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PHOTOGRAPHIC PROCESSING METHOD UTILIZING FROZEN AQUEOUS SOLUTIONS

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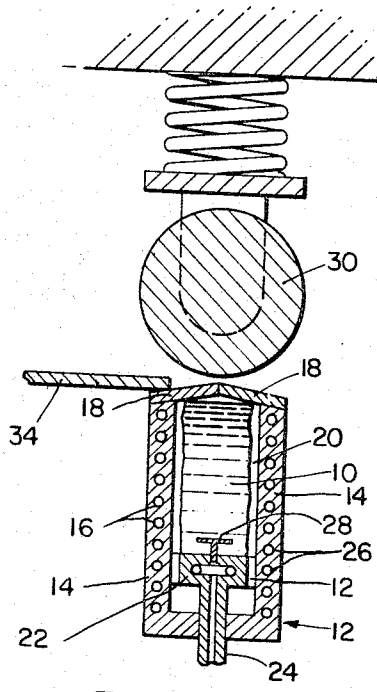


FIG. 1

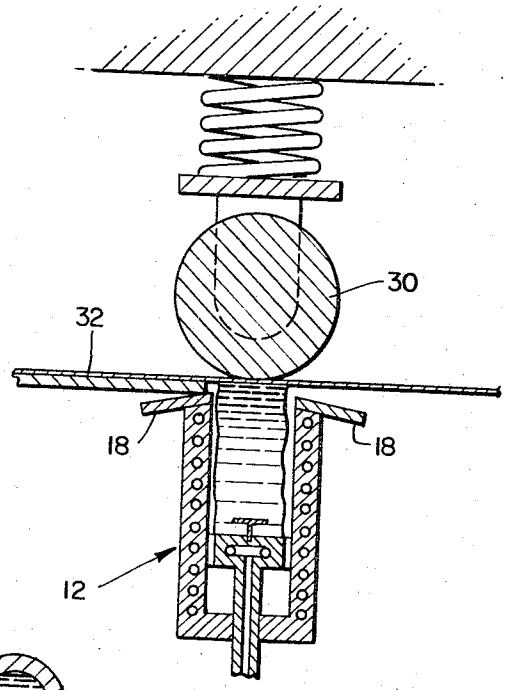


FIG. 2

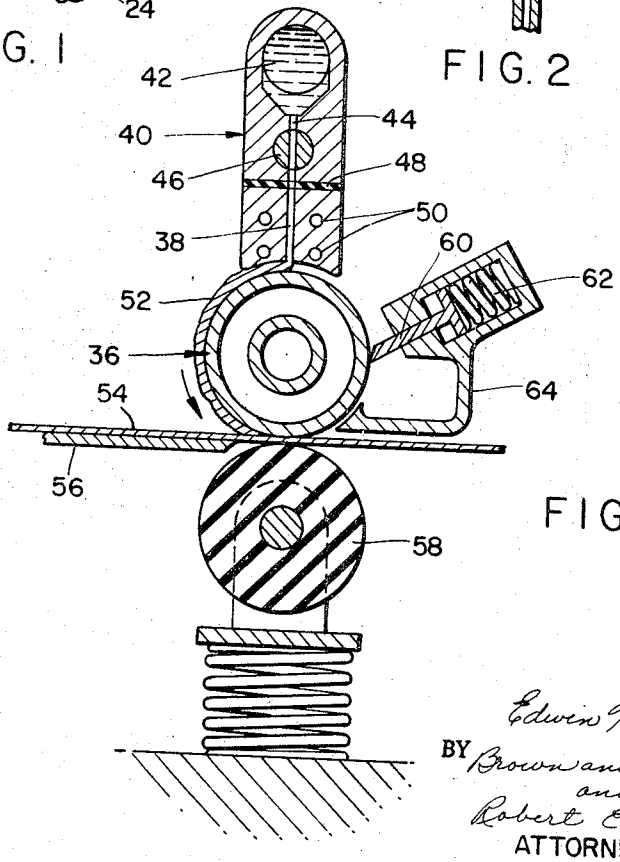


FIG. 3

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PHOTOGRAPHIC PROCESSING METHOD UTILIZING FROZEN AQUEOUS SOLUTIONS

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This invention relates to photographic methods and, more particularly, to methods of treating exposed photosensitive image-recording sheet material with liquids having substantially the viscosity of water to produce visible images in the sheet material.

