MULTILAYERED PHOTOGRAPHIC PROCESSING WEB

FIG. 1

FIG. 1a

FIG. 1b

FIG. 1c

FIG. 1d

FIG. 1e

INVENTOR:

ELMER S. BORNEMISZA

ATTORNEY.
MULTILAYERED PHOTOGRAPHIC PROCESSING WEB

Filed April 28, 1967

POLYMER, DEVELOPER
ACETAMIDE
POLYMER, ALKALI
ACETAMIDE
POLYMER, FIXER
SUPPORT

DEVELOPER, ALKALI
POLYMER, FIXER
ACETAMIDE
SUPPORT

INVENTOR.
ELMER S. BORNE

ATTORNEY.
MULTILAYERED PHOTOGRAPHIC PROCESSING WEB

Elmer S. Bornemisza, 36 Main St., Roslyn, N.Y. 11576
Filed Apr. 28, 1967, Ser. No. 641,727
(Filed under Rule 47(b) and 35 U.S.C. 118)
Int. Cl. G03c 5/24, 5/26, 5/38
U.S. Cl. 96—50

9 Claims

ABSTRACT OF THE DISCLOSURE

A photoprocessing web in which developing and stabilizing agents are separated by an amide-soluble organic polymer barrier, the web including an amide having a melting point of about 40°-95° C. which when heated to liquefaction, dissolves the polymer barrier thereby releasing the agents.

This invention relates to photography, and more particularly to photoprocessing webs incorporating developing and stabilizing agents and to a process for the development and stabilization of exposed photographic emulsions.

At the present time, images are developed on photographic recording media, such as paper coated with a photosensitive silver halide emulsion, by exposing the emulsion to a light image or signal and therefor dipping, spraying or coating the emulsion and paper with a liquid alkaline solution of developer which brings out the photographic image. Usually, the record is made permanent by subsequent treatment with a stabilizer solution. Thus, a two-step treatment with liquid solutions is required which is relatively time-consuming and the developer solution must usually be carefully stored.

One-step methods have been proposed which call for the incorporation of developing and stabilizing agents into the photographic recording medium. Invariably an alkali (which term hereinafter will be used to signify a material capable of providing alkalinity) is associated with and triggers the developing agent. Such systems suffer from short shelf life due to a reduction in stability of the silver halide layer, pre-reaction of the developer and silver halide, high sensitivity to moisture and reaction of the developing agent with the stabilizing agent. Close control over development and fixing is very difficult. Attempts to mitigate the above deficiencies by separating the silver halide, developer and/or stabilizer layers with interlayers of gelatin or other material have not been entirely satisfactory. Excessively high temperatures are needed to effectively join the separated reagents and effective control of the performance of the reagents is lacking.

In other one-step methods, dry development of the recording medium has been proposed by incorporating the developing and stabilizing reagents in a gel web. The intimacy of the reagents causes such "monoweb" to have a short shelf life.

It is an object of this invention to provide a one-step method of developing and fixing a silver halide recording medium. It is another object to provide such a method utilizing a dry process. It is still another object to provide a monoweb for developing and stabilizing a recording medium wherein there is a separation of developer and stabilizer, which separation is readily eliminated during processing. Other and further objects, features and advantages of this invention will become apparent from the following description thereof.

The above and other objects are accomplished by provision of a web for use in photographic processing comprising a sheet support on which has been deposited a fixing agent, a developing agent, a barrier material separating the fixing agent from the developing agent, and a barrier-dissolving material which liquefies when heated to dissolve a substantial portion of the barrier material.

The web is utilized by bringing it into contact with an exposed silver halide emulsion, the developing agent diffusing to the silver halide emulsion to develop an image thereon. If the developing agent is in a top layer, diffusion to the silver halide layer may be accomplished without heat. Very shortly thereafter, the web is heated to liquefy the barrier-dissolving material which dissolves the barrier material sufficiently to allow fixing agent to diffuse to the silver halide emulsion and fix the developed image. If the developing agent is not in a top layer, then both developing agent and fixing agent are concurrently released by heat to diffuse to the silver halide layer. Thus, a dry process is provided whereby a monoweb having a long shelf life can be used to develop and fix a silver halide emulsion. The term "dry" is used here to denote the state of the materials just prior to and after development and stabilization and the fact that it is not wet in the sense of prior aqueous systems.

