April 27, 1971 E. S. BORNEMISZA 3,576,632

MULTILAYERED PHOTOGRAPHIC PROCESSING WEB

Filed April 28, 1967 2 Sheets-Sheet 1

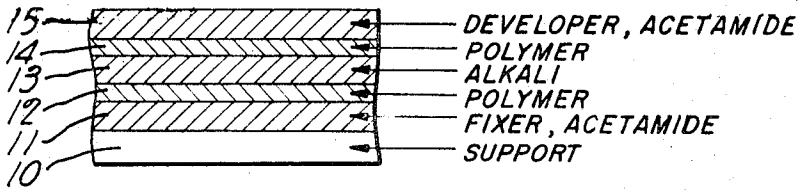


FIG. 1

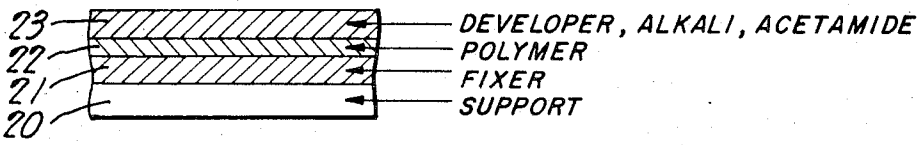


FIG. 1a

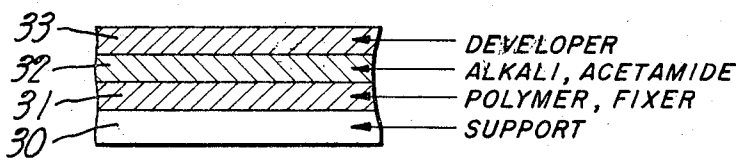


FIG. 1b

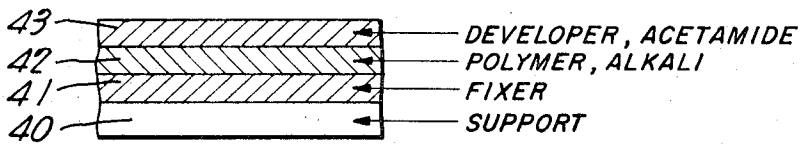


FIG. 1c

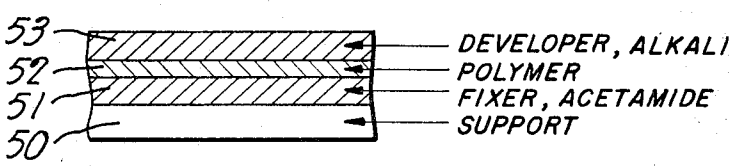


FIG. 1d

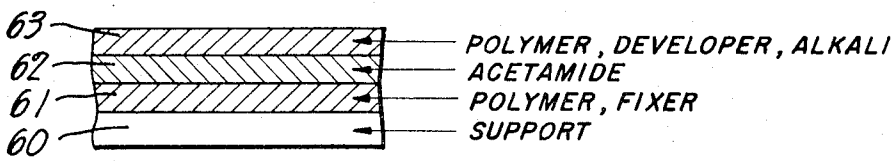


FIG. 1e

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MULTILAYERED PHOTOGRAPHIC PROCESSING WEB

Filed April 28, 1967 2 Sheets-Sheet 2

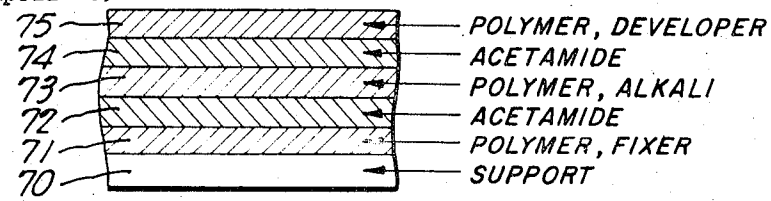


FIG. 1f

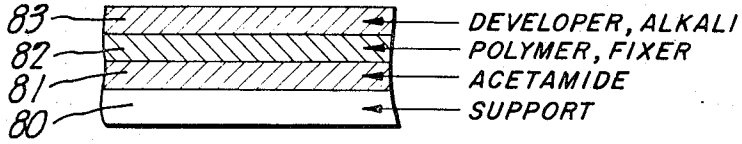


FIG. 1g

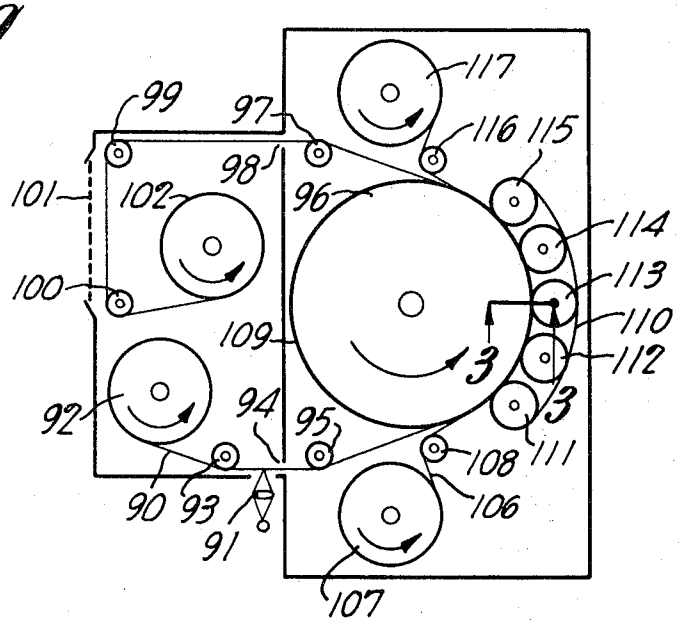


FIG. 2

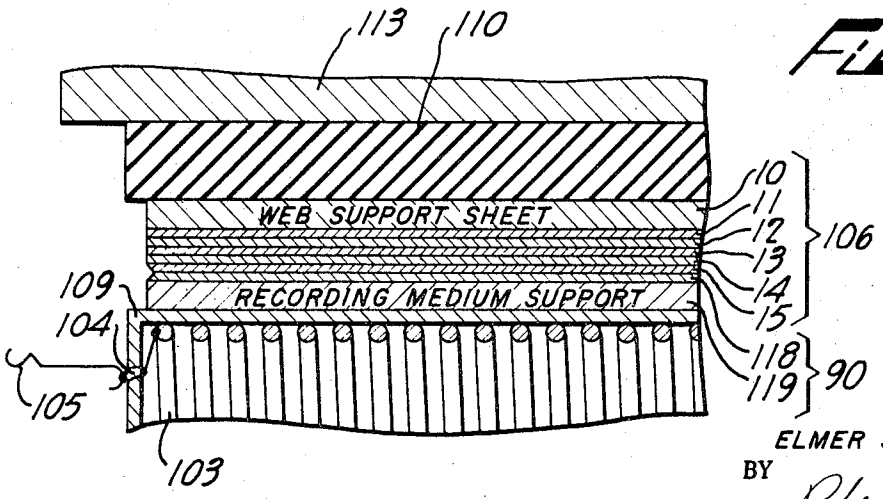


FIG. 3

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3,576,632

Patented Apr. 27, 1971

3,576,632

MULTILAYERED PHOTOGRAPHIC PROCESSING WEB

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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 thereafter 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 "monowebs" 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 polyacrylic acid, and polymers of methacrylic and ethacrylic acid, polyacrylic acid copolymers and modified polyacrylic 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-chloro-acetylacetanilide, p-ethoxydiacetanilide, N-acetylethylenediamine, N-acetylbenzylamine, o-chloroacetanilide, o-acetophenetidide, o-acetaniside, N-methyl-o-acetotoluidide, 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 accompaniying drawings in which:

FIGS. 1–1*g* 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 acetate, 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, toluhydroquinone, o-chlorohydroquinone, o-bromohydroquinone, 4-phenyl catechol, 4-t-butyl catechol, pyrogallol, 4-butylpyrogallol, nordihydroquiauretic acid, 4,5-dibromocatechol, 3,5,6-tribromo-4-phenylcatechol and 1-phenyl-3-(N-n-hexylcarboxamine) - 4 - [p-(B-hydroquinoylethyl)-phenylazo]-5-pyrazolone, ascorbic acid, Phenidone B, Metol, and the like, and mixtures thereof. Developers such as Amidol (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 thiosulfates, such as sodium thiosulfate, 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 alkalies such as 1,3-propanediamine, diethanolamine, and the like; and inorganic alkalies such as sodium hydroxide, potassium hydroxide, sodium carbonate, sodigum, dextrose, casein, and the like, and mixtures thereof.

Rather than applying the acetamide, fixer, alkali and/or developer as such, these reagents 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 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, dextrine, 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, Duponal ME, Spans, Tweens, and the like and can be added in an amount up to about 0.05 percent of the weight of the gelling agent. Fog reducers such as potassium bromide and Kodak Antifog #1 can be added in amounts up to 1% of the weight of the gelling agent.

A water releasing agent can also be added to the web preferably in asociation 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 alumino 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 function with the particular silver halide emulsion to be used and these 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 thence over a rotatable heatable drum **96**, over guide roller **97**, through light-tight opening **98**, over guide rollers **99** and **100**, where it passes beneath view window **101** and is taken up by take up roller **102**. Drum **96** is heated by an internal heating coil **103**, as shown in FIG. 3, supplied with power through ring contacts (of which one, **104**, is shown), which are engaged by brushes (of which one, **105**, is shown), connected to a suitable source of electrical power (not shown).

