

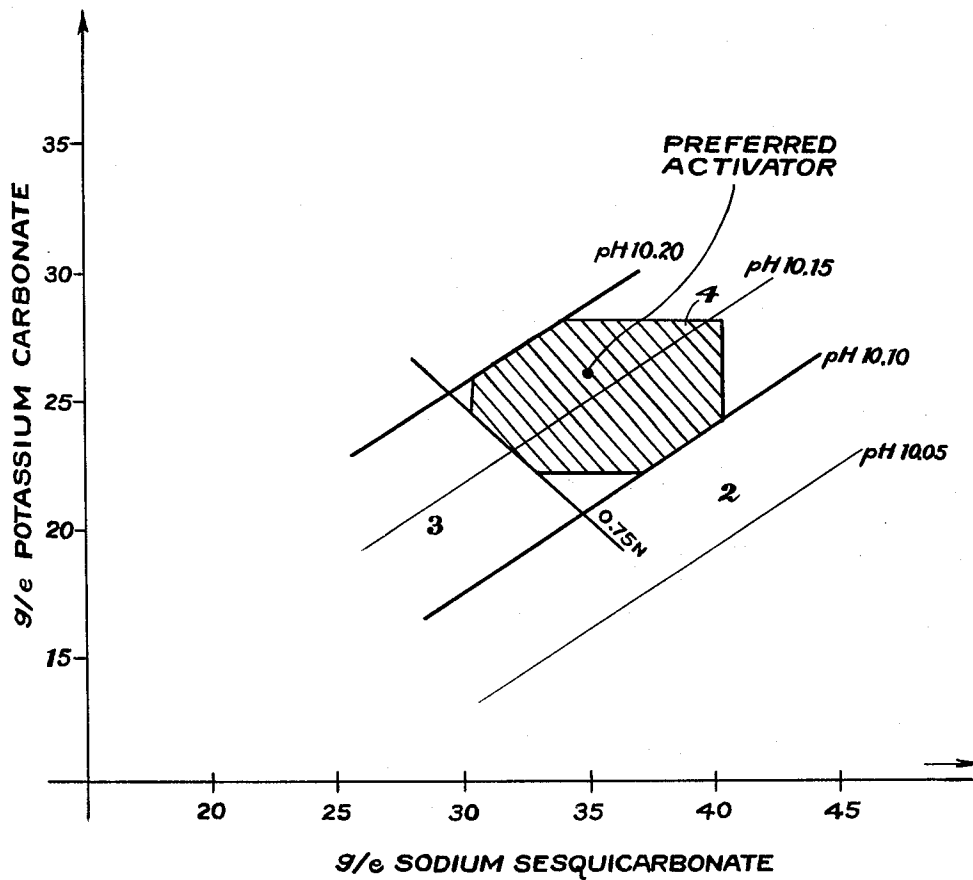
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COLLOID TRANSFER PROCESS AND ACTIVATOR SOLUTION THEREFOR

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1

3,148,060

## COLLOID TRANSFER PROCESS AND ACTIVATOR SOLUTION THEREFOR

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This invention relates to a process in photography wherein 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, known as the Colloid Transfer Process.

A typical colloid transfer process is described in the Yutzy et al. U.S. Patents 2,596,756, issued May 3, 1952, and 2,716,059, issued August 23, 1955. These patents disclose processes which embody the exposure to a subject of a substantially unhardened gelatino-silver halide emulsion layer which may contain a gelatin tanning silver halide developing agent as well as a nontanning silver halide developing agent. Upon activation of the exposed emulsion with an alkaline solution in the presence of the developing agent or agents, tanning development of the more exposed regions of the emulsion takes place corresponding to the highlights of the subject, 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. 2,716,059, above.

The developed emulsion is pressed 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 a receiving sheet. Subsequently, when the emulsion and receiving sheet are separated, a stratum of the less exposed regions of the emulsion remains on the sheet and appears as a positive image of the original subject.

The alkaline solution which has been used for activation of the exposed emulsion layer has contained a gelatin softening agent to facilitate transfer of the less exposed portions of the emulsion to the receiving sheet. Urea and certain other gelatin softening agents have been suggested for this purpose. In addition, sodium carbonate has been suggested as an alkaline component of the alkaline solution used for initiating development of the exposed emulsion.

