

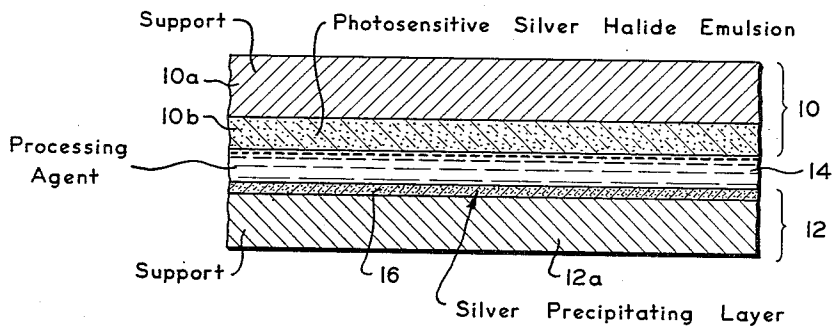
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PROCESS FOR FORMING PRINT-RECEIVING ELEMENTS

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PROCESS FOR FORMING PRINT-RECEIVING ELEMENTS

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15 Claims. (Cl. 117—34)

This invention relates to photography and more particularly to processes for the fabrication of products which are suitable as print-receiving elements in photographic transfer reversal processes.

This application is a continuation in part of my co-pending applications Serial No. 727,385, and now Patent No. 2,698,245, filed February 8, 1947, for Photographic Product and Process, and Serial No. 164,908, and now abandoned, filed May 29, 1950, for Photographic Silver Halide Transfer Product and Process.

Photographic transfer reversal processes for giving positive prints directly in silver are a recent innovation in the photographic art. In these processes, a latent image in a silver halide emulsion is developed and almost concurrently with such development a soluble silver complex obtained by reaction with the undeveloped silver halide of said emulsion is formed. This complex is transferred in solution from the emulsion to a suitable print-receiving element and the silver thereof is there precipitated to form the desired positive print in silver. A principal problem in extending the application of these processes, especially to amateur photography, has been the creation of a print-receiving element or positive sheet so constituted as to adequately precipitate the silver atoms derived from "fast" negative-type silver halide emulsions and to aggregate the silver so deposited in dense clumps which give pictures of adequate density and gamma and which are homogeneous in hue in highlight and shadow. This problem is solved according to the present invention by providing a suitable silver precipitation layer comprising a special matrix in which a silver precipitating agent is so dispersed as to effect a controlled precipitation of the soluble silver complex, the matrix serving to receive and suitably aggregate the precipitated silver to produce positives of excellent pictorial quality. It has been determined that greatly improved results are obtained when a silver precipitation layer of this type is formed by solidifying a liquid dispersion of said matrix material and said precipitating agent upon the support therefor. This provides an optimum distribution of the silver precipitating agent within the matrix which is far superior to that obtained when the matrix is first formed and the precipitating agent is thereafter introduced into the matrix as by imbibition. It is thus one object of the present invention to provide an improved process of this type for the formation of the silver precipitating layer of a print-receiving element.

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

The invention accordingly comprises the process involving the several steps and the relation and order of one or more of such steps with respect to each of the others which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention reference should be had to the following detailed description taken in connection with the accom-

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panying drawing which shows a diagrammatic, enlarged sectional view of the association of elements during one stage of the performance of a transfer process, said element being the product of the novel process of the present invention.

The product of the present invention is most useful in processes wherein the positive silver print is obtained in a single step by suitably treating a silver halide emulsion with a uniformly applied layer of processing liquid. Preferably this liquid is in a viscous condition and is spread between the photosensitive element comprising the silver halide emulsion and the print-receiving element formed in accordance with the process of the invention. The liquid develops that latent image in the emulsion and forms a soluble silver complex 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.

As silver precipitating agents in the silver precipitating layer, it has been proposed to use such materials, as for example, the metallic sulfides and selenides, thiooxalates and thioacetamides, as disclosed in my co-pending application Serial No. 7795, filed February 12, 1948, for Photographic Process. 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. Other precipitating agents have been proposed, such, for example, as the colloidal metals and specifically colloidal silver. The use of silver precipitating agents to aid in the reduction and precipitation of metallic silver from silver complex ions in the presence of a silver halide developing agent in photographic transfer reversal processes is well known in the art and does not per se constitute a feature of this invention.

