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2,774,667

PHOTOGRAPHIC SILVER HALIDE TRANSFER PROCESS

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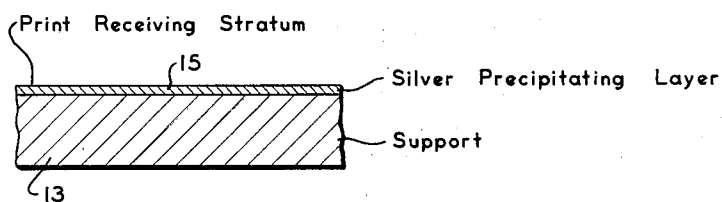


FIG. 1

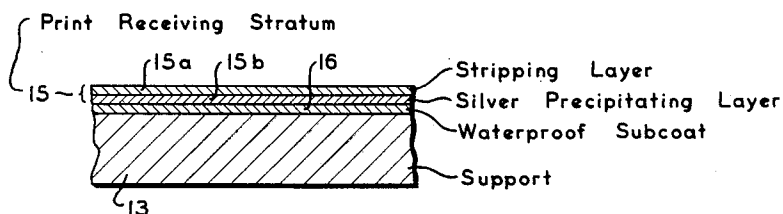


FIG. 2

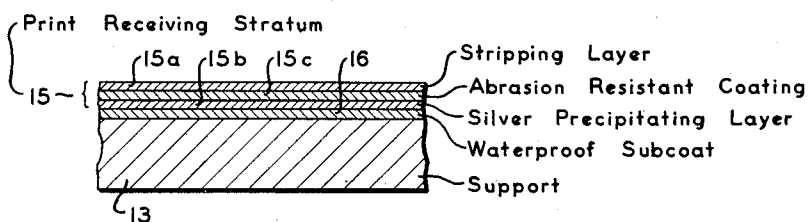


FIG. 3

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PHOTOGRAPHIC SILVER HALIDE TRANSFER PROCESS

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Application July 2, 1951, Serial No. 234,854

14 Claims. (Cl. 96—29)

This invention relates to photographic processes and more particularly to transfer processes wherein a latent image in a silver halide emulsion is developed and a soluble silver complex is obtained by reaction with the undeveloped silver halide of said emulsion, and wherein the soluble silver complex is transferred from said emulsion to a print-receiving element and the silver thereof is there precipitated to form a positive print.

One object of the present invention is to provide a novel silver halide transfer process of the foregoing type, said process being capable of giving positive images which are brilliant, which have full-tone gradation, high maximum densities, low minimum densities and homogeneity of hue in highlight and shadow, and whose color range is from black through neutral gray to white.

It is another object to provide a novel transfer process of the above character which can be performed with a great variety of silver halide emulsions and which is especially suited for giving positive prints of latent images formed in the very fast negative-type emulsions.

A further object is to provide a transfer process which can be performed not only with a great variety of photosensitive silver halide emulsions but also with most of the conventional developing agents and compositions.

A still further object of the invention is to use in a transfer process an improved print-receiving element comprising a novel silver precipitating layer adjacent one surface thereof, which layer comprises a discrete macroscopically continuous film or matrix formed of particles of colloidal silica in which there is dispersed a silver precipitating agent. Especially useful for providing the silica of this layer is the silica dispersion commercially available under the trade name "Ludox" (Soap and Sanitary Chemicals, volume 25, July issue, pages 121, 123 and 125; August issue, pages 115-117) in which the silica micelles are estimated to have a particle size from 10 to 30 millimicrons with an average of 15 millimicrons. This dispersion is applied as a layer to a suitable support to provide upon said support the matrix of silica, and care is taken to retain the silica in its colloidal unprecipitated state until it is so applied to the support. The silica matrix in its solid condition has dispersed therethrough a silver precipitating agent and this silver precipitating agent is added to the constituents of the silica matrix prior to their solidification upon the support. Preferably, the silver precipitating agent is introduced into the silica dispersion prior to its application onto the support or, alternatively, the silver precipitating agent is added to the layer of silica dispersion just after it is applied to the support but before it dries. In either case, the addition of the silver precipitating agent is made in such a way as to leave the silica particles in their colloidal condition.

