

Nov. 29, 1966

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PHOTOGRAPHIC APPARATUS AND PROCESS
FOR TREATING SHEETS WITH A LIQUID

3,288,609

Filed Oct. 12, 1964

2 Sheets-Sheet 1

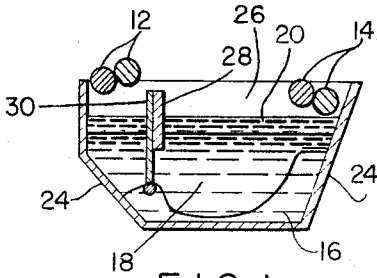


FIG. 1

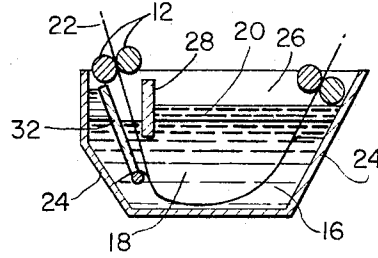


FIG. 2

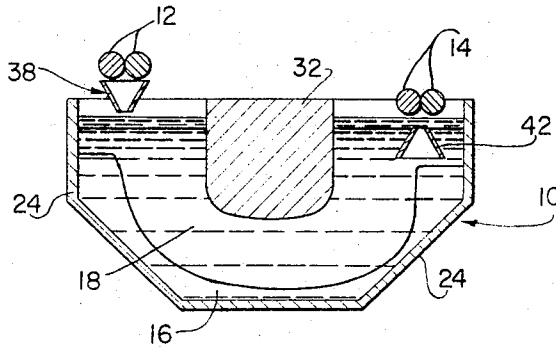


FIG. 3

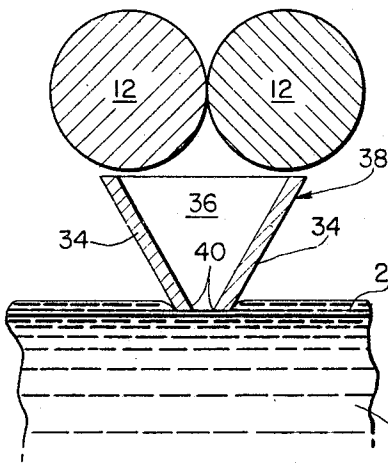


FIG. 4

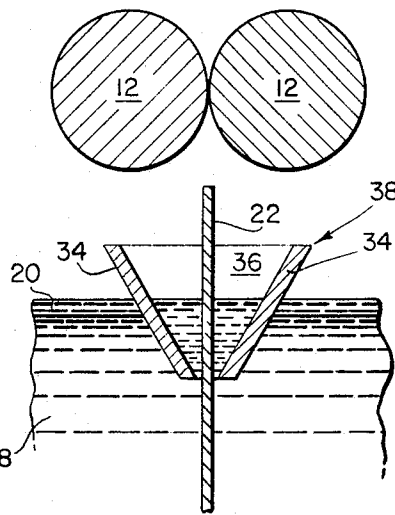


FIG. 5

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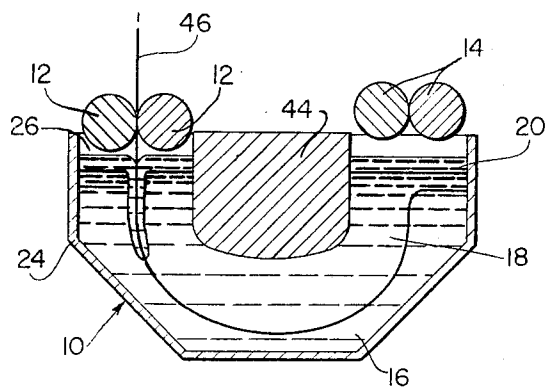


