United States Patent [19]

Fisch

[11] **3,785,824**

[45] **Jan. 15, 1974**

[54] **PHOTOGRAPHIC AQUEOUS DISPERSION CONCENTRATES**

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[73] Assignee: **Minnesota Mining and Manufacturing Company**, St. Paul, Minn.

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[21] Appl. No.: **183,703**

[52] **U.S. Cl.** ..... **96/66 R**, 96/66.1

[51] **Int. Cl.** **G03c 5/30**

[58] **Field of Search** 96/66, 114, 66.1; 252/364, 356; 260/78.5, 23

[56] **References Cited**

UNITED STATES PATENTS

2,286,215	9/1942	Lowe	96/114
3,418,118	12/1968	Thommes et al.	96/20
1,976,679	10/1934	Fikentscher et al.	252/356
3,141,897	7/1964	Crecelius et al.	252/356
3,385,834	5/1968	Merijan	252/356
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3,589,902	6/1971	Himmelmann et al.	96/66
3,615,497	10/1971	Fassbender	96/66.1
3,649,287	3/1972	De Pauw et al.	96/100

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Attorney—Alexander, Sell, Steldt & Delahunt

[57] **ABSTRACT**

A synthetic, water-soluble polymer having a hydrocarbon backbone is employed as a dispersing agent in dispersions in water of a solvent for high-boiling, water-immiscible vehicles useful in the photographic solvent-dispersion technique for the formation of coupler-containing photographic silver halide elements.

11 Claims, No Drawings

PHOTOGRAPHIC AQUEOUS DISPERSION CONCENTRATES

The present invention relates to color photographic processing, and more particularly relates to developer solutions, solution concentrates, and methods for color development.

One system of silver halide color photography employs silver halide photographic elements which have a plurality of silver halide layers, each layer having a photographic color coupler dispersed therein by the solvent dispersion technique. This technique involves dispersing, in a silver halide emulsion, very fine droplets of a high-boiling, water-immiscible liquid vehicle such as tricresyl phosphate, in which is dissolved a color coupler. Reference is made to U. S. Pat. Nos. 2,332,027 and 2,801,170. During color development of the so-described silver halide element, silver halide is reduced by the developing agent to silver, and the developing agent is oxidized. The oxidation product of the developing agent "couples," i.e., reacts, with the color coupler which is included within the very fine droplets dispersed in the silver halide emulsion, to form a dye.

Color development working solutions ordinarily include, in addition to a p-phenylenediamine color developer and other photographic adjuvants, a solvent for the droplets of the high-boiling, water-immiscible vehicle referred to above. Such solvents (such as aromatic alcohols (e.g., benzyl alcohol) and the like) are believed to promote access of the oxidized developer to the couplers, thereby promoting the dye-forming reaction and enabling dye images of the proper density to be obtained. Reference is made to British Pat. No. 546,347.

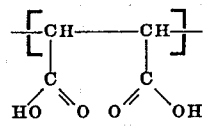
Color developer working solutions are often prepared by the user from photographic developer "kits," the user merely combining and diluting the kit contents to form the desired developer solution. Such kits may contain two or more separately packaged compositions. One such composition, for example, may include a concentrated aqueous acidic solution of a photographic p-phenylenediamine developer. Another package may contain a concentrated aqueous alkaline solution, antioxidants, and the like. A third package may contain, in concentrated form, the solvent referred to above. Since this solvent is a solvent for the high-boiling, water-immiscible, coupler-containing vehicles used in the solvent dispersion technique, such solvents ordinarily exhibit a very limited solubility in water. In order to permit such solvents to be incorporated into concentrates for use in kit form, and yet to promote rapid dissolution of such solvents during preparation of a photographic developer working solution, it has been proposed that such solvents be incorporated in a concentrated water solution which also includes a simple glycol co-solvent to promote solubility (U. S. Pat. No. 3,574,619).

