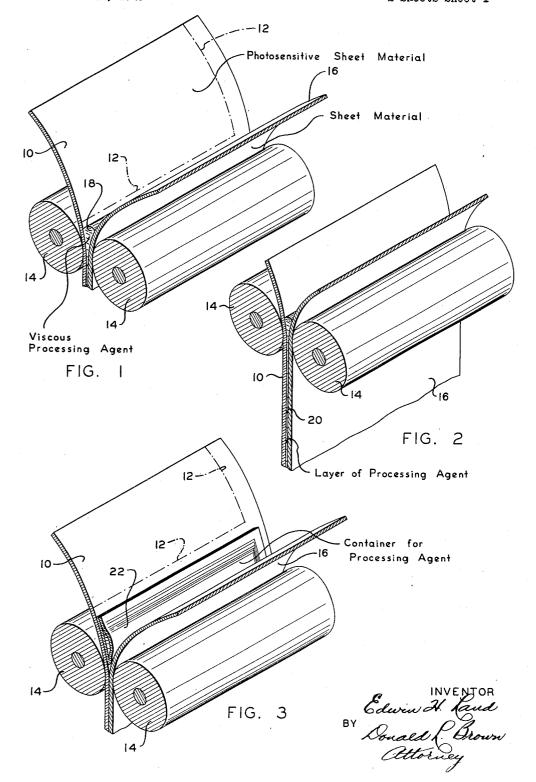
ONE STEP PHOTOGRAPHIC TRANSFER PROCESS

Filed Feb. 12, 1948

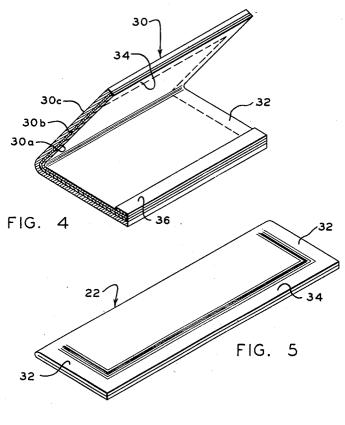
2 Sheets-Sheet 1

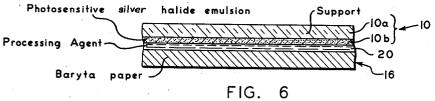


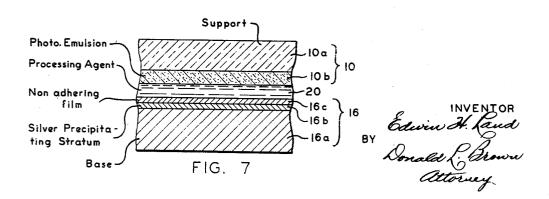
ONE STEP PHOTOGRAPHIC TRANSFER PROCESS

Filed Feb: 12, 1948

2 Sheets-Sheet 2







UNITED STATES PATENT OFFICE

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ONE STEP PHOTOGRAPHIC TRANSFER PROCESS

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17 Claims. (Cl. 95—88)

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This invention relates to photography, and more particularly to improved methods for treating a photosensitive material with a liquid processing agent.

This application is a continuation-in-part of application Serial No. 576,254, filed February 5, 1945, for Photographic Process, Apparatus and Product, now abandoned.

One object of the present invention is to provide a novel method for treating a predetermined area of a photosensitive material with a liquid processing agent, which method is characterized by the fact that no liquid baths are necessary and such equipment as distributes the processing agent throughout the area to be treated is not 15 wetted by the liquid, the method being thus particularly adapted for use in a camera or other photographic apparatus to predeterminedly process a given area of a photosensitive material shortly after photo-exposure of said area in said 20 apparatus.

Another object is the provision of a novel method of the foregoing type for processing a photosensitive material comprising as its photosensitive layer a silver halide emulsion or the like 25 containing a latent image to cause the formation of a visible positive image of the subject matter of said latent image.

