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3,248,219

PHOTOGRAPHIC ELEMENT FOR DRY PROCESSING

Filed Sept. 6, 1960

FIG_1

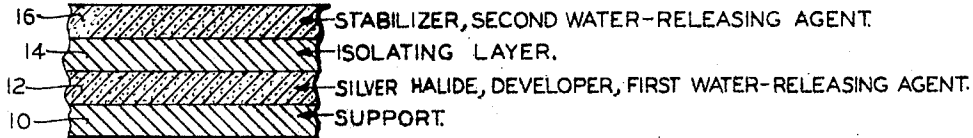


FIG_2

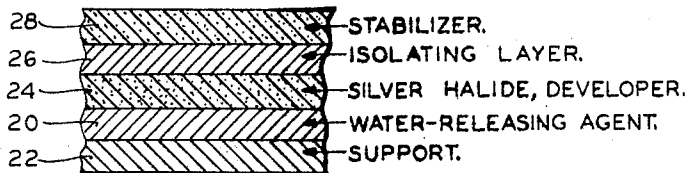


FIG_3

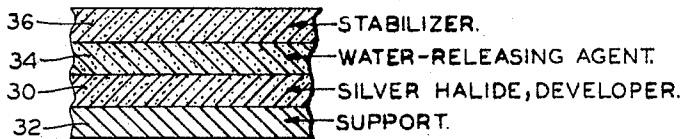


FIG_4

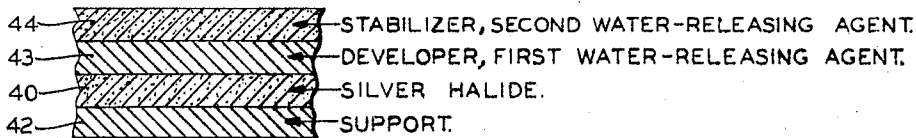
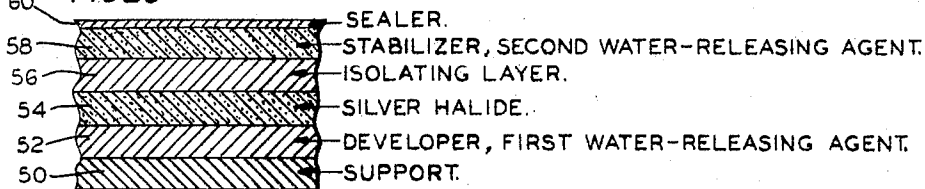


FIG_5



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PHOTOGRAPHIC ELEMENT FOR DRY PROCESSING

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2 Claims. (Cl. 96—76)

This invention, which is a continuation-in-part of my co-pending application Serial No. 777,613, filed December 2, 1958, now abandoned, relates to photography, and more particularly to the dry processing of photosensitive media such as photographic paper.

At the present time, images are developed on photographic record media such as paper coated with a photosensitive emulsion by exposing the emulsion to a light image or signal and thereafter dipping, spraying or coating the emulsion and paper with a liquid solution of developer which brings out the photographic image. Usually, the record is made permanent by subsequent treatment with a stabilizer solution. This requires a two-step treatment with liquid solutions of developer and stabilizer, and is relatively time consuming. Moreover, the developer solution must usually be carefully stored, and usually the entire roll of film is developed at one time.

This invention provides a high speed process for developing and stabilizing photosensitive emulsions without requiring the presence of a liquid developer solution or stabilizer solution, and has great utility where rapid access photography is required because the exposed portion of a film can be developed and examined immediately without exposing or developing the remainder of the film.

In work such as dynamic recording with photographic paper used to record a variable signal, very short access time is desirable. The term "access time" is used to indicate the time interval between the exposure of a photosensitive recording paper to a signal to be recorded and the presentative of the resultant record for visual observation. The terms "photographic paper" and "recording paper" are used throughout the specification and claims to include photosensitive emulsions disposed on any suitable support such as paper, film or other usable medium.

Wind tunnel and flight testing are examples of test procedures wherein rapid access is of considerable value because operational conditions can be changed with greater facility when the test results are recorded and visually observed in a brief, rather than a prolonged, interval of time.

Previously, the conventional photographic recording techniques generally referred to as "oscillography" have involved the exposure of an entire roll of a record paper to the information to be recorded with subsequent and separate chemical development and stabilization of the exposed roll. In the conventional procedure, the record roll of, say, approximately 200–400 feet in length, is entirely exposed before its removal from the recorder, and is subsequently developed by conventional means. This procedure thus represents a rather long access time of minutes, or even hours.

