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SILVER HALIDE DEVELOPER COMPOSITIONS CONTAINING POLYOXYALKYLENE ETHERS OF HEXITOL RING DEHYDRATION PRODUCTS

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9 Claims. (Cl. 95—88)

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This invention relates to photography. More particularly, it relates to novel photographic developer compositions and to processes of developing silver halide images therewith.

An object of this invention is to obtain improved silver images. Another object is to provide improved processes for the development of silver halide images. A further object is to provide improved photographic developer solutions. A still further object is to provide novel developer compositions which produce enhanced speed and contrast results in the development of silver halide images. Still other objects will be apparent from the following description of the invention.

It has been found that the inclusion of the polyoxyalkylene ethers of hexitol ring dehydration products in photographic developer solutions leads to beneficial changes in the effective photographic emulsion speed of exposed silver halide emulsion layers and the contrast of the developed images. The compounds can be used in various amounts, e. g., from 0.1 to 2.5 grams of the ethers per liter of developer solution. With most of the ethers, however, the optimum concentration is about 0.5 gram per liter.

The polyoxyalkylene ethers of hexitol ring dehydration products are commercially available. They are essentially non-ionic in character and have been found to have good wetting and dispersing properties. They can be made by reacting a hexitol ring dehydration product, such as a hexitan or a hexide, with an alkylene oxide, e. g., ethylene oxide or propylene oxide, in an amount sufficient to introduce a plurality of oxyalkylene groups into the molecule. For instance, the reaction may be carried out in a manner similar to that described in British Patent No. 443,559 and United States Patent 2,380,166. In general, the alkylene oxide should be used in an amount sufficient to form an ether group on one of the oxygen atoms of the hydroxyl groups of the hexitan or hexide and introduce at least two of the alkylene groups (—R—O— wherein R is an alkylene radical, e. g., ethylene, propylene, butylene, etc.). The alkylene oxide may, however, react with several of the hydroxyl groups of the hexitans or hexides and introduce several oxyalkylene chains. For example, one to four of the hydroxyl groups of the hexitan or one to two of the hydroxyl groups of the hexide may react and form a chain or chains of oxyalkylene groups of two to 20 or more of such groups.

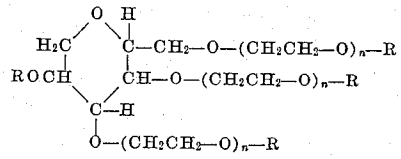
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The resulting polyoxyalkylene ethers of the hexitans or hexides may then be reacted with a monofunctional etherification agent or esterification agent to introduce a lipophilic group, e. g., an aliphatic hydrocarbon chain of 8 to 18 or more carbon atoms or the hexitans or hexides may be first esterified or etherified with such agents and the resulting long chain ethers or esters later reacted with an alkylene oxide. Suitable long chain etherification or esterification reactants include normal alkyl halides of 8 to 20 carbon atoms, e. g., n-octylchloride, n-dodecyl bromide, n-tetradecylchloride, n-octadecyl bromide, and n-hexadecylbromide, or a fatty acid halide of 8 to 20 carbon atoms, e. g., octadecoylchloride, dodecoylchloride, tetradecoyl bromide, n-oleyl chloride, etc. The introduction of two oxyalkylene ether groups into the hexitan or hexide is enough to form the products used in accordance with this invention. It is possible that the alkyl halides or acid halides react with the hydroxyl group at the end of the oxyalkylene chain when etherification with alkylene oxides is effected first. However, if the hexitan or hexide is first esterified or etherified with a long chain monofunctional etherification or esterification agent, the lipophilic groups become linked to an acyclic oxygen atom thereof.

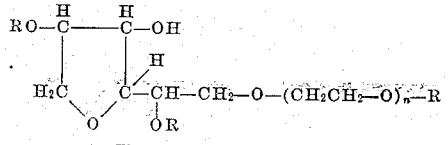
When hexitols are dehydrated, they generally result in a mixture of ring compounds, namely hexitans and hexides, which can be separated by fractional crystallization or extraction. For the purposes of this invention, the ring dehydration products need not be completely separated and mixtures of hexitans and hexides may be utilized to prepare the products used in accordance with this invention.

