

1

3,379,528

ACTIVATOR SOLUTION REJUVENATION

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This invention concerns activators for use with the photographic process known as the colloid transfer process.

In the colloid transfer process, an image in soft adhesive organic colloid is formed photographically and a discrete stratum of the image is transferred to a receiving sheet to provide a reproduction of the subject. The process is described in the Yutzy et al. U.S. Patents 2,596,756, granted May 3, 1952 and 2,716,059, granted Aug. 23, 1955, and embodies the exposure to a subject of a substantially unhardened gelatin silver halide emulsion layer which may contain a gelatin tanning silver halide developing agent as well as a non-tanning silver halide developing agent. These patents are incorporated herein by reference.

Upon activation of the exposed gelatin emulsion with the alkaline solution in the presence of the developing agent or agents, tanning development of the most exposed regions of the emulsion corresponding to the highlights of the subject proceeds, although some development of the less exposed regions also takes place to provide visual density for the transferred image, as explained in more detail in U.S. Patent 2,716,059. Thereafter, the developed emulsion is placed into contact with an absorbent receiving sheet such as paper to cause the less exposed regions, and thus the less developed regions, of the emulsion to adhere to the receiving sheet. Subsequently, when the emulsion on the matrix sheet and receiving sheet are separated, a stratum of the less exposed regions of the emulsion remains on the receiving sheet and appears as a positive silver image of the original subject.

The colloid transfer process has been used extensively for office copying purposes and it has been desirable to provide activator solutions for processing the exposed silver halide emulsion. Various activator solutions have been disclosed in the following U.S. patents: Yackel, 2,596,754; Yutzy et al., 2,596,756; Yutzy et al., 2,725,298; Yutzy et al., 2,739,890; Clark et al., 2,763,553; Cowden et al., 2,835,575; Kendall, 2,852,371; Chain et al., 2,865,745, etc.

In addition, the following U.S. patent applications also disclose activator solutions for use in the colloid transfer process: Fruchard et al., U.S. Ser. No. 242,526, filed Sept. 5, 1962; Cowden, U.S. Ser. No. 310,897, filed Sept. 23, 1963, and Yost, U.S. Ser. No. 227,562, filed Oct. 1, 1962.

Colloid transfer activator baths, in general, are alkaline solutions which serve to activate the developer contained in the silver halide emulsion. However, various improvements over the basic alkaline solution have been made. For instance, certain activator solutions desensitize the emulsion for roomlight handling, reduce the tendency for salts to crystallize out of the solution, incorporate gelatin hardeners, improve the temperature latitude, and the like.

All activator solutions have reduced usefulness following the activation of a number of matrices containing the silver halide emulsion and it has been desirable to find a method of replenishing the activator solutions with a universal replenisher which would essentially restore the solution to working strength without the necessity of discarding the complete solution and replacing with fresh activator. Therefore, it has been desirable to find a replenisher which would preserve the particular characteristics of the activator solution, for example, temperature latitude, gelatin softening, or the like, but which would permit satisfactory use of the activator for a larger number of ma-

2

trices than has customarily been possible. It has also been desirable to provide ease of replenishing the activator so that after a certain number of matrices have been processed, a predetermined amount of replenisher is added.

We have discovered a method of replenishing used activator solution using lithium hydroxide coated matrix sheets or coated sheets which can be packaged in a predetermined manner with the sensitive matrix sheets.

One object of this invention is to provide a method of replenishing a used or depleted activator solution. Another object is to provide a process of packaging colloid transfer matrices with a replenishing agent for the activator solution. An additional object is to provide interleaving sheets which can be used to replenish an alkaline activator solution which would raise the pH to that found in the fresh activator solution. Additional objects will be apparent from the following specification.

Lithium hydroxide is used as the alkaline material as an alkali which is compatible with all activator solutions. A particularly useful form of the lithium hydroxide is as its monohydrate. Sufficient lithium hydroxide is added to restore the activator to about its original pH. In a useful embodiment, the lithium hydroxide is coated onto a separate sheet of paper in a suitable binder.

The coated sheet is immersed in the activator solution for a time sufficient to remove at least half of the lithium hydroxide by dissolving it into the activator solution.