This invention provides a recording medium and a method for developing it in which a light signal can be recorded, developed, stabilized and observed almost immediately, simply by the application of heat to the paper after exposure to the light signal.

Briefly, the invention provides a photographic recording medium which includes a photosensitive material, such as a silver halide emulsion. A dry developing agent, which requires the presence of water to become active, is mixed with or disposed on the emulsion. Mixed with,

or put on, the photographic sensitive emulsion, is a compound which releases water on the application of heat to activate the developing agent. A stabilizing agent, which is activated by the presence of water is also included in the recording medium, and is disposed so that it is activated by the release of water after the activation of the developing agent.

The photographic recording medium is utilized by exposing it to the light image to be recorded, and heating it to release water so that developer is first activated to develop the image, and so the stabilizer is thereafter activated to stabilize the developed image. For example, if the photosensitive material is silver halide, a conventional complexing agent such as sodium thiosulfate may be used as the stabilizing agent to combine with the undeveloped silver halide and form a complex which is colorless and non-light-sensitive.

In one form of the invention, a single water-releasing agent is used to supply water to both the developer and the stabilizer. Preferably the stabilizer is in a layer spaced farther from the photosensitive material than the developer, which may even be mixed with the photosensitive material.

In another form, separate water-releasing agents are used to furnish water to the developer and stabilizer, and in this case, it is the presently preferred practice to have water-releasing agents with different activation temperatures, the agent with the lower activation temperature being associated with the developer so it is activated first.

These and other aspects of the invention will be more fully understood from the following description taken in conjunction with the accompanying drawing in which FIGS. 1 through 5 are schematic sectional elevations of five embodiments of this invention.

Referring to FIG. 1, a support 10, which may be conventional paper or transparent film, is covered on one side with a first layer 12, which may be any conventional photosensitive material, such as a silver halide emulsion. The layer 12 also includes a developer, which may be of conventional type, such as hydroquinone. Alternatively, the photosensitive material layer 12 may include a special developer molecule which is a combined sensitizing dye and developing agent as explained in more detail below.

The first layer 12 also includes a first water-releasing agent which gives up water on heating. Suitable agents are Glauber salt, borax, sodium triphosphate, sodium metasilicate, sodium alginate, or sugar. Of this group, the presently preferred compound is sodium alginate because it serves the triple function of acting as a binder, a water-release agent, and an alkaline supplier. In addition, it is the most sensitive of the listed group to heat for releasing water. That is, sodium alginate gives up water at a lower temperature than any of the other listed materials. The sugar materials are useful because they also serve as binders or carriers, and, on heating form enediol compounds, which are good, clean developing agents. Moreover, the sugar tends to hold some water in an amorphous layer.

An isolating layer 14 is disposed on top of the photosensitive material layer and may be made of any suitable water-permeable material such as gelatin, polyvinyl alcohol (sold by Du Pont under the trade name "Elvanol"), or methoxy cellulose. A layer 16 of a suitable stabilizing material such as sodium thiosulfate or ammonium thiosulfate, is disposed on top of the isolating layer. A second water-releasing agent is mixed with the layer 16, and may be any one of the agents listed above.

In preparing the photosensitive medium shown in FIG.

1, a solution containing developer and the first water-releasing agent is applied to the layer of photosensitive material, such as a silver halide, already in place on the support. The solution of developer and water-release agent softens the silver halide emulsion so that the developer and water release agent penetrate the emulsion to make a layer of the three materials as indicated in FIG. 1, i.e., silver halide, developer and first water-releasing agent. The film is dried, and a thin film of the isolating layer, say gelatin solution, is applied to the silver halide-developer-water release agent layer. The gelatin layer is dried and thereafter coated with the stabilizer layer, which may be a saturated solution of sodium thiosulfate and the second water-releasing agent. The foregoing procedure is described in more detail in Example A given below.

The thickness of the layers and support shown in FIG. 1, as well as the other figures, are not to scale, and will of course vary, depending on the materials used. Ordinarily the total thickness of the layers deposited on the support is less than .001".

In using the medium shown in FIG. 1, a light image is focused on the silver halide layer 12. The light may come through the over-lying layers, or if they have a tendency to be opaque, the light can be directed onto the silver halide through the support, which may be transparent film. After exposure, the medium is heated in the dark so that the first water release agent in the silver halide layer 12 releases water to activate the developer and develop the image. The isolating layer retards the diffusion of water to the stabilizer layer. Heating of the medium continues until the second water release agent in the stabilizer layer 16 releases water to activate the stabilizer and permit it to diffuse through the isolating layer to the silver halide, which is then made insensitive to light by well known chemical reactions.