A class of especially useful products have a structure which is exemplified by the following hexitans and hexide derivative formulae:

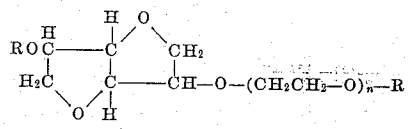
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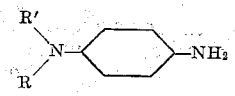


wherein in the formulae one of the R's is an alkyl radical of 8 to 20 carbon atoms or an acyl radical of the formula R—CO— wherein R is of the same order and the other R's are hydrogen and n is 2 to 20 or more. When only one

$$(CH_2CH_2—O)_n$$

radical is present then n should be 6 or more.

The polyoxyalkylene ethers or hexitol ring dehydration products are useful with a wide variety of photographic developing agents including hydroquinone, chlorohydroquinone, pyrogallol, p-aminophenol, ferrous-oxalate, N-methyl-p-aminophenol sulfate, 2,4-diaminophenol, N-dialkyl phenylenediamines of the formula



and their water-soluble salts, where R and R' are the same or different lower alkyl radicals, e. g., methyl and ethyl, 1,4-diaminobenzene, 1,4-diaminonaphthalene, p-aminodiethyltoluidine, and mixtures of two or more of such agents, etc.

The developers may contain the usual sulfites, e. g., sodium sulfite, potassium sulfite, potassium metabisulfite; alkalies, e. g., sodium or potassium carbonate, sodium hydroxide, borax; soluble neutral salts, e. g., sodium bromide, potassium bromide; boric acid, formaldehyde, aldehyde-bisulfite complexes, etc.

In making the novel developer solutions of this invention, it is merely necessary to add the polyoxyalkylene ethers of the hexitol ring dehydration products to the aqueous solution in the same manner that the other ingredients, for example, the sulfites and developing agents, are added. The aforesaid ethers readily dissolve or disperse in aqueous solutions. It is usually most convenient to add the aforesaid ethers as a solution. Water and ethyl alcohol are suitable solvents and a 10% by weight solution in such solvents affords a practical means for adding the ethers to the developer solution.

It has been found that the addition of 0.1 to 2.5 grams of a polyoxyalkylene ether of a hexitan or a hexide or a mixture of such compounds to a developer solution is sufficient to change the induction period of development. Induction period can be defined as the time necessary to produce a density of 0.02 above fog. More can be used if desired. This reduction is more marked in the case of developer solutions which are less active than those which normally have short induction periods.

The invention will be further illustrated by the following examples. The parts are by weight.

Example I

A negative type photographic film bearing a gelatino-silver iodobromide emulsion layer was exposed to an object. The exposed film was then divided into parts, one of which was developed in the following developer and one each was developed in the respective developing solutions made by adding 0.5 gram of the respective polyoxyalkylene ethers of hexitans and hexides to the developer with the results listed in the following table. In each case the time of development required to produce a density of .02 above fog was measured. The results are reported in a relative way as fractions of the control.

N-methyl-p-aminophenol sulfate	grams	0.74
Sodium sulfite (anhydrous)	do	90.4
Hydroquinone	do	1.0
Borax	do	2.7
Potassium bromide	do	0.14
Water to	liter	1.0

Developer	Relative Induction Period
Unmodified	1.0
Modified with A	0.64
Modified with B	0.60
Modified with C	0.70
Modified with D	0.70
Modified with E	0.90

A is mannitan monolaurate polyoxyethylene ether containing approximately 20 oxyethylene groups per molecule divided in 3 chains.

B is sorbitan monolaurate polyoxyethylene ether containing approximately 20 oxyethylene groups per molecule divided in 3 chains.

C is mannitan monostearate polyoxyethylene ether containing approximately 20 oxyethylene groups per molecule divided in 3 chains.

D is sorbitan mono-oleate polyoxyethylene ether containing approximately 20 oxyethylene groups per molecule divided in 3 chains.

E is sorbitan trioleate polyoxyethylene ether containing approximately 20 oxyethylene groups per molecule in one chain.

Example II

Strips of photographic paper comprising a baryta coated paper base bearing a gelatino-silver iodobromide emulsion layer of a standard enlarging type were given a suitable step wedge exposure simultaneously on a sector wheel sensitometer of the intermittent time-scale type.