The method of the invention finds particular utility in a photographic process in which a visible positive image is formed in a sheet from an exposed silver halide emulsion by diffusion-transfer reversal effected by an aqueous alkaline liquid, having the viscosity of water and including a silver halide developing agent, impregnated into the sheet. In processes of this type, it is important not only that the quantity of the liquid impregnated into the sheet be accurately controlled and the liquid be uniformly distributed, but liquid agents of this type are subject to and must be protected against deterioration, e.g., evaporation, aerial oxidation, pH changes, etc., when exposed to the atmosphere.

Objects of the invention are: to provide in a photographic process of the type described, a novel and improved method of applying a predetermined quantity of a liquid processing agent having the viscosity of water to a surface of a photosensitive image-recording sheet for impregnation into the sheet; and to provide a method as described in which the liquid is uniformly distributed in the sheet material over a predetermined area thereof and is confined, handled and applied in such a manner as to preclude spillage of the liquid and protect the liquid against deterioration due to exposure to the atmosphere.

Other objects of the invention are: to provide a substantially dry method of applying a non-viscous photographic developing liquid to one side of an image-recording sheet for impregnation into said sheet; and to provide a method as described in which the processing liquid is protected against deterioration due to exposure to the atmosphere by freezing the liquid into a solid body, and said liquid is applied to the sheet by pressing and moving the solid body of frozen liquid against one side of the sheet.

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

The invention accordingly comprises 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 fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description taken in connection with the accompanying drawing wherein:

FIGS. 1 and 2 are somewhat schematic sectional views of apparatus for performing the method of the invention illustrating said method, and

FIG. 3 is a similar view of another form of apparatus illustrating the method of the invention.

The present invention is particularly concerned with a method of treating a succession of exposed sections of a combination photosensitive image-recording and image-receiving sheet material with a non-viscous liquid, that is, a liquid having substantially the viscosity of water, to form visible positive prints in the exposed and processed sections of the sheet material. Typical sheet materials and processes useful in the method of the invention are disclosed in the copending U.S. patent applications of Edwin H. Land, Ser. Nos. 368,621 and 368,622 filed May 19, 1964, both now abandoned. The sheet material employed in the process comprises, for example, a support, such as paper, 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 photo-exposure of the light-sensitive layer therebetween 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 processing according to the method of the invention is, in the preferred form, designed to contain processing liquid sufficient to process a succession of exposed sheets or sections of a sheet and apply the liquid to each exposed section. An example of the composition of a processing liquid suitable for this purpose and useful in the method of the invention 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 preferably applied to the same side of the sheet material as the translucent layer for impregnation into the light-sensitive image-recording material, i.e., silver halide, to form a visible silver image by diffusion transfer of image-forming substances from the image-recording material.

The process may be considered to be substantially dry when and because the liquid is confined or contained in such a way as to preclude spillage or contact with components of the apparatus outside of the container prior to application to the sheet and is applied to one side of the sheet, rather than to both sides of the sheet as is the case when the sheet material is immersed in a container of the liquid, and the wet portion of the sheet is prevented from contacting components of the sheet. In other words, in the "dry" method of liquid application described and constituting the invention, the liquid contacts only the container, the applicator and the sheet material, and quantities of the liquid are stored prior to application so as to prevent spillage and protect the liquid from deterioration. Dry methods of applying non-viscous liquids pose the additional problems of applying a predetermined quantity of the liquid uniformly over the section of the sheet material to be treated.

According to the method of the invention, the dry application of a predetermined quantity of non-viscous aqueous liquid uniformly to a section of photosensitive sheet material while protecting the liquid against deterioration due to contact and reaction with the atmosphere, is achieved by rapidly freezing the liquid to form a solid body and then pressing and moving the solid body of frozen liquid against the surface of the sheet to be impregnated. The liquid is frozen rapidly to prevent evaporation and separation of the reagents and, in the frozen solid condition, the reagents comprising the liquid react extremely slowly, if at all, with the atmosphere so that little or no precautions are required to prevent contact between the liquid and the atmosphere.