FIG. 6

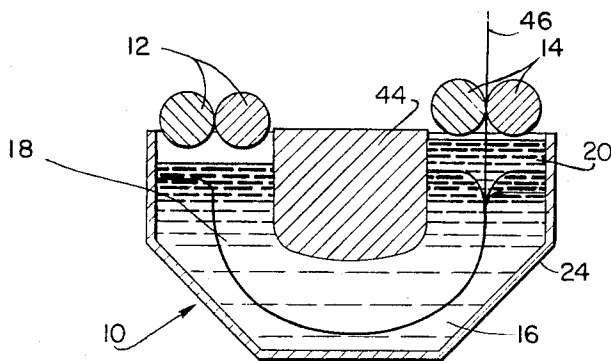


FIG. 7

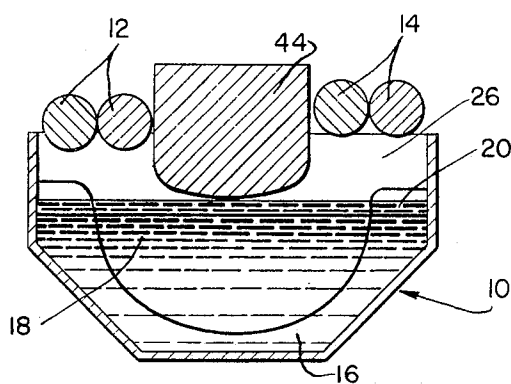


FIG. 8

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PHOTOGRAPHIC APPARATUS AND PROCESS FOR TREATING SHEETS WITH A LIQUID

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19 Claims. (Cl. 96—50)

This invention relates to photographic methods and apparatus, and particularly to methods of treating exposed photosensitive image-recording sheet material with liquids to produce visible images in the sheet material and apparatus therefor.

A number of photographic processes, particularly diffusion-transfer reversal processes, involve the immersion of a sheet including an exposed photosensitive image-recording material such as silver halide in a processing liquid, including, for example, a silver halide developer, to produce a visible image in the sheet. The liquid is conveniently held in a tray or similar open container and the sheet is passed into, through and from the liquid at a controlled rate such that the sheet absorbs a predetermined quantity of the liquid. Most liquid processing agents of this type and particularly those containing silver halide developers are subject to deterioration, e.g., evaporation, aerial oxidation, pH changes, etc., when exposed to the atmosphere, so that protection of such liquids from exposure to the atmosphere has posed a problem of long standing.

Objects of the invention are: to provide a novel and improved method of treating photographic sheet material by immersion in a liquid processing agent while protecting the liquid against contact with the atmosphere; and to provide a method as described in which the sheet material is impregnated with the liquid by immersion therein and is similarly protected from the atmosphere upon emergence from the liquid.

In the copending U.S. patent applications of Edwin H. Land, Serial Nos. 368,622 and 368,621, filed May 19, 1964, there is described a photographic process in which an area of a photosensitive image-recording sheet is exposed to form an image and thereafter treated with a liquid to produce a visible image in the exposed area. The sheet material employed in the process comprises a support such as paper and a layer (or layers) including a light-sensitive image-recording material such as a silver halide emulsion and a translucent outer layer permeable to the liquid processing composition for supporting a visible image, e.g., silver, formed by diffusion transfer of image-forming substances from the light-sensitive image-recording material; and the processing liquid employed is aqueous and alkaline and includes a silver halide developer. This process results in a positive transfer image on a white background and most importantly, involves a single sheet rather than the two sheets normally associated with diffusion-transfer reversal processes, so that the sheet itself, upon emergence from the aqueous liquid, can be protected against contact with the atmosphere.

Other objects of the invention are: to provide a photographic method as described in which the surface of a body of an aqueous liquid is covered with a layer of another liquid which is substantially nonvolatile and immiscible with the aqueous liquid to protect the aqueous liquid from the atmosphere and the exposed photosensitive image-recording sheet material is advanced into and from the body of aqueous liquid through the surface

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thereof; to provide a method as described in which the sheet material is advanced from the aqueous liquid through the layer of other liquid to provide a protective coating of the other liquid on the surfaces of the sheet material; and to provide a method, as described, including novel methods of removing the layer of other liquid from an area of the surface of the body of aqueous liquid and introducing the sheet material into the aqueous liquid through this area.