One of the strips was developed for 75 seconds at 68° F. in a developing solution of the following composition and another in the said developer modified by the addition of 0.5 gram of mannitan monolaurate polyoxyethylene ether containing an average of 20 oxyethylene groups per molecule divided in 3 chains, with the results indicated below:

N-methyl-p-aminophenol sulfate	grams	1.2
Sodium sulfite (anhydrous)	do	19.0
Hydroquinone	do	4.0
Sodium carbonate	do	26.0
Potassium bromide	do	0.4
Water to	liter	1.0

Developer	Net Densities for—	
	High Exposure	Low Exposure
Unmodified	1.68	0.10
Modified	1.85	0.18

Example III

A perforated motion picture negative type film bearing a gelatino-silver iodobromide emulsion layer is exposed to an object field and divided into two parts. One of the parts is developed in the following solution and the other in the solution modified by the addition of 0.5 gram of mannitan monolaurate polyoxyethylene ether containing an average of 20 oxyethylene groups per molecule divided in 3 chains. The development in each case is for three minutes and twenty seconds at 68° F. and gives the following results:

Sodium sulfite (anhydrous)	grams	90.0
p-Phenylenediamine-hydrochloride	do	10.0
p-Hydroxyphenyl amidoacetic acid	do	2.0
Water to	liter	1.0

Developer	Relative Densities for Equal Exposures
Unmodified	100
Modified	200

Example IV

Strips of positive type motion picture film bearing a gelatino-silver iodobromide emulsion layer were given a suitable step wedge exposure simultaneously on a sector wheel sensitometer of the intermittent time-scale type. One of the strips was developed in a solution of the following composition for three minutes at 68° F. and the other for the same period in said developer modified by the addition of 0.5 gram per liter of mannitan monolaurate polyoxyethylene ether containing an average of 20 oxyethylene groups per molecule divided in 3 chains, with the results listed in the following table:

Sodium sulfite (anhydrous)	grams	40.0
N-methyl-p-aminophenol sulfate	do	0.3
Hydroquinone	do	6.0
Sodium carbonate (monohydrated)	do	22.5
Potassium bromide	do	0.9
Citric acid	do	0.7
Potassium metabisulfite	do	1.5
Water to	liter	1.0

Developer	Relative Densities for Equal Exposures
Unmodified	100
Modified	108

Example V

Strips of a photographic film element bearing a silver iodobromide emulsion layer wherein the binding agent for the silver halide grains is a hydrophilic hydrolyzed ethylene/vinyl acetate copolymer prepared after the manner of the similar polymer used in Example II of U. S. P. 2,397,866 were exposed as in Example II. One film strip was developed in the developer solution of Example II and the other in said solution modified by the addition of sorbitan monolaurate polyoxyethylene ether containing an average of 20 oxyethylene groups per molecule divided in 3 chains for 3 minutes at 68° F. The results are given in the following table:

N-methyl-p-aminophenol sulfate	grams	1.2
Sodium sulfite (anhydrous)	do	19.0
Hydroquinone	do	4.0
Sodium carbonate	do	26.0
Potassium bromide	do	0.4
Water to	liter	1.0

Developer	Relative Densities for Equal Exposures
Unmodified	100
Modified	109

Example VI

A photographic film of the kind described in Example III was exposed as described therein and separated into two parts which were, respectively, developed for 12 minutes at 68° F. in the solution of the following composition and that modified by the addition of 0.5 of a gram per liter of mannitan monolaurate polyoxyethylene ether containing an average of 20 oxyethylene groups per molecule divided in 3 chains. The results are given in the table.

N-methyl-p-aminophenol sulfate	grams	5.0
Sodium sulfite (desiccated)	do	100.0
Sodium metaborate	do	2.0
Sodium thiocyanate	do	1.0
Potassium bromide	do	0.5
Water to	liter	1.0

Developer	Relative Densities for Equal Exposures
Unmodified	100
Modified	75

Example VII

Strips of a standard blue base X-ray film element bearing a light-sensitive iodobromide emulsion layer on each surface were given an X-ray exposure under an aluminum step wedge of the usual type and strips of a negative type cine film of the type described in Example III were exposed as described in that example. One strip of each film was developed in (*a*) a solution of ferrous oxalate (made by pouring 750 cc. of 18.5% potassium oxalate into 250 cc. of 18.5% ferrous sulfate aqueous solution) and (*b*) such a solution modified by the addition of 0.5 gram per liter of mannitan monolaurate polyoxyethylene ether containing an average of 20 oxyethylene groups per molecule divided in 3 chains. The developments were continued for four minutes at 68° F. with the following relative densities for equal exposures.