The barrier material is such as to allow effective separation of the fixing and developing agents and yet is sufficiently soluble in the liquefied barrier-dissolving material so as to be effectively removed as a separation when moderate heat is applied. In general, it is preferred that the barrier material be an organic polymer. Examples of suitable polymers include acrylics, such as polycrylic acid, and polymers of methacrylic and ethacrylic acid, polycrylic acid copolymers and modified polycrylic amides; vinyls, such as polyvinyl alcohol, polyvinyl acetate, modified vinyl methyl ethers and maleic anhydride polymers; natural resins, such as shellac; proteins, such as zein and casein plastic; and mixtures thereof.

The barrier-dissolving material is preferably an organic material that is solid at room temperature and somewhat above, e.g., about 40° C., so as to be storable yet can be liquefied at moderate temperatures, e.g., up to about 95° C., so as to function without adversely affecting the silver halide emulsion. In general, any organic material that has a melting point of between about 40 and about 95° C. and which is stable when liquid in that temperature range can be used. It is preferred to use amides and their derivatives as such materials are generally more effective in dissolving the polymeric barrier material. Examples of suitable amides, and derivatives thereof, include acetamide, diacetamide, triacetamide, p-chloroacetylacetanilide, p-ethoxyacetanilide, N-acetylmethylendiamine, N-acetylbenzylamine, o-chloroacetanilide, o-acetophenidide, o-acetanilide, N-methyl-o-acetotoluamide, N-methyl-N(4-tolyl)-acetic acid amide, N-phenyl-N-propylacetic acid amide, m-acetotoluidide, and the like. Acetamide is particularly preferred as it is readily available and particularly effective.

The above and other aspects of the invention will be more fully understood from the following description taken in conjunction with the accompanying drawings in which:

FIGS. 1–1g are schematic sectional elevations of eight embodiments of this invention;

FIG. 2 is a schematic diagram of an apparatus for
developing and stabilizing a silver halide emulsion in accordance with a process of this invention; and FIG. 3 is an enlarged view taken along line 3--3 of FIG. 2.

Referring to FIG. 1, a support 10, which may be paper, cloth or other art-known web support, is covered on one side with a first layer 11 which may be any conventional silver halide fixer (stabilizer), in this case sodium thiosulfate. Layer 11 also includes acetamide as a barrier-dissolving material as discussed above. A layer 12 of polymeric barrier material, in this case an 80:20 copolymer of acrylic acid and ethyl acrylate, is disposed on top of layer 11. A layer 13 of alkali, in this case diethanolamine, is disposed on top of polymeric layer 12. Another polymeric layer 14 which may be the same or different from layer 12, but in this case is the same, is disposed upon alkali layer 13. A layer 15 of developer, which may be any conventional type, in this case hydroquinone, is disposed on layer 14. Layer 15 also includes a barrier-dissolving material which can be the same or different than the material in layer 11, but in this case is the same and is acetamide.

In preparing the monoweb shown in FIG. 1, hot liquid acetamide, containing the fixer dispersed or dissolved therein, e.g., in about 10 weight percent, is applied to the support 10 and allowed to cool and solidify. A preformed sheet of polymer can be applied with moderate pressure to form layer 12. The alkali is then coated as layer 13 over polymer layer 12 and polymer layer 14 coated thereon. Alternatively, a sandwich of polymer-alkali-polymer can be applied to the fixer-acetamide layer 11. Finally, the developer and acetamide, e.g., in about equal proportions, can be applied by pressure contact to the polymer 14.

For developing agents, suitable materials that can be used include catechol, hydroquinone, toluidinequinone, o-chlorohydroquinone, o-bromohydroquinone, 4-phenyl catechol, 4-butyly catechol, pyrogallol, 4-butylypyrogallop, nordihydroguaiaretic acid, 4,5-dibromocatechol, 3,5,6-trihydroxy-4-phenylcatechol and 1-phenyl-3-(N-ox yhexyleav- boxamine) - 4 - r-(B-hydroxyquinolyethyl)-phenylazo]-5- pyrazolone, acorbic acid, Phenidone B, Metol, and the like, and mixtures thereof. Developers such as Amidosol (2,4-diaminophenol hydrochloride) which do not require the presence of alkali to develop an image, may also be used. In this latter case, alkali may be omitted from the web. It may also be advantageous to add an auxiliary developing agent such as monomethyl-p-amino phenol or a 3-pyrazolidone, which appear to act synergistically in combination with a primary developer.

