators listed below. They are then treated as sample 1. After drying and exposure they are developed for 7 minutes at 20°C . in a solution consisting of:

Water	cm. ³	800
Monomethyl-p-aminophenol sulphate	g	2
Hydroquinone	g	5
Sodium sulphite (anhydrous)	g	100
Borax	g	10
Boric acid	g	5
Potassium bromide	g	0.5
Water up to 1000	cm. ³	

SENSITOMETRIC RESULTS

Sample	Compound added	Relative Sensitivity	Gamma	Fog
1	None	100	0.75	0.06
2	0.34 g. polyglycol average m.w.: 400.	98	0.71	0.06
3	0.34 g. polyglycol average m.w.: 1,000.	103	0.59	0.08
4	0.34 g. compound of prepar. 1.	113	0.76	0.06
5	0.34 g. polymer of prepar. 2.	129	0.77	0.06

Example 2

The following results were obtained in exactly the same manner as described in Example 1.

Sample	Compound added	Relative Sensitivity	Gamma	Fog
1	None	100	0.58	0.06
2	3.4 g. polyglycol average m.w.: 400.	88	0.56	0.06
3	3.4 g. polyglycol average m.w.: 1,000.	111	0.60	0.08
4	3.4 g. compound of prepar. 1.	127	0.67	0.04
5	3.4 g. compound of prepar. 2.	180	0.65	0.05

Example 3

The following results were obtained in exactly the same manner as described in Example 1.

Sample	Compound added	Relative Sensitivity	Gamma	Fog
1	None	100	0.65	0.10
2	0.34 g. polyglycol average m.w.: 300.	98	0.65	0.10
3	3.4 g. polyglycol average m.w.: 300.	93	0.65	0.10
4	0.34 g. compound of prepar. 3.	114	0.67	0.13
5	3.4 g. compound of prepar. 3.	119	0.68	0.14
6	0.34 g. compound of prepar. 4.	100	0.62	0.10
7	3.4 g. compound of prepar. 4.	103	0.65	0.11

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Example 4

The following results were obtained in exactly the same manner as described in Example 1.

Sample	Compound added	Relative Sensitivity	Gamma	Fog
1	None	100	0.61	0.13
2	0.34 g. compound of prepar. 5.	120	0.63	0.14
3	3.4 g. compound of prepar. 5.	124	0.70	0.14
4	27.2 g. compound of prepar. 5.	133	0.93	0.25
5	0.34 g. compound of prepar. 6.	114	0.62	0.14
6	3.4 g. compound of prepar. 6.	108	0.63	0.14
7	0.34 g. compound of prepar. 9.	104	0.71	0.14
8	3.4 g. compound of prepar. 9.	110	0.76	0.15
9	0.34 g. compound of prepar. 10.	112	0.72	0.16
10	3.4 g. compound of prepar. 10.	125	0.78	0.16

Example 5

A washed coarsely grained gelatino silver iodo-bromide emulsion wherein the silver halide consists of 98.2 mol percent silver bromide and 1.8 mol percent silver iodide is ripened at 42°C . After addition of a stabilizing agent such as 5-hydroxy-7-methyl-s-triazolo-(4,5a)-pyrimidine and of other usual ingredients, the emulsion is coated onto a suitable support (sample 1).

Further samples were prepared by adding to the same emulsion prior to coating and, per mol silver halide present, the amounts of developing accelerators listed below. They are then treated as sample 1. After drying and exposure they are developed for 4 minutes in a solution consisting of:

Water	cm. ³	800
Mono-methyl-p-amino phenol sulphate	g	4
Sodium sulphite (anhydrous)	g	65
Hydroquinone	g	10
Sodium carbonate (anhydrous)	g	45
Potassium bromide	g	5
Water up to 1000 cm. ³		

SENSITOMETRIC RESULTS

Sample	Compound added	Rel. Sens.	Gamma	Fog	After 36 hr. of incubation		
					Rel. Sens.	Gamma	Fog
1	None	100	3.27	0.04	100	2.89	0.09
2	0.2 g. prep. 7.	131	3.28	0.05	120	3.00	0.11
3	0.2 g. prep. 8.	131	3.02	0.06	135	2.89	0.16

Example 6

Two samples of an emulsion such as that of Example 1 are considered. To sample 1 are added per mol of silver halide and before coating, 0.40 g. polyglycol with an average molecular weight of 6000. To sample 2 of the same emulsion is added before coating, instead of 0.40 g. of polyglycol with an average molecular weight of 6000, 0.40 g. of the compound of Preparation 2.