According to the process of the present invention, a processing agent is spread in a thin layer between a photosensitive material and another sheet material throughout an area at least coextensive with the area of the photosensitive material to be processed. The processing agent contains all the liquid required for the processing, and also contains a film-forming material which imparts thereto a predetermined high viscosity. The inclusion of the film-forming material serves several functions. In addition to increasing the viscosity of the agent to permit more uniform and controlled spreading thereof, the film-forming material provides for a more rapid and uniform wetting of the photosensitive material by the liquid of the agent. It serves to bond together at least temporarily the two sheet materials tightly enough to prevent separation or relative movement thereof during processing.

In a preferred form of the process, the processing agent is located between the photosensitive sheet material and the other sheet material adjacent to the area to be processed thereby in sufficient bulk to carry out the desired processing, and is thereafter spread in a thin layer throughout the area to be processed by progressively squeezing together successive increment areas of said sheet materials in the direction of the area

to be processed. This makes possible a relatively close control of the thickness of the layer of processing agent and also of the area through which the processing agent is spread, and in turn makes unnecessary the excess of liquid which would be required if the distribution were non-uniform or uncontrollable as to the area of spread. In addition, the spreading of a viscous liquid between two sheets of material in this manner makes possible the processing of the photosensitive emulsion without any contact taking place between the liquid and the mechanism which accomplishes the spreading.

Moreover, by spreading the photographic reagent between two sheet materials, a lamination is formed whose outer layers prevent the penetration to any substantial extent of oxygen from the atmosphere to the intermediate thin layer of liquid processing agent, thereby maintaining at a minimum the oxidation of the materials of the processing agent and making it possible to render the reagents in the processing agent inert to oxygen during the period of processing so that upon separation of the two sheets no further oxidation takes place.

It is possible by means of the process of the invention to carry out such photographic processes as require the predetermined permeation of a photosensitive material with a liquid processing agent. The processing agent spread between the photosensitive material and another sheet material contains all the liquid for carrying out the processing, but such photographic reagents as may be desired in the liquid to treat the photosensitive layer may either be dissolved or otherwise contained in the processing agent prior to the spreading thereof, or these reagents may be in part or wholly added to the agent as it is spread between the sheet materials, being so located on or adjacent the surface of one or both of said sheet materials as to be dissolved by or otherwise interacted with the liquid agent when the latter wets said surfaces.

Various photosensitive materials may be processed in accordance with the present invention. For example, a diazo print may be developed with a processing agent containing an alkali, or a ferric salt print may be developed with a processing agent which is an acidic aqueous solution, or a leuco dye base print may be treated by a processing agent which is an alkaline aqueous solution. Similarly, a photosensitive silver halide emulsion or the like may be developed, or it may be developed and at least partially fixed, or a silver image in the photosensitive layer may be subjected to a predetermined toning or bleaching.

The process of the invention is, however, particularly advantageous for so processing a photosensitive silver halide emulsion layer or the like containing a latent image as to form a visible image of the subject matter of said latent image, which image is preferably a positive of said subject matter. In the performance of this preferred form of the process, the processing agent, when spread in a layer, is capable of developing a latent image in the area of the photosensitive 10 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 provide the positive image in a layer other than the photosensitive layer.

In one form of this process, 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 25 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 an- 30 other layer of the lamination to form a positive image. As the liquid content of the intermediate layer of the liquid processing agent is absorbed by the two sheets between which it is spread and is in part evaporated through said 35 sheets, the intermediate layer tends to solidify and to provide a coating of the film-forming material between the sheet materials. The silver of the soluble complex may be caused to precipisaid film and partly in a surface stratum of the other sheet material, or almost entirely in a surface layer of the other sheet material.

In other processes which may be carried out in accordance with the invention, the imagewise distribution of the developer or of the oxidation 45 product of the developer, resulting from the development of a latent image in the photosensitive layer, is used to create said visible image in another layer of the lamination. In one such process, the imagewise distribution of the unused 50 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 other sheet material 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 nonsolarized 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 65 as the Herschel effect.

In general, therefore, the process of the invention is particularly adapted for performing transfer processes wherein the layer of liquid composition which is located between the sheet material comprising the photosensitive layer and another sheet material 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 75 tion thereof is superposed with respect to the

other sheet material or the solidified film-forming material of the liquid layer 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 thereto, of a material which thereafter acts to 15 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 tempo-20 rarily 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.