Further objects of the invention are: to provide novel and improved apparatus for practicing the method of the invention including means for shifting at least portions of the layer of other liquid on the surface of the body of aqueous liquid; and to provide apparatus of the type described having a simple and inexpensive construction, and is dependable in its operation.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the apparatus possessing the construction, combination of elements and arrangement of parts and the process involving the several steps and the relation and order of one or more of such steps with respect to each of the others which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

For a further understanding of the nature and objects of the invention, reference should be had to the following detailed description taken in connection with the accompanying drawings wherein:

FIGS. 1 and 2 are somewhat diagrammatic sectional views of liquid processing apparatus embodying the invention and illustrating steps of the method of the invention;

FIG. 3 is a view similar to FIG. 1 showing another embodiment of the process and apparatus of the invention;

FIGS. 4 and 5 are fragmentary views of components of the apparatus of FIG. 3 illustrating steps in the method and details of the construction and operation of the apparatus; and

FIGS. 6, 7 and 8 are views similar to FIGURE 1 illustrating another embodiment of the apparatus and steps in another embodiment of the method.

The present invention is particularly concerned with a method of treating a succession of exposed, combination, photosensitive image-recording and image-receiving sheets with a liquid to form visible positive prints in the exposed and processed areas of the sheets. A typical sheet material useful in the method of the invention is disclosed in the aforementioned applications and comprises, for example, a paper support having thereon a layer of a light-sensitive silver halide emulsion and an outer layer comprising a translucent material such as finely divided titanium dioxide, calcium carbonate, magnesium oxide, etc., dispersed in a suitable permeable colloidal carrier or matrix such as gelatin which is permeable to the processing liquid. This outer layer may also contain silver precipitating nuclei and is sufficiently transparent to permit photoexposure of the light-sensitive layer therebeneath while, at the same time, being sufficiently opaque to provide the requisite background for a positive silver image transferred thereto and to mask the negative image formed thereunder.

The process performed with this photosensitive sheet material is particularly useful for duplicating documents so that the apparatus employed for the processing is, in the preferred form, designed to contain the processing liquid and process a succession of exposed sheets by passing the sheets through the processing liquid. An exam-

ple of the composition of a processing liquid suitable for this purpose is as follows:

Water	cc.	8400
Sodium sulfite	gm.	675
Sodium hydroxide	gm.	180
Potassium thiosulfate	gm.	207
4-amino-2,5-dimethylphenol	gm.	180

This aqueous and highly alkaline liquid processing agent is obviously susceptible to deterioration due to exposure to the atmosphere resulting, for example, from evaporation, reduction of the pH due to carbon dioxide in the atmosphere and aerial oxidation. The usual method of treating sheet materials with processing liquids such as this is to contain the liquid in a tray or other suitable container and advance successive sheets into, through and from the liquid at a controlled rate such that a predetermined amount of the liquid is absorbed by the sheets. This general method of processing has the advantage of assuring uniform impregnation of the sheets and is subject to fairly accurate control over the amount of liquid absorbed. However, the surface of the liquid is exposed to the atmosphere continuously in the simpler forms of apparatus for performing the process; or rather complicated mechanisms have been required for handling the processing liquid so as to limit exposure of the liquid to the atmosphere.

Reference is now made to FIGS. 1 and 2 of the drawings wherein there is illustrated a method of and apparatus for treating successive exposed photosensitive sheets by immersion in an aqueous alkaline developing liquid while protecting the liquid against contact with the atmosphere. The apparatus comprises a relatively shallow tray or container 10 having sloped sides and open at the top, a pair of juxtaposed feed rolls 12 for feeding sheets into the container adjacent one side thereof and a pair of juxtaposed wringer rolls 14 disposed adjacent the opposite side of the container for withdrawing sheets from the container as they emerge from liquid within the container. Wringer rolls 14 preferably include at least surface layers of elastomeric material and are biased toward one another so as to compress the sheets and squeeze excess liquid therefrom. Mounted within the container are a plurality of guide members 16 for engaging a sheet as it is moved downwardly into the tray by rolls 12, changing the direction of movement of the sheets and guiding the sheets upwardly so that they emerge from the tray in alignment with the bite of wringer rolls 14. The path length of the sheets and the speed of the rotation of the rolls may be easily controlled to provide for immersion of the sheets in the liquid within the tray for a precisely predetermined period.

