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DEVELOPMENT OF PHOTOGRAPHIC SILVER HALIDE ELEMENTS

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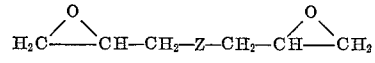
U.S. Cl. 96—66.3 20 Claims

ABSTRACT OF THE DISCLOSURE

A process is described for developing an exposed photographic silver halide element wherein the development is carried out in the presence of a water-soluble non-polymeric compound obtained by reaction of a bisepoxide of the formula:



Z being oxygen or the group —O—Y—O— wherein Y is a straight-chain or branched-chain C_2–C_8 alkylene group

with a monoalkyl or monoaryl ether of ethylene glycol or a polyoxyethylene glycol. The speed and developability of the silver halide element is substantially increased by the presence of this polyaddition compound. By infectious development of silver chloride and silver chlorobromide emulsions it is possible by means of these compounds to obtain very contrasty line and screen images and sharply defined screen dots, and to reduce the formation of peppers when using somewhat exhausted developing baths.

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

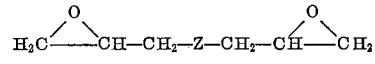
It is known that the development of continuous tone images by means of the usual developers such as a hydroquinone/p-methylaminophenol developer can be accelerated by the use in the photographic material or the developing bath of polyoxyalkylene compounds, preferably those having an average molecular weight above 1500, such as 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 (cfr. United States patent specifications 2,240,472 of Donald R. Swan issued Apr. 29, 1941, 2,423,549 of Ralph Kingsley Blake, William Alexander Stanton and Ferdinand Schulze issued July 8, 1947, 2,400,532 of Ralph Kingsley Blake and Walter Diney Baldsiefen issued May 21, 1946 and 2,716,062 of Burt H. Carroll and Norman F. Beach issued Aug. 23, 1955 and United Kingdom patent specification 748,745 filed June 28, 1954 by Kodak Co.). By the favourable effect of these compounds on the development, the final sensitivity of the silver halide emulsions is increased.

It is also known e.g. from German patent specification 1,141,531 filed Jan. 24, 1962 by Perutz Photowerke G.m.b.H. that polyoxyalkylene compounds when used in combination with so-called lith-developers (infectious development), which are developers comprising a bisulphite addition product of an aliphatic aldehyde or ketone such as formaldehyde bisulphite, and hydroquinone as the sole developing substance, restrain the development rate while increasing the gradation. On account of the very contrasty development obtained therewith, polyoxyalkylene compounds were found very suitable for use in the "lithdevelopment of silver halide emulsions of the graphic arts type i.e. of the type used for photomechanical reproduction of line or half-tone images, which are generally silver chloride and silver bromochloride emulsions comprising at most 50 mole percent of bromide.

Polyoxyalkylene compounds, however, when used in silver halide emulsion layers, impair the keeping qualities of these layers, particularly at high temperatures and elevated degrees of relative humidities in that they induce a substantial increase of fog. It was also found that when these polyoxyalkylene compounds are incorporated into silver halide emulsions to increase the speed, they very often impair the image tone of the developed silver by forming brown and reddish-brown images. Moreover, polyoxyalkylene compounds when used in infectious development greatly increase the formation of "peppers".

"Peppers" are black spots of a very high density which are irregularly produced during the development in the areas of the light-sensitive emulsion which are slightly exposed. These "peppers" when they are present in a high amount markedly degrade the quality of a half-tone image reproduction by deforming the screen dots and/or soiling the areas which were practically unexposed. The phenomenon of "pepper" particularly arises when partly air oxidized or somewhat exhausted developing baths are used.

It has now been found that the developability and sensitivity of photographic silver halide emulsions can be substantially increased on development—the keeping qualities of the said emulsions not being impaired to a noteworthy extent—by carrying out the development in the presence of water-soluble nonpolymeric compounds obtained by reaction of a bisepoxide corresponding to the formula:



wherein:

Z stands for oxygen or the group —O—Y—O— wherein Y is a straight-chain or branched-chain alkylene group which has from 2 to 8 C-atoms such as ethylene, tetramethylene and 1-methyltrimethylene,

with a monoalkyl ether or monoaryl ether of ethylene glycol or a polyoxyethylene glycol, the hydrogen atoms of the hydroxyl groups in the reaction products obtained being optionally wholly or partly substituted.