To apply a predetermined quantity of the liquid uniformly to one side of a sheet, a quantity of the liquid at least sufficient to process a section of sheet material is frozen to form a solid body, preferably elongated and having a dimension approximately equal to one dimension of the section or area (e.g., rectangular) of image-recording sheet to be treated. The elongated body is pressed against the surface of the sheet so as to make contact therewith over an area extending from edge to edge of the section to be treated and is moved transversely of its long dimension across the section to be treated. The pressure of the body of frozen liquid against the sheet causes melting of the liquid in the region of contact between the frozen body and sheet and the liquid as it melts is immediately absorbed by the sheet so that there is no separation or deterioration of the constituents of the liquid. Melting and application of the liquid in the region of contact can be further promoted by sliding the frozen body relative to and in contact with the sheet and, in the preferred form of the invention, a combination of rolling and sliding contact is achieved. The quantity of liquid applied to the sheet in this manner is dependent upon such factors as the pressure applied to hold the body against the sheet, the temperature of the liquid, the rate of movement of the frozen body and sheet relative to one another and, in the embodiment in which substantially all of the frozen liquid is utilized, the quantity of liquid initially present and composing the frozen body. These factors are obviously subject to reasonably accurate control so that the amount of liquid (which is very small) absorbed into the exposed image-recording sheet material can be predetermined with substantial accuracy. Moreover, in accordance with the invention, the liquid is in a solid condition during the major portion, if not all, of the time it is outside of a container and in contact with the sheet material so that it is protected against deterioration due to exposure to the atmosphere and spillage, and contamination of other components of the apparatus are prevented.

In the embodiment of the method of the invention illustrated in FIGS. 1 and 2, a quantity of the liquid sufficient to treat a plurality of sections of exposed image-recording sheet material is rapidly frozen to form an elongated body **10** having a length preferably equal to one dimension, e.g., width, of the section of sheet material to be treated. Body **10** is stored in a container **12** having walls **14** with channels **16** through which a refrigerant is circulated to maintain body **10** in a solid condition; and a cover comprising two sections **18** movable from the closed position shown in FIGURE 1, to the open position shown in FIG. 2. Container **12** provides a recess or chamber **20** for containing frozen liquid body **10** and includes a backing member **22** engaged between the walls of the container and mounted on a reciprocating shaft **24** for movement within chamber **20** toward and away from the open end of the chamber. Backing member **22** and shaft **24** are also formed with channels **16** through which a refrigerant is circulated, and backing member **22** is formed with peripheral grooves for allowing the atmosphere within chamber **20** to pass from side to side of the backing member during reciprocal movement of the backing member.

Body **10** of the frozen liquid is frozen with a retaining member **28** adapted to be releasably coupled with backing member **22** embedded in the body for coupling the body with the backing member.

Container **12** is mounted with the open side thereof uppermost, beneath a roll **30** rotatable about an axis extending in the direction of elongation of body **10**, and functions to support a sheet **32** against body **10** and move the sheet relative to the body in contact therewith. The apparatus also includes a support plate **34** for guiding sheet **32** in a generally horizontal plane, container **12** and roll **30**, means for rotating the roll, means for moving cover sections **18** to an open position as a sheet **32** is moved into the space between the roll and container, and means for moving rod **24** upwardly to lift frozen body **10** upwardly into contact with the lower surface of the sheet which is supported against the frozen body by roll **30**. The pressure between the frozen body and sheet may be controlled easily and may be retained constant by providing a compression spring between shaft **24** and the means for moving the shaft, or between roll **30** and whatever the fixed means on which roll **30** is mounted.

