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PROCESS FOR THE REGENERATION OF FIXING PHOTOGRAPHIC SOLUTION

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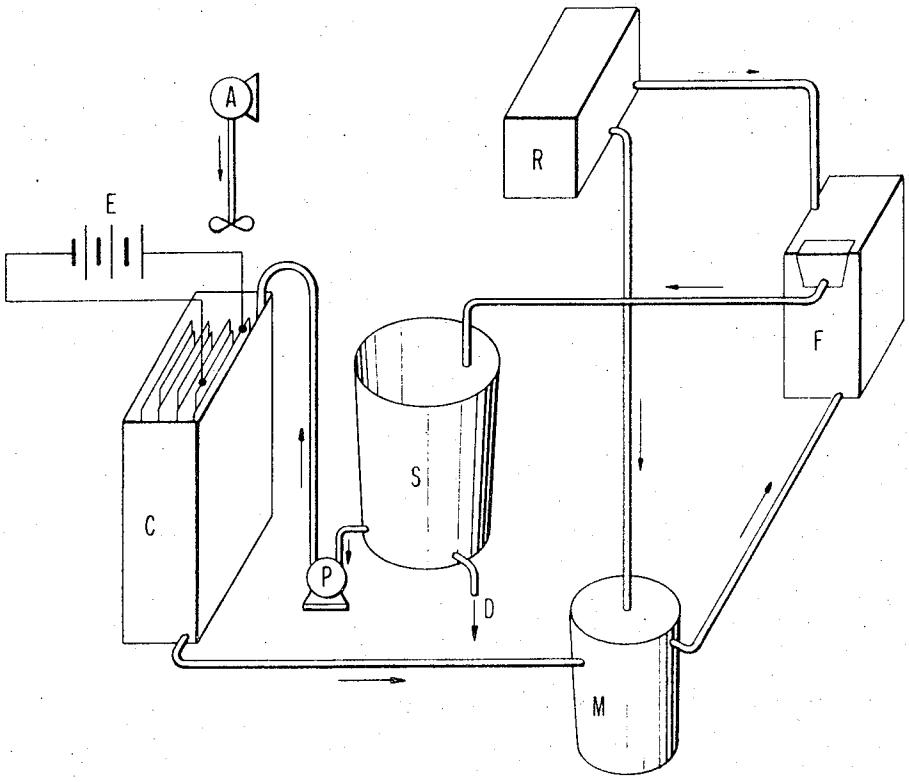

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PROCESS FOR THE REGENERATION OF FIXING PHOTOGRAPHIC SOLUTION

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ABSTRACT OF THE DISCLOSURE

A process for the regeneration of a photographic fixing solution comprising contacting the used fixing solution containing dissolved silver with a polyethylene glycol or derivative thereof and electrolyzing the thus contacted fixing solution to recover the silver is disclosed.

BACKGROUND OF THE INVENTION

(1) Field of the invention

This invention relates to a process for regenerating a photographic fixing solution used in the processing of photographic silver halide light-sensitive materials and to a process for using the fixing solution thus generated repeatedly.

(2) Description of the prior art

In general, to obtain photographic images from silver halide light-sensitive materials, the silver halide light-sensitive material are exposed and developed, whereby the exposed silver halide is reduced to form silver images. Then, after the unexposed silver halide is dissolved away using a fixing treatment, the developed silver images remain on the processed materials. In color development of color photographic light-sensitive materials, the exposed silver halide is reduced with the formation of a dye image but the reduced silver is oxidized and converted into a silver salt in a bleaching step. Then the silver salt is dissolved away in the subsequent fixing step.

In both cases, the remaining silver salt is dissolved away in a fixing bath with sodium thiosulfate. The step is shown by the following reaction.

$$AgX + n Na_2S_2O_3 \rightarrow Ag(S_2O_3)_n^{+2n} + 2n Na^+ + X^-$$

wherein n is believed to be 2 or 3 and X represents a halogen atom.

Accordingly, during the fixation of photographic materials the silver salt and the halide gradually accumulate and the content of free thiosulfate decreases in the fixing solution.

With the increase of such accumulations, the activity of the fixing solution is reduced gradually causing a so-called "exhaustion of fixing solution" and in the extreme case the silver salt is not removed and insufficient fixing results.

