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DEVELOPING COMPOSITIONS USED IN PHOTOGRAPHIC TRANSFER PROCESSES

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This invention relates to developing compositions for use in photographic transfer processes and those processes in which such developing compositions are employed. These compositions contain as the major substituents the alkali metal salt of cyclic sulfonic acid, and alkali and a polyethylene glycol.

The reproductions of designs, printed matter, or the like, has been of considerable interest in recent years. One procedure of reproducing designs or printed matter was developed by Henry C. Yutzy and Edward C. Yackel and is described in their U.S. Patents Nos. 2,596,756, 2,716,059 and 2,592,368. That procedure involved exposing a photographic product consisting of a substantially unhardened light-sensitive gelatino-silver halide emulsion layer on paper or some other support with the emulsion surface in contact with the front of a sheet carrying printed matter or the like, following which the exposed emulsion was subjected to differential hardening by means of a tanning developing agent and treatment with an alkaline solution containing also an activator thereby conditioning the emulsion layer for transfer to a paper sheet such as bond paper upon contact therewith accompanied by pressure.

The activator which has been regarded heretofore as suitable for use in the alkaline developing solution has been a gelatin softener on the order of urea, formamide, ethylene chlorohydrin or sodium nitrate. Occasionally some disadvantage might be encountered with one or the other of these activators and, therefore, it is desired to have an activator available that for any given situation that most suitable for use may be selected.

One object of my invention is to provide a developing composition for photographic transfer processes of excellent stability. Another object of my invention is to provide a developing composition for photographic transfer processes having a better latitude of operation than that of developing compositions for similar purposes available at the present time. A further object of my invention is to provide a developing composition for transfer processes free of deposits or solids formation upon standing and hence readily adapted to be supplied in concentrated form. A still further object of my invention is to provide a developing composition for use in transfer processes which provides better densities of subsequent copies than obtained with developing compositions available at the present time. A still further object of my invention is to provide a photographic transfer process employing as the developing composition therein an aqueous solution, the principal constituents of which are an alkali metal salt of a cyclic sulfonic acid, an alkaline material and a polyethylene glycol.

In its broadcast aspects my invention is based on the finding that compositions of alkaline material, alkali metal salts of cyclic sulfonic acids and certain polyethylene glycols give considerably improved properties of developing compositions available at the present time for photographic transfer processes.

The alkali metal salts of cyclic sulfonic acids which are useful are those which have at least 6 and not more than 18 carbon atoms per molecule. Some acids whose alkali metal salts are useful in this connection are toluene sulfonic acid, xylene sulfonic acid, nitrobenzene

sulfonic acid, dimethylamino benzene sulfonic acid and the like. The salts of these compounds are used in the developing composition in the proportion of 5–50 grams per liter of solution or 0.5–5% concentration therein. The alkaline material which is employed is an alkali metal carbonate, an alkali metal hydroxide or their mixture. It is desirable that the developing composition have a pH within the range of 12.5 to 10.5. If the sulfonic acid compound is added in the form of the acid, some of the alkaline material which is added will serve to convert the sulfonic acid to its salt. Ordinarily the alkali will be used in a concentration on the order of 2%.

Also incorporated in the developing composition in accordance with my invention is a polyethylene glycol, any of the polyethylene glycols up to those of 6 carbon atoms being especially useful. This glycol is ordinarily present in a proportion within the range of 1–10% as amounts within this range exhibit optimum properties. The preferred range is 2–5% concentration. Polyethylene glycols which are especially useful are the di, tri, or tetra ethylene glycols. Other additives are sometimes desirable in addition to those which are considered essential; for instance the use of a sequestering agent is desirable particularly where water having more than a low mineral content is employed, thus overcoming any effect which might be experienced from calcium ion or the like. Also in some cases, the handling of the developing composition might involve foaming, hence, in those cases the use of an anti-foaming agent, as is well known in the art, such as a silicone anti-foamer or an alcohol such as butyl, dodecyl or other water soluble aliphatic alcohols of at least 4 carbon atoms may be desirable to decrease foaming.