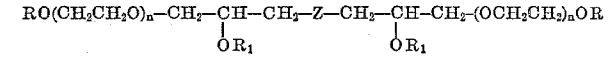
It has further been found that the development of line and/or half-tone images in silver chloride and silver chlorobromide emulsions by means of so-called "lith"-developers as described above, in the presence of the water - soluble non - polymeric compounds as defined above, produces very contrasty silver images, yields very sharply defined screen dots and occurs with the formation of a smaller number of peppers than is the case with known polyoxyalkylene compounds, and furthermore can take place within a broad interval of time without harm to the image quality.

Therefore, in accordance with the present invention there is provided a process of developing photographic materials comprising exposed silver halide, wherein the development is carried out in the presence of a water-soluble non-polymeric compound as defined above.

The invention further provides photographic light-sensitive silver halide materials and photographic developing compositions comprising a water-soluble non-polymeric compound as defined above.

In the preparation of the non-polymeric water-soluble compounds as defined above, the reaction products are generally made to react in a stoichiometric ratio, though the use of one of them in an amount exceeding the stoichiometric amount is not harmful since the reaction proceeds very smoothly and generally not in an exothermic way.

The reaction products obtained substantially consists of compounds corresponding to the following general formula:



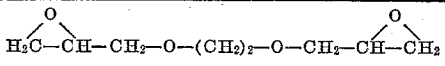
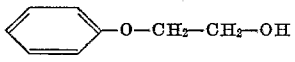
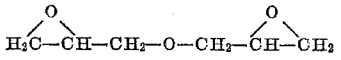
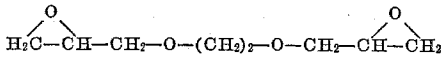
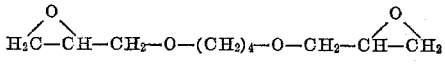
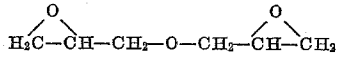
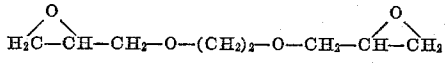
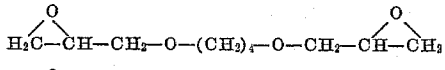
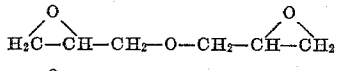
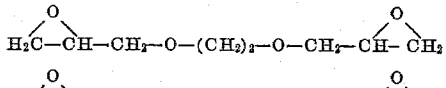
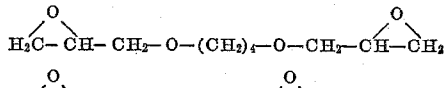
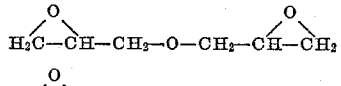
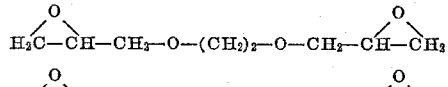
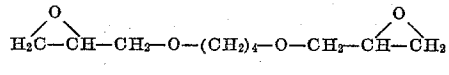
wherein:

Z has the same significance as above,
R stands for alkyl, preferably C_1–C_5 alkyl or aryl,
n stands for an integer from 1 to 20, and
R_1 stands for hydrogen, an alkyl group, a substituted alkyl group e.g. a cyanoethyl group, a —COR_2 group, a —$CONHR_2$ group or a —SO_2R_2 group wherein R_2 stands for a monovalent saturated or unsaturated aliphatic group, for example alkyl and alkenyl, a —COCH=CH—COOH group or its busulphite addition product, an aryl group or a heterocyclic group or such groups carrying one or more substituents.

The following general procedure can be given for the preparation of the compounds of use according to the present invention.

To 2 moles of the monoalkyl or monoaryl ether of ethylene glycol or a polyoxyethylene glycol a catalytic amount of sodium methylate is added and then the mixture is preheated to a temperature of approximately 100° C. Then 1 mole of bisepoxide is added portion-wise with stirring whereupon the reaction mixture is heated to a temperature from between 150 and 180° C., and preferably 170° C. (except compound I of the table, which has been prepared in a sealed tube) and kept at this temperature for a certain time (see table: reaction time). Quantitative yields of well water-soluble products are obtained.