Any of the common binders used in photographic products can be used, such as proteins, for example, gelatin, casein, zein, etc.; cellulose ethers, e.g. methylcellulose, carboxymethylcellulose, hydroxyethylcellulose, etc.; water permeable polymeric materials, e.g. copoly ethylacrylate acrylic acid, polyvinyl alcohol, etc. It will be understood that the binder is not critical provided it is of water permeable material. In a particularly useful embodiment of the invention, a solution of lithium hydroxide in a binder is coated on a paper support in sufficient amount to contain at least 0.5 gram per square foot in the dried coating.

The following examples are intended to illustrate our invention but not to limit it in any way:

Example 1

A liquid activator having the following formula

Potassium carbonate	g./l.	40.0
Ethylenediamine tetraacetic acid, sodium salt	g./l.	4.5
p-Toluenesulfonic acid (monohydrate)	g./l.	15.0
Potassium hydroxide, dilute solution to neutralize acid, then to pH=11.0.		

was exhausted by using 200 matrices, making three copies per matrix. After every fifteen matrices, an 8½ inch by 11 inch sheet containing approximately one gram lithium hydroxide per square foot was soaked for 60 seconds, and the bath solution was maintained with the activator diluted 2:1. Satisfactory copies were obtained.

Example 2

A liquid activator having the following components was prepared:

Potassium carbonate	g./l.	40.0
Ethylenediamine tetraacetic acid, sodium salt	g./l.	4.5
Diethylene glycol	cc./l.	40.0
p-Toluenesulfonic acid, (monohydrate)	g./l.	10.0
Potassium hydroxide, dilute solution to neutralize acid, then to pH=11.0.		

This formula was exhausted by using to process 1000 matrices, making one copy per matrix, with approximately

225 single copy colloid transfer matrices, letter size. The remainder were colloid transfer multiple copy, letter size, and were used to make three copies per matrix. After an average of 16 matrices, 8½ by 11 inch sheets containing approximately one gram lithium hydroxide per square foot were soaked in the activator for 60 seconds. The solution level was maintained with undiluted fresh activator. A total of 62 interleaving sheets and 7080 cc. (including the 1800 cc. starting volume) of activator were employed in this example.

The quality of the copy obtained with the activation time range of 10 to 20 seconds was maintained throughout the testing period. The number of legible multiple copies increased slightly and there was no sign of image "bleeding," on either the single copy or multiple copy material. Maximum reflection density of the first copy was 0.81 in the fresh activator and 0.76 after 1000 sheets. The almost negligible drop in quality during the last several hundred sheets of the exhaustion test indicated that the composition of the bath reached equilibrium and copy could be made indefinitely. Each matrix sheet comprised a polyethylene coated paper support having thereon an unhardened colloid silver halide emulsion containing a colloid hardening silver halide developer and a non-hardening silver halide developer.

Example 3

Anhydrous lithium hydroxide (450 grams) was dissolved in 4500 cc. of solution which contained 5% methylcellulose in 30% dimethylformamide and 70% ethylene chloride. This composition was coated on a polyethylene coated support and the solvent evaporated to leave a coverage of about 0.6 gram of lithium hydroxide per square foot as determined by conventional titration procedures. The coatings were used as described in Example 1.

Example 4

To 1500 ml. of a 9.1% solution of the sodium salt of copoly (ethylacrylate-acrylic acid) at 40° C., there was added 27.4 ml. of a 17% solution of the sodium salt of oleylmethyltaurine and 6.9 ml. of 2-methyl-2,4-pentandiol. Next 137 grams of powdered anhydrous lithium hydroxide was added slowly with vigorous stirring. Stirring was continued until the lithium hydroxide was dissolved. Distilled water was then added to a total volume of 2000 ml.

Example 5

The activity of the liquid activator, similar to that of Example 1, was maintained by affixing a small amount of lithium hydroxide to each matrix processed. Strips of lithium hydroxide coating prepared according to Example 1 were cut to ¾ inch by 8½ inches and attached to the reverse side of a colloid transfer matrix. The coating contained 0.68 gram of available lithium hydroxide per square foot. One hundred of these modified matrices were processed normally in the activator, making three copies per matrix. At the end of this test, the pH of the activator had dropped from 10.95 to 10.85 and copy quality and latitude remained excellent. A similar test without the lithium hydroxide strip on each matrix, showed the drop to be from 11.0 to 10.35, at which point an acceptable copy was no longer available.