Preferably, the medium shown in FIG. 1 is heated from the back, i.e., through the exposed surface of the support so that the developer and its water release agent are heated and activated before the stabilizer. In this way, the film is properly developed before the silver halide emulsion is stabilized. This action is enhanced by having the stabilizer layer spaced from the silver halide layer by the isolating layer, and using the second water release agent which requires a higher temperature before giving up its water to activate the stabilizer. When sodium alginate is used as the first water release agent in the silver halide-developer layer, a good water release agent for the stabilizer layer is sodium triphosphate. Sodium alginate is a seaweed product, sold under the trademark "Halltex."

In the arrangement shown in FIG. 2, a common water release agent layer 20 is disposed on a support 22 and covered by a layer 24 of silver halide and developer. The layer 24 is covered by an isolating layer 26, which in turn is covered by a stabilizer layer 28.

In using the medium shown in FIG. 2, the silver halide layer 24 is exposed to a light image, and subsequently developed and stabilized by applying heat to the medium through the support layer 22. The water-releasing agent, say sodium metasilicate, gives up its water first to the silver halide-developer layer 24 so that the image is developed. The water then penetrates the isolating layer to the stabilizer so that it is activated to stabilize the record.

In the embodiment of FIG. 3, a silver halide-developer layer 30 is disposed on a support 32, and covered with a layer 34 of a water-releasing agent, which in turn is covered with a layer 36 stabilizer.

In using the medium of FIG. 3, the silver halide is exposed, and the medium heated to release water to both the developer layer and the stabilizer layer. However, since the developer layer is closer to the silver halide than the stabilizer layer, the developer reaches the silver

halide first because the stabilizer must diffuse a greater distance.

In the arrangement shown in FIG. 4, a silver halide layer 40 is disposed on a support 42 and covered by a layer 43, which is a mixture of developer and first water-releasing agent such as sodium alginate, which releases water at a relatively low temperature. A layer 44 of a stabilizer and a second water-releasing agent is disposed on the layer 43 of the developer and first water-releasing agent. The second water-releasing agent gives up water at a higher temperature than the first, and may be a material such as sodium triphosphate or Glauber salt.

In using the material of FIG. 4, the silver halide layer 40 is exposed to a light image, and developed by heating the material through the support 42. The first water-releasing agent gives up water first and activates the developer, which develops the image. The second water-releasing agent subsequently gives up water to activate the stabilizer, which diffuses through the developer layer 43 to stabilize the record.

The arrangement shown in FIG. 5 includes a support layer 50, a layer 52 of developer and a first water-releasing agent, a layer 54 of silver halide, or other suitable photosensitive material, an isolating layer 56, and a layer 58, which is a mixture of stabilizer and a second water-releasing agent that gives up water at a higher activation temperature than the first agent.

In the medium shown in FIG. 5, the silver halide is exposed to a light image, which is subsequently developed by applying heat to the medium through the support 50. The first water-releasing agent gives up water to the developer, which develops the image in a silver halide layer. Thereafter, the second water-releasing agent gives up water to the stabilizer, which diffuses through the isolating layer 56 and stabilizes the record in layer 54.

In the embodiment of FIG. 5, the exposed surface of the stabilizer layer 58 is coated with a thin film of a sealer 60, which may be a vegetable gum, gum tragacanth, gum arabic, or a pine resin such as the resin sold under the trade name "Durez." The sealer prevents the inadvertent wetting of the stabilizer or developer prior to exposure of the photographic recording medium. Of course, the embodiments shown in FIGS. 1 through 4 can also include a sealing film.

In one form, the water-releasing compound is a hydrated salt. In another form, the water-releasing agent is an adsorbent material such as porous, crystalline sodium or calcium aluminosilicate which contains water that is bound up in its pores, and is released only on heating.

The following are specific examples of how to make and use a photographic recording medium such as that shown in FIG. 1.

Example A

300 grams of borax is added to one liter of a developer solution having the following composition:

6-nitrobenzimidazole	-----grams	1/2
Sodium sulfite	-----do	30
Benzotriazole	-----do	20
Caustic soda	-----do	10
1-phenyl-3-pyrazolidone	-----do	10
Hydroquinone	-----do	10
Potassium carbonate	-----do	20
Duponol 80 (wetting agent)	-----ml	2
Teepol	-----ml	2
Water added to make 1 liter of solution.		

