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3,589,902

**PHOTOGRAPHIC DEVELOPER CONCENTRATE**  
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1 Claim

## ABSTRACT OF THE DISCLOSURE

Developer concentrates having added copolymer of polyethylene glycol with an olefinically unsaturated carboxylic or sulfonic acid or added copolymer of a polyethylene glycol ester of an unsaturated carboxylic acid with a vinyl compound containing a carboxylic or sulfonic acid group. Such copolymers compensate for the contrast loss otherwise produced by a developer made by diluting an aqueous-organic solution of the developer concentrate.

The present invention relates to liquid developer concentrates which comprise two components that are mixed together and diluted with water to produce a photographic developer bath.

Photographic developers have already been produced on a commercial scale in the form of developer concentrates. In such concentrates, the organic developer substances in combination with agents which protect against oxidation, e.g. sulphites, are dissolved in an acid or neutral concentrate while the alkaline inorganic additive, alkalies, water softeners, antifogging agents such as potassium bromide, and development accelerators are dissolved in an alkaline concentrate.

Such concentrates have the advantage of avoiding all the problems inherent in the preparation of solutions. Furthermore, one can prepare without weighing the desired quantity of concentrate for a developer bath, ready for use, simply by mixing the two parts of the concentrate and then diluting with water.

A limiting factor in the preparation of concentrates, especially photographic developer concentrates, is that the individual photographic chemicals, especially the developer substances, are not particularly soluble in water in the required concentrations. It is therefore necessary, especially in the preparation of highly concentrated developer solutions, to use organic solubilising agents which are miscible with water, for example, methanol, glycols, glycol ether, methylene glycols or dimethylformamide, for the developer substances which are usually benzene- or naphthalene derivatives substituted by hydroxyl or amino groups. In many cases, however, such solubilising agents have been found to have an adverse effect on photographic development. In particular it has been found that developer concentrates used in reproduction work with photographic emulsion layers which have a very steep gradation, have a much lower utilisation of sensitivity than a developer solution which has been prepared with water alone. In addition, a flattening of the gradation curve frequently occurs in developers when solubilising agents are used.

The object of the invention is to provide developer concentrates which contain development accelerators that are equal in efficiency to those developers prepared in aqueous solution.

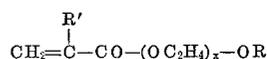
It has now been found that the disadvantages mentioned above do not occur if there is used as accelerator, water-soluble derivatives of polyethylene glycols or alkyl-ethers of polyethylene glycol which are produced by (1) co-

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polymerisation of polyethylene glycol esters of unsaturated carboxylic acids with vinyl compounds containing carboxylic or sulfonic acid groups or by (2) graft polymerisation of polyethylene glycol or derivatives thereof with olefinically unsaturated carboxylic or sulfonic acids.

The following are especially suitable:

(1) Copolymers of (a) reaction products of polyethylene glycols or monoalkylether of such glycols with unsaturated polymerisable acid chlorides or acid esters (e.g. with the chlorides or esters of acrylic acid, methacrylic acid, or vinyl sulfonic acid) (b) with polymerisable monomers containing carboxyl or sulfo groups, e.g., monomers such as acrylic acid, methacrylic acid, vinyl sulfonic acid or styrene sulfonic acid. Reaction products of the above mentioned (a) type which are particularly suitable are those of the following formula:



wherein:

R is a hydrogen atom, an alkyl group containing up to 18 C-atoms, preferably up to 5 C-atoms, a phenyl group which may be substituted, an acyl group, in particular an acyl radical which can be derived from an aliphatic carboxylic acid;

R' is a hydrogen atom or an alkyl group containing up to 3 C-atoms, especially methyl;

x is an integer from 8 to 200.

(2) Graft co-polymers of polyethylene glycols containing preferably 8 to 200 ethylene oxide units, with polymerisable monomers of the above mentioned type which contain carboxyl or sulpho groups.

The graft polymers are prepared by polymerisation of the monomers in the presence of polyethylene glycol or its derivatives, with peroxides or persulphates as catalysts.

The copolymers or graft polymers preferably have a molecular weight of 1,000 to 20,000. In both types of polymers, the proportion by weight of the polyethylene oxide to the polymerised monomers is about 10:1 to 1:10, preferably about 4:1 to 1:3.

The polyethylene oxide chain may also contain small quantities of other alkylene oxides such as propylene oxide, trimethylene oxide etc. The polymeric chain containing vinyl groups may also contain units of other monomers in small quantities, especially those which do not impair the solubility in water, such as low vinyl alkyl ethers, e.g. vinyl ether.

If the polyethylene glycol residue is sufficiently large (at least 8 ethylene glycol radicals) cross-linking does not occur and compounds which are readily soluble in water are obtained. Owing to the presence of the carboxyl or sulpho groups, of the compounds of the present invention in comparison with the known development accelerators such as quaternary salts of the corresponding simple polyalkylene oxides are readily soluble and are not precipitated or salted out from concentrates, even at elevated temperatures.