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 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,

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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:

Figure 1 is a diagrammatic enlarged sectional view illustrating one form of the novel print-receiving element of the present invention;

Fig. 2 is a view similar to Fig. 1 illustrating another embodiment of the print-receiving element; and

Fig. 3 is a view similar to Fig. 1 of still another form of the print-receiving element of the invention.

It has previously been proposed to employ silver halide transfer processes otherwise identified as "diffusion-transfer reversal processes" for the purpose of forming positive prints upon print-receiving elements. Certain of these proposals have been directed to processes of limited application suitable essentially for the graphic arts, such as reflex and direct positive printing. These last-mentioned processes are performed with slow emulsions and in a plurality of steps. They require a washing or toning operation subsequent to image formation and also require for their performance the immersion of the photosensitive and print-receiving elements in baths of the processing agent ("A New Principle of Reversal; Reversal-Transfer by Diffusion" by Andre Rott in Science et Industrie Photographique (2) 13: 151-152, July-August 1942, and I. G. F. French Patent No. 879,995).

In the following patent and applications of Edwin H. Land: Patent No. 2,543,181, issued February 27, 1951, for Photographic Product Comprising a Rupturable Container Carrying a Photographic Processing Liquid; application Serial No. 662,000, filed April 13, 1946, now Patent No. 2,584,029, for Photographic Product and Process; application Serial No. 726,982, filed February 7, 1947, now Patent No. 2,584,030, for Photographic Product and Process; application Serial No. 727,382, filed February 8, 1947, now Patent No. 2,698,238, for Photographic Product and Process; application Serial No. 727,383, filed February 8, 1947, now Patent No. 2,644,756, for Photographic Product and Process; application Serial No. 727,385, filed February 8, 1947, now Patent No. 2,698,245, for Photographic Product and Process; application Serial No. 7,795, filed February 12, 1948, now Patent No. 2,647,056, for Photographic Process; application Serial No. 37,252, filed July 6, 1948, now Patent No. 2,635,048, for Photographic Product and Process; application Serial No. 88,832, filed April 21, 1949, now Patent No. 2,662,822, for Photographic Transfer Processes and Products and Compositions for the Practice of said Processes; application Serial No. 164,908, filed May 29, 1950, now abandoned, for Photographic Silver Halide Transfer Product and Process; and application Serial No. 176,963, filed August 1, 1950, now abandoned, for Photographic Transfer Processes and Compositions for the Practice of said Processes; there have been disclosed silver halide transfer processes capable of (a) operating with fast (negative) emulsions; (b) directly producing stable prints, i. e., prints requiring no washing, toning or other after treatment for their permanency; (c) directly giving positive prints having adequate density, homogeneous hue in highlight and shadow and full-tone gradation; (d) operating over a wide range of ambient temperatures; and (e) being performed in a camera without baths and with a minute quantity of liquid contained within the film. According to the present invention, there is provided an improved print-receiving element universally useful in the transfer processes described in the foregoing patents, patent applications and publications for giving prints of improved pictorial quality and color characteristics.

In one of its simplest forms the product of the present

invention comprises, as shown in Fig. 1, a support 13 and a silver precipitating layer 15 coated or otherwise applied upon said support. Support 13 may be formed of almost any rigid or flexible supporting material which is mechanically stable in the presence of conventional photographic developing compositions. For example, for forming positives which are to be viewed in reflected light, support 13 may be a photographic paper base, such as baryta paper, and for giving positive transparencies said support may be one of the transparent film bases.