In another method, benzyl alcohol or other solvents are provided in concentrated form as aqueous dispersions using, as dispersing agents, such materials as cellulose derivatives (e.g., hydroxymethyl cellulose), water-soluble polymeric carbohydrates and water-soluble polymeric amides (Belgian Pat. No. 727,705). By virtue of the fact that such dispersing agents are naturally-occurring materials, a variation in the properties thereof can be expected to lead to inconsistent dispersion characteristics and thus to inconsistent photographic developing characteristics in photographic developer working solutions. In addition, cellulosic materials are often subject to certain chemical reactions (e.g., hydrolysis), causing degradation thereof.

It is an object of the present invention to provide a storage-stable dispersed concentrate of a solvent for high-boiling, water-immiscible liquid vehicles employed in the solvent dispersion technique.

It is another object of the invention to provide a dispersed concentrate of a solvent for the high-boiling, water-immiscible liquid vehicles employed in the solvent dispersion technique which employs a storage-stable, photographically-acceptable dispersing agent for the solvent.

Briefly, the invention relates to a concentrated dispersion in water of a solvent selected from the group consisting of aromatic alcohols, alkyl glycol ethers, aryl glycol ethers, alkyl polyglycol ethers and aryl polyglycol ethers, which solvent is soluble in water to an extent of about 10 g/l to about 100 g/l. The dispersion includes a dispersing agent which is a synthetic, water-soluble polymer prepared from ethylenically unsaturated monomers and having essentially a hydrocarbon backbone. In a preferred embodiment, the dispersing agent is an anionic polymer, and in its most preferred embodiment the dispersing agent is a water-soluble addition polymer hydrolyzate having recurring units of the formula



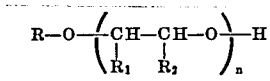
such as, for example, hydrolyzates of copolymers of maleic anhydride and ethylenically unsaturated comonomers such as styrene, ethylene and methyl vinyl ether.

The polymeric dispersing agents of the invention, as noted, are prepared from ethylenically unsaturated monomers such as maleic anhydride, and accordingly have a backbone which consists essentially of a hydrocarbon chain. The polymeric dispersing agents are water-soluble; that is, they are immediately soluble in water (e.g., polyvinyl alcohol, sulfonated polystyrene, etc.) or can be made soluble in water by hydrolysis of the pendant groups thereof (as for example the maleic anhydride copolymers referred to above). The term "water soluble" as used herein refers to polymers of both types. The polymers of the invention further are preferably anionic; that is, the polymers will dissolve and ionize in water to form a negatively charged polymeric species. Examples of such polymers are the maleic anhydride copolymers referred to above, sulfonated polystyrene, and copolymers of vinyl sulfonic acid.

Most preferred as dispersing agents in the present invention, however, are water-soluble addition polymer hydrolyzates of the formula set forth above, which polymers may be formed from maleic anhydride and ethylenically unsaturated comonomers by techniques known to the art. Of particular importance are the copolymers of maleic anhydride with styrene, ethylene and methyl vinyl ether. The mer ratio of units derived

from maleic anhydride to units derived from other ethylenically unsaturated monomers must be such as to render the hydrolyzate of such polymers readily soluble in water. As is known to the art, maleic anhydride copolymers themselves generally have limited solubility in water. Upon addition of such polymers to water, hydrolysis of the anhydride groups of the maleic anhydride mer units is believed to occur, thereby rendering the polymers highly soluble in water.