In the method illustrated by FIGS. 1 and 2, a sheet **32** or section thereof to be treated, is advanced along support plate **34** into the space between roll **30** and the container and as the leading edge of the section to be treated enters the space, cover sections **18** are opened and the frozen body is raised by backing member **22** into contact with the lower surface of the sheet at the leading edge of the section to be treated. Roll **30** is rotated to move the sheet across and in contact with the frozen body of liquid and as the trailing edge of the section to be treated reaches the frozen body, the latter is lowered into chamber **20** and cover sections **18** are closed. Chamber **20** is maintained at a temperature just low enough to maintain body **10** of frozen liquid in a solid condition and prevent any melting thereof, and a small portion of the body is raised from the container only long enough for the liquid to be applied to a sheet so that melting of the frozen body occurs only at the portion thereof in contact with the sheet. Chamber **20** is preferably slightly larger than frozen body **10** in order to allow for freedom of movement of the body while maintaining the walls of the chamber as close as possible without contacting the sides of the body, thereby facilitating retention of the body in a frozen condition. The walls of the container may, if desired, be tapered slightly to further insure against adherence of the body of frozen liquid to the container walls.

In the embodiment of the method of the invention described with respect to FIGS. 1 and 2, the liquid processing agent is rapidly frozen to form a solid body at some time prior to application of the liquid to the image-recording sheet, and this time may range from minutes to months so long as the liquid is retained in a solid frozen condition such that no melting occurs. It is possible to store the solid, frozen developing liquid without deterioration in an ordinary atmosphere containing such gases as oxygen and carbon dioxide, which would ordinarily react with the constituents of the developing liquid to cause deterioration thereof.

In another embodiment of the method of the invention illustrated by FIG. 3, freezing of the developing liquid is effected immediately prior to application to the image-recording sheet primarily for the purpose of facilitating application of a predetermined uniformly distributed quantity of the liquid in a manner which could be termed "dry." In this embodiment, the liquid is rapidly frozen as a thin layer on the surface of a cylindrical heat-absorbing roll or drum and, immediately following freezing, that is, within a few seconds at most, the layer of frozen liquid on the drum is pressed into and moved in contact with the image-recording sheet to melt the liquid and apply it to the sheet for absorption therein.

Apparatus for performing this method is illustrated by

way of example in FIG. 3, and comprises a cylindrical applicator roll or drum **36** constructed to provide for the circulation of a refrigerant within the drum in order to maintain the drum at a temperature such that the developing liquid will freeze almost instantaneously as it is applied as a sheet to the drum. Drum **36** is rotated and the liquid is applied to an upper portion of the rotating drum by means providing a narrow elongated passage **38** through which the liquid emerges as a sheet equal in length to the width of the section of sheet material to be processed. Passage **38** is formed in a nozzle **40** including a chamber **42** containing the processing liquid, a passage **44** between chamber **42** and a passage **44** for conducting the liquid from chamber **42** to passage **38**, a valve **46** within passage **44** for controlling the flow of liquid through the passage, and a thermal insulating member **48** between the section of nozzle **40** including chamber **42**, passage **44** and valve **46** and the section thereof including passage **38**. This latter section is formed with passages **50** through which a refrigerant can be circulated for cooling the developing liquid prior to emergence from passage **38** and deposit and freezing upon drum **36**.

The width of passage **38** and the adjustment of valve **46** are such that the developing liquid emerges from the passage as a thin sheet which is immediately frozen upon contacting the drum to form a solid body or sheet **52** on the surface of the drum composed of a predetermined quantity of liquid such that substantially all of the liquid is applied to the sheet. The means for applying the liquid to an image-recording sheet, designated **54**, include a guide member **56** and a backing roll **58** mounted in juxtaposition with drum **36** beneath the drum with the axes of the drum and roll in the same plane and spring biased upwardly toward drum **36**. Roll **58** is preferably rotated so that its surface moves at a faster linear rate than the surface of drum **36** so that a sheet advanced between the drum and roll by rotation of the roll is held by the roll in both rolling and sliding contact with layer **52** of the frozen developing liquid. This arrangement is preferred because it promotes friction between the sheet and frozen layer tending to cause melting of the frozen layer and more complete utilization by absorption by the sheet of the frozen developing liquid coated on the drum.