The novel structure of the silver precipitating layer 15 is uniquely effective in providing the type of environment required for the formation of positive prints which are brilliant and which have full-tone gradation, high maximum densities, low minimum densities and homogeneity of hue in highlight and shadow. Certain of the conditions which must be satisfied in the achievement of such a print have been described in the article entitled "One step photography" by Edwin H. Land in the *Photographic Journal*, Section A, January 1950, pages 7 through 15. It is there pointed out that the silver precipitating layer must be suitably constituted to build up the deposited silver atoms into arrays of large enough diameter for absorbing visible light and that these arrays must also have adequate constancy in diameter so that the highlight and shadow of the positive are of the same hue. Undue migration or aggregation of the silver precipitants in the silver precipitating layer will cause silver precipitation to initiate at many points so that an enormous number of highly dispersed silver grains form, thereby diminishing the density of the positive and giving a print which has a yellowish hue. For example, colloidal silver dispersions in a protective colloid, such as gelatin, if used as print-receiving layers, induce precipitation of silver in this highly dispersed form and give prints having a yellow to light brown color. Attempts to correct this by the inclusion of conventional blue-black toning agents with the colloidal silver in the silver precipitating layer are partially effective in giving a more nearly black and white image, but this improvement is made at the sacrifice of gradation in density between highlights and shadows. Thus, a product formed in this manner finds its principal application in the graphic arts for document duplication. A different attack upon the problem of silver precipitation which has resulted in the production of excellent photographic prints suitable for all photographic purposes is represented by the improvements embodied in the Polaroid Land film. As first made publicly available, this film gave warm sepia prints. The concepts which have contributed to this advance in the art of forming positive prints by silver halide transfer involve not only the provision of a proper environment for the precipitation of silver but also a closely interrelated chemical environment so constituted as to avoid the hazards to print stability. In solving the first problem so as to obtain prints which have full-tone gradation and homogeneity of hue, several important concepts were combined among which were the use of lead ions for giving improvements in density and color (application Serial No. 662,000); the use of heavy metal sulfides and selenides in combination with an excess of heavy metal ions capable of trapping the sulfide ions to confine the latter to their original site (application Serial No. 164,908); and the use of certain inert dispersing media without specific regard to the extent of their dispersion to provide the initial desirable aggregation of the metallic sulfides or selenides (application Serial No. 727,385). These concepts have provided extremely effective mechanisms for achieving print quality, especially when used in combination.

Another mechanism effective for controlling the silver precipitation during image formation is the provision of the silver precipitants in the viscous processing agent rather than in the surface portion of the solid print-receiving element. These precipitants are provided as substantially insoluble salts and in a highly dispersed essentially colloidal condition (application Serial No.

88,832). This approach tends to precipitate the silver almost entirely in the layer of processing composition. These mechanisms in specially selected combinations are capable of giving prints which not only possess the desiderata of a good photographic print, e. g., excellent gradation, homogeneity of hue, high maximum densities and low minimum densities but are also substantially black and white in color. However, this approach depends upon the interaction of several components or concepts for the proper control of the silver precipitation and upon achieving a proper balance between the components. The present invention provides a more universal solution to the problem of obtaining high quality, brilliant prints in a color range of from black through neutral gray to white. The product of the present invention tends, whatever the circumstances, to aggregate the precipitated silver atoms into arrays such that the highlight and shadow of the positive are white and black, respectively, and the gradations are neutral gray. These results are achieved by providing as a principal component of the print-receiving layer a macroscopically continuous film or matrix of silica in which suitable silver precipitating agents are dispersed, said matrix being deposited from a dispersion in which the silica micelles are present in colloidal form. This dispersion is regarded as either a colloidal solution of hydrated silica or a polymerized form of siliceous acid in solution. It preferably contains 30% of the silica and also a small amount of alkali which serves as a stabilizing agent to prevent the precipitation or gelation of the silica. One available form of this colloidal silica is the product sold by Du Pont under the trade name "Ludox." In this connection it is to be noted that some equivalency has been observed between silica and other protective colloids in maintaining colloidal metals in their colloidal condition in liquid suspensions thereof in a strictly non-photographic application (*Journal of the Washington Academy of Science*, volume V, 1915, pages 68-71), but for the purposes herein disclosed, namely, the achievement of a solid matrix serving as a vehicle for the silver precipitating agent and for receiving and precipitating silver, there is a vast and dramatic difference between the functioning of silica and other suspending and dispersing media and also between silica in this hydrated and colloidal condition and silica in its other states of aggregation.

The silver precipitating agents are preferably introduced into the silica dispersion prior to its application to the support 13 and in quantities and under such conditions as to clearly preclude any gelation or precipitation of the silica of the dispersion. Preferred as silver precipitating agents are the metallic sulfides, selenides and selenosulfides, these terms being understood to include the polysulfides and polyselenides. Also suitable as precipitants are such colloidal metals as silver, gold and mercury, provided that the same are introduced into the silica matrix in intimate mixture with a protective colloid capable of preserving their colloidal state. The amounts of protective colloid necessary for this purpose are relatively trivial in comparison to the mass of the silica of the matrix so that the essential physical and chemical characteristics of the matrix are not appreciably modified by the presence of the protective colloid. Still other satisfactory silver precipitating agents are dithiooxamate and its lead and zinc complexes, potassium dithiooxalate and the lead complexes thereof and thioacetamide.

