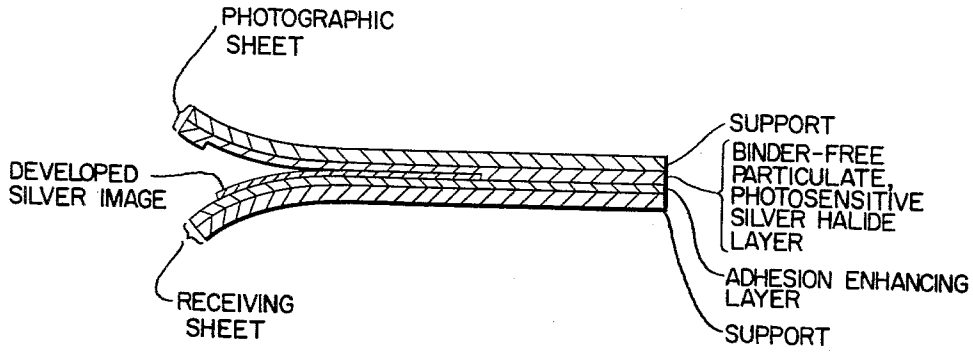
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PHOTOGRAPHIC PROCESSES

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# PHOTOGRAPHIC PROCESSES

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The present application is a continuation in part of copending U.S. application Serial No. 840,973 filed September 18, 1959, now abandoned.

This invention relates to photography, and more particularly to novel photographic transfer processes.

A number of photographic transfer processes are known and currently in use. Among the more important of such is the diffusion transfer process in which photosensitive sheet material bearing a silver halide emulsion is exposed to form a latent image. The image is developed with a processing composition, fo rexample, an aqueous, solution of a silver halide developer, a silver halide solvent, and an alkali. During development, the emulsion surface is maintained in superposed relationship with an image-receiving surface or transfer sheet for a predetermined processing period. During this period, the exposed silver halide of the photosensitive material is reduced to silver, and the unreduced silver halide forms a water-soluble, complex silver salt which diffuses through the processing composition to the transfer sheet where, upon being reduced to silver, it forms a visible image.

In yet another process, similar to the diffusion transfer process, an exposed photosensitive sheet material is treated to form dye silver salts. The fully exposed areas of the treated photosensitive material are hardened in an activator but the unexposed areas are dyed to form the salts and do not harden. Hence, upon superposing the developed photosensitive sheet material with a transfer sheet a dye silver salt is transferred to the latter to form a visible image.

An additional known transfer process is an electrostatic process, now known as xerography, which is based upon creation of an electrostatic image upon a photoconductive plate formed, for instance, of selenium. The plate is first given a uniform electrostatic charge and is then exposed to an optical image which destroys the charge selectively according to the intensity of the image portions. A powder, charged oppositely to the plate, is then dusted on the latter and is electrostatically bound wherever the appropriate charge is present. The powder image thus formed may be transferred to a receiving sheet, such as paper, as by pressure, and fixed to the surface of the latter, as by heating.

This latter process being based upon electrostatic phenomena, is not concerned with photosensitive silver salts, nor the transfer of silver images. The other transfer processes mentioned above are based upon the photosensitivity of silver halides. But both of these latter transfer processes require intermediate chemical processing to effect image transfer; in none is developed silver transferred directly. In the diffusion transfer process, the processing fluid itself acts as a medium for transferring silver complexes, and usually a special receiving sheet having silver precipitating nuclei is required to precipitate silver from the complex silver salts at the receiving sheet. On the other hand, the dye silver process requires the formation of special dye silver complex before transfer can be effected, and the transferred image is constituted of these dye complexes rather than simple silver.

Accordingly, a principal object of the present invention is to provide novel methods for producing photographic records. Particularly, the methods of the invention involve coherent images formed of developed silver particles on a substrate of silver halide and the mechanical transfer of such images from the substrate to a transfer material, thereby forming an essentially silver halide-free image upon the latter, while leaving the substrate substantially silver-free. The mechanical transfer is achieved through preferential adhesion of the developed silver images with the transfer material. Another object of the present invention is to provide a transfer process of the type described wherein is employed a photosensitive sheet material formed as a binder-free, particulate silver halide stratum on an appropriate base material.