These two samples were packed and stored for one year in a relatively moist atmosphere at temperatures fluctuating between 15 and 35°C . After this year, they were exposed to light and developed for 7 minutes in a developer such as that of Example 1.

Sample	Compound added	Rel. Sens.	Gamma	Fog
1	0.4 g. polyglycol average m.w.: 6,000.	100	0.80	0.18
2	0.4 g. compound of prepar. 2.	100	0.78	0.12

Example 7

Two samples of an emulsion such as that of Example 5 are considered. To sample 1 is added 0.2 g. of Carbowax 6000 which is the optimal allowable amount for not

producing an excess of fog. To sample 2 of the same emulsion are added such amounts of compounds according to the present invention until the same highest allowable fog is attained, and next the sensitivities obtained are checked after 4 minutes of development such as in Example 5.

Sample	Compound added	Rel. Sens.	Gamma	Fog
1-----	0.2 g. Carbowax 6000-----	100	4.00	0.06
2-----	1 g. compound of prepar. 3-----	123	3.50	0.06
1-----	0.2 g. Carbowax 6000-----	100	3.50	0.07
2-----	1 g. compound of prepar. 5-----	114	3.25	0.05

Example 8

To one sample of an emulsion according to Example 5 is added before coating 0.2 g. of Carbowax (sample 1) and to another sample 0.2 g. of compound according to preparation 8 (sample 2). Both samples are stored for some days at considerable relative humidity and high temperature, and next developed for 4 minutes in developer from Example 5.

Sample	Compound added	Rel. Sens.	Gamma	Fog
1-----	0.2 g. Carbowax 6000-----	100	2.93	0.17
2-----	0.2 g. compound of prepar. 8-----	116	2.84	0.16

Example 9

A washed coarsely grained gelatin silver iodobromide negative type of emulsion (average grain size 0.8 μ) wherein the silver halide consists of 94.5 mol percent silver bromide and 5.5 mol percent silver iodide is ripened at 45° C. After addition of a panchromatic sensitizing dye and other usual ingredients the emulsion is coated onto a suitable support (sample 1). Further samples

Sample	Compound added	Relative Sensitivity	Gamma	Fog	After 36 h. of incubation		
					Relative sensitivity	Gamma	Fog
1-----	None-----	100	0.98	0.13	100	0.80	0.16
2-----	0.34 g. Carbowax 6000 (trade name of Union Carbide and Carbon, New York, N.Y., U.S.A., for a polyalkylene glycol with aver. mol. weight of 6,000).-----	106	1.07	0.19	106	0.91	0.23
3-----	3.4 g. compound of preparation 14-----	111	1.15	0.16	112	0.88	0.26

were prepared by adding prior to coating to the same emulsion and per mol silver halide present the amounts of developing accelerators listed below. They are then treated as sample 1. After drying and exposure they are developed for 7 minutes at 20° C. in a solution consisting of:

Water-----	cm. ³ -----	800
Mono-methyl-p-amino phenol sulphate-----	g-----	2
Hydroquinone-----	g-----	5
Sodium sulphite (anhydrous)-----	g-----	100
Borax-----	g-----	10
Boric acid-----	g-----	5
Potassium bromide-----	g-----	0.5
Water up to 1000 cm. ³ -----		

SENSITOMETRIC RESULTS

Sample	Compound added	Relative Sensitivity	Gamma	Fog
1-----	None-----	100	0.60	0.10
2-----	0.34 g. polyethylene glycol (average m.w.: 300).-----	98	0.65	0.10
3-----	3.4 g. polyethylene glycol (average m.w.: 300).-----	93	0.65	0.10
4-----	0.34 g. compound of preparation 13-----	105	0.64	0.11
5-----	5.3 g. compound of preparation 13-----	109	0.64	0.12
6-----	0.34 g. compound of preparation 14-----	111	0.64	0.11
7-----	3.4 g. compound of preparation 14-----	128	0.74	0.12
8-----	3.4 g. compound of preparation 15-----	132	0.85	0.13

Example 10

The following results were obtained in exactly the same manner as described in Example 9.