In the following table a survey of suitable starting products and reaction conditions is given. The possible epoxide groups in the final product obtained, which may be due to unreacted bisepoxide or which are terminal epoxide groups in part of the reaction products formed, are determined by titration with perchloric acid in acetic acid medium comprising hexadecyl trimethyl ammonium bromide. The residual epoxide groups are given on a percentage basis of the milliequivalents of epoxide groups found relative to the milliequivalents of epoxide groups used on starting the reaction.

Compound	Monoalkyl or monoaryl ether used—	Bisepoxide used—	Reaction time (hours)	Residual epoxide groups, percent
I	$H_3CO-CH_2-CH_2-OH$		32	4
II	$N_9C_4O-CH_2-CH_2-OH$	Same as above	60	5.5
III		do	34	7
IV	$H_3CO-(CH_2CH_2O-)_2H$		32	None
V	$H_3CO-(CH_2CH_2-O)_2H$		32	1.5
VI	$H_5C_2O(CH_2CH_2O)_2H$	Same as above	36	2.5
VII	$H_9C_4O(CH_2CH_2O)_2H$	do	62	5
VIII	$H_3CO-(CH_2CH_2O-)_2H$		32	3
IX	Monomethyl ether of polyoxyethylene glycol having an average molecular weight of 350 which can be represented by: $H_3CO-(CH_2CH_2O)_7H$.		56	1
X	do		56	7
XI	do		32	None
XII	Monomethyl ether of polyoxyethylene glycol having an average molecular weight of 550 which can be represented by: $H_3CO-(CH_2CH_2O)_{12}H$.		56	None
XIII	do		56	4
XIV	do		32	None
XV	Monomethyl ether of polyoxyethylene glycol having an average molecular weight of 750 which can be represented by: $H_3CO-(CH_2CH_2O)_{16}H$.		56	1.5
XVI	do		32	4
XVII	do		32	None

The hydrogen atoms of the free hydroxyl groups in the compounds obtained may be partly or wholly substituted by reaction with compounds which are reactive with respect to an active hydrogen atom of a hydroxyl group for example an acid chloride or acid anhydride such as acetic anhydride, succinic anhydride, maleic anhydride and sulphobenzoic anhydride, a sulphonyl chloride, isocyanates or unsaturated alkylating compounds, e.g. a vinyl compound such as acrylonitrile and methacrylonitrile. The reaction product of the said hydroxyl containing compound with maleic anhydride may further be allowed to react with a bisulphite thus forming a bisulphite addition product. The bisulphite used is preferably an alkali metal bisulphite.

The compounds used according to the present invention can be present in the developer bath or can be added to the coating composition of a silver halide emulsion layer and/or incorporated into a water-permeable layer which when coated under or on top of the emulsion layer forms a water-permeable system with the silver halide emulsion layer and is then in effective contact with the silver halide.

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

The water-soluble compounds of the invention 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 compounds of the invention are preferably added to the silver halide emulsion composition after the chemical ripening process and just before coating the emulsion.

The compounds are preferably added from a solution in water or in an aqueous mixture of water and water-miscible organic solvents such as ethanol that do not impair the photographic properties of the light-sensitive silver halide emulsion.

The optimum amount of compound added to the silver halide emulsion depends on the compound itself 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 compounds are added to the high-sensitive material in amounts ranging from 10 mg. to 5 g. per mole of silver halide. In the developing bath they are normally used in amounts ranging from 10 mg. to 5 g. per liter. If necessary, these compounds can also be added in amounts exceeding these limits.

The step of influencing the sensitometric characteristics of silver halide emulsions by means of the compounds of the invention can be combined with a method known as chemical sensitization, in which together with the above-mentioned compounds chemical sensitizers are used, e.g., sulphur-containing compounds such as allyl isothiocyanate, allylthiourea or sodium thiosulphate, reducing compounds such as the tin compounds described in the Belgian patent specifications 493,464 filed Jan. 24, 1970 and 568,687 filed June 18, 1958 both by Gevaert Photo-Production N.V., the iminoaminomethane sulphinic acid compounds described in the United Kingdom 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 described by R. Koslowsky, Z. Wiss. Phot. 46, 65–72 (1951).