Tray 10 includes a body of aqueous liquid 18 having a surface located below the level of the upper edges of the walls of the tray. A layer 20 of a second liquid is floated on the surface of liquid body 18. The second liquid, of course, has a specific gravity less than that of the aqueous liquid, and is substantially non-volatile at ordinary temperatures, substantially immiscible with the aqueous liquid and constitutes a poor solvent for gases in the atmosphere. An example of a liquid meeting these criteria and useful for this purpose is mineral oil, the commonly accepted term used to describe a mixture of hydrocarbons within the viscosity range of products commonly called oils and not volatile at normal temperatures. The depth of layer 20 is not critical and good results have been obtained, for example, with layers of the order of $\frac{1}{8}$ " to $\frac{1}{4}$ " deep. An example of a particular mineral oil found suitable for this purpose is extra heavy mineral oil produced by E. R. Squibb & Sons having a viscosity at 70° F. of approximately 200 cps. Mineral oil is particularly desirable because, in addition to the above enumerated properties, it is relatively inert at least insofar as photographic chemicals are concerned, is colorless, odorless, and any thin coating of the oil remaining on the surfaces

of a sheet following processing does not tend to become tacky or change color.

In the preferred method of the invention, an exposed photosensitive image-recording sheet, designated 22, is introduced into body of liquid 18 through a portion of the surface thereof from which layer 20 has been removed, so that the second liquid (oil) does not contact the surfaces of the sheet and inhibit or prevent absorption by the sheet of the aqueous liquid. In the form of the apparatus and process shown in FIGS. 1 and 2, tray 10 includes inclined side walls 24 and substantially vertical end walls 26 spaced from one another by a distance exceeding the width of sheet 22. Layer 20 of the second liquid is removed from an area of the surface of the aqueous liquid by providing a fixed barrier 28 in the form of a wall or panel within tray 10 extending from one end wall 26 to the other and from above the surface of layer 20 below the surface of body 18, dividing or separating layer 20 and the upper strata of the liquid body in two sections; and a movable barrier 30 also extending from one end wall to the other and from above the surface of layer 20 beneath the surface of body 18. Movable barrier 30 is mounted in a generally vertical plane for pivotal movement about its lower edge on guide members 16 and is pivotable from the initial position shown in FIGURE 1 in which layer 20 covers substantially the entire surface of body 18, in a counterclockwise direction to the open position shown in FIG. 2 to provide a space between the barriers through which sheet 22 is fed into the body of liquid by feed rolls 12. The ends of barrier 30 are constructed to, or are provided with suitable means (e.g., flexible wipers), for closely engaging end walls 26 so that the second liquid comprising layer 20 is shifted (to the left, viewing FIG. 2) and thereby removed from the portion of the surface of liquid body 18 between barriers 28 and 30. Immediately prior to introduction of sheet 22, barrier 30 is pivoted away from barrier 28 to clear the second liquid from the surface of liquid body 18 between the barriers, sheet 22 is advanced by rolls 12 downwardly between the barriers which, incidentally, function as a guide, into engagement with guide members 16 which direct the sheet through liquid body 18 and upwardly into the nip or bite of wringer rolls 14. Upon emerging from liquid body 18, sheet 22 may pass through layer 20 where it may, depending upon the nature of the second liquid, acquire a protective coating of the second liquid which inhibits deterioration, due to atmospheric contact, of the aqueous liquid absorbed by the sheet. Wringer rolls 14 compress the emerging sheet removing therefrom excess quantities of both liquids so that the sheet upon emergence may be almost factually dry. Immediately following complete introductory movement of sheet 22, barrier 30 is returned to its initial position so that liquid body 18 is immediately completely protected from contact with the atmosphere.

