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PHOTOGRAPHIC SILVER HALIDE TRANSFER PROCESS AND THE PRINT-RECEIVING PRODUCTS USEFUL IN CONNECTION THEREWITH

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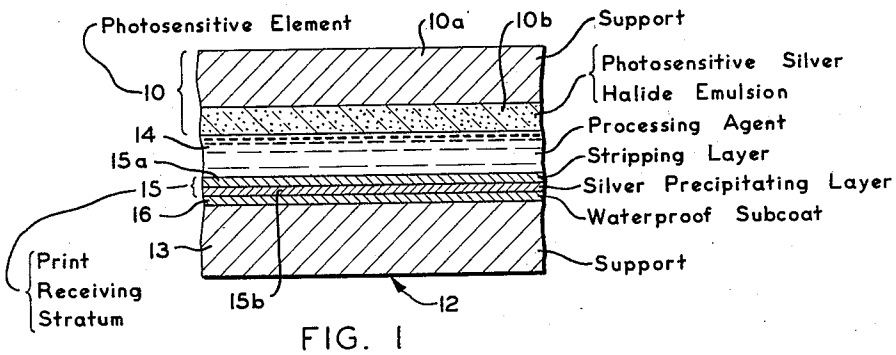


FIG. 1

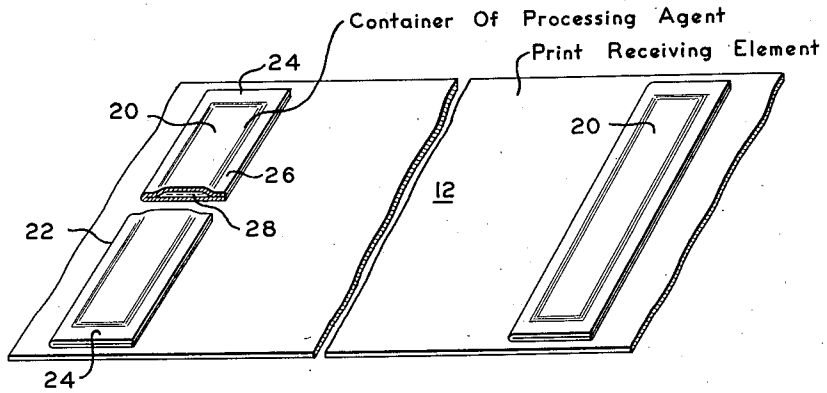


FIG. 2

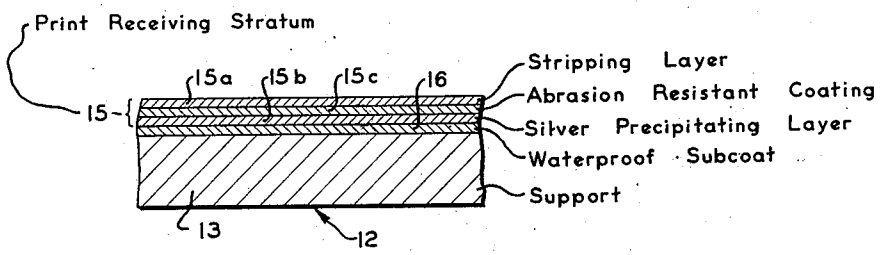


FIG. 3

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PHOTOGRAPHIC SILVER HALIDE TRANSFER PROCESS AND THE PRINT-RECEIVING PRODUCTS USEFUL IN CONNECTION THEREWITH

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16 Claims. (Cl. 96—29)

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

It has heretofore been proposed to form positive prints in a single step by suitably treating a silver halide emulsion containing a latent image with a uniformly applied layer of processing liquid. In one form of this print-making procedure, the processing liquid is in a viscous condition and is spread in a liquid film between the photosensitive element comprising a silver halide emulsion and a print-receiving element comprising a suitable silver precipitating layer.

It is one object of the present invention to provide improved products and processes suitable for the performance of this type of transfer process whereby there is obtained as a result of the processing a positive print which is dry immediately upon separation from the photosensitive element and which gives no evidence as far as wetness is concerned of having been in contact with a liquid processing composition. In accordance with the present invention, the print-receiving element is so constructed that the viscous continuum of processing agent separates therefrom and leaves no droplets or film of developing composition on the print-receiving layer. Moreover, the image-receiving stratum of the print-receiving element is thin, holding a mass of water so small that there is no tactual wetness and equilibrium with the environment is reached almost immediately. Consequently, the print-receiving sheet appears to the observer to be a dry sheet the instant it is peeled from the negative element which carries the viscous developer layer. It thus becomes possible, in accordance with the present invention, to achieve the benefits which are ordinarily associated with liquid processes and yet to have a dry product immediately upon the completion of the treatment thereof. The foregoing is accomplished by confining the permeability of the print-receiving element to a very thin surface stratum. It also becomes possible by virtue of this improved structure to obtain increased overall reliability in the print formation since a more precise control of the film spread between the photosensitive element and the print-receiving element is achieved.