The combination of a silver precipitating agent and a discrete macroscopically continuous matrix of silica thus provides an environment in which the silver atoms will deposit in aggregates having high enough conductivity and large enough diameter to be black, like those or ordinary positive paper, without requiring any special reagents for confining the silver precipitant to its original site. The use of such reagents may, however, assist in increasing the density and improving the stability of the positive print. The novel precipitating layer so precipitates and aggregates the silver as to give it a very high covering

power in the order of five times that of the silver in the negative.

One example of a process for forming print-receiving elements comprising a support 13 and a silver precipitating layer 15 is the following:

EXAMPLE 1

A solution is formed by mixing together:

	Cc.
10% solution of silver nitrate (AgNO ₃)	6.30
Water	14.0
2 N Sodium hydroxide (NaOH)	1.88

A precipitate is obtained which is thereafter dissolved by being washed in 3 cc. of a 10% solution of ammonium hydroxide (NH₄OH).

This solution is then added to 100 cc. of a 2% gelatin solution and the mixture is heated in a water bath and after heating is permitted to stand for approximately fifteen hours. The solution is then evaporated in an evaporating dish and the dry residue is redissolved in 20 cc. of water. 3.6 cc. of the resulting solution are added to 300 cc. of "Ludox" and the mixture thus formed is applied as a coating 15 to a support 13.

A further type of silver precipitating agent which is useful is the silver-protein composition synthesized in accordance with the procedure outlined in Dansk. Tids. Farm. 18, pages 53 to 83, 1944, and a satisfactory coating composition for layer 15 is one formed from a mixture of 400 cc. of "Ludox" and 1.58 grams of said silver-protein composition.

A positive sheet so constructed may be employed in a process similar to that described in my above-mentioned copending application Serial No. 7,795, with a processing composition comprising:

Water	cc.	398
Sodium carboxymethyl cellulose (high viscosity)	grams	15.25
Sodium sulfite	do	25.6
Sodium hydroxide	do	15.2
Sodium thiosulfate	do	5.4
Hydroquinone	do	52
6-nitrobenzimidazole	do	5
Metol	do	5

The print-receiving elements of the present invention may be suitably employed to form transfer prints when used with a great variety of photosensitive emulsions. For example, satisfactory results can be had with any of the following films:

Eastman films

Photoflure (PF-470)
 Verichrome
 Plus-X (rolls and packs)
 Super-XX (rolls and packs)
 Plus-X (35 mm. and bantam)
 Panatomic-X
 Super-XX (35 mm. and bantam)
 Fine Grain Positive
 High Contrast Positive
 Micro-File
 Super, Panchro-Press, Sports Type
 Tri-X
 Super Panchro-Press, Type B
 Super-XX (sheet films)
 Portrait Panchromatic
 Panatomic-X
 Ortho-X
 Super Ortho-Press
 Super Speed Ortho Portrait
 Commercial
 Infrared
 Tri-X Aero
 Super-XX Aero
 Infrared Aero

Contrast Process Ortho
 Contrast Process Pan
 Kodabromide
 Royal Bromide
 Eastman Background X

Anso films

Plenachrome
 Superpan Press
 Triple "S" Pan
 Isopan
 Triple "S" Ortho
 Commercial Ortho

Defender films

Arrow Pan
 XF Panchromatic
 Fine Grain Pan

Du Pont films

High Speed Pan Type 428
 Photowrit K
 Varigam R
 High Speed Varigam
 Arrow Pan
 XF Pan

A great variety of silver halide developers may be used in the processing composition which participates in the formation of the transfer print. For example, any of the following developers may be satisfactorily employed:

Hydroquinone
 p-Aminophenol hydrochloride
 Bromohydroquinone
 Chlorohydroquinone
 Diaminophenol hydrochloride
 Diaminophenol dihydrochloride
 Toluhydroquinone
 Monomethyl-p-aminophenol sulfate
 p-Hydroxyphenylaminoacetic acid
 Pyrogallol
 p-Aminophenol
 Pyrocatechin

