Nov. 24, 1964 D. J. SHANEFIELD 3,158,481

DRY PHOTOGRAPHIC PROCESS

Filed April 2, 1962

Fig. 1.

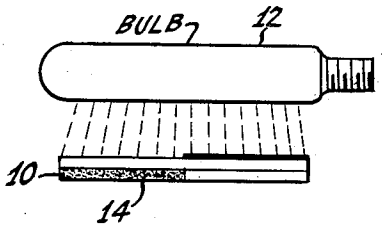


Fig. 3.
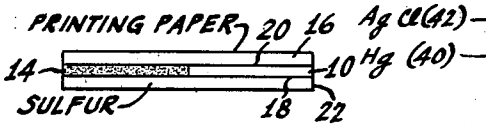
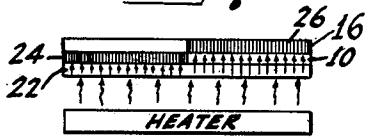
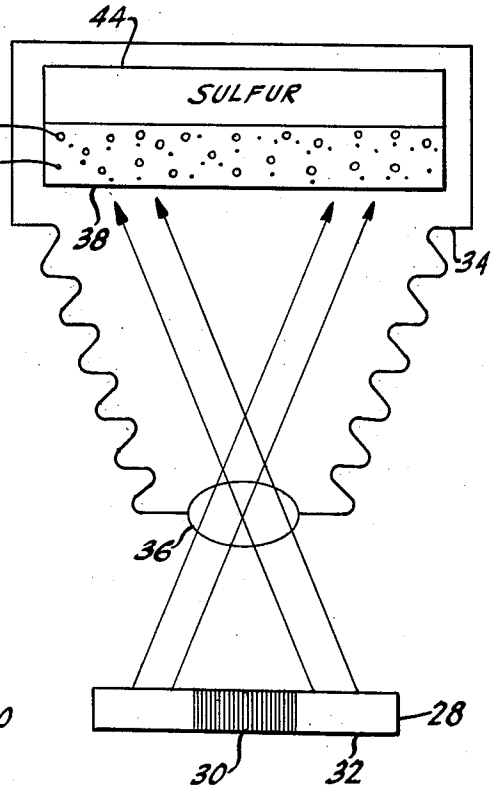




Fig. 2.



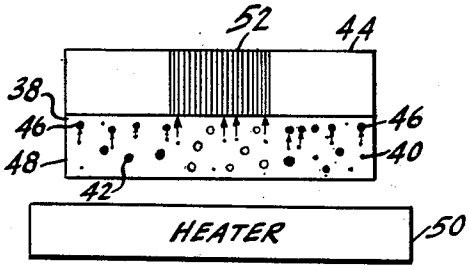


Fig. 5.

Fig. 4.

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United States Patent Office 3,158,481 Patented Nov. 24, 1964

3,158,481

DRY PHOTOGRAPHIC PROCESS

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Filed Apr. 2, 1962, Ser. No. 184,237
5 Claims. (Cl. 96—48)

This invention relates to photography, and particularly to the formation of fixed, stable photographic prints or images by a dry process.

A variety of photographic techniques have been developed which operate by liquid diffusion, that is, by transfer in a liquid of a soluble or dispersible image-forming substance from a layer of photosensitive material to a second, image-receiving layer.

The image forming substance in the photosensitive layer is rendered incapable of dissolution or dispersion in the liquid in selected areas, e.g., by exposure to light and/or chemical treatment, and thus can be picked up and transferred to the image-receiving layer only in areas not so modified. This permits creation of an image which is the reverse of an image in the photosensitive layer.

In these techniques, a liquid agent normally is located between the two layers and upon demand dissolves or disperses the image-forming substance in the photosensitive layer, and along with the dissolved or dispersed substance diffuses over to the image-receiving layer, where the image-forming substance creates the desired image.