Sample	Compound added	Relative Sensitivity	Gamma	Fog
1-----	None-----	100	0.48	0.08
2-----	0.34 g. compound of preparation 16-----	102	0.48	0.09
3-----	3.4 g. compound of preparation 16-----	106	0.54	0.09
4-----	3.4 g. compound of preparation 17-----	105	0.50	0.09
5-----	3.4 g. compound of preparation 17-----	115	0.58	0.12

Example 11

The following sensitometric results are obtained in the same manner as described in Example 9, but the samples are developed for 7 minutes at 20° C. in a solution of the following composition:

Water-----	cm. ³ -----	800
Monomethyl-p-aminophenol sulfate-----	g-----	6
Hydroquinone-----	g-----	3
Sodium sulphite (anhydrous)-----	g-----	75
Sodium carbonate (anhydrous)-----	g-----	5
Borax-----	g-----	10
Water up to 1000 cm. ³ -----		

Example 12

A washed coarsely grained gelatine silver iodobromide emulsion wherein the silver halide consists of 98.2 mol percent silver bromide and 1.8 mol percent silver iodide is ripened at 42° C. After addition of a stabilizing agent such as 5-hydroxy-7-methyl-s-triazolo-(2,3a)-pyrimidine and of other usual ingredients, the emulsion is coated onto a suitable support (sample 1).

Further samples were prepared by adding to the same emulsion prior to coating and, per mol silver halide present, the amounts of developing accelerators listed below. They are then treated as sample 1. After drying and

exposure they are developed for 4 minutes in a solution consisting of:

Water	-----cm. ³	800
Mono-methyl-p-amino phenol sulphate	-----g	4
Sodium sulphite (anhydrous)	-----g	65
Hydroquinone	-----g	10
Sodium carbonate (anhydrous)	-----g	45
Potassium bromide	-----g	5
Water up to	1000 cm. ³	

SENSITOMETRIC RESULTS

Sample	Compound added	Relative Sensitivity	Gamma	Fog	After 36 h. of incubation		
					Relative sensitivity	Gamma	Fog
1	None	100	3.10	0.04	111	3.24	0.09
2	2 g. compound of preparation 14	121	3.46	0.05	120	3.32	0.12
3	4 g. compound of preparation 16	121	3.20	0.04	127	2.97	0.09
4	0.8 g. compound of preparation 17	116	3.12	0.04	124	2.89	0.08
5	1.6 g. compound of preparation 17	128	3.22	0.05	130	2.81	0.10

Although in the above examples gelatine silver halide emulsions are described, our invention is not limited to such colloid emulsions. Emulsions based on other water-permeable colloids may equally well be treated according to the present invention. Among such colloids are for instance to be mentioned: agar-agar, zein, collodion, water-soluble cellulose derivatives such as hydrolyzed cellulose acetate; cellulose esters of hydroxycarboxylic acids, for example lactic or glycolic acid; alkali metal salts of cellulose esters of dicarboxylic acids such as phthalic acid; polyvinyl alcohol, and partially hydrolyzed polyvinyl acetate and interpolymers of vinyl acetate with unsaturated compounds such as styrene and maleic acid, water-soluble polyvinyl acetals and other hydrophilic synthetic or natural resins or polymeric compounds.

The new developing accelerators may be used for sensitizing the known types of silver chloride, silver bromide, silver iodide emulsions and emulsions containing mixtures of these halides.

Furthermore, the methods as described in the above examples are not limited, as far as the quantity and the nature of the developing accelerator to be added or the moment of the addition are concerned. Indeed, for obtaining an optimum effect, all particular techniques in the preparation of light-sensitive emulsions should be taken into account.

An advantage of this invention is the compatibility of the new developing accelerators with color couplers and optical sensitizing dyes, which fact is of great importance for using the new developing accelerators for increasing the general light-sensitivity of color photographic material containing one or more light sensitive layers.