Yet another object of the present invention is to provide novel transfer processes by which a single image or a plurality of successive images, can be obtained from a single latent image by mechanical transfer of developed silver through adhesion.

Other objects of the present invention will in part be obvious and will in part appear hereafter. The invention, accordingly, comprises the methods and compositions respectively comprising the steps and procedures, and combination of elements, 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 present invention, reference should be had to the following detailed description, taken in connection with the accompanying drawing in which is shown an exemplary embodiment of the invention. The methods of the present invention preferably employ a photographic element such as photosensitive sheet material comprising a binder-free, particulate stratum of silver halide mounted upon an appropriate base material as shown in the drawing; particularly a silver halide deposited upon the base sheet in the form of an evaporated film as by vacuum deposition techniques. Among appropriate base materials are baryta paper (paper coated with, for example, barium sulphate in gelatin) vitreous materials such as glass; cellulose esters, e.g., cellulose acetate, cellulose butyrate, cellulose proprionate; synthetic polymeric resins such as Mylar (polyethylene terephthalate), polystyrene, polyvinyl chloride, vinyl chloride-vinyl acetate copolymer; and other polyesters, polyamides and the like. This base material may be transparent to radiation actinic to the silver halide, or opaque depending upon the desired form of the image to be obtained and the method of exposure to be used. The silver halide is in the form of a light-sensitive silver salt such as silver bromide, silveriodobromide, and others. Examples of photographic media of this type are disclosed, for instance, in U.S. Patent No. 1,970,496 issued August 14, 1934 to De Boer et al.; and U.S. Patent 2,945,771 issued July 19, 1960 to H. Mansfeld.

Media of this type have some pronounced advantages over gelatin emulsion films in that they are free from limitations imposed by the gelatin binder. In standard photographic emulsions the silver halide is usually imbedded in a gelatin matrix. This limits the speed of the development process because the developer reagent generally must diffuse through the binder before it can react with the halide grains. Processing of ordinary emulsion film also involves fixation of the developed image by chemical removal of the undeveloped silver halide. Additionally, in developed emulsions, oxidation products are bound in the gelatin in the areas where development has taken place; this creates a loss in acutance. The separation of the halide grains and any subsequently developed silver by the emulsion adversely affects resolution. In the present invention, however, because there is no binder, diffusion by the developer reagent is no factor, and no extra reagent is necessary to provide gelatin saturation.

In addition, the images produced by the present invention in some instances do not necessarily require fixation to remain substantially permanent with respect to actinic radiation. The lack of binder, of course, provides superior resolution and acutance in that developed silver grains may be contiguous and no organic oxidation can occur. Unlike a developed silver image in a gelatin matrix, the images formed in the preferred photographic media are formed of binder-free silver, and this permits the separation of the silver from the silver halide to be effected mechanically by adhesion rather than chemically.

Photosensitive sheet material of the type described may be exposed to actinic radiation to form a developable latent image in the silver halide stratum, as by contact printing, direct exposure to an optically formed image, by reflex printing, or the like. The latent image thus formed is developable by an alkaline silver halide developing solution containing a silver halide developing agent, with or without a silver halide solvent depending upon the variation of the process desired. Silver halide developing solutions such as Eastman Kodak's D–19 comprising an aqueous solution of p-methylaminophenol, sodium sulfite, hydroquinone, sodium carbonate and potassium bromide may be used. If it is desired to retard the speed of development, in view of the binder-free nature of the photosensitive stratum, it is preferred to dilute the D–19 by forming a solution of 70% thereof with 30% of a 5% gelatin solution. Another developing solution adapted for use in the present invention and preferred as a surface developer comprises

| | | |
|---|---|---|
| p-Methylaminophenol sulfate | g— | 0.67 |
| Hydroquinone | g— | 2.5 |
| Sodium sulfite | g— | 26.0 |
| Sodium carbonate | g— | 26.0 |
| Potassium bromide | g— | 0.67 |
| Gelatin | g— | 1.67 |

Water to make 1 liter.

