Aug. 21, 1956 E. H. LAND 2,759,825

PHOTOGRAPHIC IMAGE TRANSFER PROCESS

Original Filed Feb. 12, 1948 2 Sheets-Sheet 1

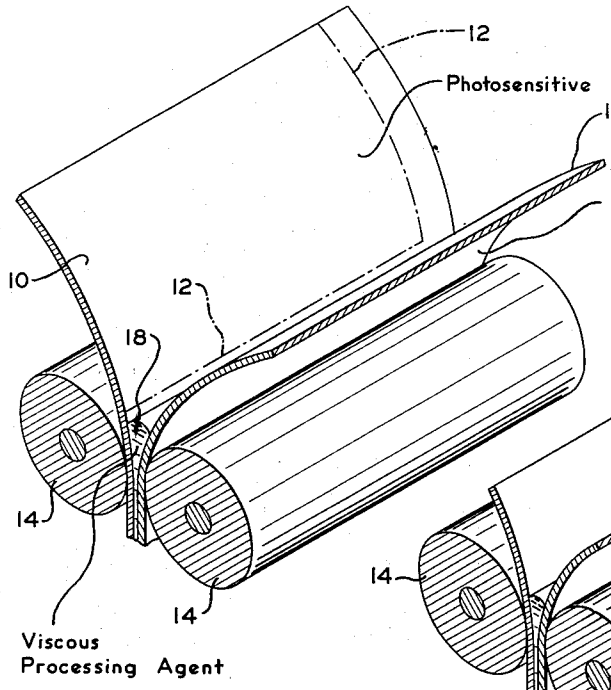


FIG. 1

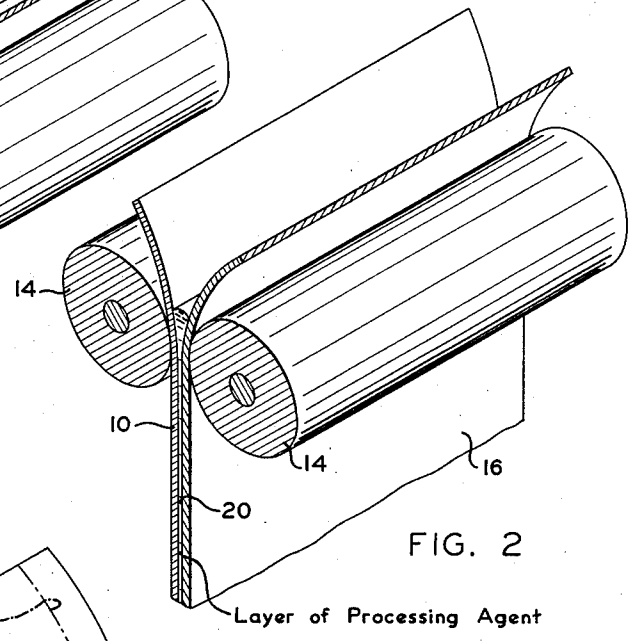


FIG. 2

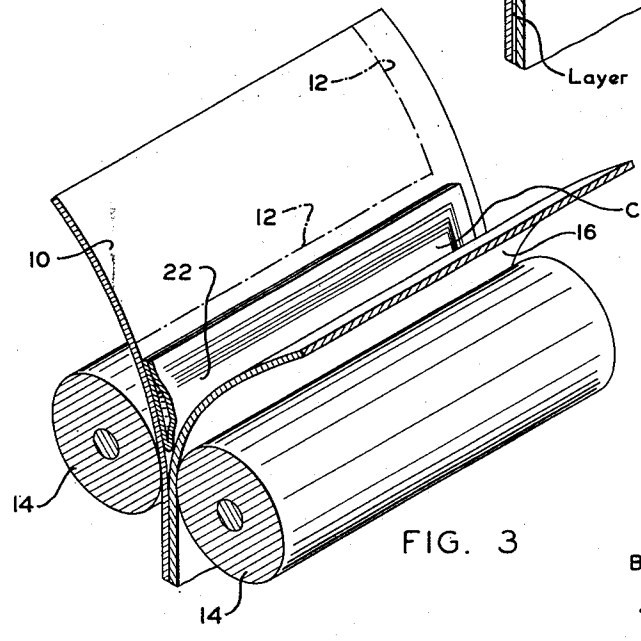


FIG. 3

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PHOTOGRAPHIC IMAGE TRANSFER PROCESS