Inasmuch as the colloid transfer system is used extensively for making copies in business offices, it has been desirable to have an activator solution which would have a long life and which would be active satisfactorily near the depletion point. Moreover, the activator should have a relatively long temperature range during which several copies can be made from a single matrix or emulsion and the activator should be free from crystallization in the tray used for immersing the matrix to initiate development. It has also been desirable to have an activator solution which would result in a large number of copies being formed than have previously been obtainable.

Inasmuch as the success of the Colloid Transfer Process depends upon a differential hardening of the emulsion layer, it is desirable to avoid either too rapid hardening or too slow hardening. However, in attempting to reach a satisfactory equilibrium of the hardening-softening rate, it has been necessary to also consider the other factors referred to above of activator life, temperature range, and salt crystallization.

In some instances the very first masters treated in a new bath are not quite sufficiently hardened after 20 seconds of activation and, accordingly, show an excessive tendency to adhere to the copying paper, particularly if

2

the surface of the latter is not perfectly smooth. This usually decreases after treatment of three or four masters and disappears after about fifteen masters.

We have discovered an activator solution which has a moderate pH and which maintains a desirable hardening-softening equilibrium but which is free from the tendency to crystallization in the activator trays and which produces satisfactory results at temperatures above room temperature.

One object of this invention is to provide an improved activator solution for use with the colloid transfer process. An additional object is to provide an activator solution which will enable several copies to be made from a colloid transfer emulsion at temperatures as high as 88° F., as well as at room temperature. Another object is to provide an activator which can be prepared in powder form which is easy to dissolve and forms a solution which has no tendency to crystallization. A further object is to provide an activator which has a moderate pH and which promotes a desirable hardening-softening equilibrium. A still further object is to provide an activator which has the desirable tanning-softening equilibrium which does not tend to crystallize in the trays and which gives optimum results when first used.

The activator according to our invention is an aqueous solution of sodium sesquicarbonate, potassium carbonate, and urea. Advantageously, it contains in addition, a sequestering agent such as the tetrasodium salt of ethylenediamine tetraacetic acid, trisodium aminotriacetate, or the like, and also a small quantity of alkaline or alkaline earth chloride.

In the accompanying diagram is shown the concentration of sodium sesquicarbonate (plotted on the X axis) and potassium carbonate (plotted on the Y axis) in the activator solution. In the area under consideration, the proportions giving constant pH values are substantially on parallel straight lines.

The diagram has been divided into 4 areas according to the working characteristics of the activator. Area 1 shows that a pH higher than 10.20 is too favorable to hardening. Area 2 shows that a pH lower than 10.10 (for a fresh activator) reduces the development too much and prolongs the activating time when the bath is half exhausted. Area 3 shows that for a pH between 10.10 and 10.20 a total alkalinity lower than 0.7500 N renders insufficient the number of emulsion coated matrix sheets that can be treated with a given volume of solution. Area 4 is the preferred working area. The hatched area shows the relatively narrow concentration which corresponds to the concentration of the activator of this invention.

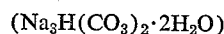
The above objects are attained by mixing sodium sesquicarbonate, potassium carbonate, urea and a sequestering agent such as the sodium salt of ethylenediamine tetraacetic acid or trisodium aminotriacetate.

The following is my preferred embodiment:

	Grams/liter
Sodium sesquicarbonate	35
Potassium carbonate	26
Urea	26
Trisodium aminotriacetate	1
Water to make one liter.	

This activator solution has a pH of about 10.10 to 10.20. The proportions may be varied from 30-40 g./l. sodium sesquicarbonate, 22-28 g./l. potassium carbonate, 20-30 g./l. urea, and 1.0-5.0 g./l. sequestering agent.

Instead of sodium sesquicarbonate



an equivalent molar mixture of sodium carbonate and sodium bicarbonate with 2 mols of water may be used

( $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ ), and is intended to be within the scope of the term sodium sesquicarbonate as used herein.