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 the 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 diatate in this intermediate coating, or partly in 40 grammatic view in perspective illustrating one stage in carrying out the process of the present invention:

> Fig. 2 is a view similar to Fig. 1 illustrating another step in the process of the present invention:

> 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 which may be used in the process of the invention to provide the processing agent in a condition for spreading in a thin layer, 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;

Fig. 6 is a diagrammatic, enlarged, sectional view illustrating one embodiment of the process in operation; and

Fig. 7 is a view similar to Fig. 6 of another embodiment of the process in operation.

Referring to the drawings, and particularly to Figs. 1 and 2, there is illustrated one manner of performing the process of the present inven-A photosensitive sheet material 10 of tion. 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 another sheet material 16 is introduced between said pressure-applying members so that a por-

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 10 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, 15 spreading said processing agent 18 in a thin layer 20, as shown in Fig. 2.

The separation of the pressure rollers and the thickness 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 25 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. $_{30}$

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 spread- 35 ing.

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 40 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 45 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 50 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 55 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 60sheet 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 65 suitable container of this type is formed from a single multilayer sheet of material 30 (Fig. 4) comprising three layers, 30a, 30b and 30c. Layer 30a, 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 75 an aqueous alkaline solution so that the proc-

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 30a. Layer 30b contiguous to layer 30a 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 30c, for example of kraft paper, is provided and makes possible the use of thinner layers 30a and 30b.

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 of the invention wherein there is formed a positive image of the subject matter of a latent image contained in a photosensitive silver halide emulsion or the like, 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 filmforming material. When this agent is spread between a photosensitive silver halide emulsion and another sheet material, 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 may be transported from the emulsion to another stratum of material of the lamination to form in said other stratum 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

essing 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 5 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 alkalies 10 and which contain none of the chemical groups, such as the ester and acid chloride groups, that are unstable to alkalies. The polymers also contain groups such as the hydroxyl and/or carboxyl groups which tend to solubilize in aqueous alka- 15 line solutions. Suitable examples 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 deriva- 20 tives such as polyvinyl alcohol and the sodium salts of polymethacrylic acid and polyacrylic

A high viscosity for the processing agent is very desirable since it makes possible the relatively 25 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 30 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 35 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 40 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, xylohydroo-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 imagereceiving layer are given below, but it is to be expressly understood that these examples are 75 modified by employing any one of the following

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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: Grome

G.	Lamo
Water	1860
Sodium carboxymethyl cellulose	117
Sodium sulfite	78
Sodium hydroxide	74.6
Sodium thiosulfate	14.5
Citric acid	38.5
Hydroquinone	52
Hydroqumone	011

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 another sheet material 16 to form a laminate comprising sheet 10, a layer 20 of the processing agent, and sheet 16 (Fig. 6). Sheet 10 may comprise a support 10a of paper or transparent film base such as a cellulosic ester or a cellulose mixed ester and a photosensitive silver halide emulsion 10b 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, and sheet material 16 is a baryta paper with the baryta coated surface thereof constituting its inner surface. 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 10b and the surface portion of sheet material 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 sheet 16 is stripped from sheet 10, leaving a finished positive image on sheet 16. The carboxymethyl cellulose is present in a continuous solid phase on the surface of the baryta paper and an appreciable amount of the silver which forms the positive image is precipitated in this carboxymethyl cellulose so that the image is at least partly formed therein. There is no appreciable wetting of the outer surfaces of sheet material 10 or 16 during the processing, the liquid being present in sufficiently small quantities to be substantially completely absorbed by the sheets.

Example 2

The processing agent of Example 1 may be

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developing agents in substantially the same quantity as the hydroquinone:

p-Aminophenol hydrochloride; bromohydroquinone; chlorohydroquinone; diaminophenol hydrochloride; diaminophenol dihydrochloride; 5 toluhydroquinone; monomethyl-p-aminophenol sulfate; a mixture consisting by weight of onehalf hydroquinone and one-half p-hydroxyphenylaminoacetic acid; and a mixture consisting by weight of one-fourth hydroquinone and threefourths p-hydroxyphenylaminoacetic acid.