The compounds employed in the present invention can also be used in combination with stabilzers and fog-inhibiting compounds for the silver halide emulsion, for instance with mercury compounds such as those described in Belgian patent specifications 524,121 filed Nov. 7, 1953 by Kodak Co. and 677,337 filed Mar. 4, 1966 by Gevaert-Agfa N.V. and in published Dutch application 6715932 filed Nov. 23, 1967 by Gevaert-Agfa N.V., with organic sulphur-containing compounds that form an insoluble silver salt with silver ions, with heterocyclic nitrogen-containing thioxo compounds such as benzothiazoline-2-thione and 1-phenyl-2-tetrazoline - 5 - thione, the compounds described in the Belgian patent specifications 571,-916 and 571,917 both filed Oct. 10, 1958 by Gevaert Photo-Producten N.V. and tetra- or pentaazaindenes especially those substituted by hydroxyl or amino groups. Examples of the latter compounds have been described by Birr, Z. Wiss. Phot. 47, 2–58 (1952). The combination with sensitizing and stabilizing cadmium salts such as cadmium chloride in the light-sensitive material as well as in the developing bath can also be applied.

In addition to the above stabilizing and chemical sensitizing agents 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 tetra-alkylammonium alkylpyridinium salts, bis-alkylene-pyridinium salts, alkylquinolinine salts, trialkyl-sulphonium salts, onium derivatives of amino-N-oxides as described in United Kingdom patent specification 1,121.696 filed Oct. 7, 1965 by Gevaert-Agfa N.V. and iodonium compounds for instance diphenyl iodonium chloride as described in United Kingdom patent specification 1,119,075 filed Oct. 7, 1965 by Gevaert-Afga N.V. can be used together with the compounds 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, plasticizers, and wetting agents, can also be added to the emulsion 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 compounds. These products can be applied for accelerating the development of X-ray emulsions as well as of a wide range of spectrally or non-spectrally sensitized emulsions. They can be incorporated into the photographic emulsion either with or without spectral sensitizers and can be used for increasing the sensitivity of negative emulsions as well as of positive emulsions. As noted above the compounds of the invention are also particularly suitable for the development of silver chloride and silver chlorobromide emulsions comprising at most 50 mole percent of silver bromide for reproducing line and half-tone images with hydroquinone/formaldehyde bisulphite developers.

The following examples illustrate the present invention.

EXAMPLE 1

A conventional ammoniacal high-sensitive gelatino silver bromoiodide (4.2 mole percent of iodide) emulsion ready for coating, which comprised per kg. an amount of silver halide corresponding to 50 g. of silver nitrate, 625 mg. of 5-methyl-7-hydroxy-s-triazolo[1,5-a]pyrimidine as a stabilizer as well as other emulsion addenda such as hardener and coating aid, was divided into several aliquot portions. To each of these portions one of the compounds listed in the table below was added as development accelerator in the amount given. The emulsion portions were then coated on a paper support and dried.

The materials obtained were then exposed under identical circumstances through a grey wedge and developed

for 8 min. at 20° C. in a developer of the following composition:

Water (52° C.)	ml	750
p-Monomethylaminophenol sulphate	g	2
Sodium sulphite (anhydrous)	g	100
Hydroquinone	g	5
Borax, granular	g	2

Water to make 1000 ml.

The values of the speed and fog for materials developed immediately after coating (fresh materials) and materials that before development was conditioned for 36 hours at 57° C. and 34% relative humidity (stored materials) are listed in the table below. The values given for the speed are relative values; the value of 100 was given to the speed of the freshly prepared material comprising no development accelerating compound.

TABLE

Compound added	Mg. per kg. emulsion,	Fresh materials Fog	Fresh materials Speed	Stored materials Fog	Stored materials Speed
		0.16	100	0.22	100
Polyethylene glycol having an average molecular weight of 6,000	100	0.34	168	0.39	200
Compound V	300	0.18	100	0.20	142
	1,000	0.16	142	0.22	168
Compound X	300	0.18	100	0.24	168
	1,000	0.17	119	0.22	142
Compound XIII	300	0.18	119	0.24	200
	1,000	0.22	119	0.23	235
Compound XVI	300	0.22	100	0.24	168
	1,000	0.20	100	0.24	200

The above results show that the compounds of the invention have a favourable speed increasing effect while not influencing the fog to a noteworthy extent as does the polyethylene glycol. When using instead of the above compounds according to the invention, polycondensation products of the same epoxide with a nonetherified polyethylene glycol (cfr. United States patent specification 3,158,484 of Jozef Frans Willems, Robrecht Julius Thiers, Joseph Louis De Munck issued Nov. 24, 1964) e.g. triethylene glycol it is also possible to obtain a favourable speed increasing effect; the use of such compounds however is accompanied with a substantial increase in fog, even exceeding that of the polyethylene glycol with average molecular weight of 6000.