Developer	X-ray Film	Cine Film
Unmodified	100	100
Modified	41	89

Example VIII

Strips of a lithographic film element bearing a gelatino-silver halide emulsion layer were given an exposure behind a graduated step wedge in a sensitometer of the intensity-scale type. Then the strips were developed in the following developer and that developer modified by the addition of 0.1 gram, 0.5 gram, and 2.5 grams per

liter of compound A of Example I for two and one-half minutes at 68° F. with the results listed in the table below:

Water	cc.	500.0
Sodium sulfite (desiccated)	grams	30.0
Paraformaldehyde	do	7.5
Potassium metabisulfite	do	2.5
Boric acid, crystals	do	7.5
Hydroquinone	do	22.5
Potassium bromide	do	1.5
Cold water to make	liter	1.0

Developer	Speed [1]	Gamma	Fog
Plain	2.40	6.2	.01
1/10 gram of A (Example I) per liter	2.45	7.3	.01
2/10 gram of A (Example I) per liter	2.10	13.0	.01
2½ grams of A (Example I) per liter	1.95	14.8	.01

[1] A speed figure in which each unit represents a full camera stop.

In place of the specific developing agents described in the above examples, there may be substituted other developing agents with similar results. Likewise other polyoxyalkylene ethers of ring dehydration products as disclosed above can be substituted for those in the examples with similar results.

In the above examples the quantity of oxyethylene groups is approximate. The invention, however, is not limited to the specific polyoxyalkylene ether derivatives described in the examples but, on the contrary, any of such derivatives having the characteristics prescribed above may be substituted in like manner. Thus mannitan mono-, di-, and tri-oleates, -stearates, -palmitates, -margarates, etc., containing from 2 to 20 oxyalkylene groups which are distributed in from 1 to 3 chains are useful. Similarly the corresponding mannides containing one of said fatty acid groups and a similar amount of oxyalkylene groups per molecule. Other suitable compounds including the mannide ether esters, e. g., the palmitates, margarates, stearates, oleates, which contain from 2 to 20 oxyalkylene groups and especially oxyethylene groups

$$(—O—CH_2—CH_2—)$$

which are distributed in from 1 to 3 chains. Mannitan, mannide, sorbitan and sorbide, decyl, dodecyl, tetradecyl, hexadecyl and octadecyl ethers containing the same number of oxyalkylene, especially oxyethylene groups are also useful. The compounds are useful in simple and mixed silver halide emulsions of various types including those containing silver chloride only and those containing one or more other light-sensitive silver halides, e. g., silver bromide and silver iodide.

It is not known why the above ethers confer beneficial results in the development of silver halide images. The compounds alter the induction period of development. Perhaps in doing so, latent image centers which were not previously developable are made developable. In some cases they are apparently rendered less developable.

How these compounds alter the induction period is not known. It is suspected, however, that adsorption forces must play a part as it has been observed that all of the effective compounds are more or less strongly adsorbed to silver halide grains.

What is claimed is:

1. The process of developing a silver halide image with a developer solution containing a photographic silver halide developing agent and from 0.1 to 2.5 grams of a polyoxyalkylene ether of a hexitol ring dehydration product per liter of solution.

2. The process of developing a silver halide image with a developer solution containing a photographic silver halide developing agent and from 0.1 to 2.5 grams of a polyoxyethylene ether of a hexitol ring dehydration product per liter of solution.

3. The process of developing a silver halide image with an alkaline developer solution containing hydroquinone and from 0.1 to 2.5 grams of a polyoxyethylene ether of a hexitan per liter of solution.

4. The process of developing a silver halide image with an alkaline developer solution containing hydroquinone and from 0.1 to 2.5 grams of a polyoxyethylene ether of mannitan monolaurate per liter of solution.

5. An aqueous developer solution containing a photographic silver halide developing agent and from 0.1 to 2.5 grams of a polyoxyalkylene ether of a hexitol ring dehydration product per liter of solution.

6. An aqueous alkaline developer solution containing hydroquinone and 0.1 to 2.5 grams of a polyoxyethylene ether of a hexitol ring dehydration product per liter of solution.

7. An aqueous alkaline developer solution containing hydroquinone and 0.1 to 2.5 grams of a polyoxyethylene ether of a hexitan per liter of solution.

8. An aqueous alkaline developer solution containing hydroquinone and 0.1 to 2.5 grams of a polyoxyethylene ether of a hexide per liter of solution.

9. An aqueous alkaline developer solution containing hydroquinone and 0.1 to 2.5 grams of a polyoxyethylene ether of mannitan monolaurate per liter of solution.

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