Example 3

The process of Example 1 may be carried out by employing the following processing agent in 15 lieu of the processing agent described in Example 1:

Watercc_	1000
Sodium sulfiteg_	70
Hydroquinoneg_	33
Sodium thiosulfateg_	14
An aqueous solution of Hercules or Dow	
carboxymethyl cellulose, sodium salt, me-	
dium viscosity, consisting of 200 g. of	
the latter compound in 1000 cc. of	
watercc_	200
Sodium hydroxide, 10% solutioncc	112

The foregoing materials may be mixed in the same way as the materials of Example 1, or in the alternative, the sodium sulfite, hydroquinone, and sodium thiosulfate are dissolved in the water, and the sodium carboxymethyl cellulose solution is then added and thoroughly mixed therewith. The solution thus obtained is cooled to a temperature between 65° and 75° F. and thereafter the sodium hydroxide solution is added thereto.

Example 4

The process of Example 1 may be carried out by employing the following processing agent in lieu of the processing agent described in Example 1:

Watercc_	1500	
Hydroquinoneg_	28	
Sodium sulfiteg_	200	•
Metolg_	15.5	
Sodium thiosulfateg_	100	
Aqueous solution of medium viscosity so- dium carboxymethyl cellulose consisting of 200 g, of the latter compound in 1000		į
cc. of waterg_	1000	
Sodium hydroxideg_	56	

Example 5

The process of Example 1 may be carried out ⁵⁵ by employing the following processing agent in lieu of the processing agent described in Example 1:

	G.	
Sodium hydroxide	. 5	1
Sodium thiosulfate	1.5	
Sodium sulfite		

are dissolved in 65 cc. of water, and the solution is added to 190 g. of a 10% solution of a high viscosity polyvinyl alcohol (du Pont PVA RH 391). There is added to the resulting mixture 5.2 g. of hydroquinone.

Example 6

The process of Example 1 may be carried out 70 by employing the following processing agent in lieu of the processing agent described in Example 1:

500 grams of hydroxyethyl cellulose, for example the product sold by Carbide and Carbon 75 the process, for example, improved image color

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Chemical Corp. and identified as Hydroxyethyl Cellulose (71.2 cps.), is dissolved in 1000 cc. of water and 200 cc. of this solution is mixed with 500 cc. of a solution comprising the following.

	G.
Sodium sulfite	180
Sodium hydroxide	37.5
Hydroquinone	180
Sodium thiosulfate	50
Water to make	1500

Example 7

The process of Example 1 may be carried out by employing the following processing agent in lieu of the processing agent described in Example 1:

		u.
	Sodium sulfite	78
	Sodium hydroxide	110
'	Sodium thiosulfate	15
	Citric acid	
	Hydroguinone	

are dissolved in 2860 cc. of distilled water, and there is added to this solution 102 g. of high molecular weight polymethacrylic acid. The resulting mixture is preferably treated in a vacuum pump to exclude oxygen and to remove the air content thereof, and comprises as its film-forming material the sodium salt of polymethacrylic acid, the polymethacrylic acid being neutralized in the alkaline solution.

If a relatively white and nontransparent film is to be formed by the liquid processing agent, there may be incorporated in any of the foregoing processing agents a suitable pigment such as titanium dioxide or mixtures of titanium dioxide and magnesium oxide or magnesium carbonate. The addition of titanium dioxide equivalent to from 10% to 20% by weight of the composition has given good results. These pigments also serve as fillers for increasing the viscosity of the composition.

Although sheet material 16 is preferably a baryta paper, 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 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., 60 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 each of the preceding processing agents of Figs. 1 through 7 is substantially increased, being preferably quadrupled. Improvements in the photographic characteristics of the positive image may also be obtained by suitably treating the surface of sheet material 16 before the same is used in

and contrast may be obtained by properly applying to the surface of the sheet material suitable 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 sulnickel selenide, lead selenide, manganous selenide and antimony selenide, and such other substances as dithiooxamide and its lead and zinc complexes, potasium dithiooxalate and the lead complexes thereof, and thioacetamide.