A small quantity of alkaline or alkaline earth chloride added to the above activator solution improves the development, the tanning and the reproduction of the emulsion. When the activator is used according to the invention, with the addition of the chloride, a perfect balance of tanning and of softening is obtained for the normal activation of 20 seconds. This avoids the tendency for the first matrices treated in a fresh activator to be tanned insufficiently after 20 seconds of activation causing excessive adhesion to the receiver sheet, especially when the surface is not perfectly smooth.

The action of the chloride ions, at a small concentration, on the tanning has not been actually completely explained. However, for the concentrations used according to the invention comprising between 0.2 g./liter to 3 g./liter no notable decrease of the sensitivity of the matrices treated in this modified activator results. Instead there is obtained a reduced sensitivity to under exposure.

Substitution for the chloride by an equivalent quantity of bromide, results in retardation of development and diminution of photographic sensitivity of the matrices. A small quantity of iodide such as potassium iodide is practically without effect. It is thus evident that the chloride ions are critical in this particular application.

#### Example 1

A substantially unhardened gelatino silver halide emulsion (having a hardness as defined in the above patents) is prepared as described in U.S. Patent 2,716,059, above, containing a mixture of tanning and substantially nontanning silver halide developing agents such as 4-phenol catechol and 4-methoxy- $\alpha$ -naphthol. The emulsion is coated on a paper support and dried. The resultant sensitive element is then exposed to a two-tone subject (a line or half-tone subject) if desired by reflex methods and placed in the following alkaline solution of the invention to initiate development.

	Grams
Sodium sesquicarbonate -----	60
Potassium carbonate -----	50
Urea -----	50
Trisodium amino triacetate -----	2
Water to make $\frac{1}{2}$ U.S. gallon.	

While development in the above alkaline solution is proceeding, light should be excluded to the extent required by the particular silver halide present in the emulsion. With daylight working emulsions, limited exposure to room lights may be given during the exposure and development steps. Other emulsions may require the use of the usual safelights during the exposure and processing steps.

When the proper amount of exposure has been given, gelatin tanning silver halide development occurs principally in the highly exposed areas of the emulsion and little or no tanning development in the other areas. When development is complete as determined by trial with the particular emulsion and conditions of operation in use, the sensitive element is pressed into contact with an absorbent sheet such as paper by means of a squeegee blade or rollers. Immediately thereafter, the sensitive element and receiving sheet are separated leaving a stratum of the less exposed and thus less hardened regions of the emulsion adhered to the receiving sheet. The result is a positive line or half-tone silver containing image affixed to the sheet. If desired, the transfer operation may be repeated a number of times by merely rewetting the sensitive element with the alkaline solution and squeegeeing to a fresh reception sheet.

The reception sheet for the colloid transfer process is advantageously prepared as described in the Chan et al. U.S. Patent 2,865,745, issued December 23, 1958, comprising a paper sheet on the surface of which is a mixture

of an intensifying agent such as thiourea and a development suppressing agent such as sodium formaldehyde bisulfite.

#### Example 2

An activator solution was prepared as in above Example 1 with the omission of potassium carbonate. The solution exposed to the air was found to form crystals in the activator container due to evaporation. When an activator solution was prepared as in Example 1 with the omission of the sodium sesquicarbonate, it was found that the hardening of the emulsion was more rapid than the softening and that only about half as many copies could be made with the same matrix as using the activator solution of Example 1. It was also found that a pH higher than a 10.20 resulted in faster hardening action than softening and a diminution of the number of copies obtained.

#### Example 3

An identical emulsion to that of Example 1 is exposed to an original and immersed during 20 seconds in an activator of the following composition:

	G.
Sodium sesquicarbonate -----	35
Potassium carbonate -----	26
Urea -----	26
Sodiumaminotriacetate -----	1
Sodium chloride -----	0.5
Water to make 1 liter.	

Copies are obtained of optimum quality although in the absence of sodium chloride, the first matrices treated in the new bath need to be exposed for a longer time (about 10%) than the matrices treated in the used activator.

#### Example 4

Replacing the sodium chloride used in Example 3 by an equal part of potassium chloride also provides satisfactory results.

#### Example 5

Replacing the sodium chloride used in Example 3 with an equal part of sodium bromide or potassium bromide results in a necessary increase by 10 to 20% in the duration of exposure of the matrices and three times the duration of development in order to obtain satisfactory copies.