For fixers, suitable materials that can be used include thioureas, such as sodium thiourea, ammonium thiosulfate, and potassium thiosulfate; thiocyanates, such as ammonia, sodium and potassium thiocyanates; other thio derivatives, such as thiourea and thiazole; and the like, and mixtures thereof.

For alkali, suitable materials that can be used include organic alkalis such as 1,3-propanediolamine, diethanolamine, and the like; and inorganic alkalis such as sodium hydrosulfite, potassium hydrosulfite, sodium carbonate, sodium, dextrose, casein, and the like, and mixtures thereof.

Rather than applying the acetamide, fixer, alkali and/or developer as such, these materials may be applied dissolved or dispersed in a conventional water-carrying organic colloid, e.g., gelatin. In this procedure, a solution of gelatin containing fixer and acetamide is coated on support 10 and solidified as layer 11. Polymer layer 12 is applied as before followed by alkali layer 13 also dispersed or dissolved in the gelatin. Polymer layer 14 is applied as before and a final layer of gelatin containing developer and acetamide is applied thereon as layer 15.

Other gelling agents may be used and suitable materials include gelatin, agar, polyvinyl alcohol, polyhydric alcohol (e.g., ethylene glycol, glycerol, polyethylene glycol, such as Dow Polyglycol P-400, E-1450, and the like) methylcellulose, sodium alginate, dextrin, locust bean gum, dextrose, casein, and the like, and mixtures thereof.

Other materials known to the art can be added to the gelling agent to improve various aspects of the web. Such materials include wetting agents such as Aerosol OS and OT, Nacconal NK, Nekal BA-75, Duponol ME, Spans, Tweenes, and the like and can be added in an amount up to about 0.5 percent of the weight of the gelling agent. Fog reducers such as potassium bromide and Kodak Antifog 1 case in quantities up to 1% of the weight of the gelling agent.

A water releasing agent can also be added to the web preferably in association with the developer, fixer and/or alkali. Such agents include hydrated salts as are known to the art and adsorbent material such as porous, crystalline sodium or calcium aluminum silicates which contain bound water that is released only on heating. Suitable specific agents include Glauber salt, borax, sodium triphosphate, sodium metasilicate, sodium alginate or sugar.

The developer, fixer and alkali are in amounts sufficient to perform their functions, with the particular silver halide emulsion to be used and the amounts are well known in the art. The organic barrier or polymer-dissolving material is present in about 5 to 100 weight percent or more of the amount of the polymer. The thickness of the layers and support shown in FIG. 1, as well as in the other figures, are not to scale, and will, of course, vary depending on the materials used.

To illustrate the use of the webs of this invention reference is made to FIGS. 2 and 3. A schematic diagram of an apparatus for developing and stabilizing one type of silver halide recording paper that can be used in this invention, a continuous silver halide recording paper, is shown in FIG. 2. An image is focused by lens system 91 on the silver halide emulsion side of a continuous strip of recording paper 90 which moves from a supply roller 92 over guide roller 93. Then strip 90 moves through light-tight opening 94, over guide roller 95 and thereupon, the acetamide of layer 11 liquefies and dissolves the developer and acetamide layer. The dissolved developer and acetamide make the strip more electrically conductive to the incoming image which is then written on the strip. The strip is then dried and the process is repeated.