In utilizing the developing composition in accordance with my invention a substantially unhardened light-sensitve gelatin-silver halide emulsion on a support is first exposed to a sheet carrying a design or printed matter thereon accompanied by light. The exposed layer is then developed in the presence of a tanning development agent, preferably incorporated in the emulsion layer as described in U.S. Patent No. 2,592,368. The emulsion is then developed in an aqueous alkaline solution such as a 2% solution of sodium hydroxide and/or sodium carbonate containing the cyclic sulfonic acid which facilitates the transfer of the stratum of the emulsion containing the image to a paper pressed against the developed emulsion. Also present therein is the polyethylene glycol which contributes to the stability of the developing solution and improves the ease of transfer and the sensitometric properties of the photographic material. The photographic element containing the emulsion after processing and while still moist is pressed against a paper sheet whereby transfer of the image to said sheet is obtained.

I have noted that the developing composition in accordance with my invention is an improvement over developing compositions which have been used heretofore for the described purpose. For instance, in the making of subsequent copies I have noted that retained density is better than in the use of the developing compositions now available. I have found that, because of this retention of density, at least one more usable copy is ordinarily available from a given matrix than in the case of development of the matrix by previously described procedures.

I have found that the developing compositions in accordance with my invention operate at a greater pH tolerance and at a greater temperature range than with previous compositions. For instance, with previous developing compositions it has been desirable for good results to limit the pH range to 11.0–10.5. With the developing compositions of the invention a pH range of 12.5–10.5 is tolerated without derogatory effect on the copies ob-

tained. I have found that developing compositions in accordance with my invention are free from deposit or the formation of solid material, particularly of a crystalline nature, upon standing of the composition. Because of this, solutions in which the materials are concentrated can be made up and supplied to customers because of their good stability and the absence of unwanted formations. These compositions are suscetpible to a larger concentration latitude than with conventional developing solutions for transfer processes and in addition the evaporation rate represents a reduction of as much as 10–40% from that of the conventional solutions.

The following examples illustrate the types of compositions which may be prepared for use in photographic transfer processes in accordance with my invention:

Example 1

A composition was prepared as follows:

Paratoluene sulfonic acid ----------grams--	17
45% potassium hydroxide in aqueous solution --ml--	9.5
Potassium carbonate ----------grams--	40
Tetraethylene glycol ----------ml--	40
Ethylene diamino tetraacetic acid ----------grams--	4.5
Water to make 1 liter.	

The potassium hydroxide gave a pH of 11±.05 in the developing composition. It was found that this developing composition when used in a photographic transfer process gave good sharp copies particularly in the first 3 or 4 copies which were prepared. This composition upon standing was free of any formation of solids material particularly in crystalline form.

Example 2

80 parts of paratoluene sulfonic acid, 160 parts of potassium carbonate, 24 parts of potassium hydroxide and 120 parts of tetraethylene glycol were dissolved in water to make up 4000 parts of solution. The resulting solution was used as an alkaline developer in a photographic transfer process as described above and copies of printed material of good sharpness were obtained.

Often in alkaline developer solutions it is desirable to include a dye to decrease the passage of light through the solution. Some water soluble dyes especially useful in this connection are:

(1) Direct Deep Black EA concentrate C.F. (color index 582).
(2) Nigrosine (color index 865).
(3) Rhodamine BI (color index 749).

The dyes are conveniently employed in a proportion of ½–1 gram per liter of developer solution.

The following example illustrates developer compositions including dye therein:

Example 3

An alkaline developer solution useful in photographic transfer processes was prepared having the following composition:

	Parts
Potassium paratoluene sulfonate ----------	27
Potassium carbonate ----------	40
Tetraethylene glycol ----------	20
Disodium ethylene diamine tetra acetate ----------	4½
Direct Deep Black EA conc. C.F. ----------	0.5
Water to make 1000 parts.	