According to the present invention, the silver precipitating agents are dispersed in a suitable matrix formed of particles, preferably colloidal in size, of a chemically inert, adsorbent material. It is preferable that these particles have a relatively low coefficient absorption for light as compared to silver and satisfactory examples of materials of this type are: colloidal silica, such as silica aerogel, fuller's earth, diatomaceous earth, kieselguhr, wood flour, infusorial earth, bentonite, filter aids such as Celite and Super-Floss, and finely powdered glass, talc, mica or zinc oxide. According to the present invention, particles of matrix material and the silver precipitating agent are dispersed together in a suitable liquid dispersing medium, preferably water, and this dispersion thereafter cast upon the support of the print-receiving element and dried to provide the solid, macroscopically continuous film of the matrix throughout which is dispersed the substantially lesser concentration of the particles of the silver precipitating agent.

Where the silver precipitating agent is one or more of the heavy metal sulfides or selenides, it is preferable to prevent the diffusion and wandering of the sulfide or selenide ions, as the case may be, by also including, in the silver precipitating layer or closely adjacent thereto, 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 which are difficultly soluble in the processing agent and which give up their sulfide or selenide ions to silver by displacement. Accordingly, in the presence of sulfide and selenide ions, the metal ions

of the more soluble salts have the effect of immediately precipitating the sulfide and selenide ions from solution. These more soluble or ion-capturing salts may be the soluble salts of any of the following metals: cadmium, cerium(ous), cobalt(ous), iron, lead, nickel, manganese, thorium and tin. 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.

According to the present invention, the print-receiving element is provided with a silver precipitating layer containing the silver precipitating agent, the ion-capturing salts and the matrix material by forming an aqueous dispersion of the matrix material to which there is added a suitable quantity of one or more of the ion-capturing salts. Thereafter, a substantially lesser molar quantity of a soluble sulfide or selenide, such for example, as sodium sulfide, is added. The anions of sulfide and the cations of the ion-capturing salts combine to precipitate from the solution relatively insoluble crystals of the sulfide of the metal of the ion-capturing salts, thereby converting a portion of the latter to the sulfide. This produces an essentially colloidal dispersion of the insoluble sulfide in the dispersion of the matrix material while leaving in solution the remainder of the ion-capturing salts. However, as noted above, the invention is not restricted to a silver precipitating layer which includes the ion-capturing salts and a silver precipitating layer comprising only the matrix material and the silver precipitating agent may be formed according to the foregoing process by using stoichiometric proportions of the soluble salts which provide the insoluble metallic sulfide. Similarly, colloidal metals may be introduced into the aqueous dispersion from which the silver precipitating layer is formed by the reduction of the suitable metallic salts in said dispersion. This reduction produces a colloidal dispersion of the metallic precipitate in the aqueous dispersion of the matrix material.

The support upon which these dispersions of the matrix material and the silver precipitating agent are cast may be formed of such materials as paper, regenerated cellulose, polyvinyl alcohol, cellulose ethers such as methyl cellulose, ethyl cellulose, or their derivatives, such as sodium carboxymethyl cellulose and hydroxyethyl cellulose, and other natural and synthetic gums and resins which will form continuous films and which are relatively stable, mechanically, in the presence of water and alkali. A transparency is ultimately obtained as the print where the support is transparent.

It will be readily appreciated that the performance of a photographic processing, which involves the formation of a positive print by means of a single liquid application, without recourse to baths of liquid, is to be greatly desired where this can be accomplished to give a positive print of good pictorial quality from emulsions of high speed as can be had by following the practices described hereinabove. However, because the usual developing solution is a highly alkaline solution containing a developing agent which rapidly oxidizes in an alkaline environment, it will also be appreciated that under normal circumstances this type of liquid processing provides in the print-receiving element a material which, upon exposure to air, tends to form undesirable stains. Unless the print is subjected to a thorough washing, this condition will normally adversely affect with time the quality of an image formed in a print-receiving layer. However, as pointed out in my U. S. Patent No. 2,584,030, issued January 29, 1952 and in my copending applications Serial No. 727,383, filed February 8, 1947, for Photographic Product and Process, and Serial No. 37,252, filed July 6,

1948 for Photographic Product and Process, it is possible to avoid this stain by including in the print-receiving layer one or more substances which substantially eliminate the stain-forming propensity of the developing solution in the print-receiving layer.