Because the exhausted fixing solution contains silver complex salts, it is economically quite profitable to recover silver from the fixing solution using either a chemical method or an electrolytic method. Heretofore, a chemical recovery method has generally been employed but when the recovery of silver in the fixing solution is conducted using an electrolytic method, the thiosulfate bonded to the silver ions is liberated forming free ions. Therefore, the employment of the electrolytic recovery method has the advantages that the fixing solution recovers its fixing activity and can be used repeatedly. However, with repeated use of the fixing solution, the properties of the fixing solution are reduced gradually although the concentration of the free thiosulfate is sufficiently high.

Thus, the fixing rate is lowered and insufficient fixation results. Consequently, even employing the electrolytic recovery method, there is a limit in repeating the use of the fixing solution. In general, because the electrolytic recovery of silver from a fixing solution requires a large cost for the equipment used in the electrolysis and the electric power used, it is important to attempt an economical use of the fixing solution by increasing the number of recycled uses of the fixing solution. For the purpose, it is economically quite profitable to prevent the fixing solution from being deteriorated during the repeated electrolysis and reuse.

An object of the present invention is to provide an economical electrolytic recovery process by preventing the deterioration of a fixing solution during the repeated uses thereof and increasing the number of repeated uses.

SUMMARY OF THE INVENTION

The inventors have discovered that when an exhausted or deteriorated fixing solution, the activity of which cannot be recovered by electrolytic methods, is treated with polyethylene glycol or a derivative thereof, the activity of the fixing solution can be recovered and can be used again as a fresh fixing solution and the economical repeated use of the fixing solution thus regenerated is possible.

Polyethylene glycols which can be effectively used in this invention are polyethylene glycol and the nonionic, aninonic and cationic derivatives thereof, having a molecular weight for the polyoxyethylene chain of greater than 400, preferably greater than 1,000, and having good solubility in or good swelling characteristics by water. For example, the following various kinds of compounds can be used in this invention.

If the molecular weight in polyoxyethylene chain of polyethylene glycol or its derivatives is less than 400, the effect of the invention is not obtained. As the molecular weight increases, the better the effect obtained. Therefore, the upper limit of the molecular weight is not limited. For example, polyethylene glycols having a molecular weight of 500,000 have been prepared.

(I) Nonionic compounds

(1) Polyethylene glycol having a molecular weight of greater than 400

Suitable examples are Carbowax 1540, Carbowax 4000, and Carbowax 1200, made by the Union Carbide and Carbon Chemical Corp., U.S.A. For example, Carbowax 1540 has an average molecular weight of from 1300 to 1600, a specific gravity of 1.15 and a solidifying temperature of from 43 to 46° C.

(2) Polyethylene glycol methyl phenyl ether having a molecular weight of greater than 500

For example, one having a polymerization degree of 50 or 25 in the polyoxyethylene chain is made by Nippon Emulsion K. K., Japan.

(3) Polyoxyethylene alkyl ether

Suitable examples are polyoxyethylene lauryl ether (HLB 9.5) made by Atlas Co., U.S.A. and polyoxyethylene lauryl ether having a polymerization degree of 20 in the oxyethylene group, polyoxyethylene oleyl ether having a polymerization degree of 50 in the oxyethylene group, and polyoxyethylene octyl ether having a polymerization of 50, each made by Nippon Emulsion K. K.

(4) Polyoxyethylene nonyl phenyl ether

For example, one having a polymerization degree of 50, 40 or 30 is made by Nippon Emulsion K. K.

(5) Polyoxyethylene sorbitan ester

Suitable examples are polyoxyethylene sorbitan monooleate (HLB 15.0), polyoxyethylene sorbitan mono-

stearate (HLB 14.9) which are made by the Atlas Co., and polyoxyethylene sorbitan monolaurate having polymerization degree of 30 or 50 made by Nippon Emulsion K. K.

(6) Polyoxyethylene polyoxypropylene block polymer

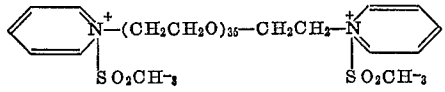
Suitable examples are Pluorinics L–61, L–62, L–64, L–68 and L–75, which are made by Wyandotte, U.S.A.

(7) Polyoxyethylene alkyl ester

Suitable examples are polyoxyethylene monostearate (HLB 17.9) made by the Atlas Co., polyoxyethylene dilaurate having a polymerization degree of about 23 made by Nippon Yuski, K.K., Japan, and polyoxyethylene monolaurate having a polymerization degree of 50 made by Nippon Emulsion K.K.

(II) Cationic compounds

(8) Polyoxyethylene bispyridinium methane sulfonate



This compound can be produced by the process described in the specification of U.S. Patent No. 2,950,970.