For use with the foregoing faster films, these precipitating materials are preferably applied to the surface of the baryta 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. Examples of suitable compositions for treating the baryta paper to form the sheet material 16, which, when used in any of the foregoing transfer processes, particularly with the faster emulsions, will give a picture of improved quality, are the following:

Example 8

40%	aqueous tate	solution	of	neutral	lead _cc	192
ace	aerogel (Cantocal (٦,		g	30
Sinca	queous sol	samocer C	//	n sulfide	8	60
1% a	queous soi queous soli	unon of so)urur	n agetata	00	66
1% a	queous son	ntion or co)hhe	Lacetate.		
15%	aqueous so	lution of	asco:	rdic aciu-	_00	30

A thin coating of this material is applied to the baryta surface of the baryta paper, as by being rubbed thereon.

Example 9

1% solution of sodium sulfidecc_	280
Silica aerogel (Santocel C)g_	30
Solution containing 30 g. of cadmium ace-	
tate, 1 g. neutral lead acetate, and 30 g. of	
zinc nitrate dissolved in 100 cc. of	00
watercc_	94

This mixture of materials is applied as a thin coating to the baryta surface of the baryta layer.

Example 10

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

Cadmium acetateg_	9
Neutral lead acetates_	.3
Neutral lead acetate	18
Zinc nitrateg_	100
Watercc_	TOO

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

Waterc	C	270
Cadmium acetate	g	27.8
Lead acetate	g	9.3
Zinc nitrate	g	55.6
Zinc nitrate	a D	30
Silica aerogel (Santocel C)	5	04.77
3% solution of sodium sulfidec	U	94.1

The sheet is preferably dipped into this mixture 70 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.

In each of the foregoing examples, the filmforming substance contained in layer 20 adheres 75 12

to sheet material 16 and strips away from emulsion 10b when sheets 16 and 10 are separated from one another, the positive image being formed in a stratum of the lamination comprising said sheet material 16 and the solid film obtained from said film-forming material. The process of the present invention may also be carried out by causing the film-forming material of layer 20 to adhere to photosensitive sheet matefide, and such metallic selenides as zinc selenide, 10 rial 10 instead of sheet material 16, so that the solid plastic film obtained from said film-forming material sticks to said photosensitive material 10 when the latter is stripped from sheet material 16.

By controlling the stratum in which the positive image is formed so that it is either on the surface or in the surface portion of sheet material 16, and then stripping from said sheet material the film obtained by the solidification of the film-forming material in layer 20, there is provided a positive print on sheet material 16 from which there has been stripped a substantial proportion of the substances which might otherwise in time deleteriously affect the positive print. In these processes, sheet material 16 comprises a base layer 16a (Fig. 7), for example of baryta paper, having one surface thereof suitably treated so that there is provided thereon or therein a precipitation stratum 16b. 30 Over stratum 16b there is applied a layer 16c, preferably very thin, 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 35 which it contacts. In the event emulsion 10b is a silver halide gelatin emulsion and the filmforming material in layer 20 is sodium carboxymethyl cellulose, layer 16c may be, for example, gum arabic, cellulose acetate-hydrogen 40 phthalate, polyvinyl alcohol, hydroxyethyl cellulose, methyl cellulose, ethyl cellulose, cellulose nitrate, sodium alginate, pectin, and polymethacrylic acid. Layer 16c preferably has a thickness of the order of 1 to 3 microns, although if 45 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 10b may also be increased by applying to said surface or 50 by incorporating adjacent said surface in said emulsion a substance which tends to insolubilize sodium carboxymethyl cellulose by causing crosslinking of the molecules of the latter, examples of such substances being lead acetate and zinc 55 acetate. The photosensitive emulsion may be treated with these materials by being dipped in a solution thereof. The affinity between emulsion 10b and the film-forming material of layer 20 may also be appreciably increased by applying to 60 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 16b containing precipitation nuclei, a sheet of baryta paper may have the baryta surface thereof coated as described in Example 10, or it may be processed as follows:

Example 11

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

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

Water

Either of the sheets processed in accordance with Examples 10 and 11 and thereby provided with an image-receiving stratum 16b may be suitably processed to be provided with a stripping overcoat 15c, for example in the following 5 manner:

Example 12

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 13

The processed sheet is dipped into a 2% solution of cellulose acetate, the cellulose acetate 20 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 25 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 14

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 16c 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 50 the film-forming material. For example, when the film-forming material in the processing agent is sodium carboxymethyl cellulose the surface of layer 10 may be treated as follows:

Example 15

A 5% water solution of sodium carboxymethyl cellulose is applied to layer 10b 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 10b 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 16c and stratum 16b, 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 16a, for example as follows:

Example 16

270

A solution consisting of:

	Water
,	Cadmium acetateg_ 27.8
	Neutral lead acetateg_ 9.3
	Zinc nitrate
	has mixed therewith a composition comprising:
0	Silica aerogel (Santocel C)g_ 30 1% solution of sodium sulfidecc_ 93.3
5	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 acetateg_ 9

3	Cadmium acetateg_	9
•	Neutral lead acetateg_	.3
	Zinc nitrateg_	
	Watercc_	100

Example 17

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

		Cc.
	8% solution of polyvinyl alcohol	220
30	4% solution of sodium sulfide	12
	12% solution of neutral lead acetate	6

Example 18

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

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

$Example\ 19$

A sheet of baryta paper has roll coated thereon in a layer of a thickness approximating .002 45 inch a composition comprising:

		Cc.
	50% solution of egg albumen	100
	50% solution of gelatin	5
	48% solution of neutral lead acetate	48
0	1% solution sodium sulfide	15
	15% solution ascorbic acid	9

As pointed out hereinabove, it is also within the purview of this invention to provide one or more of the ingredients which participates in the desired processing of the photosensitive layer in or on either of the faces of the two sheet materials between which the composition is spread during the processing. These ingredients are preferably provided on said sheet materials in a condition such that they are rendered effective to perform their required function when dissolved in the liquid of the processing composition. For example, it is possible to provide the ions, e. g., thiosulfate, cyanide, or thiocyanate ions, which form the soluble silver complex with the unexposed silver halide in the foregoing process by providing a thiosulfate, cyanide, or thiocyanate salt on the image-receiving layer 16 which will dissolve in the processing liquid.

An example of this type of processing is, for example, the following:

Example 20

A sheet of baryta paper is dipped for sixty 75 seconds in a bath which contains fifty grams of

lead acetate and 100 cc. of water. This sheet is squeegeed and dried after the immersion and is then dipped for thirty seconds in another bath which contains 25 g. of sodium thiosulfate and 100 cc. of water. This second treatment causes the formation of lead thiosulfate in the surface of the baryta paper. The coating of lead thiosulfate may also be provided, for example, by adding to a 20% water solution of neutral lead acetate a 5% water solution of sodium thio- 10 sulfate and then rubbing the precipitate produced by this mixture onto the baryta paper. The baryta paper treated in either of these ways may then be employed as sheet 16 in the process of the invention with its treated surface in con- 15 tact with a layer 20 of processing agent comprising the following ingredients:

Watercc	1860
Sodium carboxymethyl celluloseg_	93
Sodium sulfiteg_	78
Sodium hydroxideg_	74.6
Citric acidg_	38.5
Hydroquinoneg_	52

Sheet 10 may have as its emulsion layer 10b 25 one of the faster emulsions such as the relatively high speed orthochromatic film or the extremely high speed panchromatic films. Examples of these emulsions are the Eastman Kodak Verichrome and Super XX Pan films. Layers 16 and 30 10 are held superposed for approximately one minute, at the end of which time the positive image is formed in the laminate comprising sheet 16 and the layer of film-forming composition formed by the liquid composition. The film 35 strips readily from the gelatin of the photosensitive emulsion and adheres to the baryta paper when the latter is separated from the photosensitive material.