Another object is to provide a novel product useful as a print-receiving element in a silver halide transfer process in which the processing liquid is spread in a thin viscous layer over the surface of said element, said product being so constructed as to give not only a dry but also a curl-proof print at the completion of the process. By the term "curl-proof" is meant proof against the type of curling or distortion which results from the differential effect of atmospheric conditions upon different layers of

a film. It has heretofore been the practice to provide special coatings to compensate for the tendency of a composite sheet to curl in response to the greater contraction or expansion of one of its layers with respect to other of its layers. By making the print-receiving stratum as thin as it is in the structure of the present invention, this tendency to curl is avoided, avoiding the need for the application of such special layers.

Still another object is to provide a novel print-receiving element having a thin stratum adjacent one surface thereof which includes a silver precipitating layer and in which the positive print is formed, said stratum being separated from the remainder of the print-receiving element by a layer which is substantially impervious to the processing liquid used in the formation of the transfer print and being provided with a surface from which the viscous film of processing agent may be readily stripped.

Other objects are the provision of a novel silver halide transfer process useful with a wide range of silver halide emulsions, including the high speed negative type emulsions, to give positive transfer prints of good quality and stability and novel products capable of serving as print-receiving elements in the said process.

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

The invention accordingly comprises the several steps and relation and order of one or more of such steps with respect to each of the others, and the product possessing the features, properties and the relation 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 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 the association of elements during one stage of the performance of a transfer process and showing as one of the elements an embodiment of the novel product of the present invention, the thicknesses of the various materials being exaggerated;

Fig. 2 is a perspective view, with parts broken away, of one form of print-receiving element upon which containers of the processing agent are so positioned as to be capable of distributing their contents between the print-receiving element and a photosensitive element; and

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

The present invention comprehends improved processes and products of the type whereby a positive print is obtained in a single step by suitably treating a silver halide emulsion containing a latent image with a uniformly applied layer of processing liquid. The processing liquid is in a viscous condition and is spread in a liquid film between the photosensitive element comprising the silver halide emulsion and a print-receiving element comprising a suitable silver precipitating layer. The liquid develops the latent image in the emulsion and forms a soluble silver complex, e. g., a thiosulfate, with undeveloped silver halide. This soluble silver complex is at least in part transported in the direction of the print-receiving element and the silver thereof is largely precipitated in the silver precipitating layer of said element to form a positive image in silver. To render the processing composition viscous, a solid thickening agent is dispersed therein. In one preferred form of the processing composition, the thickening agent is a high molecular weight film-forming polymer.

It has been proposed to use, in the formation of the silver transfer prints by the foregoing process, certain

compounds and elements whose presence during the process has a desirable effect on the amount and character of the silver precipitated during image formation. For this purpose, such materials as, for example, the metallic sulfides and selenides, the thiooxalates, the thioacetamides and others have been disclosed in my copending applications Serial No. 727,385, filed February 8, 1947, for Photographic Product and Process, now Patent No. 2,698,245, Serial No. 7,795, filed February 12, 1948, for Photographic Process, now Patent No. 2,647,056, and Serial No. 164,908, filed May 29, 1950, for Photographic Silver Halide Transfer Product and Process, now abandoned. Other silver precipitating agents have been proposed such, for example, as colloidal silver.

It has also been disclosed in my said copending applications that the precipitation and aggregation of silver obtained by using the silver precipitating agents, including the above-mentioned materials, are very greatly improved by providing in the print-receiving element as a vehicle for said agents a macroscopically continuous matrix consisting essentially of submacroscopic agglomerates of particles of a water-insoluble, inorganic, chemically inert, adsorbent substance. The word "submacroscopic" refers to a class of sizes which includes as a subclass those sizes known as submicroscopic. The substance preferably has a low coefficient of absorption for light as compared to silver and the matrix formed therefrom is essentially free of protective colloid action for silver. One example of such a matrix is a layer of silica such as is formed by drying a layer of the hydrated colloidal silica dispersion available under the trade name "Ludox" or a layer of the dispersion of the silica aerogel available under the trade name "Santocel C."

According to the present invention, the print-receiving element is constructed in a novel manner so that only a surface portion thereof, hereinafter characterized as the print-receiving stratum, is capable of being permeated to any appreciable extent by the ionic reagents contained in the liquid processing composition. The outer surface of this print-receiving stratum contacts the layer of processing composition and preferably this surface is so constituted as to have a lesser adhesion for the solid residue of the liquid processing composition than does the photosensitive element. As a result, the photosensitive element, when stripped from the print-receiving element, carries with it the residue of the processing composition. The entire print-receiving stratum may be essentially formed of a material having the desired stripping properties or preferably a thin film of a suitable stripping composition may constitute the outer surface portion of the print-receiving stratum, while the remainder of said print-receiving stratum is formed of a vehicle more suitable for carrying the silver precipitating agents. These silver precipitating agents for controlling and aggregating the silver precipitate that produces the positive image are dispersed throughout a part at least of the thickness of the print-receiving stratum. The remainder of the print-receiving element serves as a support for the print-receiving stratum and has contiguous to said stratum a surface which is substantially impervious to the liquid of the processing composition, which surface may be obtained by having a liquid-impervious layer provided between the print-receiving stratum and a suitable supporting member for said stratum, or said liquid-impervious surface may be the surface portion of a supporting sheet which is entirely formed of liquid-impervious material.