It is to be observed that the ion-capturing salts, to which reference has been made hereinabove, may also serve the function of improving the stability of the positive print provided that they possess, in addition to the aforementioned characteristics, the requisites specified in my above-mentioned Patent No. 2,584,030. For example, if the ion-capturing salt is a salt of a metal which slowly forms insoluble or slightly soluble metallic hydroxides with the hydroxyl ions in the alkaline processing liquid, it will suitably control the alkalinity of the print-receiving element to substantially, if not totally, prevent the formation of undesirable developer stains.

The stabilizing salt should not be a fogging agent and preferably should be white or lightly colored and should give hydroxides which are also white or light in color. It should not decompose in aqueous nonalkaline solutions. For this purpose, the acetates and nitrates, especially of lead, zinc, nickel and cadmium, are preferred. Of the salts hereinabove set out as being satisfactory for preventing the sulfide ions from wandering, all except the hydroxide will function satisfactorily as stabilizing agents. In addition, the soluble salts, for example of aluminum, may be used to stabilize although they will not serve to trap the wandering sulfide ions.

The use of the products produced in accordance with the present invention in the performance of a silver halide transfer process is illustrated diagrammatically in the drawing, wherein 10 represents a photosensitive element comprising a support 10a and a photosensitive silver halide emulsion layer 10b, 14 represents a layer of relatively viscous processing agent, and 12 is one embodiment of the novel print-receiving element of the invention upon which a transfer print is obtained by the process. As shown, print-receiving element 12 comprises a suitable support 12a and a silver precipitating layer 16. Liquid layer 14 may be obtained by spreading the processing agent, for example, in a manner disclosed in my copending application Serial No. 7795, and the processing agent may be one of the film-forming processing agents disclosed in said copending application. Element 12 is formed by applying to a suitable support 12a, for example of baryta paper, a coating of a suspension or sol of the matrix-forming particles and the silver precipitating agent. This suspension is permitted to dry and provides layer 16 through which is distributed the silver precipitating agent. As noted above, suspension of the matrix material is obtained by dispersing the said material, for example colloidal silica, in a suitable liquid suspending medium such as water and then adding the silver precipitating agent either directly or by introducing into the suspension reagents whose reaction product is the precipitating agent. Examples of processes of forming a print-receiving element 12 provided with a suitable silver precipitating layer 16 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

The baryta-coated surface portion of a strip of baryta paper is immersed in a mixture comprising the following ingredients:

1% solution of sodium sulfide	cc.	280
Silica aerogel	grams	30
Solution containing 30 g. cadmium acetate, 1 g. neutral lead acetate and 30 g. zinc nitrate dissolved in 100 cc. of water	cc.	92

to provide a thin coating of these materials on said surface. As the baryta paper is removed from the bath, the excess mixture on said surface is removed from the

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sheet as, for example, by the action of a soft buffer roll on said sheet as it leaves the bath.

Example 2

To 24 cc. of a 10% solution of lanthanum chloride there are added 4 g. of silica aerogel (Santocel C) and 6 cc. of a 1% solution of sodium sulfide, and these ingredients are thoroughly mixed in a mechanical mixer. A layer of the resulting mixture is then applied to the baryta-coated surface of a sheet of baryta paper, and the sheet is permitted to stand for approximately 15 seconds. Thereafter, the excess of the liquid mixture is removed as by a soft buffer roll from the surface of the sheet.

Example 3

The process of forming the sheet described in Example 2 may be performed by substituting for the mixture therein a mixture of the following materials which gives a coating of silica containing palladium sulfide:

24 cc. of a 10% solution of palladium chloride
4 g. of silica aerogel
4 cc. of a 1% solution of sodium sulfide

Example 4

The process of forming the sheet described in Example 2 may be performed by substituting for the mixture therein a mixture of the following materials which gives a coating of silica containing nickelous sulfide:

40 cc. of a 15% solution of nickelous chloride
7.5 g. of silica aerogel
20 cc. of a 1% solution of sodium sulfide

Example 5

The process of forming the sheet described in Example 2 may be performed by substituting for the mixture therein a mixture of the following materials which gives a coating of silica containing cadmium sulfide:

96 cc. of a 20% solution of cadmium acetate
15 g. of silica aerogel
30 cc. of a 1% solution of sodium sulfide

Example 6

The process of forming the sheet described in Example 2 may be performed by substituting for the mixture therein a mixture of the following materials which gives a coating of silica containing zinc sulfide:

20 cc. of a 37.5% solution of zinc nitrate
7.5 g. of silica aerogel
30 cc. of a 1% solution of sodium sulfide

Example 7

The process of forming the sheet described in Example 2 may be performed by substituting for the mixture therein a mixture of the following materials which gives a coating of silica containing magnesium sulfide:

48 cc. of a 40% solution of magnesium acetate
7.5 g. of silica aerogel
18 cc. of a 1% solution of sodium sulfide

Example 8

The process of forming the sheet described in Example 2 may be performed by substituting for the mixture therein a mixture of the following materials which gives a coating of silica containing lead selenide:

96 cc. of a 40% neutral lead acetate solution
15 g. of silica aerogel
30 cc. of a 1% sodium selenide solution

Example 9

To 15 grams of Ludox, a solution containing approximately 30% of hydrated colloidal silica in water, there are added 90 grams of water. Thereafter 24 cc. of a solution formed by adding 3 grams of sodium sulfide to

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46 cc. of water is added to this suspension, followed by the addition of 12 cc. of a solution formed by dissolving 2.6 grams of lead acetate in 20 cc. of water.

The resulting mixture is rubbed by hand on the surface of the print-receiving support. It is preferable to wipe off any excess of the mixture from the paper after the rubbing operation.

To obtain different precipitating agents in the silver precipitating layer that is formed according to the process of Example 9, there may be substituted for the 2.6 grams of lead acetate one of the following salts in the following quantities:

	Grams
15 Zinc acetate -----	1.42
Cupric acetate -----	1.34
Manganous acetate -----	1.60
Cadmium acetate -----	1.92

Example 10

To assure the presence of a sufficient excess of cations for capturing the sulfide or selenide ions of any of the print-receiving elements 12 of the foregoing Examples 1 through 9, said elements may be suitably treated as follows: The surface of the element containing the silica suspension is dipped for 30 seconds in a solution consisting of:

10 g. cadmium acetate
1 g. lead acetate
30 g. zinc acetate
100 cc. of water

Excess moisture is removed from the sheet as it leaves the solution, for example with a glass rod, and the sheet is dried.

For the baryta paper of any of the foregoing examples, there may be substituted a film of plastic such, for example, as polyvinyl alcohol, hydroxyethyl cellulose, sodium carboxymethyl cellulose, regenerated cellulose or other self-supporting sheetlike materials upon which the novel silver precipitating layer of the present invention may be deposited. A transparent plastic as a support will, of course, give a transparency.

In another form of the product of the present invention, it may be desirable to provide a coating on the silver precipitating layer 16 of a material, such as a plastic, more abrasion resistant than the silica of the precipitating layer in order to protect said layer. This overcoat of a plastic material may also serve as a layer which prevents the adhesion to the element 12 of the film-forming material of the layer of processing liquid 14 so that when said element 12 is stripped away from the photosensitive film 10 at the completion of the processing, the film-forming material remains attached to the photosensitive layer 10b. This overcoat may be formed by applying over layer 16 a thin coating of a film-forming material which may be, for example, gum arabic, cellulose acetate-hydrogen phthalate, polyvinyl alcohol, hydroxyethyl cellulose, methyl cellulose, ethyl cellulose, cellulose nitrate, sodium alginate, pectin and polymethacrylic acid. This overcoat preferably has a thickness of the order of 1 to 3 microns although, if it is relatively water permeable, its thickness may be appreciably greater. It may contain one or more of the neutralizing agents which may improve the stability of the finished print.

To provide any of the print-receiving elements 12 of Examples 1 through 10 with a protective coating of a more abrasion-resistant plastic which may also serve as a layer for minimizing the adhesion between the film-forming material of layer 14, particularly where said material is sodium carboxymethyl cellulose, said elements 12 of each of said examples may be processed as follows:

Example 11

The processed sheet has roll-coated thereon against a smooth surface such, for example, as the polished sur-

face of a metal drum, a 5% aqueous solution of polyvinyl alcohol in a layer whose thickness is of the order of .001 inch. An equivalent amount by weight of hydroxyethyl cellulose or polymethacrylic acid may be substituted for the polyvinyl alcohol of this example.