EXAMPLE 2

An emulsion as described in Example 1 was divided into several aliquot portions. To each of these portions one of the compounds listed in the table below was added as development accelerator in the amount given. The emulsions were then coated on a subbed film support and dried.

After exposure and processing as described in Example 1 the following results were attained.

TABLE

Compound added	Mg. per kg. emulsion,	Fresh materials Fog	Fresh materials Speed	Stored materials Fog	Stored materials Speed
		0.05	100	0.05	100
Compound VIII	300	0.05	168	0.07	200
	1,000	0.07	119	0.07	142
Compound IX	300	0.05	119	0.06	142
	1,000	0.05	119	0.06	200
Compound XI	300	0.06	168	0.06	200
	1,000	0.05	168	0.07	282

EXAMPLE 3

Example 2 was repeated with the difference that the compounds listed in the table below were used. The following results were attained.

TABLE

Compound added	Mg. per kg. emulsion,	Fresh materials Fog	Fresh materials Speed	Stored materials Fog	Stored materials Speed
		0.05	100	0.05	100
Compound I	300	0.05	142	0.06	168
	1,000	0.05	142	0.05	168
Compound IV	300	0.05	142	0.06	119
	1,000	0.05	142	0.05	142

When using instead of the compounds of the present invention products obtained by reaction, in a similar way as the compounds of the present invention, of a monomethoxy polyethylene glycol with a bisepoxide of closely related structure e.g. the product obtained by reaction for 10 hours at 125° C. of N,N-di(2,3-epoxypropyl)isopropylamine with the monomethyl ether of diethylene glycol (4.5% residual epoxide groups) and the product obtained by reaction for 10 hours at 125° C. of N,N-di(2,3-epoxypropyl)isopropylamine with the monomethyl ether of polyoxyethyleneglycol having an average molecular weight of 750 which can be represented by the formula $H_3CO(CH_2CH_2O)_{16}H$ (6% residual epoxide groups) it is also possible to obtain a favourable speed increasing effect; the use of such compounds, however, is accompanied with a substantial increase in fog, even exceeding that produced when using polyethylene glycols.

EXAMPLE 4

To a series of identical chemically ripened silver chlorobromide emulsions (25 mole percent of bromide) suitable for the reproduction of line and halftone images, which contain 5-methyl-7-hydroxy-s-triazolo[1,5-a]pyrimidine, cadmium chloride and a spectral sensitizer, one of the compounds listed in the table below were added in an amount of 100 mg. per mole of silver halide.

After the addition of coating aid, 25% by weight of a latex-plasticizer calculated on the weight of gelatin and formaldehyde as hardening agent, the emulsion samples were all coated in a similar way on a cellulose triacetate support and dried.

In a first experiment, the materials were exposed through a continuous wedge in order to examine the formation of "peppers" due to infectious development.

The examination of the peppers occurs visually after development for 2.5 minutes at 20° C. in a developing bath of the following composition:

	G.
Sodium bisulphite	1.5
Hydroquinone	17
Formaldehyde bisulphite	60
Anhydrous sodium carbonate	60
Anhydrous sodium bicarbonate	15
Potassium bromide	1

Water to make 1000 ml.

A value of 0 to 4 is given to the number of peppers observed, which values should be interpreted as follows:

0 stands for no peppers
1 stands for very few peppers
2 stands for a few peppers
3 stands for a number of peppers still acceptable but less desirable
4 stands for many peppers (poor quality material)
5 stands for too many peppers (useless material)

The results attained are listed in the table hereinafter.

In a second experiment, the materials were developed for 4 minutes at 20° C., without being previously ex-

posed, in a normal hydroquinone-p-monomethylaminophenol developer having the following composition:

Water (40° C.)	ml	800
p-Monomethylaminophenol sulphate	g	1.5
Anhydrous sodium sulphite	g	50
Hydroquinone	g	6
Anhydrous sodium carbonate	g	32
Potassium bromide	g	2

Water to make 1000 ml.