For certain purposes, especially when a viscous processing composition is to be used and spread over the surface of the print-receiving element during the performance of the process, it is desirable to so construct the print-receiving element as to confine the permeability thereof to a very thin surface stratum and also to so construct the surface of the element that the viscous continuum of the processing composition separates therefrom and leaves no droplets or film of developing composition on the print-receiving layer. As a result of this construction, prints are obtained which are dry immediately upon separation from the photosensitive element and which do not curl or distort as a result of changes in atmospheric conditions. Also, as a result of this construction, such of the stain-forming reactants as are retained by the print-receiving element after the formation of the positive print are primarily confined to the thin print-receiving stratum. Because the print-receiving stratum constitutes such a small proportion of the total thickness of the material permeated by the liquid, there is, in effect, a lesser mass of these undesirable stain-forming reactants in the print-receiving element than would exist if a greater thickness of said element were penetrated by the liquid processing agent.

One embodiment of this type of print-receiving element is illustrated in Fig. 2 and, as shown, comprises a suitable support 13 and a print-receiving stratum 15, the latter in turn comprising a stripping layer 15a, preferably of from 1 to 3 microns in thickness, which constitutes the outer surface portion thereof and a silver precipitating layer 15b, also preferably of from 1 to 3 microns in thickness. Between the print-receiving stratum 15 and the support 13 there is a water-impermeable layer or subcoat 16. Support 13 may be formed of a water-permeable material, such as an uncoated or gelatin-coated paper or of a substantially water-impermeable material, such as a cellulose ester, for example, cellulose nitrate, cellulose acetate butyrate, cellulose acetate or cellulose propionate. If support 13 is water permeable, layer 16 constitutes a

separate film of one of the water-impermeable materials and is coated on said support in sufficient thickness to prevent any appreciable penetration of the liquid therein during the transfer process. If support 13 is substantially water impermeable, layer 16 may be just an integral extension of said support.

It is to be noted also, in connection with water-impervious layer 16, that its primary purpose is to prevent any substantial penetration of the liquid processing agent beyond print-receiving stratum 15 during the performance of the transfer process and that in general the process for forming the positive print takes less than five minutes for its completion and more usually only about one minute. Accordingly, the water impermeability of layer 16 need only be such as will prevent any penetration of an aqueous liquid therethrough during this time, and the term "water-impermeable," as used hereinafter, in connection with layer 16, is to be understood as pertaining to an impermeability of this order. It may be desirable in some instances to provide layer 16 with a further thin subcoat (not shown) for improving the adhesion between layer 16 and stratum 15.

Stripping layer 15a minimizes the adhesion between the essentially solid residual film, formed when a viscous processing agent is used, and the print-receiving element so that upon separation of the print-receiving and photosensitive elements the solid residual film will adhere to the photosensitive element and will be stripped therewith from the print-receiving element.

Examples of a print-receiving element comprising a thin print-receiving stratum and capable of being stripped from the solid residue of a viscous processing composition are the following:

EXAMPLE 2

There is applied, as by roll coating, on the baryta-coated surface of a baryta paper 13, a solution consisting of:

Polyvinyl butyral (unplasticized)-----	grams--	35
Isopropyl acetate -----	cc--	525
Methanol -----	cc--	175

to provide said support 13 with a subcoat 16 of the polyvinyl butyral thick enough to be water impermeable.

A solution A is formed by mixing together:

Lead acetate -----	grams--	0.21
Cadmium acetate -----	do----	2.28
Zinc acetate -----	do----	3.80
Water -----	cc--	100.0

A solution B is made by mixing 100 grams of sodium sulfide in 100 cc. of water, adding thereto 90 grams of powdered selenium and then adding water to make 1000 cc. A coating composition is then formed comprising:

Solution A -----	cc--	10.0
"Ludox" -----	cc--	400.0
Sodium hydroxide -----	grams--	.3
Solution B -----	cc--	15.0

This composition is then applied, as by roll coating, upon the subcoat 16 and forms the further layer 15b. The composition is roll-coated in a thickness which gives a layer 15b approximately 2 to 3 microns thick. To expedite the application of this layer 15b upon subcoat 16, a small quantity of wetting agent may be added to the composition. Thereafter, stripping layer 15a is formed on the surface of silver precipitating layer 15b by roll coating thereon against a smooth surface, such for example as the polished surface of a metal drum, a 5% aqueous solution of polyvinyl alcohol in a layer which gives a polyvinyl alcohol coating of a thickness of approximately one to two and one-half microns.