Other developing solutions may be used, typically, solutions containing developing agents such as hydroquinone derivatives, 1-phenyl-3-pyrazolidone, phenylhydrazine, phenylhydroxalamine and many others. Such developing solutions may be directly flushed onto the exposed silver halide stratum as in a bath, or may be sprayed on as a fine mist, or may be used by being absorbed in a carrier such as a sponge, blotter or the like, which is then applied to the silver halide stratum to release the developing agent.

Upon exposure and development, the silver halide microcrystals which are developed in photographic media of the type employed, are converted essentially to pure silver particles resting on a substrate of the original silver halide. The adhesion between silver particles and silver halide microcrystals is poor. Thus, the transfer process of the present invention is accomplished by placing the silver image of a developed photographic sheet of the preferred type in superposed relation with an appropriate transfer element or receiving sheet to create adhesion between the latter and the image as shown in the drawing. The term "adhesion" as used herein applies to the tendency of matter to cling to other matter through the interaction of strong molecular forces established by molecules that come into relatively intimate contact with one another. The term "adhesion" is intended to include adhesion of any nature, whether brought about because of the plasticity of a surface, the smoothness of a material, or the use of normally tacky "adhesives" such as gums and glues or the like. Adhesion between the silver image and the superposed receiving sheet can be effected merely by pressure and the selection of an appropriate transfer element which exhibits selective adhesion with respect to the silver, i.e., where adhesion forces are created between the receiving sheet and the silver which are greater than the adhesion forces between the silver and the silver halide. Such a receiving sheet also preferably exhibits substantially less adhesion with respect to the silver halide than the base material upon which the silver halide has been deposited, thereby insuring that the silver halide will not transfer. Where the base material of the photographic sheet would normally exhibit inherently poor adhesion with respect to silver halide deposited thereon, an adhesion enhancing layer or bonding layer of adhesive material may be deposited upon the receiving sheet to form a substrate for silver halide deposition thereon.

Because the forces of adhesion increase inversely as a function of distance, ti is desirable to have the receiving sheet brought into very close contact with the silver image intended to be transferred thereto. The smoothness, i.e. the freedom from surface irregularities of the receiving sheet can contribute in this respect. Thus glass, polymeric materials such as polyethylene terephthalate, polyvinyl acetate, and the like, capable of being calendered, cast or ground into smooth sheets, are appropriate in this respect. Additionally, the adhesion characteristics of the receiving sheet may be enhanced, in some instances, by selecting a material for the receiving sheet which is capable of being softened slightly by the application thereto of heat.

Other transfer materials or receiving sheets exhibiting preferential adhesion for a developed silver image on a binder-free silver halide layer may also be employed. For instance, a sheet formed of a pressure-sensitive adhesive or having an adhesion enhancing coating thereof may be employed as shown in the drawing. Typical pressure-sensitive, adhesive-coated tapes or sheets are commercially available from Minnesota Mining and Manufacturing Company under the trade name of "Scotch" brand tapes and from other manufacturers. A typical tape of this type can be formed of a flexible support such as cellophane, polystyrene, polyvinyl acetate, cellulose acetate, polyethylene glycol terephthalic acid film or the like, coated with an adhesive comprising an elastomer such as a natural rubber latex, a tackifier such as a coumarene-indene resin, and a filler such as zinc oxide, titanium dioxide or aluminum hydrate, with a stabilizer or antioxidant such as 2,6 ditertiary butyl-p-cresol if desired. A specific adhesive useful in the present invention and requiring no tackifier is one containing metal salts of esters of maleic anhydride-styrene copolymers. The use of this pressure-sensitive material as a transfer or receiving sheet allows the latter to be placed in superposition with the developed surface silver image on a binder-free halide layer, and when pressure is applied thereto substantially normal to the surface of a silver image, adhesion is effected between the receiving sheet and the silver.