Original Filed Feb. 12, 1948 2 Sheets-Sheet 2

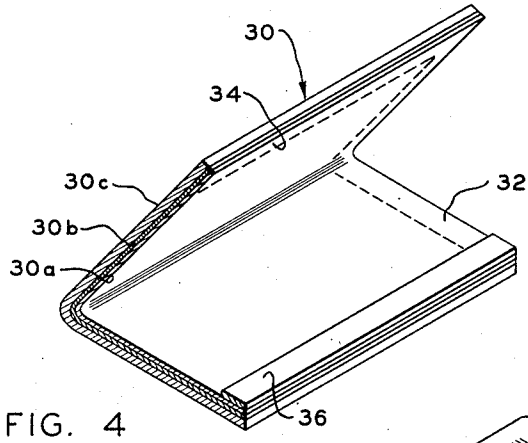


FIG. 4

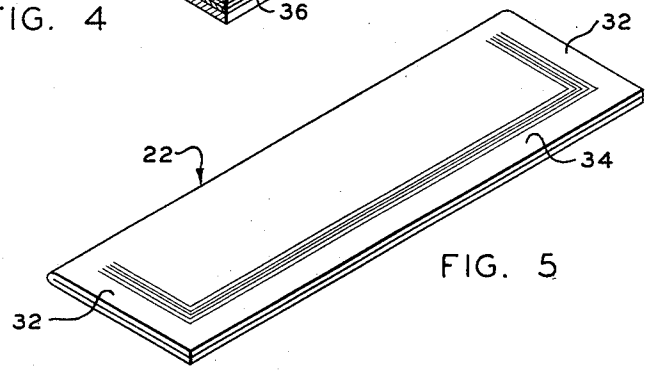


FIG. 5

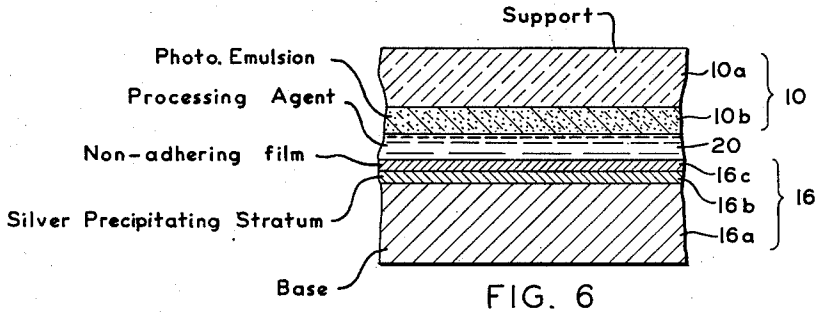


FIG. 6

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PHOTOGRAPHIC IMAGE TRANSFER PROCESS

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Original application February 12, 1948, Serial No. 7,795. Divided and this application February 9, 1951, Serial No. 210,125

11 Claims. (Cl. 95—88)

This invention relates to photographic processes and more particularly to transfer processes wherein a latent image in a silver halide emulsion is developed and wherein components are transferred from said emulsion to a print-receiving element to form a positive print in the latter.

This application is a division of my copending application Serial No. 7795, filed February 12, 1948, for One-Step Photographic Transfer Process (now Patent No. 2,647,056, issued July 28, 1953).

One object of the present invention is to provide a novel transfer process in which the processing liquid is spread in a thin layer over the surface of a print-receiving element and a photosensitive element, and the print-receiving element is provided with a surface from which the viscous film of processing agent may be readily stripped.

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 accompanying drawings wherein:

Figure 1 is an enlarged fragmentary and diagrammatic view in perspective illustrating one stage in the process of the present invention;

Fig. 2 is a view similar to Fig. 1 illustrating another step in the process;

Fig. 3 is a view similar to Fig. 1 in which there is illustrated an alternative method for introducing the liquid processing agent between the two sheet materials;

Fig. 4 is a fragmentary enlarged perspective view illustrating the construction of the container of Fig. 3, the thicknesses of the laminations of the sheet materials from which the container is formed being greatly exaggerated;

Fig. 5 is a perspective view of the filled and sealed container; and

Fig. 6 is a diagrammatic enlarged sectional view illustrating one embodiment of the product of the present invention shown in use in the performance of a transfer process.

The present invention is particularly useful in processes wherein a photosensitive, silver halide emulsion layer or the like containing a latent image has a positive of the subject matter of said latent image formed upon a separate print-receiving element. In the performance of such processes, the processing agent, when spread in a layer, develops a latent image in the area of the photosensitive layer over which it is spread and the development of this latent image produces an imagewise distribution throughout the photosensitive layer and/or the liquid processing layer adjacent thereto of a material which thereafter acts

to provide the positive print in the print-receiving element, the latter being superposed upon the photosensitive layer during this processing with the layer of processing agent located between it and the photosensitive layer.

In one form of this type of processing, there is provided in the spread liquid composition a developing agent for the latent image and a material capable of forming a soluble complex with the photosensitive material of the emulsion. The complex-forming material and the developing agent react with the photosensitive layer in such a manner that the latent image is developed and a soluble complex is formed with the relatively unexposed, undeveloped photosensitive material of the emulsion. This complex is transported from the photosensitive layer and the silver thereof is caused to precipitate and aggregate in a print-receiving element to form a positive image.