The copolymers or graft polymers according to the invention are prepared by known methods. The preparation of some polymers is described in detail as follows:

### POLYMER 1

Preparation of bisacrylic acid ester of a polyethylene glycol having a molecular weight of 4000:

$\frac{1}{100}$  mol (40 g.) of a polyethylene glycol of molecular weight 4000 were dissolved in 600 cc. absolute acetone at 35-40° C., 8 g. of sodium bicarbonate were added and  $\frac{1}{25}$  mol (3.6 g.) acrylic acid chloride was then slowly added dropwise to the mixture with stirring. The mixture was then stirred for about another 6 to 7 hours until the pH had risen to 7 (a small quantity of potassium car-

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bonate is added at the end). The salts are filtered off and the residual mixture is evaporated to dryness in vacuo (at 40° C.). The waxy residue is used direct for polymerisation.

Preparation of the copolymer with acrylic acid (quantities are in the proportion of 1:1).

100 g. of the above reaction product are dissolved in 500 cc. water and 100 g. of acrylic acid are added. The mixture is adjusted to pH 7 with sodium hydroxide solution and 2 g. of potassium persulphate are added as catalyst. The pH is maintained at 7. The polymerisation time is always one hour (at 70° C.). The clear solution is cooled and poured into methanol. The precipitate is washed several times with methanol and dried. To remove any monomeric polyethylene glycol or polyethylene glycol derivative still present, the dried residue is dissolved in the smallest possible quantity of water and again precipitated from methanol (the operation of purification may be repeated several times). A 10% solution of the copolymer in water has a viscosity of about 10 cp. at 20° C. Yield: 190 g.

#### POLYMER 2

A polymer similar in nature to Polymer 1, but containing a different polyethylene oxide chain, is obtained when a polyethylene oxide having an average molecular weight of 1000 is used instead of the polyethylene oxide mentioned above.

#### POLYMER 3

A polymer similar in nature to Polymer 1 but with a different polyethylene oxide chain is obtained by using a polyethylene oxide having an average molecular weight of 6000 instead of the polyethylene oxide used in preparing Polymer 1.

#### POLYMER 4

A polymer similar in nature to Polymer 1 but with a different polyethylene oxide chain is obtained by using a polyethylene oxide having an average molecular weight of 12,000 instead of the polyethylene oxide used in preparing Polymer 1.

#### POLYMER 5

45 g. of a mixture of monoalkylethers of dodecaethylene glycol (the alkyl groups contain 16 to 18 C-atoms) having a molecular weight of about 1500 were dissolved in 600 cc. of dry acetone. 7.2 g. of sodium bicarbonate are added to this and then, while the mixture is stirred vigorously 6 g. of acrylic acid chloride are added dropwise. The mixture is stirred at room temperature until it has a pH of 7 (about 6 hours). Some soda may be added if necessary. The salts are then filtered off under suction and the solvent is evaporated in vacuo. The compound may be used without further purification. Polymerisation with acrylic acid (quantitative ratio 1:1):

100 g. of the above reaction product are dissolved in 500 cc. of water and 100 g. of acrylic acid are added. The mixture is adjusted to pH 7 with sodium hydroxide solution. 2 g. of potassium persulphate are then added and the mixture is heated to 70° C. with stirring (average polymerisation time is 1 to 2 hours). The clear viscous solution is cooled and the product precipitated with acetone. After washing with acetone, the polymer is dried and is precipitated from a small quantity of water with acetone.

#### POLYMER 6

Copolymer with vinyl sulphonic acid:

75 g. of the reaction product of polyethylene oxide and acrylic acid ester used in the preparation of Polymer 1 are dissolved in 1 litre of water (oxygen-free) together with 100 g. of sodium vinyl sulphonate. 3 g. of potassium persulphate are added to the mixture as catalyst and the mixture is polymerised while stirring constantly for 20 hours at 70° C. The mixture is then dialysed for 24 hours in a cellophane tube (Kalle) to remove the major portion of low molecular weight products. The solution

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is concentrated by evaporation to give a viscous residue, and the product is then precipitated by the addition of acetone and triturated many times over with acetone and dried. It is then reprecipitated from a small quantity of water using acetone. Yield 130 g.

#### POLYMER 7

27 g. of methacrylic acid and 20 g. of polyethylene glycol of molecular weight 4000 were dissolved in 100 cc. of water and the mixture adjusted to pH 7 using sodium hydroxide solution. After the addition of 0.5 g. of potassium persulphate in 50 cc. of water, the mixture was polymerised at 70° C. for about 7 hours. The mixture was cooled and the polymer was precipitated with methanol. The precipitate was triturated several times with methanol, dried and then reprecipitated from a small quantity of water with methanol. Yield: 45 g.