The reagent side of a continuous web 106, e.g., of FIG. 1, from supply roller 107 passes over guide roller 108, is pressed firmly against the recording strip 90 by the surface of heatable drum 96 and endless belt 110 which passes around pressure rollers 111, 112, 113, 114 and 115. Web 106 then separates from recording strip 90 after leaving drum 96, passes over guide roller 116 and is taken up on the web take up roller 117. Endless belt 110 can optionally include a heating element (not shown). FIG. 3 is an enlarged view taken on line 3--3 of FIG. 2 and shows web 106 in contact with the emulsion side 118 of recording strip 90 and the drum 96 in contact with the recording medium support paper 119. The web 106 is that of FIG. 1 with web support sheet 10 and layers 11--15. In operation, recording strip 90 moves around drum 96, where heat is applied; e.g., up to about 50°C as required to melt the barrier-dissolving material. In this case, a temperature somewhat below 50°C is applied, since acetamide is being used as the barrier-dissolving material. As recording strip 90 moves on to drum 96, layer 15 of FIG. 1, web 106, contains polymer aceta mide, contacts the silver halide emulsion 118 of recording strip 90. The layers are compressed by endless belt 110 by means of pressure rollers 111--115. The acetamide of layer 15 liquefies and dissolves polymer layer 14 whereupon alkali and developer diffuse to the silver halide emulsion 118 to develop the image thereon. Concurrently, or shortly thereafter, the acetamide of layer 11 liquefies and dis-
solves polymer layer 12 whereby the fixer of layer 11 diffuses to the silver halide emulsion 118 and stabilizes the developed image. Upon leaving the drum 96, the aceta-
mide cools and solidifies on web 106, web 106 being taken up by take up roller 117. Recording strip 90 moves over guide rollers 97, 99 and 100 and is taken up by take up roller 102. The developed and stabilized image can be viewed through window 101 thereafter stored for later reference on take up roller 102. The take up rollers 102 and 117 pull the recording strip 90 and web 106 through the above stages by means of a synchronized drive mecha-
nism (not shown).

The objectives of this invention are obtained by the separation of developer and stabilizer and, optionally, the separation of developer and alkali. A single polymer layer can be used with developer and alkali together in one layer or in separate layers; or the alkali may be located in the polymer layer. Similarly, developer can be located in a polymer layer, alone or with alkali. The fixer may be located in a polymer layer, alone or with alkali. The aceta-
mide, or other barrier or polymer-dissolving material, can be in more than one layer as in FIG. 1 or can be located in one layer, alone or together with developer, with alkali, with developer and alkali, or with the fixer. Regardless of the arrangement of the developer, it is preferred that the developer be in such physical position that it contacts the silver halide emulsion prior to, or at least concurrently with, contact of the stabilizer with the silver halide.

The polymer can separate developer and fixer by its physical presence as a layer or by separately encapsulating the developer and stabilizer. In this latter case, separate encapsulated developer and stabilizer may be located in one polymer layer and both released simultaneously by dissolving the polymer layer with liquefied acetamide or other barrier-dissolving material.

In the arrangement shown in FIG. 1a, a support 20 is covered on one side with a layer 21 which, in turn, is covered by a polymer layer 22 covered, in turn, by a layer 23 of developer, alkali and acetamide, which layer 23 may be contained in gelatin or other like material. The developer can be any of the developing materials men-
tioned above, e.g., catechol, which may be combined with an equal amount of a synergist such as monomethyl p-
amino phenol.

In the embodiment of FIG. 1b, a support 30 is covered on one side with a polymer layer 31 which layer 31 also contains a fixer such as sodium thiosulfate. Layer 31 is covered with an alkali layer 32 which also contains acet-
amide and a polymer 33 is covered with a layer 34 which can be incorporated in gelatin containing a hydrated salt which releases water on the application of heat, such as sodium alginate.

In the arrangement shown in FIG. 1c, a support 40 is covered on one side with a layer 41 of fixer which, in turn, is covered with a layer 42 of polymer. The polymer layer 42 also contains alkali dispersed therein and is covered with a layer 43 of developer and acetamide.

In the embodiment of FIG. 1d, a support 50 is covered on one side with a layer 51 of fixer and acetamide which, in turn, is covered with a layer 52 of polymer which, in turn, is covered with a layer 53 of developer and alkali.

In the embodiments of FIGS. 1-1d, the uppermost lay-
er containing developer, can be contained in a water carrying organic colloid such as gelatin which can act as a physical carrier and protector for the developer and other reagents as well as a means for incorporating ancillary materials into the above.

In the arrangement shown in FIG. 1a, a support 60 is covered on one side with a layer 61 of polymer which has fixer dispersed therein. Layer 61 is coated with a layer 62 of acetamide which, in turn, is covered with a polymer layer 63 which also contains developer and alkali. A polymer layer 70 is covered on one side by a layer 71 of polymer which also contains fixer dispersed therein and is, in turn, covered by a layer 72 of acetamide, followed by a layer 73 of polymer which also contains alkali dispersed therein, followed by a layer 74 of acetamide and finally by a layer 75 of polymer which also contains developer dispersed therein.