The fog produced in the materials developed immediately after preparation and materials that were developed after having been stored for 36 hours at 57° C. and 34% of relative humidity is listed in the table hereinafter.

TABLE

Compound added	Peppers (infectious development)	Fog (hydroquinone/p-monomethyl aminophenol development)	
		Fresh materials	Stored materials
Polyethylene glycol having an average molecular weight of 4,000	3-4	0.10	0.31
Compound I	0.5-1	0.06	0.20
Compound V	1-2	0.06	0.23
Compound XIII	0-0.5	0.07	0.16
Compound XVI	2	0.07	0.25
Compound XVII	1-2	0.08	0.24

From the above results appears that contrary to the compounds of the present invention polyethylene glycols when used in materials for the reproduction of line and half-tone images give rise to the formation of a large number of peppers after infectious development.

The results also show that after development in a conventional hydroquinone/p-monomethylaminophenol developer the compounds of the present invention give less fog than polyethylene glycols.

EXAMPLE 5

A photographic material as described in Example 4, with the difference that to the emulsion none of the compounds listed in the table of Example 4 was added, was divided into two strips.

The strips were exposed for 4 seconds through a graphic magenta contact screen and a yellow filter in order to examine the formation of "peppers" due to infectious development in a partly air-oxidized developer.

The first strip was developed for 2.5 min. at 20° C. in a developing bath of the composition given in Example 4 to which per litre 0.05 g. polyethylene glycol having an average molecular weight of 4000 had been added.

The second strip was developed for 2.5 min. at 20° C. in a developing bath of the composition given in Example 4 to which per litre 0.05 g. of Compound XIII has been added.

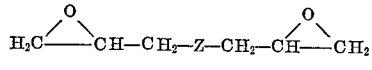
The values of the peppers observed in each strip are given in the following table. These values should be interpreted as described in Example 4.

TABLE

Developer containing—Peppers	
The above polyethylene glycol	2-3
Compound XIII	0

What we claim is:

1. A process for developing an exposed photographic material containing light-sensitive silver halide, wherein during the development a water-soluble non-polymeric compound obtained by reaction of a bisepoxide corresponding to the formula:

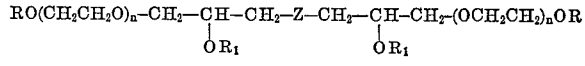


wherein:

Z stands for oxygen or the group —O—Y—O— wherein Y is a straight-chain or branched-chain alkylene group which has from 2 to 8 C-atoms;

with a monoalkyl ether, or a monoaryl ether of ethylene glycol or a polyoxyethylene glycol, is present in an amount sufficient to enhance development without a substantial increase in fog.

2. A process according to claim 1, wherein the said water-soluble non-polymeric compound corresponds to the formula:



wherein:

Z stands for oxygen or the group —O—Y—O— wherein Y is a straight-chain or branched-chain alkylene group which has from 2 to 8 C-atoms;

R stands for alkyl or aryl,

n stands for an integer from 1 to 20, and

R_1 stands for hydrogen, an alkyl group, a $—COR_2$ group, a $—CONHR_2$ group or a $—SO_2R_2$ group wherein R_2 stands for a monovalent saturated or unsaturated aliphatic group for example alkyl and alkenyl, a

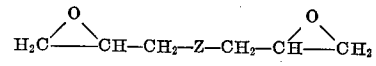
—COCH=CH—COOH

group or its bisulphite addition product, an aryl group or a heterocyclic group.

3. A process according to claim 1, wherein Z stands for $—O—(CH_2)_2—O—$ or $—O—(CH_2)_4—O—$.

4. A process according to claim 1, wherein a silver chloride or silver chlorobromide emulsion, which comprises at most 50 mole percent of bromide, suitable for the production of line and half-tone prints is developed with a hydroquinone formaldehyde bisulphite developer.

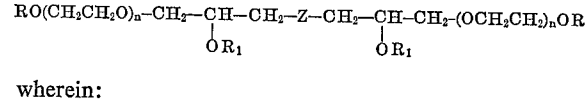
5. A photographic light-sensitive material which comprises a silver halide emulsion layer or a water-permeable layer adjacent to a silver halide emulsion layer containing a water-soluble non-polymeric compound obtained by reaction of a bis-epoxide corresponding to the formula: wherein:



Z stands for oxygen or the group —O—Y—O— wherein Y is a straight-chain or branched-chain alkylene group which has from 2 to 8 C-atoms;

with a monoalkyl ether, or a monoaryl ether or ethylene glycol of a polyoxyethylene glycol in an amount sufficient to enhance development of said material after exposure and during development without a substantial increase in fog.