The liquid diffusion process, and the various techniques employed to carry it out, have serious disadvantages. For example, exacting control of each step and composition is necessary; in most such transfer processes the liquid developer-solvent must diffuse first into the photosensitive layer and then over into the superimposed image-receiving layer. Diffusion of a liquid first in one direction and then in a reverse direction is difficult to control.

Another disadvantage is the need for a liquid for development and solvent transfer. The liquid requires special containers, and liberation of it at the desired time normally is a problem. In some such techniques, the liquid is contained in pods and a special machine is required to free the liquid and spread it evenly. In other techniques the liquid is open to the air, and it requires frequent replacement because of oxidation. Furthermore, deposits in the liquid system form on the equipment, and must be cleaned frequently; in any event, the liquid must be removed from the system after use. A still further disadvantage is that the liquid system tends to form stains in the final image layer. At best, therefore, the liquid diffusion photographic process, and the various techniques for practicing it, have inherent disadvantages.

It is an object of the present invention to provide a diffusion process for creating on an image-receiving layer, an image which is the reverse of an image in an image-containing, or first layer superimposed thereon, by a means which operates in the absence of a liquid.

It is a further object to provide such a diffusion process which operates by passage of an image-transfer agent from the image-containing layer to the image-receiving layer, without the need for difficultly controlled back diffusion.

Still another object is to provide such a diffusion process in which the image-transfer agent is not susceptible to oxidation or other change on exposure to air, and therefore need not be replaced periodically.

Still a further object is to provide a diffusion process which does not depend on dissolution and transfer of a substance in a liquid, and which therefore does not result

in the formation of deposits on equipment upon evaporation or precipitation of solids from such a liquid system.

Still another object is to provide such a diffusion process which has no material present which will form stains on the image layer or require frequent cleaning of equipment. These and other objects of the invention will be made apparent by the detailed description which follows.

It has now been found, quite surprisingly, that a clear and precise image, which is the reverse of an image in a first or image-containing layer, can be created in a second or image-receiving layer, by a process which operates in the absence of a liquid, by providing a first layer permeable to a gas and having an image therein which obstructs passage of said gas through the image area of this first layer, providing a second or image-receiving layer which contains a material which is converted to a visible condition by contact with said gas, superposing said first and second layers and causing said gas to pass from permeable portions of said first layer to said superposed second layer, and permitting the gas to convert the material in the second layer to a visible condition.

The operation of the present process will now be described more fully with reference to the attached drawings, in which FIGS. 1, 2 and 3 are diagrammatic cross-sectional representations of the steps of the preferred embodiment of the present invention; and, FIGS. 4 and 5 are a diagrammatic cross-sectional representation of another embodiment of the invention.

Referring now to the preferred embodiment described with reference to FIGS. 1 to 3, a first layer, 10 of photographic film is provided, containing a photothermographic substance such as silver succindiamide oxime, mercurous oxalate, or other material which can be sensitized with formation of a latent image on exposure to light, and developed, that is caused to precipitate a metal such as silver or mercury in sensitized areas, upon being heated. This layer 10 is exposed to light from a light source 12 passed through an object to be copied. This creates a latent negative image 14 in the first layer 10.

The resulting exposed film is superposed on a second layer 16 of photographic printing paper containing a material such as mercurous amido nitrate which may be made visible by exposure to a gas, e.g., sulfur vapor, or iodine vapors, which suitably are formed by heat. The vapor will pass through the photographic film layer 10, but will be absorbed by, and therefore will not pass through, the metal formed upon heating of the photothermographic substance.

The face 18 of the first layer 10, opposite the face 20 of first layer 10 which contacts the second layer 16, is then placed in contact with the gas source 22, which may be a sheet of paper containing solid sulfur which vaporizes upon heating, thereby liberating sulfur vapor. The assembly is then subjected to heat, and the metal in the latent image 14 is caused by the heat to form a negative image 24 of metal particles, while simultaneously sulfur gas is formed which passes in the direction of the arrows into the image of metal particles in layer 10 where it is absorbed, and therefore stopped, and through areas not exposed and developed into the second, printing paper, layer 16 where it reacts with and converts the mercurous amido nitrate therein to a darkened, positive image 26.