In FIGS. 1e and 1f, the developer is dispersed or dis-
solved in the soluble polymer which acts not only to sepa-
rate it from the fixer but also to physically protect and support it and other ancillary agents.

In the arrangement shown in FIG. 1g, a support 80 is covered on one side with a layer 81 of acetamide which, in turn, is covered with a layer 82 of polymer which con-
tains a fixer dispersed therein. Layer 82 is covered with a layer 83 of developer and alkali which is dispersed in gelatin, as optional in FIGS. 1-1d. Alternatively, the uppermost surfaces 15, 23, 33, 43, 53, and 83 of FIGS. 1-1d and 1g can optionally be covered with a thin film of gelatin or of polymer as a sealing layer. A sealing layer protects the uppermost layer prior to use and prevents ambient reaction.

Arrangements of the layers other than above can read-
ily be envisioned. However, it will be appreciated that a permutation of the various combinations of layers that can be used will unnecessarily burden this disclosure and not add significantly to the above descriptions; one skilled in the art can devise other arrangements which will fulfill the objectives of this invention. All of the embodiments of FIGS. 1a through 1g can be used in the same manner as the embodiment of FIG. 1. Other arrangements will now be apparent to those skilled in the art and changes may be made by those skilled in the art without departing from the spirit of the invention.

I claim:

1. A web for use in photographic processing compris-
ing a support on which has been deposited a fixing agent, a developing agent, an amide-soluble organic polymer as a barrier material interposed between the fixing agent and the developing agent, said barrier material being coated as a layer on said support and a barrier-dissolving component which is solid at room temperature and which when heated to its melting point forms a liquid to dissolve a substantial portion of the barrier material, said barrier-
dissolving component being coated as another layer on said support and comprising an amide having a melting point of about 40-95° C., said developing agent and fixing agent being relatively disposed on said support whereby said developing agent is released concurrently with or prior to said fixing agent.

2. The web of claim 1 wherein said barrier-dissolving component is a layer 75 of a polymer.

3. A web for use in photographic processing compris-
ing a support on which has been deposited a layer of fixing agent having a barrier-dissolving component asso-
ciated therewith, said barrier-dissolving component compr-
isng an amide having a melting point of about 40°-95° C., a layer of developing agent and an amide-soluble organic polymer as a barrier material layer between said developing agent layer and said fixing agent layer, the barrier-dissolving component being solid at room temperature and when heated to its melting point forming a liquid to dissolve a substantial portion of the barrier ma-
terial, said developing agent and fixing agent being rela-
tively disposed on said support whereby said developing agent is released concurrently with or prior to said fixing agent.

4. The web of claim 3 containing alkali.

5. The web of claim 4 wherein said alkali is separated from the fixing agent by the barrier material.

6. The web of claim 5 containing an additional layer of barrier material separating the developer from the alkali.

7. The web of claim 6 wherein said developer layer additionally contains, as a component, an amide having a melting point of about 40°-95° C.

8. The web of claim 7 wherein said barrier-dissolving component, in each case, acetamide.
9. A process for treating an exposed photographic recording medium which comprises contacting said recording medium with the reagent side of the web of claim 1 and heating said web to the melting point of said barrier-dissolving component whereby to liquefy the barrier-dissolving component.

References Cited

UNITED STATES PATENTS

<table>
<thead>
<tr>
<th>Patent Number</th>
<th>Date</th>
<th>Inventor(s)</th>
<th>Class</th>
</tr>
</thead>
<tbody>
<tr>
<td>3,041,952</td>
<td>7/1962</td>
<td>Schreck</td>
<td>96—61</td>
</tr>
<tr>
<td>3,179,517</td>
<td>4/1965</td>
<td>Tregillus et al.</td>
<td>96—76</td>
</tr>
</tbody>
</table>

3,236,650 2/1966 Limberger 96—48
3,260,598 7/1966 Yutzy et al. 96—29
3,348,946 10/1967 Jones 96—61
3,438,776 4/1969 Yudelson 96—66
3,413,181 11/1968 Goldhammer et al. 96—76

NORMAN G. TORCHIN, Primary Examiner
M. F. KELLEY, Assistant Examiner

U.S. Cl. X.R. 96—61, 63, 66, 76,