It is to be noted that the coating composition which provides layer 15b contains but a small proportion of solid reagents other than the colloidal silica micelles and

includes a sufficient amount of sodium hydroxide to maintain the silica particles in their colloidal state.

EXAMPLE 3

For the coating composition which provides the silver precipitating layer 15b of Example 2 there is substituted a composition comprising the following:

	Cc.
"Ludox" -----	300.0
10 Solution B of Example 2-----	22.4
.025 molar solution of lead nitrate-----	13.6

EXAMPLE 4

For the coating composition which provides the silver precipitating layer 15b of Example 2 there is substituted a composition comprising the following:

	Cc.
"Ludox" -----	200.0
10 Solution B of Example 2-----	40.0

EXAMPLE 5

For the coating composition which provides the silver precipitating layer 15b of Example 2 there is substituted a composition comprising the following:

	Cc.
25 "Ludox" -----	300.0
Solution B of Example 2-----	5.6
.05 molar solution of lead nitrate-----	13.6

Waterproof subcoat 16 may, for example, be formed of such other materials as cellulose nitrate, cellulose acetate, cellulose butyrate or cellulose acetate propionate. Stripping layer 15a may be, for example, gum arabic, cellulose acetate-hydrogen phthalate, polyvinyl alcohol, hydroxyethyl cellulose, sodium alginate, pectin or polymethacrylic acid. Layer 15a may also be formed of such less permeable materials as methyl cellulose, ethyl cellulose and certain of the methacrylic esters, but in the latter case it is preferably very thin, having a thickness of from one to three microns.

The products of the present invention are especially well suited for the formation of substantially grainless positive transparencies which are capable of being enlarged by projection to a substantial extent without appreciable loss in definition. A print-receiving element capable of giving positive transparencies is formed by coating upon a transparent support of cellulose acetate one of the silver precipitating layers 15 or 15b of the above-noted examples.

In another embodiment of the print-receiving element, as shown in Fig. 3, a layer 15c is provided between stripping layer 15a and silver precipitating layer 15b, said layer 15c serving to improve the abrasion resistance of the silver precipitating layer and also to minimize the ionic penetration into layer 15b of certain of the stain-forming components of the processing composition. Very satisfactory results are obtained with this arrangement when stripping layer 15a is selected from such of the materials noted above as being suitable for the stripping layer as are relatively soluble in an aqueous alkaline solution and layer 15c is a less soluble, although relatively permeable, material. For example, satisfactory results have been obtained by forming stripping layer 15a from gum arabic and abrasion-resistant layer 15c from polyvinyl alcohol. Similar satisfactory results may be obtained by using two polymeric materials whose chemical structures are the same but whose molecular weights differ. For example, a low molecular weight polyvinyl alcohol could be used as stripping layer 15a whereas a substantially higher molecular weight polyvinyl alcohol would be satisfactory in this case as abrasion-resistant layer 15c. Also useful are mixtures of the same materials in different concentrations. For example, both layers may be formed from mixtures of gum arabic and polyvinyl alcohol with layer 15c comprising a sub-

stantially higher concentration of polyvinyl alcohol than layer 15a.

A modification of the print-receiving element of Figs. 2 and 3 is obtained by applying a thin silver precipitating layer 15b, for example of from 1 to 3 microns in thickness, on the subcoated or otherwise water-impervious support 13 and omitting the abrasion-resistant coating and the stripping layer. This type of sheet is particularly useful with emulsions which are relatively thick and in processes wherein the processing composition is spread in a very thin viscous film between the photosensitive emulsion and the print-receiving element. When the print-receiving element is so processed and is thereafter separated from the photosensitive element, the plastic content of the processing composition strips with the print-receiving element and provides thereon a thin protective film. Because of the thinness of this residual plastic layer and of the print-receiving layer, especially as compared to the thickness of the emulsion of the photosensitive element, essentially all of the stain-forming components of the process are carried away with the photosensitive emulsion.