In other processes which may be carried out in accordance with the invention, the imagewise distribution of the developer or the oxidation product of the developer resulting from the development of the latent image in the photosensitive layer is used to create a visible image in the print-receiving element. In one such process, the imagewise distribution of the unused developing agent acts to form a substance which produces the visible image. In another modification, the oxidized developer is employed to react with a substance in a surface stratum of the print-receiving element to form, for example, a dye image. This dye image is a negative of the subject matter of the latent image in the event the photosensitive emulsion is the ordinary non-solarized emulsion, and is a positive of the subject matter of the latent image in the event the emulsion is of the type which gives direct positives upon exposure and development, e. g., emulsions which have been optically or chemically solarized or which use other reversal effects such as the Herschel effect.

In general, therefore, the print-receiving elements of the present invention are particularly useful in the performance of transfer processes wherein the layer of liquid composition which is located between the sheet material comprising the photosensitive layer and the print-receiving element acts to develop a latent image in said photosensitive layer, and such development produces an imagewise distribution of a material which is capable of providing said print-receiving element with a visible positive or negative image record of the latent image. The inclusion of the film-forming material in the liquid composition in connection with these transfer processes serves further functions. It provides a spacer for the two sheet materials which tends to hold the same far enough apart so that there is a reservoir therebetween for the ions and molecules that must enter and leave the sheet materials during the processing while keeping the surfaces of said sheet materials near enough together so that the image-forming particles which are translated from the photosensitive layer are made up of components which have arrived along a relatively short radius of diffusion. The presence of the film-forming material in the liquid processing agent also serves to cause the latter to temporarily bond together the two sheet materials tightly enough to prevent such separation or relative movement thereof as might tend to diffuse the image being formed by the transfer process.

In accordance with the present invention, the print-receiving element is so constituted that when the same is stripped from the photosensitive element the film formed by the processing agent adheres to the photosensitive element so that a minimum of the reaction products of the processing which produces the positive print in the print-receiving element remains upon said print-receiving element, thereby tending to greatly improve the stability of the print.

Referring to the drawings, and particularly to Figs. 1 and 2, there is illustrated one manner of performnig the process of the present invention. A photosensitive sheet material **10** of which a predetermined area **12** is to be processed has a portion thereof, in advance of said area, located between a pair of pressure-applying members such as a pair of pressure rollers **14—14** and a print-receiving element **16** is introduced between said pressure-applying members so that a portion thereof is superposed with respect to the portion of said photosensitive material located between said members. There is introduced into the troughlike cavity formed adjacent the pressure-applying members by sheet materials **10** and **16** a mass **18** of the viscous film-forming processing agent in a quantity at least sufficient to carry out the processing of said area, said mass of processing agent being preferably distributed throughout a length parallel to and coextensive with the linear dimension of said area which it adjoins. Thereafter, the sheet materials are moved in superposed relation between said pressure rollers so that the latter progressively apply a compressive force to successive increment areas of said sheet materials, spreading said processing agent **18** in a thin layer **20**, as shown in Fig. 2.

The separation of the pressure rollers and the thicknesses of the sheet materials predetermine the maximum thickness of the layer of the liquid processing agent that is obtained between said sheet materials. Said sheet materials may be moved with respect to said pressure rollers by being pulled therethrough manually, or by rotating the rollers to cause the frictional engagement between said rollers and said sheet materials to advance the latter therebetween, or by fixing the edges of said sheet materials extending through said rollers with a suitable clamp and then moving the rollers with respect to the sheet materials.

Other types of pressure-applying members such, for example, as a pair of nonrotatable bars or a pair of plates or a pair of jaw-shaped members or a plate and a roller may be employed instead of the pressure rollers to effect the spreading.

The processing agent may be dispensed between the sheet materials from a suitable container as, for example, a tubular, collapsible, metallic container of the type used for containing tooth paste, shaving cream, and the like. It will be observed (Fig. 1) that the liquid is located, upon dispensation, in a fairly concentrated mass **18** having a relatively small exposed surface area and that the relatively thin layer **20** of large surface area which is thereafter obtained by the spreading of the agent (Fig. 2) is protected on both sides thereof by the two sheet materials between which it is spread, thus minimizing the effects of oxidation.

The liquid composition may also be provided in a condition to be dispensed and spread between said sheet materials **10** and **16** by being contained in an elongated container **22** which has a length at least equal to a transverse linear dimension of the area **12** of photosensitive material **10** to be processed. Container **22** is located between the two sheet materials adjacent and substantially parallel to an edge of said area which parallels said linear dimension.

Container **22**, which may be attached to one of sheet materials **10** and **16**, is preferably inexpensive and disposable and so constructed as to be capable of retaining the processing 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 **30** (Fig. 4) comprising three layers, **30*a***, **30*b*** and **30*c***. Layer **30*a***, which provides the internal surface layer of the container, is formed of a material which is chemically inert to 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 of a developer for silver halide or the like, 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 particularly satisfactory as inner coating **30*a***. Layer **30*b*** contiguous to layer **30*a*** 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. Backing layer **30*c***, for example of kraft paper, is provided and makes possible the use of thinner layers **30*a*** and **30*b***.