A second typical system for operating the present dry photographic process will now be described with reference to FIGS. 4 and 5.

In FIG. 4, object 28 having image areas 30 and non-image areas 32, and which is to be copied, is photographed with camera 34 through lens 36, to a sheet 38 containing finely divided mercury 40 and silver chloride 42, and superposed on a second sheet 44, containing sulfur.

As shown in FIG. 5, the silver chloride is converted to silver particles 46 by the light in areas 48 correspond-

ing to non-image areas 32 on object 28. The superposed sheets are then subjected to heat from heater 50 with the result that the mercury particles 40 are vaporized. The vapors are obstructed by the silver particles 46 in layer 38, and pass into the sulfur-containing layer 44 in the direction of the arrows, in areas in which the silver chloride has not been converted to silver. Where the mercury vapors pass into layer 44 they react with the sulfur in this layer, forming a dark image 52 corresponding to the image 30 copied by the photographic process shown in FIG. 4. Sheet 44 is then stripped from sheet 38, and the latter is discarded, with sheet 44 now containing a reproduction of object 28.

The present process operates simply and precisely without the use or formation of any liquid which could be difficult to handle, and which would lead to the formation of undesirable deposits requiring frequent cleaning and liquid replacement. Furthermore, it does not depend upon diffusion of dissolved or dispersed developer or back diffusion, and therefore eliminates several sources of difficulty in control.

It will be apparent that the exposure of the photothermographic film can be accompilshed by other means, and that the formation of the metallic image in the film by heating can be accomplished before combination of the first layer with the printing paper layer. Likewise, the two layers can be assembled before the first layer is exposed to light, with the composite being handled as a unitary product.

Furthermore, other gases than sulfur can be employed, and other material developable with the gas can be employed in place of the materials shown with reference to the drawings. Typical useful gaseous systems include chlorine, oxygen, bromine and mercury, as well as sulfur vapors.

Other materials developable by the various vapors or gases are; with mercury vapor, sulfur; with sulfur or halogen vapor, gold chloride, yellow lead oxide, or a dye such as fluorescein which has been reduced and can be reconverted to dye condition by oxidation with the vapor. Silver metal, or anything that will combine with sulfur to form a sulfur dye, such as p-methylaminophenol or p-phenylene diamine, can be converted to a visible image by contact with sulfur vapor.

Likewise, alternate means of providing the image in the first, or image-containing negative layer can be employed. The typical silver emulsion systems employed in photography, silver bromide carried in gelatin, or silver oxalate likewise carried in gelatin, can be used in this step with advantage.

The process is well suited to the production of colored prints. The material in the image-receiving, or second, layer may be a latent dye oxidizable by oxygen, sulfur, chlorine or other gas to form the dye in areas made visible. The image can be created in the image-receiving layer by causing a visible image to form as a lighter color in a dark photographic layer, as well as by formation of a dark image in a lighter layer.

The gas can be formed in situ in the process, as in the illustrated method of FIGS. 1 to 5, that is by heat or other means, or it may be introduced as a gas from a tank or cylinder, or formed by the reaction of chemicals. Preformed gas would be of particular utility in office copying machines where use of a cylinder or other source of gas is not objectionable.

The amounts of gas, and of image-forming material in the image-receiving layer, as well as of the gas-obstructing material in the image-containing layer, may be determined readily for each application, and generally speaking, it is important to employ amounts of each which will balance. That is, it is necessary in the first or image-containing layer to have an amount of gas-obstructing material which will absorb or otherwise stop all of the gas in the desired areas, while permitting gas to pass through sparsely exposed areas to provide shading, and through unexposed areas to provide a dark image.

The present process is conducted over a period of time which is effective to create the desired image in the image-receiving layer, and normally over on the order of 10 seconds to 10 minutes; the exact time required will depend on the vapor and the image-producing materials employed, the temperature at which the operation is carried out, film thicknesses, and the desired degree of contrast.