Another embodiment of the method and apparatus of the invention is illustrated in FIGS. 3 through 5, wherein the same numerals have been employed to denote the same parts previously shown and described. The basic distinction here is in the method of and means for removing layer 20 from a portion of the surface of liquid body 18 to permit introduction of sheet 22 into the aqueous liquid without contacting the second liquid comprising layer 20. In this embodiment, tray 10 is provided with guide members 16, a body of aqueous liquid 18, a layer of second liquid 20, and the apparatus includes feed rolls 12 and wringer rolls 14 all constructed substantially as shown in FIGS. 1 and 2 and described. Mounted within container 10 is a fixed barrier 32 extending from end to end of the tray and from above the surface of layer 20 well beneath the surface of liquid body 18, separating layer 20 and the upper strata of liquid body 18 into two sections. Fixed barrier 32 is substantially enlarged so as to reduce the areas of the surface of liquid body 18 which must be protected from the atmosphere. The means for removing

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layer 20 from a portion of the surface of liquid body 18 comprise a pair of elongated convergent side panels 34 joined by end panels 36 to form a V-shaped trough 38 having a length exceeding the width of sheet 22. The trough defined by the side and end panels includes a narrow opening 40 defined by the lower edges of the panels and extending from end to end of the trough. Trough 38 is normally located in a raised position, shown in FIG. 3, in which the lower edges of the side and end panels are located above the surface of layer 20 between one of side walls 24 and fixed barrier 32 in alignment with feed rolls 12. Immediately prior to introduction of sheet 22 between rolls 12, trough 38 is moved downwardly through layer 20 until the lower edges of side panels 34 defining opening 40 are beneath the surface of liquid body 18, as shown in FIGS. 4 and 5, and the upper edges of the trough are above the level of the surface of layer 20. During the downward movement of the trough the lower edges of the side panels displace layer 20 outwardly, as shown in FIG. 4, due to the surface tension and viscosity of the liquid comprising layer 20 so that substantially none of the second liquid comprising layer 20 remains on the surface of liquid body 18 within trough 38 and sheet 22 may be advanced downwardly between feed rolls 12 into the trough and through opening 40 beneath the surface of liquid body 18 without contact the second liquid of layer 20.

As an example of this embodiment of the process and apparatus, a trough was formed with side panels 34 approximately $\frac{3}{16}$ " thick having an opening $\frac{1}{4}$ " wide and the lower edges of side panels 34 were shaped to lie substantially in a common plane. Trough 38 was displaced downward through a $\frac{3}{16}$ " deep layer of the aforementioned mineral oil to provide a surface of liquid body 18 within the trough free of the mineral oil comprising layer 20. Immediately following complete immersion of sheet 22, trough 38 is raised above the surface of layer 20 to protect the surface from contact with the atmosphere.

It may be desirable to advance sheet 22 from the body of aqueous liquid without contacting the second liquid comprising layer 20 and for this purpose, in the embodiment shown in FIG. 3, a second trough 42, similar to trough 38, is provided on the opposite side of barrier 32 initially positioned entirely beneath the surface of liquid body 18. Trough 42 is inverted and is raised as trough 38 is lowered until the upper edges of trough 42 are above the surface of layer 20. As the upper edges of trough 42 are raised above the surface of layer 20, the layer is displaced from the surface of the liquid body within the trough permitting the sheet to emerge from the liquid body through the trough into the bite of rolls 14 without contacting the liquid of the protective layer. A simple construction would be to mount troughs 38 and 42 on a single pivotable support.

Reference is now made to FIGS. 6 through 8 of the drawings wherein there is illustrated another embodiment of the method and apparatus of the invention, the latter comprising a tray 10, feed rolls 12, wringer rolls 14, guide members 16, a body of aqueous liquid 18 and a layer of a second liquid 20, all substantially as shown and described. Mounted within tray 10 is a barrier 44 extending from above the surface of layer 20 into liquid body 18 well beneath the surface thereof separating layer 20 and the upper strata of liquid body 18 into two sections. In this embodiment of the invention, the second liquid comprising layer 20 is removed from the section of the surface of the liquid body between barrier 44 and one side of the container by rapidly advancing a carrier sheet 46, which may comprise paper or another flexible material to which the second liquid will adhere, downwardly through layer 20 and through the body of liquid to the opposite side of barrier 44. As sheet 46 is advanced downwardly through layer 20, the second liquid adheres to the sheet, as shown in FIG. 6, and is drawn by the sheet through liquid body 18 to the opposite side of the barrier as shown in FIG. 7,