The solvents of the invention include aromatic alcohols such as benzyl alcohol, as reported in British Pat. No. 546,347. Of particular interest are alkyl glycol ethers, aryl glycol ethers, alkyl polyglycol ethers or aryl polyglycol ethers, such as are described in the copending application Ser. No. 186,675 of H. Santemma and R. Fisch entitled "Color Photographic Developing Solution". The latter solvents are characterized by the formula



wherein R is a $C_1 - C_{10}$ alkyl group or an aryl group having no more than 10 carbon atoms, R_1 and R_2 each independently represent a hydrogen atom or a $C_1 - C_3$ alkyl group with the proviso that at least one of R_1 and R_2 is hydrogen, and n is an integer of from one to five. The concentrates of the invention employ the solvents as described above in a concentration which exceeds the miscibility of the solvent in water. The weight ratio of water to dispersed solvent is desirably maintained between about 1/1 and 25/1. The dispersions of the invention either do not separate into separate layers or, if some tendency to form layers occurs, the solvent can be readily redispersed upon moderate agitation.

In addition to the solvent referred to above, and a dispersing agent therefor, the dispersed concentrates of the invention may additionally include such photographic adjuvants as color developers of the p-phenylenediamine type, black and white developers such as hydroquinone, and hydroxylamine salts such as hydroxylamine sulfate. The dispersed concentrates of the invention may include hydroxylamine sulfate in a quantity limited only by the solubility of this compound in the concentrate. Preferably, however, hydroxylamine sulfate is employed in a salt/water weight ratio of from about 0.1/100 to about 33/100.

The concentrates of the present invention may be easily prepared by incorporating a suitable quantity of dispersing agent in water, and then adding thereto, with vigorous agitation, a selected solvent such as benzyl alcohol. The concentrates of the invention are preferably adjusted to about neutral pH, e.g., in the range of from about pH 5 to about pH 9.

In use in photographic kit form, the dispersed concentrate of the invention is combined with the ingredients of other packages thereof such as an aqueous, acidic developing agent concentrate and an aqueous, alkaline solution concentrate, to form, with water, a photographic color developer working solution. The poorly-soluble solvents of the invention, in dispersed form, are readily dissolved during preparation of the working solution, thereby permitting the working solution to be rapidly prepared, and avoiding problems associated with incomplete mixing of the various ingredients of the solution.

Although the above description has been directed primarily to photographic color developing solution kits for producing working developer solutions, it will be understood that this description also refers to replenisher kits which are employed to provide replenisher solutions; i.e., solutions which are used to replenish depleted photographic color processing working solutions.

The invention may be more readily understood by reference to the following illustrative, non-limiting examples:

EXAMPLE 1

A three-package color development replenisher kit was prepared as follows:

Part A
- Hydroxylamine sulfate—2.1 g.
- Benzyl alcohol—12.6 ml.
- Maleic anhydride-methyl vinyl ether copolymer (Gantrez AN 169, a trademarked product of General Aniline and Film Corporation) (10 percent aqueous solution)—2.0 ml.
- Water to—20.0 ml.

Part B
- Potassium carbonate—40.3 g.
- Sodium sulfite—2.3 g.
- Potassium bromide—0.16 g.
- Sequestering agent (Antical-3, a product of Eastman Kodak Co.)—1.6 g.
- Water to—57.5 ml.

Part C
- Sodium sulfite—3.0 g.
- Developing agent (4-amino-N-ethyl-N-(β-methanesulfonamido ethyl)-m-toluidine sesquisulfate)—5.0 g.
- Water to about—13.0 ml.

Part A above was in the form of a practically stable dispersion. Parts A, B and C were added in order to 800 ml. of water to form, upon further dilution to 1,000 ml., and with minimal stirring, a photographic color developer replenisher solution.

EXAMPLE 2

A two-package photographic color developer replenisher kit was prepared as follows:

Part A
- Potassium hydroxide (45 percent aqueous solution) 173 ml.
- Boric acid 118.4 g.
- Sodium sulfite 6.78 g.
- Water to 325 ml.

Part B
- Developing agent (4-amino-N-ethyl-N-(β-methanesulfonamido ethyl)-m-toluidine sesquisulfate)—50.0 g.
- Sodium sulfite—2.24 g.
- Benzyl alcohol—30.0 ml.
- Maleic anhydride-methyl vinyl ether copolymer (Gantrez AN 149, a product of General Aniline and Film Corp.), 10 percent aqueous solution—9.0 ml.
- Water to—200 ml.