The container **22** (Fig. 5) is preferably formed by taking the single sheet of material **30** and folding the same medially, as shown in Fig. 4, and thereafter securing the end marginal portions **32** and the longitudinal portions **34** of the two folded faces to one another, providing a central space or cavity for containing the processing agent. To fill the container, it is possible to adhere together the opposite longitudinally extending marginal portions **34** and the end marginal portions **32** at one end only of the container, the container being filled through the other end, which is thereafter sealed.

The longitudinal seal between marginal portions **34** is preferably such that upon application of a predetermined compressive force to the walls of the container there may be created within the container a sufficient hydraulic pressure to separate the marginal portions **34** throughout substantially their entire length. To insure this, the bond securing together said marginal portions **34** is somewhat weaker than the bond which secures together end marginal portions **32**. For example, the end portions may be secured by pressing the two polyvinyl butyral inner surfaces together and applying heat thereto while a sealing strip **36** may be provided between the longitudinal marginal portions, which sealing strip is adapted to adhere to the inner layers of polyvinyl butyral with a lesser affinity than said layers adhere to one another in a direct polyvinyl butyral to polyvinyl butyral bond. Strip **36** may be formed of a material such as ethyl cellulose or a mixture of ethyl cellulose and paraffin.

For carrying out the process a preferred form of the processing agent comprises a water solution of a developer, an alkali for imparting to the solution a sufficiently high alkalinity to permit the developer to carry out its developing function, a substance for forming a soluble complex with silver halide, and a film-forming material. When this agent is spread between a photosensitive silver halide emulsion and a print-receiving element, the developer in the agent acts to develop any latent image in the emulsion and the silver halide solvent forms a soluble complex with the relatively unexposed silver halide during the development, which complex is transported from the emulsion to the print-receiving element to form in said element a positive image comprising silver of the developed image in the emulsion. The film-forming material, which is preferably a high molecular weight polymer, imparts to the composition a predetermined high viscosity and is of such character as to retain its viscosity-imparting and film-forming properties in an aqueous alkaline solution so that the processing agent, once its ingredients have been mixed and have attained an equilibrium, remains uniformly viscous for any given temperature for long periods of time.

The film-forming material in the foregoing alkaline composition is preferably one of the class of high molecular weight polymers which include in their chemical structure such groups as, for example, the ether, alkyl, hydroxyl, carboxyl and acetyl groups that are stable to alkalis and which contain none of the chemical groups, such as the ester and acid chloride groups, that are unstable to alkalis. The polymers also contain groups such as the hydroxyl and/or carboxyl groups which tend to solubilize in aqueous alkaline solutions. Suitable ex-

amples of such polymers are the alkali-inert and water-soluble cellulose derivatives such as sodium carboxymethyl cellulose and hydroxyethyl cellulose, and the alkali-inert and water-soluble polyalkane derivatives such as polyvinyl alcohol and the sodium salts of polymethacrylic acid and polyacrylic acid.

A high viscosity for the processing agent is very desirable since it makes possible the relatively uniform spreading of the composition and insures a complete coverage of the desired area by said composition. The film-forming material is preferably contained in the composition in suitable quantities to impart to the composition a viscosity in excess of 1,000 centipoises at a temperature of approximately 24° C. and preferably of the order of 1,000 to 200,000 centipoises at said temperature. These high viscosities are important for any commercial application of said composition in view of the order of nonuniformity of commercially available materials and pressure-applying means to be used in connection therewith.

Examples of developers useful in the foregoing composition alone or in mixture with one another are hydroquinone, monomethyl-p-aminophenol sulfate (Elon, Metol), p-aminophenol hydrochloride (Kodelon), p-hydroxyphenylaminoacetic acid (Athenon, Glycin), p-phenylenediamine, o-phenylenediamine, pyrocatechin (pyrocatechol, catechol), diaminophenol dihydrochloride (Amidol), diaminophenol hydrochloride (Acrol), pyrogallol, chlorohydroquinone, dichlorohydroquinone, tetrachlorohydroquinone, bromohydroquinone, toluhydroquinone, xylchydroquinone, o-aminophenol, 2-amino-5-diethylaminotoluene hydrochloride, p-tertiary butyl catechol, hydroquinone disulfonic acid (potassium salt), 2,5-ditertiary butyl hydroquinone, and p-aminodiethylanaline.

Examples of materials which may be used in the composition for the purpose of forming a soluble silver complex with the undeveloped silver halide of the photosensitive layer are sodium thiosulfate, sodium thiocyanate, ammonium thiosulfate, ammonia and sodium cyanide. When a compound is toxic, such as sodium cyanide, precautions should be taken in the use thereof.

The composition may also contain sodium sulfite which acts in part as a preservative, and may also function as a silver halide solvent.