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leaving the section of the surface of liquid body 18 underlying feed rolls 12 substantially free of the second liquid. This is very easily accomplished if the second liquid comprises a viscous material such as the mineral oil mentioned, and sheet 46 is moved through the liquid at a fairly rapid rate. Returning the second liquid to its original position is a simple matter and merely involves raising barrier 44 above the surfaces of liquid body 18 and layer 20, as shown in FIG. 8. The ends of barrier 44, of course, are required to closely engage end walls 26 of tray 10 to prevent flow of the second liquid around the end of the barrier.

In the process of the invention, the aqueous processing liquid is completely protected from the atmosphere except for very brief periods during which only a relatively small area (or areas) of the surface of the aqueous liquid is uncovered. Complete protection is assured because it is provided by a liquid and the protection from atmospheric contact is extended to the liquid impregnated sheet without additional operations or difficulty. Coating of the sheet with the protective liquid, specifically oil, has the further advantages of protecting the wringer rolls against contact with the corrosive aqueous liquid and effectively prevents adherence of the sheet material to the rolls. The apparatus for performing the process is also characterized by a simplicity, which makes it inexpensive, and dependability of operation.

Since certain changes may be made in the above process and apparatus without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description or shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. The method of treating an exposed photosensitive image-recording sheet with a liquid to produce a visible image therein comprising:

providing a body of an aqueous liquid including reagents capable of reacting with differentially exposed photosensitive image-recording material to produce a visible image;

floating a layer of another liquid substantially non-volatile at normal temperatures and immiscible with said aqueous liquid on the surface of the latter to protect said body of aqueous liquid from the atmosphere; and

advancing said sheet into and from said body of liquid at a rate such that said sheet absorbs a predetermined amount of said aqueous liquid.

2. The method of treating an exposed photosensitive image-recording sheet with a liquid to produce a visible image therein comprising:

providing a body of an aqueous liquid including reagents capable of reacting with differentially exposed photosensitive image-recording material to produce a visible image;

floating a layer of another liquid substantially non-volatile at normal temperatures and immiscible with said aqueous liquid, on the surface of the latter to protect said body of aqueous liquid from the atmosphere;

advancing said sheet into and from said body of liquid at a rate such that said sheet absorbs a predetermined amount of said aqueous liquid;

guiding said sheet within said body of liquid so that during emergence therefrom said sheet passes through said layer of said other liquid; and

immediately upon emergence of said sheet from said liquids, advancing said sheet between compression members to remove excess liquid from the surfaces thereof.

3. The method of claim 2 in which said sheet is advanced into said body of said aqueous liquid through and in contact with said layer of said other liquid.

4. The method of claim 2 in which said sheet is advanced into said body of said aqueous liquid through a portion of the surface thereof which is substantially free of said other liquid.

5. The method of claim 2 in which said surface of said body of said aqueous liquid is substantially completely covered with said layer of said other liquid to protect said surface from the atmosphere.

6. The method of claim 5 in which said layer of said other liquid is removed from a section of said surface immediately prior to introduction of said sheet, said sheet is introduced into said aqueous liquid through said section of said surface substantially without contacting said other liquid and said section of said surface is covered with said layer of said other liquid immediately following complete introduction of said sheet.

7. The method of claim 2 in which said surface of said body of aqueous liquid is divided by a barrier extending through said surface into two separated sections, said sheet is introduced into said body through one of said sections of said surface and is guided within said aqueous liquid so as to emerge from said body through the other of said sections.

8. The method of claim 7 in which said layer of said other liquid is substantially removed from at least a portion of said one section of said surface immediately prior to introduction of said sheet, said sheet is introduced through said portion of said section substantially without contacting said other liquid and said one section is covered with said layer of said other liquid immediately following complete introduction of said sheet into said body of said aqueous liquid.

9. The method of claim 7 in which said other liquid floated on said one section of said surface is transferred to said other section of said surface by passing a carrier sheet through said body from said one section of said surface beneath said barrier to said other section of said surface, and said other liquid is returned to provide said layer on said one section by removing said barrier from said surface.