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. In general these reactants in their dissolved condition tend to uniformly distribute themselves throughout so much of the total thickness of the superposed materials as includes the liquid of the processing composition, namely the layer of processing composition itself and so much of the thickness of the print-receiving element and the photosensitive element as is permeated by the processing composition. Because the print-receiving stratum constitutes such a small proportion of the total thickness of material permeated by the liquid, there is in effect a lesser mass of the 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. Thus, the structure of the print-receiving element is effective in minimizing, and, in some instances, making negligible some of the hazards to a finished print. These include the following: (1) the highlights of the print may turn yellow due to the oxidation of the unexhausted developing agent; (2) many oxidized developing agents may act as oxidizing agents for silver; hence, not only will the highlights turn yellow but the shadows will also fade; (3) the silver may be oxidized by other reagents as, for example, by sulfide from residual thiosulfate; and (4) the silver may be oxidized by oxidizing agents in the atmosphere.

As noted hereinabove, the print-receiving element has the viscous processing film stripped therefrom and the latter, because of its viscosity, leaves no droplets or film of developing composition upon the print-receiving element as it is stripped. Moreover, because of the thinness of the image-receiving stratum of the print-receiving element, said element holds an extremely small mass of water. Accordingly, as it is stripped, it comes at once into equilibrium with the environment and feels dry to the touch.

A further hazard to the print arises by virtue of this stripping of the processing agent in that the thin print-receiving stratum is ordinarily fairly readily susceptible to scratching and other surface abrasion effects. Provision is made in the preferred form of the present invention for the protection of the print-receiving element against this hazard and this is accomplished without any substantial increase in the thickness of the print-receiving stratum.

The use of the novel products of the present invention in the performance of the silver halide transfer process is illustrated diagrammatically in Fig. 1 wherein **10** represents a photosensitive element comprising a support **10*a*** and a photosensitive, silver halide emulsion layer **10*b***; **14** represents a layer of a relatively viscous processing composition; and **12** is one embodiment of the novel print-receiving element of the invention in which the transfer print is formed.

Liquid layer **14** may be obtained by spreading the processing agent, for example, in a manner disclosed in my said copending application Serial No. 7,795, and the processing agent may be one of the film-forming processing agents disclosed in said copending application. It may comprise, for example, a developing agent such as hydroquinone, an alkali such as sodium hydroxide, a substance, such as sodium thiosulfate, for forming a soluble silver complex with unexposed silver halide, and a high molecular weight film-forming thickening agent such as sodium carboxymethyl cellulose. All these materials are preferably in aqueous solution and are preferably contained in the processing liquid prior to the spreading thereof as a layer **14**. However, they may be in part or wholly added to the processing liquid as it is spread between elements **10** and **12**, being so located on or adjacent the surface of one or both of said elements as to be dissolved by or otherwise interacted with the liquid agent when the latter wets said surface.

The liquid processing composition may be provided for spreading as a layer **14** between elements **10** and **12** by being contained in an elongated rupturable container **20** which, as shown in Fig. 2, has a length at least equal to the transverse dimension of the area of photosensitive element **10** to which the liquid processing agent is to be applied. One or more containers **20** may be attached

to one of elements 10 and 12 and, in Fig. 2, two such containers are shown secured to the print-receiving surface of element 12, being spaced apart, lengthwise of said element, a distance equal at least to the length of a single frame of the photosensitive element 10. Said elements 10 and 12 may be connected together so that they can be superposed with the containers so positioned as to be capable of successively releasing their contents in a film between said elements. Each of containers 20 is preferably so constructed as to be capable of retaining the liquid processing agent or composition therein for relatively long periods of time without vapor loss or oxidation. One example of a suitable container of this type is formed from a single multilayer sheet of material comprising three laminae. The inner lamina, which provides the inner surface of the container, is formed of a material which is chemically inert to the reagents in the processing agent and which is impervious to the liquid of the agent. One class of materials suitable for this purpose, particularly where the processing agent is an alkaline solution, is the polyvinyl acetals, and of the acetals, polyvinyl butyral is a preferred species. A composition comprising 60% to 72% by weight of polyvinyl butyral, 10% to 23% by weight of nitrocellulose, and approximately 5% by weight of dibutyl sebacate is satisfactory as the inner lamina. The intermediate lamina is preferably impervious to the vapor of the processing agent and is formed, for example, of a metallic foil such as lead or silver foil. The outer or backing lamina is formed of a strong, deformable, relatively inexpensive sheet material such as a kraft paper.

The container 20 is preferably formed by taking the single sheet of three-ply material and folding the same medially at 22, and thereafter securing the end marginal portions 24 and the longitudinal marginal portions 26 of the two folded faces to one another, providing a central space or cavity 28 for containing the processing liquid.

To fill the container it is possible to adhere together the opposite longitudinally extending marginal portions 26 and one of the end marginal portions 24, the container being filled through the other end which is thereafter sealed.

Photosensitive element 10 may be any of the commercially available photosensitive silver halide films, the term "film" as used herein being understood to include paper-backed emulsions. The products of the present invention are particularly useful in improving the results obtained when the transfer process is carried out with one of the high-speed photosensitive silver halide emulsions such as the emulsion of the relatively high-speed orthochromatic films, e. g., Eastman Kodak Verichrome film, having an ASA speed rating of 0200 and an ASA exposure index rating in the daylight of 50, and the extremely high-speed panchromatic emulsions, e. g., Eastman Kodak Super XX Pan having an ASA speed rating of 0400 and an ASA exposure index rating in the daylight of 100, and Ansco Triple S Pan. Also satisfactory are the emulsions of Kodak Photoflure safety films and Du Pont High Speed Pan film. The products and processes of the present invention also give excellent results when used with slower emulsions, for example, the emulsions of Contrast Process Ortho film or the emulsions of chloride and chlorobromide type printing and enlarging papers.