Examples of processes for forming a positive image of a latent image contained in a silver halide emulsion by means of the transformation of undeveloped silver halide to a soluble complex and the translation thereof to a suitable image-receiving layer are given below, but it is to be 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:

Water	grams	1860
Sodium carboxymethyl cellulose	do	117
Sodium sulfite	do	78
Sodium hydroxide	do	74.6
Sodium thiosulfate	do	14.5
Citric acid	do	38.5
Hydroquinone	do	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 processing agent is then spread, for example, as shown in Figs. 1 and 2, between a photosensitive sheet material **10** and the novel print-receiving element **16** to form a laminate comprising sheet **10**, a layer **20** of the processing agent, and element **16** (Fig. 6). Sheet **10** may comprise a support **10***a* of paper or transparent film base such as a cellulosic ester or a cellulose mixed ester and a photosensitive silver halide emulsion **10***b* such as an orthochromatic, high contrast emulsion especially useful for process work, for example, the emulsion of Eastman Kodak Contrast Process Ortho film, or an emulsion of an enlarging paper such as the emulsion of Eastman Kodak Kodabromide paper. This emulsion constitutes the inner surface of sheet **10**. The layer of processing agent **20** is preferably spread between said sheet materials to a thickness of between .002 inch and .003 inch. The absorption of the liquid by emulsion **10***b* and the surface portion of element **16** promptly reduces this layer to a thickness of the order of .0001 inch to .0003 inch. Layer **20** bonds together sheet materials **10** and **16** just tightly enough so that they do not separate spontaneously during the time of processing. The lamination thus formed is kept intact for approximately one to two minutes, and at the end of this time element **16** is stripped from sheet **10**, leaving a finished positive image on element **16**.

Base or support **16***a* of element **16** is preferably baryta paper although it may be formed of such other materials as, for example, regenerated cellulose, a polyhydroxy alkane such as polyvinyl alcohol, sodium alginate, cellulose ethers such as ethyl cellulose, or their derivatives such as sodium carboxymethyl cellulose, aluminum carboxymethyl cellulose and hydroxyethyl cellulose, other papers, proteins such as gelatin and carbohydrates such as gums and starch, and mixtures of these materials where the latter are compatible.

Faster emulsions such, for example, as the emulsions available for use in amateur photography as negative materials may also be used. Examples of the faster emulsions are 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. Preferably, when these higher speed emulsions are used, the sodium thiosulfate content of the processing agent of Example 1 is substantially increased, being preferably quadrupled. Improvements in the photographic characteristics of the positive image may also be obtained by suitably applying to the print-receiving element substances for attracting and aggregating the image-forming ions. Examples of such substances are the metallic sulfides such, for example, as lead sulfide, cadmium sulfide, zinc sulfide, ferric sulfide, antimony sulfide, manganous sulfide, titanium sulfide sodium sulfide, lanthanum sulfide, palladium sulfide, nickelous sufide, and such metallic selenides as zinc selenide, nickel selenide, lead selenide, manganous selenide and antimony selenide, and such other substances as dithiooxamide and its lead and zinc complexes, potassium dithiooxalate and the lead complexes thereof, and thioacetamide.

These precipitating materials are preferably applied to the surface of the base **16***a* in mixtures of a suitable, relatively inert material such as silica aerogel (Santocel C), wood flour, clays, for example kieselguhr and bentonite, starches, ground glass, and celites. An example of suitable compositions for treating a base **16***a* of baryta paper to form thereon a silver precipitating layer **16***b* is the following:

Example 2

Baryta paper is run through a bath which is kept in contact with the baryta surface for approximately ten seconds, the bath comprising:

Cadmium acetate	g	9
Neutral lead acetate	g	.3
Zinc nitrate	g	18
Water	cc	100

The sheet thus obtained is dried and coated with a mixture comprising:

Water	cc.	270
Cadmium acetate	g.	27.8
Lead acetate	g.	9.3
Zinc nitrate	g.	55.6
Silica aerogel (Santocel C)	g.	30
3% solution of sodium sulfide	cc.	94.7

The sheet is preferably dipped into this mixture and the excess mixture is removed from the sheet as, for example, by the action of a soft buffer roll on said sheet as it leaves the bath.

To cause the film-forming material of layer **20** to adhere to photosensitive sheet material **10** instead of print-receiving element **16** so that the solid plastic film obtained from said film-forming material sticks to the photosensitive material **10** when the latter is stripped from element **16**, there is provided over stratum **16***b* a layer **16***c*. Layer **16***c* is preferably very thin and is formed of a material which has an appreciably lesser affinity for the film-forming material of layer **20** than said film-forming material has for the surface of sheet material **10** which it contacts. In the event emulsion **10***b* is a silver halide gelatin emulsion and the film-forming material in layer **20** is sodium carboxymethyl cellulose, layer **16***c* may be, for example, gum arabic, cellulose acetate-hydrogen phthalate, polyvinyl alcohol, hydroxyethyl cellulose, methyl cellulose, ethyl cellulose, cellulose nitrate, sodium alignate, pectin, and polymethacrylic acid. Layer **16***c* 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.