The rate of flow of the liquid, rotation of drum **36** and advancement of sheet **54** by roll **58** are all interrelated to achieve complete utilization of the liquid frozen on the drum. However, some residue of frozen liquid may remain on the drum and it is desirable that it be removed prior to the application of fresh liquid to the drum and for this purpose there is provided a scraper blade **60** biased against the surface of drum **36** by a spring **62** and a trough **64** located beneath the edge of scraper blade **60** where the latter contacts the drum, for collecting frozen developing liquid removed from the drum by the scraper blade. The surface of drum **36** preferably comprises or is coated with a material which is not only unaffected by aqueous alkaline developing liquids, but which is so constituted that the developing liquid will adhere to it at least sufficiently to be rubbed in contact with the image-recording sheet, whereas the material comprising the surface layer of roll **58** has a high coefficient of friction in order to engage and advance the image-recording sheet relative to the surface of the drum. It is further contemplated that in this embodiment of the invention, heating means may be provided for raising the temperature of the liquid-impregnated sheet to advance the silver halide diffusion-transfer reversal process and/or dry the sheet. Such heating means may comprise a heater within roll **58** or means located beneath the sheet for heating the sheet by radiation and/or conduction. It may also be desirable to preheat the sheet, for example, by providing heating elements in support member **56** and, in this manner, promote the thawing of the frozen processing liquid. While the heat absorbing members have been shown as including passages for the circulation of a coolant liquid, it is contemplated that other types of refrigeration systems are equally useful including, for example, thermoelectric devices.

The method of the invention provides the answers to the three most basic and important problems associated with the processing of light-sensitive sheet materials with non-viscous developing liquids, namely, preventing deterioration of the liquid during prolonged storage and/or application to the sheet material, applying a uniformly distributed predetermined quantity of the liquid to only one side of a sheet, and doing so by a process which is dry in the sense that the liquid is confined to a container, applicator and one side of the sheet. Spillage is prevented and the highly akaline liquid, including the liquid impregnated into one side of the sheet, is prevented from contacting other components of the apparatus. The liquid is stored, handled and applied by apparatus which is relatively simple, and application of the liquid is performed rapidly, accurately and reliably. Freezing of the developing liquid substantially eliminates the danger of deterioration and spillage, and application of the frozen liquid by pressing and moving a solid body of the frozen liquid against one side of the sheet insures application of an accurately predetermined quantity of liquid of unstable, but known, chemical composition evenly and uniformly distributed to only one side of a light-sensitive image-recording sheet.

Since certain changes may be made in the above process 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 drawing 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 an aqueous liquid having substantially the viscosity of water to produce a visible image in said sheet, said method comprising:

rapidly freezing a quantity of said aqueous liquid containing reagents capable of reacting with differentially exposed photosensitive image-recording material to produce a visible image, said liquid being frozen in the form of a substantially solid body having at least one dimension approximately equal to one dimension of the section of said sheet to be treated; and

while maintaining said body of frozen liquid in a substantially solid condition, supporting said body in contact with one side of said sheet over an elongated area located adjacent an edge of said section and extended to opposite edges of said section; and

simultaneously pressing said body against said sheet and moving said sheet and body relative to one another transversely of said elongated area to cause melting of said body in the region of contact with said sheet and impregnation of said sheet with said liquid resulting from said melting.

2. The method of claim **1** wherein said body is moved relative to said sheet in sliding contact therewith.

3. The method of claim **1** wherein said body is moved relative to said sheet in rolling contact therewith.

4. The method of claim **1** wherein said body is moved relative to said sheet in combined sliding and rolling contact therewith.

5. The method of claim **1** wherein said quantity of liquid is approximately equal to the amount required to treat said section of said sheet and is rapidly frozen by application to the surface of a heat absorbing member immediately prior to application to said sheet; and substantially all of said quantity of said liquid frozen on said member is applied to said section of said sheet.

6. The method of claim **5** wherein said surface of said heat-absorbing member is cylindrical and said member is mounted for rotation about the axis of said surface; said

liquid is applied to and frozen on said surface as a thin layer of substantially uniform thickness during rotation of said member; and said sheet is moved relative to said cylindrical heat absorbing member in rolling contact with said layer of frozen liquid.

7. The method of claim 6 wherein said heat-absorbing member is rotated at a rate such that the linear speed of said surface is less than the speed of said sheet relative to and past said heat-absorbing member causing said layer of frozen liquid to make sliding and rolling contact with said sheet and prolonging the period during which said sheet is in contact with said frozen liquid.

8. The method of claim 1 wherein said sheet is heated immediately following impregnation with said liquid.

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