10. The method of claim 2 in which said image-recording sheet comprises layers including a photosensitive silver halide and a material for supporting a silver image formed by diffusion transfer reversal and said aqueous liquid includes a silver halide developer and a silver halide complexing agent.

11. Photographic apparatus for treating photographic sheet material with an aqueous liquid which is subject to deterioration due to exposure to the atmosphere, said apparatus comprising, in combination:

an open container holding a quantity of said aqueous liquid;

a quantity of a second liquid, substantially non-volatile at normal temperatures, immiscible with and having a specific gravity less than said aqueous liquid, sufficient to form a layer of predetermined thickness on the entire surface of said aqueous liquid;

means for feeding said sheet material into said aqueous liquid through a first predetermined section of said surface of said aqueous liquid;

guide means within said container for guiding said sheet material through said aqueous liquid so that said sheet material emerges from said aqueous liquid through a second predetermined section of said surface; and barrier means extending from above the surface of said second liquid beneath said surface of said aqueous liquid and separating said first section of said surface and the portion of said layer of said second liquid thereon from said second section of said surface and the portion of said layer thereon, said barrier means being movable for shifting a portion of said layer of said second liquid with respect to said first section of said surface.

12. The photographic apparatus of claim 11 in which said second liquid is mineral oil.

13. The photographic apparatus of claim 11 including compression means mounted above said layer adjacent said second section of said surface for engaging said sheet material immediately upon emergence from said liquids for compressing said sheet material to remove excess liquids therefrom; and said guide means are so constructed and arranged as to direct said sheet materials from said liquids into engagement with said compression means.

14. The photographic apparatus of claim 13 in which said compression means comprise juxtaposed rolls biased toward one another and means for rotating said rolls to advance said sheet material from said liquids between said rolls.

15. The photographic apparatus of claim 11 in which said barrier means comprise first and second barrier members extending in contiguous relation from above said surface of said layer beneath said surface of said aqueous liquid, and said first barrier member is movable horizontally apart from said second barrier member to remove said layer of said second liquid from a portion of said surface intermediate said barrier members and constituting said first section of said surface.

16. The photographic apparatus of claim 11 in which said barrier means include a barrier member dividing said body of liquid in the region of said surface into two separated portions each including one of said first and second sections of said surface, and said barrier member is movable to a position completely above or below said surface to permit said second liquid to flow on said surface from one side of said barrier member to the other.

17. The photographic apparatus of claim 11 in which said barrier means comprise a pair of panels mounted in fixed position with respect to and inclined toward one another to form a V-shaped trough and having adjacent lower edges defining a narrow opening at the bottom of said trough through which said sheet material is movable, and means for moving said panels from a raised position in which said lower edges are located above the surface of said layer and a depressed position in which said lower edges are disposed beneath said surface of said body of said aqueous liquid and said panels extend above said surface of said layer, to remove said layer from the portion of the surface of said body of liquid between said panels constituting said first section of said surface of said body of aqueous liquid.

18. Photographic apparatus as defined in claim 17 including a second pair of said panels arranged to form an inverted V-shaped trough open at the top and disposed completely beneath said second section of said surface of said body of aqueous liquid, and means for moving said second pair of panels upwardly, to a position in which the opening defined by the upper edges of said second pair of panels is disposed above said surface of said layer, simultaneously with the downward movement of the first-mentioned pair of panels.

19. Photographic apparatus for treating photographic sheet material with an aqueous liquid which is subject to deterioration due to exposure to the atmosphere, said apparatus comprising, in combination:

a container holding a quantity of said aqueous liquid; a quantity of a second liquid, substantially non-volatile at normal temperatures, immiscible with and having a specific gravity less than said aqueous liquid sufficient to form a layer of predetermined thickness on a predetermined section of the surface of said aqueous liquid;

means for feeding said sheet material into said aqueous liquid through said predetermined section; and

means for shifting a portion of said layer of said second liquid with respect to the surface of said aqueous liquid at said predetermined section.

No references cited.

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