The adhesion between the carboxymethyl cellulose in layer **20** and the surface of layer **10***b* may also be increased by applying to said surface or by incorporating adjacent said surface in said emulsion a substance which tends to insolubilize sodium carboxymethyl cellulose by causing cross-linking of the molecules of the latter, examples of such substances being lead acetate and zinc acetate. The photosensitive emulsion may be treated with these materials by being dipped in a solution thereof. The affinity between emulsion **10***b* and the film-forming material of layer **20** may also be appreciably increased by applying to the surface of said emulsion a thin coating of solid film formed of said film-forming substance.

To provide a sheet **16** with a stratum **16***b* containing precipitation nuclei, a sheet of baryta paper may have the baryta surface thereof coated as described in Example 2, or it may be processed as follows:

Example 3

A sheet of baryta paper has roll coated thereon a thin layer of a composition comprising:

.25% solution of polyvinyl alcohol	cc.	110
1% solution of sodium sulfide	cc.	48
1% solution of neutral lead acetate	cc.	76

Either of the sheets processed in accordance with Examples 2 and 3 and thereby provided with an image-receiving stratum **16***b* may be suitably processed to be provided with a stripping overcoat **16***c*, for example in the following manner:

Example 4

The processed sheet has roll coated 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 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 5

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 6

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 and gum arabic and pectin may be applied as layer **16***c* 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.

In using the sheets processed in accordance with any of the foregoing examples, the adhesion between the film-forming material and the photosensitive emulsion may be increased by applying to the photosensitive emulsion a thin coating of the film-forming material. For example, when the film-forming material in the processing agent is sodium carboxymethyl cellulose the surface of layer **10***b* may be treated as follows:

Example 7

A 5% water solution of sodium carboxymethyl cellulose is applied to layer **10***b* in a darkroom as, for example, by being spread thereon by a doctor blade to a thickness of approximately .002 inch. This film, when dried, will give a very thin layer of sodium carboxymethyl cellulose and will improve the adhesion between the layer **10***b* and the solid film formed from the processing agent.

It may be desirable in some instances to provide on the surfaces of sheet **16** a single layer which combines the properties of layer **16***c* and stratum **16***b*, i. e., a single layer which serves to lessen the affinity between sheet material **16** and the film-forming material, and is so constituted as to attract the soluble silver halide complex and to precipitate the silver therefrom. Such a layer may be provided on base **16***a*, for example as follows:

Example 8

A solution consisting of:

Water	cc.	270
Cadmium acetate	g.	27.8
Neutral lead acetate	g.	9.3
Zinc nitrate	g.	55.6

has mixed therewith a composition comprising

Silica aerogel (Santocel C)	g.	30
1% solution of sodium sulfide	cc.	93.3

To 100 cc. of the resulting mixture there is added 20 cc. of a solution of gum arabic such as Arabol. The mixture thus obtained is rubbed on a sheet as, for example, by a buffing roll in a thin layer onto a sheet of baryta paper which has been previously dipped for approximately ten seconds in a solution comprising:

Cadmium acetate	g.	9
Neutral lead acetate	g.	.3
Zinc nitrate	g.	18
Water	cc.	100

Example 9

A sheet of baryta paper has roll coated thereon in a layer of a thickness approximating .002 inch a composition comprising:

8% solution of polyvinyl alcohol	cc.	220
4% solution of sodium sulfide	cc.	12
12% solution of neutral lead acetate	cc.	6

Example 10

A sheet of baryta paper has roll coated thereon in a layer of a thickness approximating .002 inch a composition comprising:

50% solution of egg albumen	cc.	100
40% solution neutral lead acetate	cc.	48
1% solution sodium sulfide	cc.	15
15% solution ascorbic acid	cc.	9

Example 11

A sheet of baryta paper has roll coated thereon in a layer of a thickness approximating .002 inch a composition comprising:

50% solution of egg albumen	cc.	100
50% solution of gelatin	cc.	5
48% solution of neutral lead acetate	cc.	48
1% solution sodium sulfide	cc.	15
15% solution ascorbic acid	cc.	9

In another form of the invention, a dye image is formed in a stratum of a sheet material **16**. The following is an example of such a process:

Example 12

A viscous film-forming composition is prepared by mixing together the following materials:

5% water solution of sodium carboxymethyl cellulose	g.	60
Pyrocatechin	g.	2
Sodium hydroxide	g.	1.5
2% water solution of Calcocid blue AX 200% (C. I. 714)	cc.	4

As the photosensitive film material **10**, there is preferably employed one of the moderately fast, orthochromatic films used as negative materials in amateur photography such, for example, as Eastman Kodak's Verichrome film.