6. A photographic material according to claim 5, wherein the said water-soluble non-polymeric compound corresponds to the formula:



wherein:

Z stands for oxygen or the group —O—Y—O— wherein Y is a straight-chain or branched-chain alkylene group which has from 2 to 8 C-atoms,

R stands for alkyl or aryl,

n stands for an integer from 1 to 20, and

R_1 stands for hydrogen, an alkyl group, a $—COR_2$ group, a $—CONHR_2$ group or a $—S_2R_2$ group wherein R_2 stands for a monovalent saturated or unsaturated aliphatic group for example alkyl and alkenyl, a

—COCH=CH—COOH

group or its bisulphite addition product, an aryl group or a heterocyclic group.

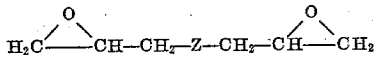
7. A photographic material according to claim **5**, wherein Z stands for —O—$(CH_2)_2$—O— or

—O—$(CH_2)_4$—O—

8. A photographic material according to claim **5**, wherein the said non-polymeric compound is present in an amount comprised between 10 mg. and 5 g. per mole of silver halide.

9. A photographic material according to claim **5**, wherein the said silver halide emulsion is a silver chloride emulsion or a silver chlorobromide emulsion, which comprises at most 50 mole percent of bromide, suitable for the production of line and half-tone prints.

10. A photographic developing composition comprising a silver halide developing agent and a water-soluble non-polymeric compound obtained by reaction of a bisepoxide corresponding to the formula:

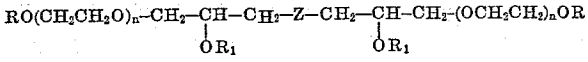


wherein:

Z stands for oxygen or the group —O—Y—O— wherein Y is a straight-chain or branched-chain alkylene group which has from 2 to 8 C-atoms;

with a monoalkyl ether, or a monoaryl ether of ethylene glycol or a polyoxyethylene glycol in an amount sufficient to enhance development without substantial increase in fog.

11. A photographic developing composition according to claim **10**, wherein the said water-soluble non-polymeric compound corresponds to the formula:



wherein:

Z stands for oxygen or the group —O—Y—O— wherein Y is a straight-chain or branched-chain alkylene group which has from 2 to 8 C-atoms,

R stands for alkyl or aryl,

n stands for an integer from 1 to 20, and

R_1 stands for hydrogen, an alkyl group, a —COR_2 group, a —$CONHR_2$ group or a —SO_2R_2 group wherein R_2 stands for a monovalent saturated or unsaturated aliphatic group for example alkyl and alkenyl, a

—COCH=CH—COOH

group or its bisulphite addition product, an aryl group or a heterocyclic group.

12. A photographic developing composition according to claim **10**, wherein Z stands for —O—$(CH_2)_2$—O— or —O—$(CH_2)_4$—O—.

13. A photographic developing composition according to claim **10**, comprising hydroquinone and formaldehyde bisulphite.

14. A photographic developing composition according to claim **10**, wherein the said non-polymeric compound is present in an amount comprised between 10 mg. and 5 g. per litre.

15. The process of claim **1** wherein the hydrogen atoms of the hydroxyl groups in the reaction product are at least partly substituted.

16. The process of claim **1** wherein the hydrogen atoms of the hydroxyl groups in the reaction product are unsubstituted.

17. The photographic light-sensitive material of claim **5** wherein the hydrogen atoms of the hydroxyl groups in the reaction product are at least partly substituted.

18. The photographic light-sensitive material of claim **5** wherein the hydrogen atoms of the hydroxyl groups in the reaction product are unsubstituted.

19. The developing composition of claim **10** wherein the hydrogen atoms of the hydroxyl groups in the reaction product are at least partly substituted.

20. The developing composition of claim **10** wherein the hydrogen atoms of the hydroxyl groups in the reaction product are unsubstituted.

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U.S. Cl. X.R.

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