As shown in Fig. 1, the novel print-receiving element 12 comprises a suitable support 13 and a print-receiving stratum 15, the latter in turn comprising, as shown, a stripping layer 15*a*, which constitutes the outer surface portion thereof, and a silver precipitating layer 15*b*. Although layers 15*a* and 15*b* are preferably formed of different materials, they may, as noted hereinabove, be of the same single material with the silver precipitating agents suitably dispersed throughout at least a portion of the thickness thereof. Between the print-receiving stratum 15 and the support 13, there is shown 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, in which case no line of demarcations, as shown in Fig. 1, actually exists between layer 16 and support 13. It is to be clearly understood, therefore, that unless specifically stated to the contrary, all future references, especially in the claims, to a water-impermeable layer and a support therefor do not preclude a structure wherein the layer and support are integral parts of a single water-impermeable sheet material such as a sheet of one of the aforementioned cellulose esters.

It is to be noted also, is 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 between layer 16 and stratum 15.

In general, stratum 15 is at least permeable to the print-forming components of an aqueous medium and has dispersed throughout a portion at least of the thickness thereof a silver precipitating agent which may be any one of the materials mentioned for this purpose in my above-noted applications but is preferably at least one of the relatively water-insoluble metallic sulfides and selenides. The latter terms are to be understood as including the polysulfides and the polyselenides within their scope. Examples of silver precipitating agents of this preferred type are the so-called "heavy metal" sulfides of zinc, chromium, gallium, iron, cadmium, cobalt, nickel, lead, antimony, bismuth, silver, cerium, arsenic, copper and rhodium and the selenides of lead, zinc, antimony and nickel.

When using one or more of these heavy metal sulfides and selenides as silver precipitating agents, it is desirable to prevent the sulfide or selenide ions of the crystals of the precipitating agent from wandering or diffusing during the precipitation of silver. To accomplish this, there is preferably dispersed throughout a portion at least of the thickness of the print-receiving stratum 15 at least one metallic salt which is substantially more soluble in the processing agent than the heavy metal sulfide or selenide used as the silver precipitating agent and which is irreducible in the processing agent. This more soluble salt has as its cation a metal whose ions form sulfides or selenides, as the case may be, which are difficultly soluble in the processing agent and which give up their sulfide or selenide ions to silver by displacement. Accordingly, when such sulfide or selenide ions are present, the metal ions of the more soluble salt have the effect of immediately precipitating the sulfide ions from solution. These more soluble or ion-capturing salts may be the salts of any of the following metals: cadmium, cerium(ous), cobalt(ous), iron, lead, nickel, manganese and thorium. Satisfactory soluble and stable salts of the above metals may be found,

for example, among the following groups of salts: the acetates, the nitrates, the borates, the chlorides, the sulfates, the hydroxides, the formates, the citrates and the dithionates. The acetates and nitrates of zinc, cadmium, nickel and lead are preferred. In general, it is also preferable to use the white or lightly colored salts, although for certain special purposes the more darkly colored salts can be employed.

It is also advantageous when using the silver precipitating agents, and especially the metallic sulfides and selenides and colloidal silver, to suitably aggregate the same and for this purpose a layer as previously described of silica or other granular, inorganic, water-insoluble, substantially chemically inert substance is preferably used. For certain photographic purposes, as, for example, for document duplication, a nongranular type of dispersing medium such as polyvinyl alcohol may be used for the silver precipitating agents.

One method of providing print-receiving layer **15***b* upon layer **16** is to form an aqueous dispersion of silica aerogel to which there is added a suitable quantity of one or more of the soluble ion-capturing salts. Thereafter, a substantially lesser molar quantity of a soluble sulfide, such as sodium sulfide, is added. The anions of sulfide and the cations of the ion-capturing salt combine to precipitate from the solution relatively insoluble crystals of the sulfide of the metal of the ion-capturing salt, thereby converting a portion of the latter to the sulfide. This produces a dispersion of the insoluble sulfide in the silica sol while leaving in solution the remainder of the ion-capturing salt. The concentration of the latter in the initial solution in relation to the added amount of the soluble sulfide is such as to give in the final layer a substantially greater amount of the ion-capturing salt in proportion to the sulfide.

This dispersion comprising the sulfide in suspension and the ion-capturing salt in solution is thereafter roll-coated or otherwise applied as a layer upon the surface of layer **16** to give, upon drying, the silver precipitating layer **15***b*.

As hereinbefore noted, the layer of processing agent **14** is preferably spread in a viscous condition, for example, from a container **20**, between the elements **10** and **12**. In order to impart to the liquid agent its desired viscosity, the liquid preferably contains in solution a water-soluble film-forming plastic so that when the liquid is removed from the processing layer **14** by absorption and/or evaporation, there remains a solid plastic film.