Following superposition which allows the silver image on the developed photosensitive sheet material to adhere to a receiving sheet, the latter is mechanically separated or stripped from the developed photosensitive sheet material. Thus a receiving sheet is obtained bearing an image comprising the large bulk of the developed silver in substantially silver halide-free form, while leaving the developed photosensitive sheet material substantially silver-free as shown in the drawing. Where the original photosensitive sheet material was developed to form a negative image, the silver transferred to the receiving sheet, of course, forms a negative image, leaving a positive image on the photosensitive sheet material in the form of undeveloped silver halide. This image can be brought out by fogging or other processing which substantially changes all of the residual silver halide to free silver, thereby creating a positive silver image on the original base material. For instance, the original silver halide can be re-exposed to light generally and then developed in a standard developer; or the silver halide can merely be flushed for sufficient time with a developer to cause fogging. Other methods are also known.

It is also possible, through the process of the present invention, to obtain a plurality of successive images from

a single exposure of the preferred photosensitive sheet material having a binder-free, silver halide stratum. As has been described previously, after a latent image is formed in such a stratum, and the image is developed with a surface developer to form a silver image, application of a receiving sheet which will adhere to the image virtually completely removes the developed image from the surface of the stratum. If proper precaution is taken to prevent the residual silver halide stratum from being further exposed, redevelopment with a surface developer will again bring out another silver surface image on the stratum, which image, on subsequent transfer, yields a second permanent copy on another receiving sheet. If the silver halide layer is thick enough and the latent image extends therethrough, the process can be repeated several times to form a series of approximately identical images, each of which is transferable by adhesion. It has been found that a silver bromide layer in binder-free form which is approximately one micron thick will yield as many as seven images in this manner.

Where it is desirable to protect the transferred silver image from mechanical damage, oxidation or the like, the silver image on the receiving sheet may be readily coated. Where, for instance, the support material of the receiving sheet is polyethylene terephthalate based film, it is especially desirable to coat the developed image unless the latter has already been fixed by one of the methods heretofore disclosed. Among the coating solutions which may be used is one containing a polymeric resin such as a terpolymer of vinyl acetate, vinyl chloride and maleic acetate (commercially available as Derex 3098 from Dewey & Almy Co.) mixed with acetic acid, acetone and ethyl acetate solvent. Other known coating compositions can also be employed.

The invention, and various aspects thereof, is illustrated in more detail in the following specific examples:

*Example 1*

A very thin (less than 0.1$\mu$) binder-free, particulate layer of silver iodobromide was formed by vacuum deposition on a sheet of polyethylene glycol terephthalate film and exposed to form a negative latent image thereon. The latent image was reduced to silver with a D–19 type of developer solution and air dried. A sheet of cellophane coated with a pressure-sensitive adhesive ("Scotch" brand tape) was superposed under pressure with the silver image to form a sandwich and then stripped from the sandwich. The silver image, in coherent form, was essentially completely transferred to the cellophane sheet.

*Example 2*

A binder-free, photosensitive layer was formed as in Example 1 and exposed to form a negative latent image. The latent image was reduced to silver using a developer of the Elonhydroquinone type substantially free from silver halide solvent. The image was transferred as in Example 1 leaving the polyethylene glycol terephthalate film with substantially silver-free and halide-free areas. The residual silver halide on its support was redeveloped by immersion in D–19 developer solution for a time sufficent to reduce all of the residual silver halide to silver. The resulting positive silver image was then superposed with another receiving sheet coated with pressure-sensitive adhesive, and pressure was applied to provide intimate contact between the latter image and the latter receiving sheet. Upon stripping the halide support from the receiving sheet, it was found that the positive coherent silver image had been almost completely transferred to the receiving sheet.

*Example 3*

A photographic element was prepared by coating a polyethylene terephthalate sheet to a thickness of approximately 1 micron with a binder-free particulate layer of AgBr, and exposed to provide a latent image extending well through the thickness of the layer. The layer was spray developed with a silver halide solvent-free developer solution to provide a surface silver image. The latter was superposed with the gelatin-urea coated (7 parts to 3) surface of a very smooth baryta paper and subjected for 5 seconds to pressure of about 10 pounds per square inch in the area including the contacted silver image. The baryta paper was stripped with silver image adhering thereto and the photographic element again spray processed to develop another surface silver image from the latent image. This silver image was transferred by adhesion to a pressure-sensitive adhesive surface of a second receiving sheet much as described in Example 2. The process was repeated to provide several separate images on dividual receiving sheets.