The above solution is kept warm (about 50° C.) to insure that all of the salts remain in solution, and applied as a coating on unexposed photographic paper, which supports a photosensitive silver halide emulsion. Any suitable paper may be used, e.g., Du Pont's Lino Writ #1 and #2. The solution penetrates the emulsion to form a layer of silver halide, developer, and water-releasing agent as shown in FIG. 1. The treated paper is dried in the dark or under a red safelight to leave a layer of dried salts

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from the above solution on the paper. The layer of dried salts is then coated with a thin film of an isolating layer of gelatin or polyvinyl alcohol, which is allowed to dry. Thereafter, a thin film of saturated sodium thiosulfate (stabilizer) at 50° C. is applied to the isolating layer and quickly dried to prevent the diffusion of the stabilizer to the silver halide. If a larger supply of water is desired, a second water-releasing agent is incorporated with the stabilizing layer. Preferably, the second water-releasing agent has a higher activation temperature than the water releasing agent mixed with the developer layer. However, the two water-releasing agents can be the same material, and heat is applied so that the developer is supplied water first.

After the dried paper is exposed to a light image, it is developed by holding the exposed paper support surface in contact with a hot platen at 150° C. The heat melts the borax and releases water of hydration, which first provides free water to activate the developer. The released water then diffuses through the isolating layer and activates the stabilizer, which stabilizes the record. Of course if a second water-releasing agent is used, it also gives up water to the stabilizer.

The amount of borax and most other water-releasing agents can be varied from about 100 to about 500 grams per liter, depending upon the nature of the paper and the particular developer used.

Example B

400 grams of borax and 200 grams of sodium citrate are added to 1 liter of developer solution which has the same composition as the developer solution given in Example A, except that only 2 grams of benzotriazole are used instead of 20 grams. The solution is prepared and applied to photographic paper as described above. The dried salts are coated with an isolating layer, which is thereafter coated with a thin film of saturated sodium thiosulfate, and a second water-releasing agent, if desired. The paper is exposed and developed as described above. The amount of borax and sodium citrate can each be varied between about 100 to about 500 grams per liter of developer solution.

Example C

300 grams of trisodaphosphate are added to 1 liter of developer solution having the composition of the developer given in Example A. The photographic paper is thereafter treated, dried, exposed, exactly as described in Example A.

Example D

400 grams of porous crystalline sodium aluminosilicate powdered to a particle size of one to five microns are mixed with one liter of the developer solution given in Example A. The pores in the aluminosilicate are of molecular dimension, i.e., 16 to 20 billionths of an inch in diameter, and they are uniform in size. The material is commercially available as "Linde Molecular Sieve." The sodium aluminosilicate is insoluble in the developer solution, so the solution is agitated to maintain the finely divided solids in suspension. The developer solution and solid particles are coated onto the emulsion of a photographic paper, and the paper dried, the solid particles being imbedded in and on the emulsion. An isolating layer is applied, coated with a thin film of stabilizer and dried. Although the final product of the emulsion, developer, and solid particles appears dry, the solid particles actually contain a substantial quantity of bound water in the small pores of the aluminosilicate.

Since the silicate particles impart a slight degree of opacity to the final product, it is desirable to use photographic film in which the support is transparent so the exposure to the light image can be made through the support.

After the paper is exposed to light, it is heated so that water absorbed in the pores of the "Molecular Sieve" is

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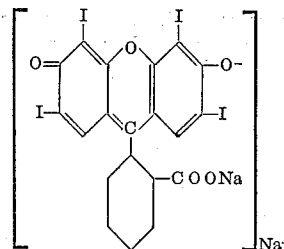
driven out to supply free water for the development of photographic emulsion. Developing action terminates when the water is completely evaporated, or, when the paper is cooled and the remaining water re-absorbed by the "Molecular Sieve."

From the foregoing examples, it will be apparent that the photographic media shown in FIGS. 2-5 are built up in the same general way as that described for FIG. 1.

Many types of photosensitive emulsions include sensitizing dyes adsorbed on the silver halide grain to expand the spectrum range to which the emulsion is sensitive. Although the exact mechanism of the action of the sensitizing dye and developer is not fully understood, the developer probably has to displace the adsorbed dye to become effective. In one embodiment, this invention uses a sensitizing dye which also includes a photo-developing functional group in its molecular structure. Such a multi-purpose chemical increases developing speed, and the competition of the developer with the dye for active spots on the emulsion (before exposure) is eliminated.