For optimum stabilizing effects in the practice of the present invention, it is desirable that this film of plastic be stripped from the print-receiving element **12** after the formation in the latter of the positive print. Accordingly, as shown in Fig. 1, there is provided as part of print-receiving stratum **15** a stripping layer **15***a* whose purpose is to minimize the adhesion between the film-forming plastic in the processing agent and print-receiving element **12** so that upon separation of elements **10** and **12** the plastic film formed by the drying of processing layer **14** will adhere to photosensitive element **10** and will be stripped therewith from element **12**.

Stripping layer **15***a* may perform the additional function of providing an abrasion-resistant coating over the surface of the silica containing silver precipitating layer **15***b*. Layer **15***a* may be, for example, gum arabic, cellulose acetate-hydrogen phthalate, polyvinyl alcohol, hydroxyethyl cellulose, methyl cellulose, ethyl cellulose, sodium alginate, pectin or polymethacrylic acid. It preferably has a thickness of the order of one to three microns. The above-mentioned plastics, suitable for coating **15***a*, are especially useful for minimizing the adhesion between the film-forming plastic of layer **14** and stratum **15** when said film-forming plastic of layer **14** is sodium carboxymethyl cellulose. It is important to note that the thickness of the stripping layer is approximately three microns or less and because of this it is possible to use materials which in thicker films would be relatively impervious during the processing of the transfer print. Typical of such materials are the cellulosic esters and methacrylic esters. It is desirable when using these materials for stripping layer **15***a* to have the same in plasticized condition; whereas, when such materials are used to provide the liquid-impervious subcoat **16**, they are preferably in unplasticized condition.

Where the permeable print-receiving stratum includes a stripping layer **15***a*, as above described, and the total thickness of said stratum is small, being of the order of 6 microns or less, a remarkably dry print is obtained upon the separation of the print-receiving element **12** and the photosensitive element **10**. The uniqueness of the phenomenon is evidenced especially by the fact that upon separation the surface of the photosensitive element **10** is perceptibly wet while the surface of the print-receiving element **12** is completely dry, the film of liquid which would ordinarily exist at the completion of a liquid treatment of the print having been totally removed from the surface of said element **12** with the viscous processing agent. The relatively high viscosity of the processing agent serves to hold the liquid therein, and the layer of processing agent, although in intimate contact with the print-receiving stratum and permitting the free transfer of ions and molecules thereto, relinquishes only a very small part of its liquid content to the print-receiving element. The mass of liquid which permeates print-receiving stratum **15** is so small that the sheet achieves an equilibrium with its environment almost instantaneously upon peeling. Accordingly, upon the separation of the said elements, element **12** is dry to the touch.

Examples of processes for forming a positive image wherein a silver halide transfer takes place and examples of the novel products of the invention when used as the print-receiving elements in the performance of said processes are given below, but it is expressly understood that these examples are merely illustrative and that the invention is not limited to the materials or proportions set out therein:

Example 1

A processing agent is prepared which comprises:

	Grams
Water	1860
Sodium carboxymethyl cellulose	117
Sodium sulfite	78
Sodium hydroxide	74.6
Sodium thiosulfate	14.5
Citric acid	38.5
Hydroquinone	52

The processing agent is prepared by dissolving the sodium carboxymethyl cellulose, for example the commercially available Hercules #1362 medium viscosity type, in the water in a mixer at room temperature, and the solution is mixed therein for approximately one hour. Thereafter, the sodium sulfite, sodium hydroxide, sodium thiosulfate and citric acid are added to the solution, the addition being effected in an inert atmosphere, for example of nitrogen. Upon dissolution of these materials, the hydroquinone is added and the solution is further mixed for an hour at approximately room temperature in a nonoxidizing atmosphere of nitrogen.

The novel print-receiving element **12** is formed by applying on the baryta-coated surface of a sheet of baryta paper a subcoat **16** consisting of unplasticized polyvinyl butyral, the latter being sufficiently water impermeable to prevent the penetration of liquid during the transfer process. Subcoat **16** is applied by roll-coating on support **13** a solution consisting of:

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

There is then applied to subcoat **16** the further layer **16***b* of a thickness of 1 to 2½ microns by roll-coating onto said subcoat the following composition:

Water	cc.	1700
Cadmium acetate	grams	19
Lead acetate	do	25
"Arabol"	cc.	135
Silica aerogel (Santocel C)	grams	800
Sodium sulfide solution	cc.	33.5

The sodium sulfide solution consists of 75 grams of sodium sulfide ($Na_2S.9H_2O$) in 100 cc. of water. Arabol is a water solution of gum arabic whose solid content varies between 57% and 61% and which has a viscosity varying between 1500 and 5000 centipoises. The surface of the print-receiving element including layer **15***b* is thereafter dipped for approximately thirty seconds in a solution consisting of:

Cadmium acetate	grams	10
Lead acetate	do	1
Zinc acetate	do	30
Water	cc.	100

Excess moisture is removed from the sheet as it leaves the solution, for example, with a glass rod, and the sheet is dried. Thereafter, stripping layer **15***a* is formed on the surface of silver precipitating layer **15***b* 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 1 to 2½ microns. Layers **15***a* and **15***b* together constitute the print-receiving stratum of the present invention.