A further advantage of the process lies in the simplicity of its general application as for instance in the manufacture of light-sensitive materials for amateur and professional photography and cinematography, for motion pictures, for graphic processes and for scientific and industrial applications.

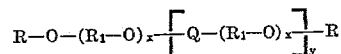
It should be appreciated that the invention is not to be construed to be limited by the illustrative examples. It is possible to produce still other embodiments without departing from the inventive concept herein disclosed.

This application is a continuation-in-part application of the Willems et al. co-pending application, Serial No. 27,484, filed May 9, 1960.

What is claimed is:

1. A light-sensitive photographic material comprising a support and at least one gelatino silver halide emulsion layer containing an alkylene oxide polymer in an amount between 0.2 g. and 7.00 g. per mol silver halide, said alkylene oxide polymer being a condensation product of

a polyalkylene glycol with a molecular weight between 100 and 1500, and an organic compound of the class consisting of an aliphatic aldehyde, an aliphatic diisocyanate, alkyl phosphites, alkyl phosphates and polyepoxides, said alkylene oxide polymer having the general formula:



wherein:

R₁ is an alkylene group of from 2 to 3 carbon atoms;

x and y each is a positive integer of from 2 to 35; Q is a member of the group consisting of

- (1) a ---CHO--- group, wherein R₂ is a member of the group consisting of hydrogen and an alkyl radical containing from 1 to 4 carbon atoms.
- (2) a $\text{---C---NH---R}_4\text{---NH---C---O---}$ group, wherein R₄ is a bivalent aliphatic hydrocarbon radical of from 2 to 20 carbon atoms;
- (3) a ---P---O--- group wherein R₃ has the same value as R₂;
- (4) a ---P---O--- group wherein R₃ has the same value as R₂; and
- (5) a $\text{---CH}_2\text{---CHOH---R}_5\text{---CHOH---CH}_2\text{---O---}$ group wherein R₅ is a member of the group consisting of a chemical bond and a bivalent polyether radical;

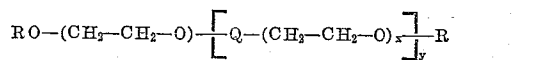
R is a member of the group consisting of

- (1) a hydrogen atom;
- (2) a ---CHOH--- group where Q represents a ---CHO--- group;
- (3) a $\text{---C---NH---R}_5\text{---NH}_2\text{---}$ group where Q is a $\text{---C---NH---R}_5\text{---NH---C---O---}$ group;
- (4) a ---P--- group where Q is a ---P---O--- group;
- (5) a ---P--- group where Q is a ---P---O--- group;
- (6) a $\text{---CH}_2\text{---CHOH---R}_5\text{---CH---CH}_2\text{---}$ group where Q is a $\text{---CH}_2\text{---CHOH---R}_5\text{---CHOH---CH}_2\text{---O---}$ group.

2. A light-sensitive photographic material comprising a support and at least one gelatino silver halide emulsion layer containing an alkylene oxide polymer in an amount between 0.2 g. and 7.00 g. per mol silver halide, said alkylene oxide polymer being a condensation product of a polyalkylene glycol with a molecular weight between 100 and 1500, and an organic compound of the class consisting of an aliphatic aldehyde, and an aliphatic diisocya-

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nate, said alkylene oxide polymer having the general formula:



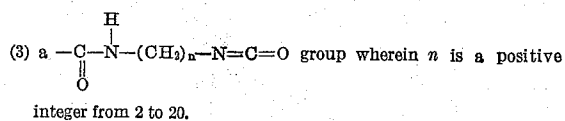
wherein x represents a positive integer from 2 to 35, y represents a positive integer from 2 to 20, Q represents a member selected from the group consisting of

- (1) a $-\overset{\text{O}}{\parallel}{C}-NH(CH_2)_n-NH-\overset{\text{O}}{\parallel}{C}O-$ group, wherein n is a positive integer from 2 to 20, 10
- (2) a $-CH_2-O-$ group,

and R is a member selected from the group consisting of

- (1) a hydrogen atom,
 (2) a CH_2OH group, 15

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