In the various compositions other polyethylene glycols such for instance as triethylene glycol or diethylene glycol may be employed as the polyhydroxy compound with equally satisfactory results.

This application is a continuation-in-part of my application Serial No. 862,096, filed December 28, 1959, and now abandoned.

I claim:

1. A composition useful in developing layers of unhardened gelatin-silver halide emulsions in a photographic transfer process, which essentially consists of an aqueous solution of an alkali metal salt of an aromatic sulfonic acid containing 6–8 carbon atoms per molecule, a polyethylene glycol containing up to 6 carbon atoms per molecule and sufficient alkaline material to impart a pH of 10.5–12.5 to the solution.

2. A composition useful in developing layers of unhardened gelatin-silver halide emulsions in a photographic transfer process, which essentially consists of an aqueous solution of an alkali metal salt of paratoluene sulfonic acid, a polyethylene glycol containing up to 6 carbon atoms per molecule and sufficient alkaline material to impart a pH of 10.5–12.5 to the solution.

3. A composition useful in developing layers of unhardened gelatin-silver halide emulsions in a photographic transfer process, which essentially consists of an alkali metal salt of paratoluene sulfonic acid, a polyethylene glycol containing up to 6 carbon atoms per molecule and sufficient alkali metal carbonate-containing alkaline material to impart a pH of 10.5–12.5 to the solution.

4. A composition useful in developing layers of unhardened gelatin-silver halide emulsions in a photographic transfer process, which essentially consists of an aqueous solution of an alkali metal salt of paratoluene sulfonic acid, tetraethylene glycol and sufficient alkali metal carbonate-containing alkaline material to impart a pH of 10.5–12.5 to the solution.

5. A composition useful in developing layers of unhardened gelatin-silver halide emulsions in a photographic transfer process, which essentially consists of an aqueous solution of an alkali metal salt of paratoluene sulfonic acid, a polyethylene glycol containing up to 6 carbon atoms per molecule and sufficient alkali metal carbonate and alkali metal hydroxide to impart a pH of 10.5–12.5 to the solution.

6. A composition useful in developing layers of unhardened gelatin-silver halide emulsions in a photographic transfer process, which essentially consists of an aqueous solution of potassium paratoluene sulfonate, tetraethylene glycol and sufficient potassium carbonate-containing alkaline material to impart a pH of 10.5–12.5 to the solution.

7. A method of photographic reproduction which comprises exposing an unhardened gelatin-silver halide photosensitive emulsion layer to a two-tone subject, developing in the presence of a tanning developing agent and treating with a composition essentially consisting of an aqueous solution of an alkali metal salt of paratoluene sulfonic acid, a polyethylene glycol containing up to 6 carbon atoms per molecule and sufficient alkaline material to impart a pH of 10.5–12.5 to the solution, thereby giving a hardened colloid image and leaving substantially unhardened colloid in the remaining area of the emulsion layer, pressing the emulsion layer while moist against a sheet having an absorbent surface to cause only said unhardened colloid portion of the layer to adhere to said sheet and separating said sheet and said emulsion layer whereby only a stratum of the unhardened colloid portion of said layer is transferred to said sheet.

8. A method of photographic reproduction which comprises exposing an unhardened gelatin-silver halide photosensitive emulsion layer to a two-tone subject, developing in the presence of a tanning developing agent and treating with an aqueous solution essentially consisting of potassium paratoluene sulfonate, potassium carbonate, potassium hydroxide and tetraethylene glycol, thereby giving a hardened colloid image and leaving substantially unhardened colloid in the remaining area of the emulsion layer, pressing the emulsion layer while moist against a sheet having an absorbent surface to cause only said unhardened colloid portion of the layer to adhere to said sheet and separating said sheet and said emulsion layer

whereby only a stratum of the unhardened colloid portion of said layer is transferred to said sheet.

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