The processing agent is spread in a layer **14** of approximately .002–.003" in thickness between the coated surface of element **12** and the photosensitive silver halide emulsion **10***b* of a photosensitive film **10**. Emulsion **10***b* is a relatively high-speed orthochromatic emulsion like the emulsion of Eastman Kodak Verichrome film, and has been exposed to predetermined subject matter to form therein a latent image of said subject matter, support **10***a* for said emulsion being a white paper. The laminations formed by the spreading of the processing agent in a layer **14** between elements **10** and **12** is kept intact for approximately one-half to one and one-half minutes, preferably one minute, and at the end of this time element **12** is stripped from element **10**. During the stripping of the photosensitive element **10** from the print-receiving element **12**, stripping layer **15***a* is cleaved and this cleavage has the further effect of diminishing the thickness of the print-receiving stratum **15** of the finished print, thereby augmenting the advantageous effects of a thin print-receiving stratum hereinabove noted. Element **12**, when so stripped, carries a positive print in silver of the subject matter of the latent image in emulsion **10***b*. The sodium carboxymethyl cellulose of layer **14** adheres to element **10**. The print obtained in this manner has good color, density and other pictorial qualities and is essentially dry as it is stripped from the photosensitive element.

Other materials may be substituted for those used in the foregoing process and the proportions may be varied to an appreciable extent. For example, the film-forming material in the processing agent which imparts the desired viscosity to the latter may be any of the high molecular weight polymers which are stable to alkalis and which are soluble in aqueous alkaline solutions. For example, such other plastics as hydroxyethyl cellulose, polyvinyl alcohol and the sodium salts of polymethacrylic acid and polyacrylic acid may be used. The plastic is preferably contained in the agent in sufficient quantity to impart to the composition a viscosity in excess of 1,000 centipoises at a temperature of approximately 24° C. Preferably, the viscosity of the processing agent is of the order of 1,000 to 200,000 centipoises at 24° C.

Other developing agents may be used, for example one of the following: p-aminophenol hydrochloride; bromohydroquinone; chlorohydroquinone; diaminophenol hydrochloride; diaminophenol dihydrochloride; toluhydroquinone; monomethyl-p-aminophenol sulfate; a mixture consisting by weight of one-half hydroquinone and one-half p-hydroxyphenylaminoacetic acid; and a mixture consisting by weight of one-fourth hydroquinone and three-fourths p-hydroxyphenylaminoacetic acid.

To form the soluble silver complex, such other complex-forming substances as sodium thiocyanate, ammonium thiocyanate and ammonia may be employed.

The waterproof subcoat **16** may, for example, be formed of unplasticized polymethacrylic acid or one of the cellulosic esters such as cellulose nitrate, cellulose acetate, cellulose butyrate or cellulose acetate propionate. Preferred however are the rubbery type of plastics such as polyvinyl butyral because such materials are more effective in eliminating cracking of the print-receiving stratum which might otherwise result from severe changes in atmospheric conditions or rough handling of the print. Stripping layer **15***a* may be formed, for example, of gum arabic, sodium alginate, pectin, cellulose acetate-hydrogen phthalate, polyvinyl alcohol, hydroxyethyl cellulose or polymethacrylic acid and, when kept thin, may be of plasticized methyl cellulose, ethyl cellulose, methyl methacrylate or butyl methacrylate. It is also preferable, in applying the print-receiving layer **15***b* to the waterproof subcoat **16**, to use a suitable wetting agent such, for example, as dibutyl phenylphenol sodium disulfonate, a sodium alkyl naphthalene sulfonate (e. g. Alkanol B), or decylbenzene sodium sulfonate. This is preferably introduced into the composition from which the silver precipitating layer **15***b* is formed in a ratio of approximately one part in forty by volume.

Example 2

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

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
"Ludox"	cc.	400
Sodium hydroxide	gram	.3
Solution B	cc.	15

and this is applied as a layer upon the subcoated surface of a suitable support **13** to form thereon a silver precipitating layer **15***b* in lieu of the layer **15***b* of said Example 1.

Example 3

For the coating and dipping mixtures that provide silver precipitating layer **15***b* of Example 1, there is substituted the following composition:

	Cc.
"Ludox"	300
Solution B of Example 2	5.6
.05 molar solution of silver nitrate solution	13.6

which is coated upon the subcoat **16** to a thickness such that the solid film obtained therefrom is from 1 to 3 microns in thickness.

Example 4

For the coating compositions which provide silver

precipitating layer **15***b* of Example 1, there is substituted the following:

	Cc.
"Ludox"	300
Solution B of Example 2	22.4
.025 molar solution of lead nitrate	13.6

In another embodiment of the print-receiving element, as shown in Fig. 3, a layer **15***c* is provided between stripping layer **15***a* and silver precipitating layer **15***b*, said layer **15***c* serving to improve the abrasion resistance of the silver precipitating layer and also to minimize the ionic penetration into layer **15***b* of certain of the components of the processing composition. Very satisfactory results are obtained with this arrangement when stripping layer **15***a* 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 **15***c* is a less soluble, although relatively permeable, material. For example, satisfactory results have been obtained by forming stripping layer **15***a* from gum arabic and abrasion-resistant layer **15***c* 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 **15***a* whereas a substantially higher molecular weight polyvinyl alcohol would be satisfactory in this case as abrasion-resistant layer **15***c*. 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 **15***c* comprising a substantially higher concentration of polyvinyl alcohol than layer **15***a*.