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

What is claimed is:

**1.** A photographic transfer process comprising the steps of: forming, by exposure, a developable latent image in a binder-free, particulate stratum of silver halide mounted on a base material; developing said latent image to form a silver image on the surface of said stratum; and transferring said silver image to a receiving element by so placing the latter in intimate contact with said silver image as to cause said silver image and said element to adhere to one another.

**2.** A photographic transfer process comprising the steps of: forming, by exposure, a developable latent image in a binder-free, particulate stratum of silver halide mounted on a base material; developing said latent image to form a silver image on the surface of said stratum; bringing said silver image into intimate contact with a surface of a receiving sheet, said surface being formed of a material capable of adhering to said image and having selectively greater adhesion for said image than for the undeveloped silver halide in said stratum; and separating said sheet, with at least a portion of said silver image adhering thereto, from said stratum.

**3.** A photographic transfer process comprising the steps of: forming, by exposure, a developable latent image in a binder-free, particulate stratum of silver halide mounted on a base material; developing said latent image to form a silver image on the surface of said stratum; bringing said silver image and a surface of a receiving sheet into contact with one another, said surface being formed of a pressure-sensitive adhesive; applying pressure to the contacted receiving sheet and silver image to effect adhesion therebetween; and separating said sheet, with at least a portion of said silver image adhering thereto, from said stratum.

**4.** A photographic transfer process comprising the steps of: forming, by exposure, a latent image in a layer of binder-free, particulate silver halide mounted on a base material, said layer being thick enough and said latent image being formed sufficiently through the thickness of said layer so that said latent image is developable to form a succession of surface silver images; developing said latent image only to form a first silver image on the surface of said layer; placing a first receiving element and said first silver image in such intimate contact with one another that enough of said first silver image adheres to said element to form a visible, coherent image thereon; separating said first receiving element, leaving said coherent image therein from said layer, repeating said steps of developing said latent image to form a succession of subsequent silver images on the surface of said layer; placing a corresponding receiving element in adhering contact with each of said successive images; and separating each of said corresponding receiving elements leaving a separate coherent image from said layer, whereby a plurality of silver images is

formed on separate receiving elements from a single latent image.

5. In a process of forming a record image by means of a recording element having a stratum of vapor deposited silver halide microcrystals adhered directly to a substrate base and cohered directly with each other, by selectively reducing a portion of said silver halide to silver along the surface of said stratum to delineate a record image, the improvement comprising the additional step of selectively separating the silver and the residual silver halide portions from each other by physically removing one portion from said element to provide a fixed silver record image.

6. In a process as set forth in claim 5, said selective separation being effected by contacting the silver and silver halide on the surface of said stratum delineating said record image with a layer of material having a greater adhesion than said element for said silver and a lesser adhesion than said element for said residual silver halide, and separating said layer of material from said stratum with said silver adhered thereto substantially free of said residual silver halide.

7. In a process as set forth in claim 6, said stratum of silver halide microcrystals having a thickness of a fraction of a micron.

8. In a process as set forth in claim 7, said thickness being about 0.1 micron.

9. In a process as set forth in claim 5, said stratum of silver halide microcrystals having a thickness of a fraction of a micron.



10. In a process as set forth in claim 5, said stratum of silver halide microcrystals having a thickness of about 0.1 micron.

11. In a process as set forth in claim 5, said stratum of silver halide microcrystals having a thickness of about one micron.

12. In a process of forming a record image by means of a recording element having a stratum of vapor deposited binder-free photosensitive silver halide microcrystals essentially continuous in phase and substantially covering a recording surface area, by selectively reducing a portion of said silver halide to silver along the surface of said stratum to delineate a record image, the improvement comprising the additional step of selectively separating the silver and the residual silver halide portions from each other by physically removing one portion from said element to provide a fixed silver record image.

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