Example 12

The processed sheet is dipped into a 2% solution of cellulose acetate, the cellulose acetate being dissolved in a mixture of methanol, ethyl acetate and methyl cellosolve, the proportions of said solvents being in the ratio of 1:3:3 by volume, respectively. The dipped baryta paper is removed from the solution in a vertical position to permit the excess liquid to drip off, a sufficient quantity of the solution remaining on the surface of the paper to provide the latter with a coating of cellulose acetate of the desired thickness.

Example 13

A 10% solution of cellulose acetate-hydrogen phthalate in acetone is roll-coated on the processed sheet in a thickness of approximately .001 inch.

In a similar manner, such other materials as methyl cellulose, cellulose nitrate, sodium alginate, ethyl cellulose, gum arabic and pectin may be applied as an abrasion-resistant coating to the processed sheet. It is, of course, understood that suitable solvents for the materials are employed, said solvents being preferably water for such materials as are readily water soluble, and may be toluene for ethyl cellulose and a mixture of methanol and ethyl acetate for cellulose nitrate.

Although the silver precipitating layer of the present invention is constituted primarily of the silica, it may contain therein a small quantity, preferably not exceeding 10% by weight of the silica, of a film-forming substance such as gum arabic, hydroxyethyl cellulose or any of the other materials heretofore mentioned as being suitable for the abrasion-resistant coating on layer 16. The addition of this small quantity of plastic facilitates application of the layer 16 onto the support therefor. An example of one way of forming a layer 16 containing a small quantity of film-forming material is the following:

Example 14

The following ingredients are mixed in the order named:

Water	cc--	595
Gum arabic	cc--	3.5
Cadmium acetate	g--	22.76
Silica aerogel	g--	36
Sodium selenide	g--	10

A sheet of baryta is dipped in the mixture, withdrawn, and the excess liquid squeezed therefrom.

Other plastics may be substituted for the gum arabic. Also, by substituting salts of other metals for the cadmium acetate different metallic selenides may be obtained in the sol.

It is to be noted from the foregoing examples that the silver precipitating agent is present in the sheet in a very small amount. Concentrations, for example, as low as 2×10^6 to 2×10^5 gram-moles for each square foot of the surface area of the print-receiving element have proven adequate. It is to be understood that the aforementioned matrix materials, while water insoluble in the strict sense that they do not become ionized and are not molecularly dispersed in water, may be present in their liquid medium in a very highly dispersed, suspended state.

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. A process for forming print-receiving elements which comprises the steps of creating a mixture, in a liquid suspending medium, of minute particles of a relatively inert, insoluble, adsorbent substance and a substantially lesser concentration of a silver precipitating agent, said substance being insoluble in water and in said liquid dispersing medium and chemically inert to silver halide emulsions and to photographic silver halide developers and fixing agents, said silver precipitating agent being dispersed among said particles of said substance and being capable of aiding in the reduction and precipitation of metallic silver from silver complex ions in the presence of a silver halide developing agent, coating the liquid dispersion so formed in a thin layer on a sheet support, and drying said coating to provide said support with a thin silver precipitation layer permeable to the ionic content of an aqueous solution of a soluble silver complex, said precipitation layer comprising a matrix of said substance throughout which is dispersed said silver precipitating agent.

2. A process for forming print-receiving elements which comprises the steps of creating a mixture, in an aqueous liquid suspending medium, of minute particles of a relatively inert, insoluble, adsorbent substance and a substantially lesser concentration of a silver precipitating agent, said substance being insoluble in the aqueous liquid and chemically inert to silver halide emulsions and to photographic silver halide developers and fixing agents, said silver precipitating agent being dispersed among said particles of said substance and being capable of aiding in the reduction and precipitation of metallic silver from silver complex ions in the presence of a silver halide developing agent, coating the liquid dispersion so formed in a thin layer on a sheet support, and drying said coating to provide said support with a thin silver precipitation layer permeable to the ionic content of an aqueous solution of a soluble silver complex, said precipitation layer comprising a matrix of said substance throughout which is dispersed said silver precipitating agent.