The present invention is 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 and in these transparencies it has been found satisfactory to eliminate the stripping layer of the above-described examples and to use a transparent cellulosic ester for support **13** so as to avoid the necessity for a separate waterproof subcoat **16**.

Example 5

One example of a print-receiving layer of this type comprises a transparent support of cellulose acetate upon which has been directly coated a silver precipitating layer having the same composition as forms the layer **15***b* of Examples 1 through 4. In this form of the invention, it is preferable to omit not only the subcoat **16** but also the stripping layer **15***a* and to have the residue of the processing composition adhere to the print-receiving layer when the latter is stripped from the photosensitive element.

Because of the relative thinness of the silver precipitating stratum of the print-receiving element of the present invention, it is sometimes difficult to incorporate within this thin permeable stratum a sufficient quantity of stabilizing agents to effect essentially complete stability. It has been found extremely effective in order to achieve stability to substitute for the sodium hydroxide of the processing composition of Example 1 a relatively volatile alkali, such as a volatile amine, e. g. diethyl amine. The effect of this substitution is to cause the alkali content of the print-receiving element to evaporate when the print-receiving element is stripped from the photosensitive element, thereby producing a reduction of the alkalinity which tends to effectively stabilize the positive print.

In still another approach to the solution of this problem there is substituted for all or a substantial part of the relatively stain-forming hydroquinone of the composition of Example 1 a reducing agent capable of functioning as a developer but which gives by-products that are substantially less stain-forming in character. An example of this type of reducing agent is ascorbic acid. Ascorbic acid is especially effective when used in combination with hydroquinone for it not only tends to supplement the developing action of hydroquinone but also serves as an antioxidant for the hydroquinone, reducing the oxidation of the latter in the print-receiving element and thus effectively minimizing the formation of stains which would affect the stability of the positive print.

Since certain changes may be made in the above product and 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. A photographic process for forming, by transfer, a print of a latent image contained in the silver halide layer of a photosensitive element, which process comprises the steps of bringing a liquid processing composition into contact with said photosensitive element so that said layer is permeated with the liquid of said composition, providing a print-receiving element in superposed relation with said photosensitive element, said print-receiving element consisting of a support and a thin silver precipitating stratum coated on said support, the surface of said support in contact with said stratum being formed of an organic plastic impervious to the liquid of said processing composition, said stratum not exceeding 6 microns in thickness and comprising a matrix of siliceous particles containing a nonsiliceous silver precipitating agent, said print-receiving element being superposed on said photosensitive element with said silver precipitating stratum adjacent said photosensitive element and with the liquid of said processing composition confined to said photosensitive element and to said silver precipitating stratum, the surface of said support providing a barrier to the penetration of said liquid into said print-receiving element beyond said silver precipitating stratum, said liquid containing, after permeation of the silver halide layer, reagents for developing exposed silver halide and for forming soluble complexes with undeveloped silver halide, maintaining said elements in their superposed relation without any appreciable penetration of said liquid into said support while said latent image is developed and until sufficient silver is transferred as a complex to said print-receiving element to form a print, and stripping said print-receiving element from said photosensitive element subsequent to said transfer, said silver precipitating stratum because of its thinness being substantially tactually dry as it is stripped from said photosensitive element.

2. The process of claim 1 wherein the said reagents are contained in the processing composition before the latter is applied to the photosensitive element.

3. A photographic process for forming, by transfer, a print of a latent image contained in the silver halide emulsion of a photosensitive element, which process comprises the steps of spreading a liquid processing composition which contains a film-forming thickening agent between said photosensitive element and a print-receiving element, said print-receiving element consisting of a support and a thin silver precipitating stratum, not exceeding 6 microns in thickness, coated on said support, the surface of said support in contact with said stratum being formed of an organic plastic impervious to the liquid of said processing composition, said stratum containing a silver precipitating agent and comprising an inner layer formed principally of inorganic, adsorbent, water-insoluble particles and an outer layer of a substantially water-soluble, organic plastic, said print-receiving element being superposed on said photosensitive element with its silver precipitating stratum adjacent said photosensitive element and with the liquid of said processing composition confined to said photosensitive element and to said silver precipitating stratum, the surface of said support providing a barrier to the penetration of said liquid into said print-receiving element beyond said silver precipitating stratum, said liquid containing, after permeation of the silver halide emulsion, reagents, including a silver halide

developer and a silver halide solvent, for developing the latent image silver halide and for forming soluble silver complexes with undeveloped silver halide, maintaining said elements in their superposed relation without any appreciable penetration of said liquid into said support while said latent image is developed and until sufficient silver is transferred to said silver precipitating stratum to form a print, and subsequent to said transfer stripping said print-receiving element from said photosensitive element and from the residual film of said thickening agent, said silver precipitating stratum because of its thinness being substantially tactually dry as it is so stripped.

4. The process of claim 3 wherein the silver halide developer and the silver halide solvent are contained in the processing composition before the latter is spread between the elements.

5. The process of claim 3 wherein the liquid processing composition is spread from a container mounted on one of said elements.