As noted previously, one of the important features of the print-receiving elements herein described is their general usefulness with a great variety of photographic emulsions and developing compositions and also in the various known types of silver halide transfer processes. A satisfactory process for using these print-receiving elements and one which is generally preferred, because of its inherent advantages, is the process disclosed in the above-noted copending application Serial No. 7,795 and the elements are also especially adapted for use in composite structures of the type shown in the aforementioned Patent No. 2,543,181. However, they may also be successfully employed in processes involving a plurality of steps and which require conventional baths of reagents for their performance. In order to make the print-receiving elements especially suited to the latter type of process, it is desirable to include as part of the structure of said elements a suitable silver halide solvent. For example, a water-soluble thiosulfate or thiocyanate salt may be used, such as lead thiosulfate. Such a salt may be dispersed throughout the surface portion of the print-receiving element so as to be readily accessible for dissolution in any liquid which permeates said surface portion.

One example of a print-receiving element which incorporates a silver halide solvent is obtained as follows:

EXAMPLE 6

On the print-receiving element of Examples 2 through 5 a thiosulfate containing layer is formed by roll coating thereon the following composition:

Water	cc	90.0
Lead acetate	grams	7.0
Polyvinyl alcohol (Du Pont PVA 70-05)	do	3.5
Sodium thiosulfate	do	10.0

Using a print-receiving element of this type, it becomes possible with any conventional type of silver halide emulsion to form a positive print of a latent negative image in said emulsion by means of standard silver halide developing compositions. The exposed photosensitive emulsion is immersed in a bath of the developing composition to develop the latent image therein and is thereafter removed from the bath and pressed into engagement with the print-receiving element. The wet photosensitive element provides the necessary liquid for dissolving the silver halide solvent from the print-receiving element and for making the solvent available for forming a soluble silver complex with the unexposed silver halide of the photosensitive element. This complex is transferred to the silver precipitating layer and the silver thereof is there precipitated to form the positive print. This same type of print-receiving element can also be satisfactorily employed when the processing is performed by means of a viscous processing composition spread

between the photosensitive element and the print-receiving element and without any intervening liquid treatments of the photosensitive element. In the latter case, the silver halide solvent ordinarily initially present in the viscous liquid processing composition may be omitted. When lead thiosulfate in the print-receiving element is the source of the silver halide solvent, it is preferable that the developer composition have a high pH.

It is to be understood, of course, that either of the compositions which may be coated in accordance with Example 1 to provide silver precipitating layer 15 of the structure of Fig. 1 may be suitably substituted for the coating compositions which provide the silver precipitating layer 15b of the structures of Figs. 2 and 3.

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 process of forming images in silver which comprises developing a latent image in a silver halide emulsion, reacting a silver halide solvent with part at least of the undeveloped silver halide of said emulsion, transferring at least part of said soluble silver complex to an image-receiving material comprising a silver precipitating agent dispersed in a silica matrix formed by the hardening in situ of a colloidal solution of hydrated silica whose silica particles have a particle size averaging less than 30 millimicrons, and precipitating the silver of said complex at said image-receiving material to form a print of said latent image among said hydrated silica.

2. The process of claim 1 wherein the silver precipitating agent is from the class consisting of the sulfides, selenides and selenosulfides.

3. The process of claim 1 wherein the silver precipitating agent is a colloidal metal.

4. The process of claim 3 wherein the colloidal metal is a noble metal.

5. The process of claim 3 wherein the colloidal metal is silver.

6. The process of claim 1 wherein the silver precipitating agent is a silver salt.

7. The process of claim 1 wherein the image-receiving material is in the form of a print-receiving layer and is provided on a support.

8. The process of claim 7 wherein the silver precipitating agent is colloiddally dispersed among the hydrated silica of the matrix.

9. The process of claim 8 wherein the surface portion of said support upon which said print-receiving layer is mounted is substantially liquid impervious.

10. The process of claim 9 wherein said print-receiving layer has a thickness less than approximately 3 microns.

11. The process of claim 1 wherein the image-receiving material is in the form of a print-receiving layer supported by paper.

12. The process of claim 1 wherein the image-receiving material is in the form of a print-receiving layer supported by a transparent film base.

13. The process of claim 1 wherein the silica particles have an average particle size of approximately 15 millimicrons.

14. The process of claim 7 wherein the silica particles have an average particle size of approximately 15 millimicrons.

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