The print-receiving element **16** is formed by casting an extremely thin layer of cellulose acetate on the baryta coated surface of a sheet of baryta paper, the layer being preferably formed by being cast from a 2% solution of cellulose acetate in a mixture of methanol, ethyl acetate and methyl cellosolve, the proportions of the three solvents being in the ratio of 1:3:3 by volume, respectively. The thin film is obtained by dipping the baryta paper into this solution and then removing the same in a vertical position to permit the excess solution to drip off, a sufficient quantity of the solution remaining on the surface of the paper to give a film of desired thickness to provide said baryta paper with a coating of cellulose acetate of the desired thickness. The liquid processing agent is spread between the coated side of element **16** and the emulsion side of photosensitive layer **10** and the developer develops the latent image in the photosensitive layer and tans the gelatin in the neighborhood of the developed portions thereof. The dye in the liquid processing agent is taken up by these tanned portions, producing an imagewise disposition of dye in the liquid composition. This dye penetrates through the coating of cellulose acetate to provide a stratum of element **16** with a positive dye image. The separation of sheet materials **10** and **16** causes the film-forming material of the liquid composition to adhere to the surface of photosensitive sheet material **10**.

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 drawings shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A method of producing visible images of a latent image contained in a silver halide layer of a photosensitive element by the transfer of components from said layer to a precipitating layer of a print-receiving element, which process comprises the steps of spreading between the said silver halide layer of said photosensitive element and a surface of said print-receiving element a viscous processing composition which comprises as a component thereof a film-forming thickening agent capable of giving a continuous solid film when the composition is dried after spreading, the stratum of said print-receiving element contiguous to said surface thereof being permeable to the liquid of said processing composition and comprising a plurality of layers, the outermost of said layers being a stripping layer which provides said spreading surface and permits the print-receiving element to be stripped from the solid thickening agent of said processing composition subsequent to the formation of the transfer print on said print-receiving element, said stripping layer comprising as its principal constituent at least one high molecular weight film-forming polymer from the class consisting of gum arabic, cellulose acetate-hydrogen phthalate, polyvinyl alcohol, hydroxyethyl cellulose, methyl cellulose, ethyl cellulose, cellulose nitrate, sodium alginate, pectin and polymethacrylic acid, another layer of said stratum beneath said stripping layer being a precipitating layer, the latter comprising particles of silica among which is dispersed a reagent capable of coacting with the processing composition to cause said transfer print to be formed in said precipitating layer, said stripping layer being substantially free of said silica and of said reagent, the liquid of said processing composition, upon permeation of said silver halide layer, containing reagents, including a silver halide developer, for developing the latent image in said silver halide layer and for forming transferable components for transfer to said precipitating layer, transferring said components to said precipitating layer to form therein a visible image of said latent image, and separating said print-receiving element from said photosensitive element, the stripping layer of said print-receiving element causing the residue of said processing composition to strip along with said photosensitive element.

2. The process of claim 1 wherein the film-forming thickening agent is a high molecular weight polymer from the class consisting of the alkali-inert, water-soluble cellulose and polyalkane derivatives.

3. The process of claim 1 wherein the film-forming thickening agent is sodium carboxymethyl cellulose.

4. A method of producing visible images of a latent image contained in a silver halide layer of a photosensitive element by the transfer of components from said layer to a precipitating layer of a print-receiving element, which process comprises the steps of spreading between the said silver halide layer of said photosensitive element and a surface of said print-receiving element a viscous processing composition which comprises as a component thereof a film-forming thickening agent capable of giving a continuous solid film when the composition is dried after spreading, the stratum of said print-receiving element contiguous to said surface thereof being permeable to the liquid of said processing composition and comprising, as its outer surface stratum, a stripping layer which provides said spreading surface and which permits the print-receiving element to be stripped from the solid, film-forming thickening agent of said processing composition subsequent to the formation of the transfer print on said print-receiving element, said stripping layer comprising polymethacrylic acid as a principal ingredient thereof, said permeable stratum also including a precipitating layer beneath said stripping layer, said precipitating layer comprising particles of a water-insoluble, inorganic substance and a reagent capable of coacting with the processing composition to cause said transfer print to be formed in said precipitating layer, said stripping layer being substantially free of said particles of inorganic substance and of said reagent, the liquid of said processing composition, upon permeation of said

silver halide layer, containing reagents, including a silver halide developer, for developing the latent image in said silver halide layer and for forming transferable components for transfer to said precipitating layer, transferring said components to said precipitating layer to form therein a visible image of said latent image, and separating said print-receiving element from said photosensitive element, the stripping layer of said print-receiving element causing the residue of said processing composition to strip along with said photosensitive element.

5. The process of claim 4 wherein the film-forming thickening agent is a high molecular weight polymer from the class consisting of the alkali-inert, water-soluble cellulose and polyalkane derivatives.