It is possible with the present process also to prepare the initial, or image-containing layer by means other than photographic. Thus an otherwise permeable film can be rendered partially or wholly impervious by sealing, its surface or interior; that is, for example, by embossing and densifying paper by heat and/or pressure alone or by flowing together particles of a heat- or pressure-softenable resin in or on the paper. Likewise, it may be sealed by coating or impregnating the layer with an impervious, or partially pervious, material in the image area, and the like. It is necessary only that the initial image in the first layer pass a suitable gas in desired areas, and obstruct its passage in other areas.

The following examples of the photographic process of the present invention are presented by way of illustration only, and are not to be considered limitative of the scope of the invention in any way.

EXAMPLE 1

Vapor-Source Layer A

Thirty grams of precipitated colloidal sulfur is stirred into a solution of 7.5 g. of gelatin and 5 g. of ammonium carbonate in 40 ml. of water. The slurry is spread onto glazed paper and allowed to dry.

First, or Image-Layer B

Twelve grams of yellow mercurous nitrate monohydrate is dissolved in a mixture of 5 ml. of water and 4 ml. of 6 normal nitric acid by stirring to about 80° C. The solution is cooled to −5° C. and filtered to produce white recrystallized mercurous nitrate. The solid is dissolved in a mixture of 2.5 ml. of 6 normal nitric acid plus 50 ml. of water, and this solution is added with stirring to a solution of 20 g. of potassium oxalate monohydrate, in 64 ml. of water. The precipitated mercurous oxalate thus formed is washed and filtered and then stirred into a solution of 15 g. of calfskin gelatin (such as Kodak No. 1099 grade) dissolved in 40 ml. of water. Carbon dioxide is bubbled into the liquid until it becomes acidic, and 10 g. of ammonium carbonate is then dissolved in the liquid. The liquid is spread onto glass and allowed to dry. The dried film is carefully peeled off the glass with a razor or other sharp edge, and the loose film is then superposed on vapor-source layer A and its paper or glass backing.

Layer B is sensitive to ultraviolet light only, and the composite layers A and B and backing is exposed to ultraviolet light in selected areas to form a latent image.

Image-Receiving Layer C

Mercurous amido nitrate is rubbed into the pores of filter paper, and the paper thus treated is pressed, salt downward, on top of the exposed composite layers A and B and backing in contact with the face of layer B which is away from layer A. This sandwich is heated from the bottom at 115° to 130° C. for 7 minutes. Upon heating, the image develops in layer B, and the ammonium carbonate sublimes and forms pores in the gelatin. Some pores had formed during drying. The sulfur vapor passes through non-image areas of layer B and into corresponding areas of layer C, and darkens the mercurous amido nitrate where it contacts it. Image-receiving layer C is then stripped off, and the other layers are discarded. A positive image is present on the image-receiving layer.

EXAMPLE 2

Substitution of mercurous oxalate sensitized by admixture of one molar portion of the oxalate with one molar portion of an equimolar mixture of mercurous iodide and silver iodide in accordance with the procedure of U.S. Patent 2,933,389, for the mercurous oxalate of Example 1, makes it possible to operate the process with white, visible light rather than with ultraviolet light, as is required for the process of Example 1.

EXAMPLE 3

The process of Example 1 can be conducted with other image-creating substances than mercurous oxalate being employed in layer B. Such other useful image-creating substances, and means for using them, include the following:

(*a*) Layer B may be composed of a paper carrying a silver oxalate-gelatin mixture applied from an emulsion of these materials. The mixture is treated to create an image in layer B by application of a catalytic material, e.g., a dilute aqueous solution containing 0.5% of sodium tetrathionate, in areas in which the image is desired followed by heating of the layer at about 100° C., as described in U.S. Patent 1,939,232. This creates an image of silver particles. Layer B can then be used as in Example 1 to form the final image in layer C.

(*b*) Silver oxalate also may be employed as a coating in a gelatin emulsion, and caused to form a latent image by exposure to ultraviolet light. This image can be converted to a silver-particle image with heat, at about 100° C. in 5 minutes to form the image in layer B, as described in U.S. Patent 1,976,302.