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 emulsion side of recording strip **90** by the surface **109** 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 95° C. as required to melt the barrier-dissolving material. In this case, a temperature somewhat above 85° 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**, containing developer and acetamide, 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 acetamide 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 mechanism (not shown).

The advantages 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 acetamide, 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 used, 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. 1*a*, a support **20** is covered on one side with a fixer 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 mentioned 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. 1*b*, 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 acetamide. Layer **32** is covered wth a developer layer **33** 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. 1*c*, 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. 1*d*, 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. 1–1*d*, the uppermost layer 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 as described above.

In the arrangement shown in FIG. 1*a*, 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.

In the embodiment of FIG. 1*f*, a support **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. 1*e* and 1*f*, the developer is dispersed or dissolved in the soluble polymer which acts not only to separate it from the fixer but also to physically protect and support it and other ancillary agents.

In the arrangement shown in FIG. 1*g*, 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 contains a fixer dispersed therein. Layer **82** is covered with a layer **83** of developer and alkali which may be contained in gelatin, as optional in FIGS. 1–1*d*. Alternatively, the uppermost surfaces **15**, **23**, **33**, **43**, **53**, and **83** of FIGS. 1–1*d* and 1*g* 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 readily 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. 1*a* through 1*g* 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 comprising 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 acetamide.

3. A web for use in photographic processing comprising a support on which has been deposited a layer of fixing agent having a barrier-dissolving component associated therewith, said barrier-dissolving component comprising 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 betweeen 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 material, 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.

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 barrier-dissolving component, an amide having a melting point of about 40°–95° C.

8. The web of claim **7** wherein said barrier-dissolving component, is 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

3,041,952	7/1962	Schreck	96—61
3,179,517	4/1965	Tregillus et al.	96—76
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

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U.S. Cl. X.R.

96—61, 63, 66, 76,