6. A photographic process for forming, by transfer, a print of a latent image contained in the silver halide emulsion of a photosensitive element, which process comprises the steps of providing a layer of an aqueous liquid processing composition which contains a film-forming thickening agent between said photosensitive element and a print-receiving element, said print-receiving element consisting of a support and a silver precipitating stratum coated on said support, the surface of said support in contact with said stratum being formed of an organic, water-impervious plastic, said stratum not exceeding 6 microns in thickness and comprising a matrix of inorganic, water-insoluble, adsorbent particles having dispersed therethrough a lesser concentration of a silver precipitating agent chemically different from said matrix particles, said print-receiving element being superposed on said photosensitive element with said silver precipitating stratum adjacent said photosensitive element and with the liquid of said processing composition confined to said photosensitive element and to said silver precipitating stratum, the said surface of said support preventing penetration of said liquid into said print-receiving element beyond said silver precipitating stratum, said liquid containing, upon permeation of the silver halide emulsion, reagents, including a silver halide developer and a silver halide solvent, for developing the latent image silver halide and for forming soluble silver complexes with the undeveloped silver halide, maintaining said elements in their superposed relation without any appreciable penetration of said liquid into said support while said latent image is developed and until sufficient silver is transferred to said silver precipitating stratum to form a print, and subsequent to said transfer stripping said print-receiving element from said photosensitive element and from the residual film of said thickening agent, said silver precipitating stratum because of its thinness being substantially tactually dry as it is so stripped.

7. The process of claim 6 wherein said matrix comprises particles of silica.

8. The process of claim 6 wherein the silver precipitating agent includes a substance from the class consisting of metallic sulfides, metallic selenides, thiooxalates, thioacetamides and colloidal silver.

9. A photographic process for forming, by transfer, a print of a latent image contained in the silver halide emulsion of a photosensitive element, which process comprises the steps of bringing an aqueous liquid processing composition into contact with said photosensitive element so that said emulsion is permeated with the liquid, providing a print-receiving element in superposed relation with said photosensitive element, said print-receiving element consisting of a support and a thin silver precipitating stratum coated on said support, the surface of said support in contact with said stratum being formed of an organic, water-impervious plastic, said stratum not exceeding 6 microns in thickness and comprising a matrix of inorganic, adsorbent, water-insoluble particles containing particles of a silver precipitating agent chemically different from said matrix particles, said print-receiving element being superposed on said photosensitive element with said silver precipitating stratum adjacent said photosensitive element and with the liquid of said processing composition confined to said photosensitive element and to said silver precipitating stratum, the surface of said support preventing the penetration of said liquid into said said print-receiving element beyond said silver precipitating stratum, said liquid containing, upon permeation of the silver halide emulsion, reagents for developing exposed silver halide and for forming soluble complexes with undeveloped silver halide, maintaining said elements in their superposed relation without any appreciable penetration of said liquid into said support while said latent image is developed and until sufficient silver is transferred as a complex to said print-receiving element to form a print, and stripping said print-receiving element from said photosensitive element subsequent to said transfer, said silver precipitating stratum because of its thinness being substantially tactually dry as it is stripped from said photosensitive element.

10. A photographic print-receiving element for having prints formed thereon by means of silver transfer from a photosensitive silver halide emulsion, said print-receiving element being substantially inert to visible light and consisting of a support and a thin silver precipitating stratum coated upon said support, said silver precipitating stratum comprising an inner layer adjacent said support and an outer layer, said inner layer being formed principally of inorganic, adsorbent, water-insoluble particles which provide a matrix and particles of a silver precipitating agent, chemically different from said matrix particles, dispersed in said matrix in a concentration substantially lower than the concentration of said matrix particles, said outer layer being formed principally of organic plastic and being more abrasion resistant than said inner layer, said silver precipitating stratum having a total thickness not exceeding 6 microns and being substantially pervious to an aqueous solution of soluble silver complex, said support having a water-impervious layer of organic plastic which provides the surface upon which said silver precipitating stratum is mounted.

11. The print-receiving element of claim 10 in which said adsorbent, water-insoluble particles are particles of silica.

12. The print-receiving element of claim 10 wherein said silver precipitating agent comprises at least one substance from the class consisting of metallic sulfides, metallic selenides, thiooxalates, thioacetamides and colloidal silver.

13. The print-receiving element of claim 10 wherein said support comprises a base of paper and said water-impervious layer is a coating of organic plastic applied to said base.

14. A photographic print-receiving element for having prints formed thereon by means of silver transfer from a photosensitive silver halide emulsion, said print-receiving element being substantially inert to visible light and comprising a base layer, a water-impervious layer of organic plastic mounted on said base layer and a print-receiving, silver precipitating stratum not greater than 6 microns in thickness mounted directly on said water-impervious layer and providing an outer surface of said element, said print-receiving stratum comprising an inner layer formed principally of inorganic, adsorbent, water-insoluble particles constituting a matrix, particles of a silver precipitating agent, chemically different from said matrix particles, being dispersed in said matrix in a concentration substantially lower than the concentration of said matrix particles, an intermediate layer formed principally of organic plastic and being more abrasion resistant than said inner layer, and an outer layer formed principally of organic plastic and being more water soluble than said intermediate layer.

15. The print-receiving element of claim 14 wherein said base is paper, said matrix particles are particles of a siliceous material and said outer layer comprises polyvinyl alcohol.

16. The print-receiving element of claim 14 which includes a container, said container holding a processing composition comprising a film-forming thickening agent capable of providing a residual, solid film when the composition is dried after spreading, said container being so mounted on the print-receiving element as to be able to dispense its contents over the surface of said silver precipitating stratum.

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