(*c*) An equimolar mixture of silver oxalate and mercurous oxalate formed by coprecipitation may be added to gelatin and used to form a photothermographic layer. As described in U.S. Patent 2,700,610, this substance is more light-sensitive than either above.

(*d*) An equimolar mixture of silver sulfide and mercuric iodide powders when heated in the absence of light and air for about 16 hours at about 200° C., forms a yellow photosensitive product which may be used as the image-creating material in layer B. It forms an image in only a few seconds when exposed to light.

Any of the above image-forming substances may be employed in place of the mercurous oxalate of Example 1 in layer B, and the procedure for providing the final image in layer C described in Example 1 followed with excellent results.

EXAMPLE 4

The mercurous amido nitrate used in the image-receiving layer C of Examples 1, 2 and 3 may be replaced with yellow lead oxide, sulfur-dioxide-bleached fluorescein or other material which is converted by a suitable vapor to a visible condition. Mercurous amido nitrate and yellow lead oxide, for example, may be converted by sulfur vapor, and the bleached fluorescein by a halogen vapor. These materials operate in the same fashion as the mercurous amido nitrate to form an image.

The terms gas and vapor are used herein coextensively, and indicate a material in gaseous state as opposed to the liquid or solid state.

Pursuant to the requirements of the patent statutes, the principle of this invention has been explained and exemplified in a manner so that it can be readily practiced by those skilled in the art, such exemplification including what is considered to represent the best embodiment of the invention. However, it should be clearly understood that, within the scope of the appended claims, the invention may be practiced by those skilled in the art, and having the benefit of this disclosure, otherwise than as specifically described and exemplified herein.

I claim:

1. Process for forming an image corresponding to an object to be reproduced, which operates in the absence of liquid reagents, comprising providing a first, continuous layer free of substantial discrete voids and of varying permeabilities to gas whereby said gas diffuses readily through non-image areas of said first layer and is obstructed against passage to varying degrees through said image areas thereof, providing a second, image-receiving, layer which contains a material which is converted to a visible condition by contact with said gas, superposing said first and second layers, causing said gas to pass through permeable portions of said first layer to said superposed second layer, and permitting the gas to convert the material in the second layer to visible condition.

2. Process of claim 1 in which the image in the first layer is created by providing in said first layer a photothermographic substance, exposing it to light to form a latent image, and developing this latent image by heat.

3. Method of claim 1 in which the gas is formed by the application of heat.

4. Process for forming an image corresponding to an object to be reproduced, which operates in the absence of liquid reagents, comprising providing a first, continuous layer free of substantial discrete voids and of varying permeabilities to gas whereby said gas diffuses readily through non-image areas of said first layer and is obstructed against passage to varying degrees through image areas thereof, providing a second, image-receiving, layer which contains a material from the group consisting of mercury compounds, silver compounds, sulfur, gold chloride, yellow lead oxide, reduced fluorescein, silver metal, p-methylamino phenol and p-phenylene diamine, which is converted to a visible condition by contact with said gas, superposing said first and said second layer, causing said gas to pass through permeable portions of said first layer to said superposed second layer, and permitting the gas to convert the material in the second layer to visible condition.

5. Method of claim 4 in which the first and second layers are superposed and heated to a temperature of 100–130° C.

References Cited in the file of this patent

UNITED STATES PATENTS

1,913,881	Heinecke	June 13, 1933
2,095,839	Sheppard et al.	Oct. 12, 1937
2,600,112	Jacobs et al.	June 10, 1952
2,600,996	Land	June 17, 1952
2,770,534	Marx	Nov. 13, 1956
2,904,432	Ross et al.	Sept. 15, 1959

FOREIGN PATENTS

619,941	Great Britain	Mar. 17, 1949

OTHER REFERENCES

Kaprelian: "A Survey of Photographic Processes and Materials," Photographic Engineering, vol. 1, No. 2, April 1950, pages 42–56.