Example 6

Efforts were made to substitute other alkaline materials for lithium hydroxide. However, when sodium, potassium or ammonium hydroxide were used, they were found to be unsuitable due to their hygroscopic nature. Weaker alkaline materials, such as sodium carbonate or sodium phosphate, were also found to be unsuitable, since they either failed to maintain a sufficiently high pH or resulted in excessive salt content.

Lithium hydroxide can be suspended satisfactorily in gelatin or similar colloid materials and coated on a suit-

able material to be used as interleaving sheets, these sheets can be packaged with silver halide emulsions in proportions that closely compensate for the amount of silver halide developed. They form a convenient, automatic means of activator rejuvenation, since introduction of the sheets into the bath at appropriate intervals will maintain the proper pH throughout the life of the bath.

In an alternative method, the lithium hydroxide can be coated on each matrix sheet in an amount of at least about 0.001 gram per square foot matrix sheet, so that it acts to replenish the activator solution at the same time that the exposed emulsion is being processed. In this particular embodiment, the coating could also be only on certain matrix sheets with the amount of lithium hydroxide coated in a larger amount per square foot. Preferably, the amount of lithium hydroxide added to the activator should be at least enough to neutralize the amount of acid released by the silver halide emulsion. Since the frequency of addition and the nature of the activator may vary, the useful amount per square foot may vary from about 0.01 to 4.0 grams per square foot or about 0.02 to 8.0 g./liter of activator solution. The pH may also vary depending upon the activator.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. A colloid transfer matrix comprising a support having thereon a substantially unhardened silver halide emulsion containing a tanning type silver halide developer and having on at least one side of the support, a coating containing at least about 0.01 gram per square foot of lithium hydroxide.

2. A method of photographic reproduction comprising developing an exposed substantially non-hardened gelatino silver halide emulsion layer on a support, said emulsion being not harder than a gelatin layer containing 0.7 gram of formaldehyde per pound of gelatin freshly coated, and containing a gelatin tanning silver halide developing agent and a substantially non-tanning silver halide developing agent and having on the reverse side of the support a coating containing at least 0.01 gram per square foot of lithium hydroxide, by activating the silver halide emulsion with an alkaline activating solution to obtain a hardened gelatin and silver image in the areas of the emulsion layer corresponding to the highlights of the subject and substantially unhardened gelatin, silver and silver halide in the areas of the emulsion layer corresponding to the shadows of the subject, said developing being such as to prevent any substantial tanning of the emulsion layer in said areas corresponding to the shadows of the subject, placing a sheet having an absorbent surface against said emulsion layer while said emulsion layer is moist to cause only the shadow areas of the emulsion layer to transfer only a stratum of said shadow areas of the emulsion layer to said sheet.

3. A method of photographic reproduction comprising developing an exposed substantially non-hardened gelatino silver halide emulsion layer on a support, said emulsion being not harder than a gelatin layer containing 0.7 gram of formaldehyde per pound of gelatin freshly coated, and containing a gelatin tanning silver halide developing agent and a substantially non-tanning silver halide developing agent and having on at least one side of the support a coating containing at least sufficient lithium hydroxide to add to the solution at least 0.02 to 8.0 g./liter during the development period, by activating the silver halide emulsion with an alkaline activating solution to obtain a hardened gelatin and silver image in the areas of the emulsion layer corresponding to the highlights of the subject and substantially unhardened gelatin, silver and silver halide in the areas of the emulsion layer corresponding to

5

the shadows of the subject, said developing being such as to prevent any substantially tanning of the emulsion layer in said areas corresponding to the shadows of the subject, placing a sheet having an absorbent surface against said emulsion layer while said emulsion layer is moist to cause only the shadow areas of the emulsion layer to transfer only a stratum of said shadow areas of the emulsion layer to said sheet.

4. A colloid transfer matrix as in claim 1 wherein said coating contains at least sufficient lithium hydroxide to neutralize the halogen acid formed by reducing the silver halide in the emulsion.

5

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6

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