The contents of parts A and B of this example, when combined and diluted to 10 l. with water, provide a photographic color developer replenisher solution.

EXAMPLE 3

The color development kit of Example 2 was duplicated except that in part B thereof, a copolymer of styrene and maleic anhydride (SMA, Monsanto Chemical Company) — 10 percent aqueous solution (8.0 ml.) was substituted for the 9.0 ml. of maleic anhydride-methyl vinyl ether copolymer. Similar results were obtained.

EXAMPLE 4

The photographic color development kit of Example 1 was duplicated except that in part A thereof, 2.0 ml. of a 10 percent aqueous solution of the copolymer of ethylene and maleic anhydride (EMA, Monsanto Chemical Company) was substituted for the 2.0 ml. of maleic anhydride-methyl vinyl ether copolymer employed therein. Similar results were obtained.

What is claimed is:

1. A concentrated photographic developing agent dispersion in water, capable of dilution to a developing solution, comprising:

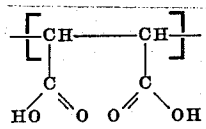
a. a solvent selected from the group consisting of aromatic alcohols, alkyl glycol ethers, aryl glycol ethers, alkyl polyglycol ethers and aryl polyglycol ethers, which solvent has a solubility limit in water of from about 10 g/l to about 100 g/l,

b. a dispersing agent which is a synthetic water soluble polymer prepared from ethylentically unsaturated monomers and having essentially a hydrocarbon backbone,

c. and at least one photographic developing agent selected from hydroxylamine sulfate or a para-phenylene diamine type developer.

2. The dispersion of claim 1 wherein said polymeric dispersing agent is anionic.

3. The dispersion of claim 1 wherein said dispersing agent is a water-soluble addition polymer hydrolyzate having recurring units of the formula



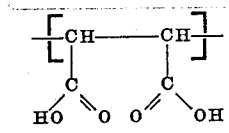
4. The dispersion of claim 3 wherein said dispersing agent is the copolymer of maleic anhydride and styrene.

5. The dispersion of claim 3 wherein said dispersing agent is the copolymer of maleic anhydride and ethylene.

6. The dispersion of claim 3 wherein said dispersing agent is the copolymer of maleic anhydride and methyl vinyl ether.

7. The concentrated dispersion of claim 1 in which the solvent is present in the dispersion in a ratio to water from about 12 g/100 ml to about 50 g/100 ml, and the dispersing agent is present in a ratio to water of from about 0.45 g/100 ml. to 1.0 g/100 ml.

8. A concentrated dispersion in water capable of use in photographic developer kits, said dispersion comprising a solvent selected from the group consisting of aromatic alcohols, alkyl glycol ethers, aryl glycol ethers alkyl polyglycol ethers and aryl polyglycol ethers, which solvent has a solubility in water of from about 10 g/l to about 100 g/l, said dispersion including, as a dispersing agent, a water-soluble addition polymer hydrolyzate having recurring units of the formula



and at least one photographic developing agent selected from the group of hydroxylamine sulfate or a para-phenylene diamine type developer.

9. The dispersion of claim 8 wherein said solvent is benzyl alcohol.

10. The dispersion of claim 8 wherein said solvent is ethylene glycol monophenylether.

11. The concentrated dispersion of claim 7 in which the solvent is present in the dispersion in a ratio to water of from about 12 g/100 ml to about 50 g/100 ml, and the dispersing agent is present in a ratio to water of from about 0.45 g/100 ml to 1.0 g/100 ml.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,785,824 Dated January 15, 1974

Inventor(s) Richard S. Fisch

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 6, line 13, after "water" insert --of--.

Col. 6, line 41, "7" should read --8--.

Signed and sealed this 19th day of November 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

FORM PO-1050 (10-69)

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* U.S. GOVERNMENT PRINTING OFFICE : 1969 O—365-334.