Example 21

A sheet material comprising a paper support 10a and a silver halide emulsion 10b, for example of the type used on Eastman Kodak Verichrome or on Super XX film, is dipped for one minute in a bath containing:

Hydroquinoneg_	2
Acetonecc_	
Tiloton	

The emulsion is then squeegeed to remove the excess liquid and then dried. To provide sheet material 16, a sheet of single weight baryta paper is first coated with a thin layer of sodium carboxymethyl cellulose, for example by being run through a bath of a 5% solution of sodium carboxymethyl cellulose, the sheet being maintained in contact with the bath for approximately ten seconds. After being dried, the sheet is run through a second bath containing:

Nicotinic acid nitrateg_	20
Lead nitrateg_	
Watercc	

and is kept in contact with this bath for approxi- 65 mately ten seconds. To further process the sheet, a mixture is prepared by adding one part by volume of a solution consisting of:

Cadmium acetateg_	60
Lead acetateg_	2
Zinc nitrateg_	
Watercc_	

to three parts by volume of a solution consisting of:

16

Sodium sulfideg_	28
Silica aerogel	300
Watercc_	2800°
77 WUCI	

To five parts by volume of the resulting mixture there is added one part by volume of a solution consisting of:

	Silica aerogelg_	30
	1% solution of sodium sulfidecc_	
`	15% solution of ascorbic acidcc	36
,	40% solution of neutral lead acetatecc	192

To fifty parts by volume of this solution there is added one part by volume of a 5% water solution of polyvinyl alcohol. Into the resulting solution there is dipped the previously prepared baryta paper and upon removal of the sheet from the bath the excess liquid is removed by means of a soft rubber buffing roll, preferably rotating in a direction opposite to the direction of travel of said sheet. Between a sheet 16 prepared in the foregoing fashion and an emulsion 10 of the foregoing type there is spread a processing agent consisting of:

	G.
Water	1860
Sodium carboxymethyl cellulose	
Sodium sulfite	
Sodium hydroxide	74.6
Sodium thiosulfate	14.5
Citric acid	

The liquid is spread in the layer approximately .002 inch to .003 inch thick, and the developer in the emulsion is dissolved by the liquid content of 35 the processing agent and caused to develop the latent image in the photosensitive emulsion and to participate in the reduction of the soluble silver halide complex to silver. Sheets 19 and 16 are kept assembled for approximately one min-40 ute, a finished positive image being formed on sheet 16 at the end of this time.

In the foregoing examples, such materials as nicotinic acid nitrate, lead nitrate, cadmium acetate, zinc nitrate, lead acetate, and ascorbic acid are applied to sheet 16 to provide an environment for the final image in which the developing agent is stable.

The process of the present invention also comprehends the spreading of a film-forming processing liquid between a photosensitive film and another layer of material to form as a result of the development of a latent image in said photosensitive layer a positive dye image of the subject matter of said latent image in another layer of the lamination. The following are examples of such processes:

Example 22

A viscous film-forming composition is prepared $_{60}\,$ by mixing together the following materials:

5% water solution of sodium carboxymethyl	
cellulose g	60
Pyrocatechin g	2
Sodium hydroxideg_	1.5
2% water solution of Calcocid blue AX 200%	
(C. I. 715) cc	4

As the photosensitive film material (0, 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.

As sheet material 16, there is provided a sheet of cellulose acetate butyrate which has been 75 coated first with a thin film of a mixture of cel-

lulose nitrate and polyvinyl alcohol, whose thickness is of the order of .0001 inch. To the coated surface of this sheet there is applied another coating which is very thin, approximately .0001 inch to .0008 inch in thickness, of gelatin, the latter being cast, for example, from a 2% water solution thereof. These coatings provide the cellulose acetate butyrate with a surface to which a film of sodium carboxymethyl cellulose will adhere. To carry out the process of the invention, the liquid film-forming composition is spread in a relatively uniform thin layer between the emulsion side of the photosensitive sheet material and the coated side of the other sheet material. The developer in the liquid composition develops a 45 latent image in the emulsion and tans the gelatin in the developed areas. The tanned gelatin takes up or has an affinity for the dye in the liquid composition. This taking up of the dye by the tanned portions of the gelatin produces an imagewise concentration of the dye in the layer of processing liquid. The two sheet materials 10 and 16 are kept in their superposed relation for approximately five minutes and then are separated, the plastic film formed by the processing fluid adhering to sheet material 16. This layer of plastic film contains therein a positive dye image of the subject matter of the latent image in the photosensitive layer. The image is a bluish-green.