3. A process for forming print-receiving elements which comprises the steps creating a mixture, in water, of minute particles of a relatively inert, insoluble, adsorbent substance and a substantially lesser concentration of a silver precipitating agent, said substance being insoluble in water and chemically inert to silver halide emulsions and to photographic silver halide developers and fixing agents, said silver precipitating agent being dispersed among said particles of said substance and being capable of aiding in the reduction and precipitation of metallic silver from silver complex ions in the presence of a silver halide developing agent, coating the liquid dispersion so formed in a thin layer on a sheet support, and drying said coating to provide said support with a thin silver precipitation layer permeable to the ionic content of an aqueous solution of a soluble silver complex, said precipitation layer comprising a matrix of said substance throughout which is dispersed said silver precipitating agent.

4. The process of claim 1 wherein the inert, insoluble, adsorbent substance is at least one material from the class consisting of silica, fuller's earth, wood flour, bentonite, powdered glass, powdered talc, powdered mica and powdered zinc oxide.

5. The process of claim 1 wherein the silver precipitating agent is a substance from the class consisting of metallic sulfides and selenides.

6. The process of claim 1 wherein the relatively inert, insoluble substance is silica.

7. The process of claim 1 wherein the relatively inert, insoluble substance is bentonite.

8. The process of claim 1 wherein the relatively inert, insoluble substance is powdered glass.

9. The process of claim 1 wherein the relatively inert, insoluble substance is powdered mica.

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10. The process of claim 1 wherein the relatively inert, insoluble substance is zinc oxide.

11. A process for forming print-receiving elements which comprises the steps of creating a mixture in water, of minute particles of a relatively inert, insoluble, adsorbent substance and a substantially lesser concentration of a silver precipitating agent, said substance being insoluble in water and chemically inert to silver halide emulsions and to photographic silver halide developers and fixing agents and being from the class consisting of silica, fuller's earth, wood flour, bentonite, powdered glass, powdered talc, powdered mica and powdered zinc oxide, said silver precipitating agent being capable of aiding in the reduction and precipitation of metallic silver from silver complex ions in the presence of a silver halide developing agent and being a material from the class consisting of metallic sulfides and selenides, coating the liquid dispersion so formed in a thin layer on a sheet support, and drying said coating to provide said support with a thin silver precipitation layer permeable to the ionic content of an aqueous solution of a soluble silver complex, said precipitation layer comprising a matrix of said substance throughout which is dispersed said silver precipitating agent.

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

13. The process of claim 1 wherein the silver precipitating agent is a substance from the class consisting of the thiooxalates and thioacetamides.

14. A process for forming print-receiving elements which comprises the steps of creating a mixture, in water, of minute particles of a relatively inert, insoluble, adsorbent substance and a substantially lesser concentration of a silver precipitating agent, said substance being insoluble in water and chemically inert to silver halide emulsions and to photographic silver halide developers and fixing agents and being from the class consisting of silica, fuller's earth, wood flour, bentonite, powdered glass, powdered talc, powdered mica and powdered zinc oxide, said silver precipitating agent being capable of aiding in the reduction and precipitation of metallic silver from silver complex ions in the presence of a silver halide developing agent and being a colloidal metal, coating the liquid dispersion so formed in a thin layer on a sheet support, and drying said coating to provide said support

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with a thin silver precipitation layer permeable to the ionic content of an aqueous solution of a soluble silver complex, said precipitation layer comprising a matrix of said substance throughout which is dispersed said silver precipitating agent.

15. A process for forming print-receiving elements which comprises the steps of creating a mixture, in water, of minute particles of a relatively inert, insoluble, adsorbent substance and a substantially lesser concentration of a silver precipitating agent, said substance being insoluble in water and chemically inert to silver halide emulsions and to photographic silver halide developers and fixing agents and being from the class consisting of silica, fuller's earth, wood flour, bentonite, powdered glass, powdered talc, powdered mica and powdered zinc oxide, said silver precipitating agent being capable of aiding in the reduction and precipitation of metallic silver from silver complex ions in the presence of a silver halide developing agent and being a material from the class consisting of the thiooxalates and thioacetamides, coating the liquid dispersion so formed in a thin layer on a sheet support, and drying said coating to provide said support with a thin silver precipitation layer permeable to the ionic content of an aqueous solution of a soluble silver complex, said precipitation layer comprising a matrix of said substance throughout which is dispersed said silver precipitating agent.

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