(III) Anionic compounds

(9) Polyethoxyethyl bissulfuric acid

$$HO_3S—O(CH_2CH_2O)_{35}—SO_3H$$

The above compound can be produced by the process described in the specification of British Patent No. 859,632.

DESCRIPTION OF THE ACCOMPANYING DRAWING

The process of this invention will now be explained by reference to the accompanyin drawing, in which an embodiment of a system for practicing the process of this invention is shown.

DETAILED DECCRIPTION OF THE ACCOMPANING DRAWING

The drawing illustrates a fixing solution circulating system of a large-scale developing machine equipped with an electrolytic recovery means. As shown in the drawing, overflowing liquid from a fixing solution tank (F) of the developing machine is collected in a storage tank (S) and then sent, by means of a pump (P), to an electrolytic cell (C), in which the fixing solution is electrolyzed by an electric current applied to the electrodes from an electric source (E) while stirred by means of an agitator (A) to deposit the silver thus electrolyzed. The desilvered fixing solution is sent back to the fixing solution tank (A) of the developing machine through a stock tank (M) and is used repeatedly. To avoid many difficulties occurring due to the deterioration of the fixing solution, an appropriate proportion of the solution can, if necessary, be discharged through a drain (D) and at the same time a fresh fixing solution can be supplied from a tank (R).

The system illustrated in the drawing is only one example and the application of this invention is not limited to this system. Practically, the process of this invention can also be applied to simpler systems having neither a storage tank nor a stock tank, a system without a tank (R) for supplying a fresh fixing solution, and a system having two or more stock tanks. The simpler systems, however, are basically the same as shown in the drawing. As a more simplified example, a system composed of a fixing tank equipped with the electrodes for conducting the electrolysis may be employed. Also, a portable electrolytic unit may be used for a small-scale developing machine.

DETAILED DESCRIPTION OF THE INVENTION

The treatment of fixing solution with polyethylene glycols according to the process of this invention can be conducted in various manners.

According to one embodiment of the process, a bag of a semipermeable membrane containing one or more of the polyethylene glycols is suspended in the storage tank of the above-described system. The fixing solution in the storage tank enters into the bag of the semipermeable membrane, wherein the fixing solution recovers its fixing activity due to the contact with polyethylene glycols in the bag, and then returns to the developing machine through a circulating system for reuse. The bag of the semipermeable membrane can be effectively used not only in the storage tank but also in the electrolytic cell, the stock tank or the fixing solution tank or in any other part of the system.

In another embodiment of the process, a filtering means is provided to a portion of the circulating system for the fixing solution, e.g., to an inlet or an outlet of the electrolytic cell. A semipermeable membrane is used as a filter for the filtering means and polyethylene glycol or a derivative thereof is placed in the filtering means between the filters of the semipermeable membrane. If necessary, a pump may be attached to the filtering means to force the circulating solution through the filtering means.

The semipermeable membrane contributes to the maintenance of the polyethylene glycol or derivative thereof inside the membrane and permits the fixing solution to flow freely through the membrane to the inside thereof to contact the fixing solution with the polyethylene glycols within the membrane. Suitable such semipermeable membranes are a cellophane sheet or a vesica of an ox or a pig can be used.

Due to the contact of the fixing solution with the polyethylene glycols as described above, the deterioration of the fixing solution can be prevented and thus the fixing solution recovers its activity sufficiently after removing the silver therefrom and the fixing solution can be used repeatedly whereby the amount of the fresh replenisher can be markedly reduced.

The amount of polyethylene glycol or derivative thereof to be used depends upon the circulation speed of the fixing solution and the manner of contacting the fixing solution and polyethylene glycol or derivative thereof. Generally speaking, the larger the amount used, the greater the effect thereof.

For example, when 1,000 feet/day of 16 mm. photographic film was processed in a developing machine having a fixing solution tank of 100 liters in volume, the fixing solution was repeatedly used for about 100 days by recycling it through the electrolytic silver recovery unit equipped with a container bag containing 1 kg. of the polyethylene glycol while the amount of replenishment was reduced to the minimum needed to keep the tank level. In the use of the polyethylene glycols, contacting the fixing solution with polyethylene glycol continuously is effective and when the polyethylene glycol is contacted with the fixing solution intermittently utilizing the standing period of development, the amount of polyethylene glycols necessary for effecting the process of this invention is increased.

If the polyethylene glycols lose their reactivating power due to their use for a long period of time, they are replaced with fresh polyethylene glycols.