6. A method of producing visible images of a latent image contained in a silver halide layer of a photosensitive element by the transfer of components from said layer to a precipitating layer of a print-receiving element, which process comprises the steps of spreading between the said silver halide layer of said photosensitive element and a surface of said print-receiving element a viscous processing composition which comprises as a component thereof a film-forming thickening agent capable of giving a continuous solid film when the composition is dried after spreading, the stratum of said print-receiving element contiguous to said surface thereof being permeable to the liquid of said processing composition and comprising, as its outer surface layer, a stripping layer which provides said spreading surface and which permits the print-receiving element to be stripped from the solid, film-forming thickening agent of said processing composition subsequent to the formation of the transfer print on said print-receiving element, said stripping layer comprising gum arabic as a principal ingredient thereof, said permeable stratum also including a precipitating layer beneath said stripping layer, said precipitating layer comprising particles of a water-insoluble, inorganic substance and a reagent capable of coacting with the processing composition to cause said transfer print to be formed in said precipitating layer, said stripping layer being substantially free of said particles of inorganic substance and of said reagent, the liquid of said processing composition, upon permeation of said silver halide layer, containing reagents, including a silver halide developer, for developing the latent image in said silver halide layer and for forming transferable components for transfer to said precipitating layer, transferring said components to said precipitating layer to form therein a visible image of said latent image, and separating said print-receiving element from said photosensitive element, the stripping layer of said print-receiving element causing the residue of said processing composition to strip along with said photosensitive element.

7. The process of claim 6 wherein the film-forming thickening agent is a high molecular weight polymer from the class consisting of the alkali-inert, water-soluble cellulose and polyalkane derivatives.

8. A method of producing visible images of a latent image contained in a silver halide layer of a photosensitive element by the transfer of components from said layer to a precipitating layer of a print-receiving element, which process comprises the steps of spreading between the said silver halide layer of said photosensitive element and a surface of said print-receiving element a viscous processing composition which comprises as a component thereof a film-forming thickening agent capable of giving a continuous solid film when the composition is dried after spreading, the stratum of said print-receiving element contiguous to said surface thereof being permeable to the liquid of said processing composition and comprising, as its outer surface layer, a stripping layer which provides said spreading surface and which permits the print-receiving element to be stripped from the solid, film-forming thickening agent of said processing composition subsequent to the formation of the transfer print on said print-receiving element, said stripping layer comprising cellulose acetate-hydrogen phthalate as a principal ingredient thereof, said permeable stratum also including a precipitating layer beneath said stripping layer, said precipitating layer comprising particles of a water-insoluble, inorganic substance and a reagent capable of coacting with the processing composition to cause said transfer print to be formed in said precipitating layer, said stripping layer being substantially free of said particles of inorganic substance and of said reagent, the liquid of said processing composition, upon permeation of said silver halide layer, containing reagents, including a silver halide developer, for developing the latent image in said silver halide layer and for forming transferable components for transfer to said precipitating layer, transferring said components to said precipitating layer to form therein a visible image of said latent image, and separating said print-receiving element from said photosensitive element, the stripping layer of said print-receiving element causing the residue of said processing composition to strip along with said photosensitive element.

9. The process of claim 8 wherein the film-forming thickening agent is a high molecular weight polymer from the class consisting of the alkali-inert, water-soluble cellulose and polyalkane derivatives.

10. A method of producing visible images of a latent image contained in a silver halide layer of a photosensitive element by the transfer of components from said layer to a precipitating layer of a print-receiving element, which process comprises the steps of spreading between the said silver halide layer of said photosensitive element and a surface of said print-receiving element a viscous processing composition which comprises as a component thereof a film-forming thickening agent capable of giving a continuous solid film when the composition is dried after spreading, the stratum of said print-receiving element contiguous to said surface thereof being permeable to the liquid of said processing composition and comprising, as its outer surface layer, a stripping layer which provides said spreading surface and which permits the print-receiving element to be stripped from the solid, film-forming thickening agent of said processing composition subsequent to the formation of the transfer print on said print-receiving element, said stripping layer comprising hydroxyethyl cellulose as a principal ingredient thereof, said permeable stratum also including a precipitating layer beneath said stripping layer, said precipitating layer comprising particles of a water-insoluble, inorganic substance and a reagent capable of coacting with the processing composition to cause said transfer print to be formed in said precipitating layer, said stripping layer being substantially free of said particles of inorganic substance and of said reagent, the liquid of said processing composition, upon permeation of said silver halide layer, containing reagents, including a silver halide developer, for developing the latent image in said silver halide layer and for forming transferable components for transfer to said precipitating layer, transferring said components to said precipitating layer to form therein a visible image of said latent image, and separating said print-receiving element from said photosensitive element, the stripping layer of said print-receiving element causing the residue of said processing composition to strip along with said photosensitive element.

11. The process of claim 10 wherein the film-forming thickening agent is a high molecular weight polymer from the class consisting of the alkali-inert, water-soluble cellulose and polyalkane derivatives.

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