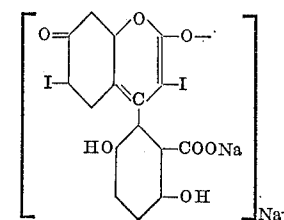
A typical photosensitive gelatin emulsion of silver bromide is sensitive to wave-lengths in the blue and violet (500μ to 400μ). By adding a dye such as erythrosine, the sensitivity of the emulsion is extended to include green.

The molecular structure of erythrosine is:



In accordance with this invention, erythrosine is modified before incorporation in the silver halide emulsion to include a silver reducing group (photo-developing functional group) of the type such as hydroquinone, methyl-para-aminophenol, eikogen, or 1-phenyl-3-pyrazolidone.

For example, a hydroquinone group is formed by the addition of two hydroxy groups to the erythrosine dye to give the following structure:

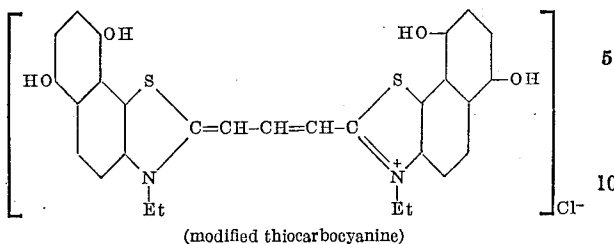


The modified dye is then incorporated in a gelatin emulsion of silver bromide in the conventional manner. An activating solution containing about 300 grams of borax, or other suitable hydratable salt, or water-releasing material, is swabbed on the unexposed emulsion and dried in the dark. The dried intermediate product is covered with an isolating layer, say, gelatin, which is then dried and covered with a film of stabilizer. Thereafter, the emulsion is exposed to a light image or signal and developed and stabilized by heating to about 125° C. to release the water of hydration from the salt and permit the developer to reduce the silver.

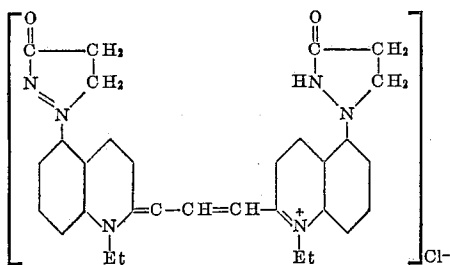
This embodiment of the invention has the advantage of (1) reducing any tendency for the developer to displace the sensitizing dye from the emulsion before exposure to light; (2) increasing developing speed because the developer does not have to displace a sensitizing dye molecule, and (3) improving selectivity and reducing the amount of water and developer required because the developer is held in close proximity to the light-activated centers.

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Other examples of modified sensitizing dyes which include a functional group for reducing silver are:



and



In the latter compound, the developing action takes place at the two pairs of CH_2 groups.

Thus, the invention provides a photographic medium which can be processed dry. No liquid developer or stabilizer solution is needed, and the image on the photographic paper can be developed and stabilized immediately after exposure simply by heating the paper. The material which supplies the water on heating also takes up water on cooling, and aids in further arresting the action of the developer when the source of heat is removed. This invention also reduces the relatively large power requirements of prior dynamic photographic recorders at high paper transport speeds, and makes possible portable units not previously practical.

I claim:

1. A photographic recording medium comprising:

- a support,
- a silver halide photosensitive material,
- a dry developing agent for the photosensitive material, the developing agent being in direct contact with the photosensitive material and requiring the presence of water to become active, the photosensitive material and developing agent being distended on the support,
- first water-releasing agent which releases water on the

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application of heat associated with the developing agent,

a layer of a dry stabilizing agent which becomes active in the presence of water to interrupt the development of the photosensitive material and make it insensitive to light, the layer of stabilizing agent being superimposed on the photosensitive material and developing agent and being spaced farther from the photosensitive material than is the developing agent, and

a second water releasing agent which releases water on the application of heat associated with the stabilizing agent, the second water releasing agent requiring a higher temperature than the first water releasing agent to release water.

2. A photographic recording medium comprising a layer of silver halide photosensitive material, a layer of dry developing agent for the silver halide, the developing agent being in direct contact with the photosensitive material and requiring the presence of water to become active, a first compound which releases water on the application of heat associated with the developing agent, a layer of sodium thiosulfate, the sodium thiosulfate being spaced farther from the photosensitive material than is the developing agent, and a second compound which releases water on the application of heat associated with the sodium thiosulfate, the second compound requiring a higher temperature than the first to release water.

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