The process for regenerating the fixing solution of this invention may be applied widely in developing laboratories. Thus, the process of this invention may be employed either in developing laboratories operating on a large scale in which several developing machines are operated simultaneously and a large amount of a fixing solution is used and is circulated through all of the developing machines or in developing laboratories operating on a smaller scale in which small developing machines and portable-type electrolytic means are used and the regeneration of the exhausted fixing solution by electrolysis is conducted overnight or over the weekend.

The process of this invention is applicable to the fixing solutions used with various light-sensitive materials such as color photographic light-sensitive materials, black and white photographic materials, cinematic films, amateur cinematic films, and X-ray photographic films. In particular, the process of this invention most effectively is applied to fixing solutions used in the fixing of a photographic material having a high-sensitive silver iodobromide emulsion layer.

The invention will be described in greater detail by reference to the following examples.

EXAMPLE 1

Using a developing machine for 16 mm. cinematic color photographic reversal films, 56 EK-type Cine Strip Machine (made by PAKO Corporation), about 10,000 feet per week of the film was developed and the silver in the fixing solution used in the process was recovered using a portable small-scale electrolytic means, Ropak 10-type silver recovering machine (made by PAKO Corporation) during the stands and the fixing solution thus regenerated was used repeatedly. During the process, the total amount of the fixing solution was maintained at a constant level by replenishing just the loss by carry-over (no overflow).

The fixing speed for the films in the fixing tank shown by the time required for making the film transparent (the clearing time), was 25 seconds at the beginning of the operation, but reached 50 seconds after 10 days, and became 70 seconds after 20 days. Finally, the adverse influences of the deterioration of the fixing solution on the qualities of the photographic images obtained due to the development were observed.

Thus, when the electrolysis was conducted at the rest of the development while a cellophane bag containing 1 kg. of polyethylene glycol having a molecular weight of about 6,000 and reinforced by a nylon net was immersed in the fixing solution tank, the speed of fixing was greatly reduced. That is, the clearing time was 30 seconds after 10 days from the starting of the operation, 40 seconds after 20 days, and the generation and the reuse of the fixing solution could be continued for a long period of time yet securing sufficiently good quality for the developed products. In addition, the efficiency in the recovery of silver was not reduced.

EXAMPLE 2

When the same procedure as in Example 1 was followed using a block polymer of polyethylene glycol and polypropylene glycol, Pluoronic L–62 (made by Wyandotte Co.), instead of the polyethylene glycol used in Example 1, the regeneration and the reuse of the fixing solution could be conducted for a long period of time as in Example 1.

EXAMPLE 3

The apparatus used in Example 1 was equipped with a storage tank to conduct the electrolytic recovery of silver when the developing processor was operated. In this apparatus, the system was so set that when the concentration of silver became higher than 0.9 g./liter in the fixing solution, the electrolysis started. A semi-permeable membrane bag containing 2 kg. of polyethylene glycol methylphenyl ether having a molecular weight of about 2,200 was immersed in the storage tank.

When the polyethylene glycol derivative was not used, the deterioration of the qualities of the photographic images finished by the developing process was observed after the operation of about 20 days, but when the polyethylene glycol derivative was used as above according to the present invention no difficulties occurred after 30 days from initiation.

What is claimed is:

1. In a process for the regeneration of a spent photographic thiosulfate fixing solution containing dissolved silver comprising electrolyzing the fixing solution and recovering the silver formed, the improvement which comprises adding to the spent fixing solution a polyethylene glycol or a derivative thereof prior to, or during electrolysis,

said polyethylene glycol or derivative having a polyoxyethylene chain having a molecular weight greater than 400.

2. The process according to claim **1**, wherein said polyethylene glycol derivative is selected from the group consisting of a polyethylene glycol methyl phenyl ether, a polyoxyethylene alkyl ether, a polyoxyethylene nonyl phenyl ether, a polyoxyethylene sorbitan ester, a polyoxyethylenepolyoxypropylene block polymer, a polyoxyethylene alkyl ester, a polyoxyethylene bispyridinium sulfonate, and a polyethoxyethyl bissulfuric acid.

3. The process according to claim **1**, wherein the contacting of the fixing solution and the polyethylene glycol or derivative thereof is conducted by the passage of the solution through a semipermeable membrane.

4. A process for the regeneration of a photographic fixing solution containing dissolved silver comprising contacting a fixing solution used in a photographic developing process with a polyethylene glycol or a derivative thereof; electrolyzing the thus contacted fixing solution and recovering the silver formed; and reusing the thus electrolyzed fixing solution in a photographic developing process.

5. The process of claim **4**, wherein said polyethylene glycol or a derivative thereof is contacted with the fixing solution by passage of the solution through a semi-permeable membrane.

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