The development accelerators according to the invention are used in developer concentrates which comprise two components. One of these parts, solution (A), contains a developer substance and a compound which protects against oxidation, e.g. sodium sulphite or formaldehyde bisulphite, usually in an aqueous organic solvent system. The organic solubilising agents for the developer substance are usually alcohols such as methanol, ethanol or propanol, glycols such as ethylene glycol, di- or triethylene glycol, glycol ethers such as ethylene glycol monoethyl- or diethylene glycol monoethyl ether, dioxane, dimethylformamide and tetrahydrofurfuryl alcohol or tetrahydrofuran.

Solution (B) contains an aqueous solution of the remaining chemicals required for the preparation of a photographic developer bath ready for use, i.e. alkali such as sodium carbonate, potassium carbonate, borax or sodium- or potassiumhydroxide, water softeners, such as ethylene diamine tetracetic acid and antifog agents such as potassium bromide. The use of mixtures of the said alkalies is preferably for the sake of increasing the solubility.

The accelerators according to the invention are preferably used in concentrates which contain hydroquinone as developer and formaldehyde bisulphite and/or sodium sulphite as an agent for protection against oxidation. They may, of course, also be used in combination with other known developers such as aminophenol, p-methylaminophenol, p-phenylenediamine etc.

The accelerators may be added both to part A and to part B of the concentrate. For example, 0.01 to 2 g. of an accelerator are employed for 500 ml. of 1 part of a concentrate containing 20 to 80 g. of hydroquinone and 80 to 180 g. of an agent protecting against oxidation, or for 80 to 300 g. of bases, in particular chemically different bases.

#### Example 1

Preparation of a developer concentrate:

Part A:

48 g. hydroquinone  
165 g. formaldehyde bisulphite  
9.3 g. boric acid anhydride  
1.2 g. ethylene diaminetetracetic acid  
10 ml. dimethylformamide  
80 ml. ethylene glycol  
80 ml. triethylene glycol  
and water up to 585 ml., filter.

Part B:

127 g. sodium carbonate sicc.  
149 g. potassium carbonate sicc.  
14 g. potassium bromide  
4.25 g. ethylene diaminetetracetic acid  
0.5 g. of polymer 1  
water up to 585 ml., filter.

To prepare a developer bath ready for use, 125 ml. of part A and 125 ml. of part B are mixed and made up to a volume of 1 litre with water.

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Strips of a black-white negative material of ultra-steep gradation (Lith gradation) which have been exposed through a step wedge are developed for 2.4 and then 6 minutes, and fixed and rinsed with water in the usual manner. Images of normal Lith gradation and sensitivity are obtained.

A similar developer which does not contain a compound according to the invention has a sensitivity which is lower by 2 to 3 shutter stops when the development time is 4 minutes.

#### Example 2

A developer concentrate is prepared using the procedure described in Example 1, except that 1 g. of polymer 7 is used instead of the accelerator described therein.

The images obtained after working up do not differ in gradation and sensitivity from images developed in a conventional developer prepared only with water.

The advantages of the copolymers and graft polymers used according to the invention in a developer concentrate are seen from the following comparison tests:

A 10% solution of copolymer 1 and a 5% solution of polyethylene glycol of molecular weight 4000 are made alkaline by the addition of dilute sodium hydroxide solution. Pure polyethylene glycol separates out as a second phase on heating while the copolymer according to the invention is not precipitated. This improvement in solubility naturally also occurs in the developer concentrates.

100 g. of polyethylene glycol of molecular weight 4000 are added to 10 cc. of developer concentrate B which has the same composition as indicated above except that the accelerator is not used. The polyethylene glycol separates completely on heating. In contrast, 200 mg., 400 mg. and 600 mg. of the copolymer mentioned above could be added without any separation of mixture, even when heated above 50° C.

We claim:

1. A process for the production of a developer bath which comprises preparing a first acid or neutral concen-

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trate containing organic developer and agents that protect against oxidation selected from the group consisting of sodium sulfite and formaldehyde dissolved in an aqueous organic solvent, preparing a second concentrate containing alkaline additive selected from the group consisting of alkaline carbonates and hydroxides and borax, ethylene diamine tetraacetic acid as a water softener and potassium bromide as an antifogging agent in suitable concentrations for photographic development in the developer bath, at least one of said concentrates containing a developer accelerator of a polymer product having a molecular weight of 1,000 to 20,000 selected from the group consisting of

(1) a copolymer obtained by free radical polymerisation of a vinyl carboxylic acid or a vinyl sulfonic acid in the presence of polyethylene glycol,

(2) a copolymer of

(a) the esterification product of polyethylene glycol and a vinyl carboxylic acid, and

(b) a vinyl compound having a carboxylic acid or sulfonic acid group,

said development accelerator being contained in its respective concentrate in the amount of 0.01 to 2 grams per 500 milliliters of concentrate; then mixing said first and second concentrates and water in a sufficient volume to provide a developer bath.

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