#### Example 6

Replacing the sodium chloride used in Example 3 with potassium iodide in an amount of 0.1-0.4 g./liter results in no difference than when the activator is used without the halide.

#### Example 7

Addition to the activator of large quantity of alkaline halide, for example more than 5 g./liter, for the chloride or the bromide or more than 1.0 g./liter of iodide, impairs the satisfactory operation of the process of reproduction.

#### Example 8

Replacing the sodium chloride in the activator of Example 3 with alkaline earth chloride, such as calcium chloride, requires increase in the amount of sequestering agent. By this means the addition of calcium chloride in the amount of 0.5 g./liter produces the same effects as sodium chloride.

The quantity of urea may be varied from that given in the above formula depending upon the requirements of the particular emulsion used in the process and the conditions of operation such as temperature, less urea being required at higher operating temperatures. Thus, while the emulsion should have a maximum hardness of the order mentioned by the above patents corresponding to a gelatin layer containing about 0.7 gram of dry formaldehyde per pound of gelatin freshly coated, more or less urea is required at different operating temperatures.

In a preferred embodiment of the invention, the gelatin tanning and nontanning developing agents are present

5

in the emulsion. However, either or both developing agents may be present in the alkaline solution and the other in the emulsion. A very useful combination of developing agents is 4-phenylcatechol with 4-methoxy- $\alpha$ -naphthol. Since the latter is self-coupling, it forms a colored compound during developing which contributes density to the print. Other useful tanning and nontanning silver halide developing agents are disclosed by the above patents.

The invention has been described in detail with particular reference to preferred embodiment 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 method of photographic reproduction which comprises developing an exposed, substantially unhardened gelatino-silver halide emulsion layer, said emulsion not being harder than a gelatin layer containing 0.7 gram of formaldehyde per pound of gelatin freshly coated, with an aqueous solution having a pH of 10.10 to 10.20 and an alkalinity of above 0.7500 N, consisting essentially of water, 22-28 grams per liter potassium carbonate, 30-40 grams per liter sodium sesquicarbonate, 20-30 grams per liter urea and 0.2 to 3.0 grams per liter of a chloride selected from the class consisting of ammonium chloride, alkali metal chlorides and alkaline earth chlorides, in the presence of both a gelatin tanning silver halide developing agent and a substantially nontanning silver halide developing agent to obtain a hardened gelatin and silver image in the areas of the emulsion layer corresponding to the highlights of the subject, and subsequently unhardened gelatin, silver and silver halide in the areas of the emulsion layer corresponding to the shadows of the subject, said development being such as to prevent any substantial tanning of the emulsion layer in said areas corresponding to the shadows of the subject, pressing 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 to adhere to the sheet, and separating the emulsion layer to transfer only a stratum of said shadow areas of the emulsion layer to said sheet.

2. The process of claim 1 wherein the gelatin tanning silver halide developing agent and the substantially nontanning silver halide developing agent are present in the emulsion layer before exposure.

3. A method of photographic reproduction which comprises developing an exposed, substantially unhardened gelatino-silver halide emulsion layer, said emulsion not being harder than a gelatin layer containing 0.7 gram of formaldehyde per pound of gelatin freshly coated, with an aqueous solution having a pH of 10.10 to 10.20 and an alkalinity of above 0.7500 N, consisting essentially of water, 22-28 grams per liter potassium carbonate, 30-40 grams per liter sodium sesquicarbonate, 1.0-5.0 grams per liter sequestering agent, 20-30 grams per liter urea and 0.2 to 3.0 grams per liter of a chloride selected from the class consisting of ammonium chloride, alkali metal chlorides and alkaline earth chlorides, in the presence of both a gelatin tanning silver halide developing agent and a substantially nontanning silver halide developing agent to obtain a hardened gelatin and silver image in the areas of the emulsion layer corresponding to the highlights of the subject, and subsequently unhardened gelatin, silver and silver halide in the areas of the emulsion layer corresponding to the shadows of the subject, said development being such as to prevent any substantial tanning of the emulsion layer in said areas corresponding to the shadows of the subject, pressing 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 to adhere to the sheet, and separating the emulsion layer to transfer only a stratum of said shadow areas of the emulsion layer to said sheet.

6

4. The process of claim 3 wherein the gelatin tanning silver halide developing agent and the substantially nontanning silver halide developing agent are present in the emulsion layer before exposure.

5. A method of photographic reproduction which comprises developing an exposed, substantially unhardened gelatino-silver halide emulsion layer, said emulsion not being harder than a gelatin layer containing 0.7 gram of formaldehyde per pound of gelatin freshly coated, with an aqueous solution having a pH of 10.10 to 10.20 and an alkalinity of above 0.7500 N, consisting essentially of water, 22-28 grams per liter potassium carbonate, 30-40 grams per liter sodium sesquicarbonate, 20-30 grams per liter urea and 0.2 to 3.0 grams per liter of a chloride selected from the class consisting of ammonium chloride, alkali metal chlorides and alkaline earth chlorides, in the presence of a gelatin tanning silver halide developing agent to obtain a hardened gelatin and silver image in the areas of the emulsion layer corresponding to the highlights of the subject, and subsequently unhardened gelatin, silver and silver halide in the areas of the emulsion layer corresponding to the shadows of the subject, said development being such as to prevent any substantial tanning of the emulsion layer in said areas corresponding to the shadows of the subject, pressing 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 to adhere to the sheet, and separating the emulsion layer to transfer only a stratum of said shadow areas of the emulsion layer to said sheet.

6. The process of claim 5 wherein the gelatin tanning silver halide developing agent is present in the emulsion layer before exposure.

7. A method of photographic reproduction which comprises developing an exposed, substantially unhardened gelatino-silver halide emulsion layer, said emulsion not being harder than a gelatin layer containing 0.7 gram of formaldehyde per pound of gelatin freshly coated, with an aqueous solution having a pH of 10.10 to 10.20 and an alkalinity of above 0.7500 N, consisting essentially of water, 22-28 grams per liter potassium carbonate, 30-40 grams per liter sodium sesquicarbonate, 1.0-5.0 grams per liter sequestering agent, 20-30 grams per liter urea and 0.2 to 3.0 grams per liter of a chloride selected from the class consisting of ammonium chloride, alkali metal chlorides and alkaline earth chlorides, in the presence of a gelatin tanning silver halide developing agent to obtain a hardened gelatin and silver image in the areas of the emulsion layer corresponding to the highlights of the subject, and subsequently unhardened gelatin, silver and silver halide in the areas of the emulsion layer corresponding to the shadows of the subject, said development being such as to prevent any substantial tanning of the emulsion layer in said areas corresponding to the shadows of the subject, pressing 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 to adhere to the sheet, and separating the emulsion layer to transfer only a stratum of said shadow areas of the emulsion layer to said sheet.

8. The process of claim 7 wherein the gelatin tanning silver halide developing agent is present in the emulsion layer before exposure.

9. An activator solution for use in the photographic gelatino-silver halide colloid transfer process consisting essentially of an aqueous solution having a pH of 10.10 to 10.20 and an alkalinity of above 0.7500 N, containing 30-40 grams per liter sodium sesquicarbonate, 22-28 grams per liter potassium carbonate, 0.2 to 3.0 grams per liter chloride selected from the class consisting of ammonium chloride, alkali metal chlorides and alkaline earth chlorides and 30-30 grams per liter urea.

10. An activator solution for use in the photographic gelatino-silver halide colloid transfer process consisting essentially of an aqueous solution having a pH of 10.10

to 10.20 and an alkalinity of about 0.7500 N, containing 30-40 grams per liter sodium sesquicarbonate, 22-28 grams per liter potassium carbonate, 20-30 grams per liter urea, 0.2 to 3.0 grams per liter chloride selected from the class consisting of ammonium chloride, alkali metal chlorides and alkaline earth chlorides and 1.0-5.0 grams per liter sequestering agent.

5

References Cited in the file of this patent

UNITED STATES PATENTS

2,716,059	Yutzy et al. -----	Aug. 23, 1955
2,843,485	Yutzy et al. -----	July 15, 1958
2,865,745	Chan et al. -----	Dec. 23, 1958
3,043,687	Linge -----	July 10, 1962
3,043,688	Weyerts et al. -----	July 10, 1962