Example 23

As photosensitive sheet material 10 there may be used a photosensitive paper such as an extreme contrast material which yields positive photo copies from positive originals upon exposure to yellow light and with normal development as, for example, the Kodagraph Autopositive Paper of Eastman Kodak. The emulsion of paper 10 is exposed to a predetermined diapositive, for example in a printing frame with a yellow filter over the glass side of the frame, the source of illumination being a 500 watt bulb which is approximately 20 inches away from the glass frame, an exposure of three minutes being sufficient. To provide sheet 16, a sheet of baryta paper is dipped in the fluid processing agent is taken up by these tanned portions, producing an imagewise disposition of dye in the fiquid composition. This dye penetrates through the coating of cellulose acetate to provide a stratum of sheet material 16 with a positive dye image. The separation of sheet materials 10 and 16 causes the film-forming material of the liquid composition. This dye penetrates through the coating of cellulose acetate to provide a stratum of sheet materials 10 and 16 causes the film-forming material of the liquid composition. This dye penetrates through the coating of cellulose acetate to provide a stratum of sheet materials 10 and 16 causes the film-forming materials 10 and 16 causes the film-forming

p-Nitrophenylacetonitrileg_	.2
Acetonecc	50
TTT 1	

for about one minute, squeegeed, and treated to provide the baryta with a magenta coupler. Thereafter, sheet 16 and photosensitive sheet material 10 have spread therebetween a layer of the 55 order of .002 inch to .003 inch of a processing agent comprising:

2-amino-5-diethylamino-toluene hydrochlo-	a
ride g Sodium carbonate g 5% solution of medium viscosity carboxy-	10
methyl cellulose g	
Water cc	15

The two sheet materials are kept in contact for ⁶⁵ approximately two minutes and at the end of this time are separated. The autopositive paper has a positive thereon of the subject matter to which it was exposed and there is obtained on the surface of the baryta paper a second positive in ⁷⁰ magenta color of this subject matter.

In another form of the process of the present invention, a dye image is formed in a stratum of the sheet material 16 and the solid film obtained 75

from the film-forming processing fluid 20 is caused to adhere to the photosensitive sheet material 10 rather than to said sheet 16. The following is an example of such a process:

Example 24

A viscous film-processing composition is provided in the same manner as in Example 22, and photosensitive sheet material 10 of the same type is employed. The other sheet material 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 cellu-25 lose acetate of the desired thickness. The liquid processing agent is spread between the coated side of sheet material 46 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 sheet material 16 with a positive dye image. The separation of sheet materials 10 and i6 causes the film-forming material of the liquid composition to adhere to the surface of photo-40 sensitive sheet material 10.

In the foregoing examples, the process of the present invention has been illustrated in connection with the formation of positive images in a stratum of the lamination comprising sheet materials 10, 16 and layer 20 other than the photosensitive emulsion of said layer. In all these processes there also takes place a predetermined treatment of the photosensitive emulsion involving at least the development of the latent image therein. It is to be expressly understood also that the process of the present invention may be performed solely for the purpose of subjecting a photosensitive emulsion to a predetermined processing such, for example, as the development or toning of a latent or visible image therein. The following are examples of this type of processing:

Example 25

A photosensitive sheet material 10 comprising as its photosensitive layer 10b a layer containing a diazonium compound such, for example, as the photosensitive sheet material sold by the Boston Blueprint Company as Blackline 202 may be used. The liquid composition, spread in a layer 20 between said photosensitive sheet material and a sheet material 16, for example of baryta paper, consists of the following:

5% solution of high viscosity sodium carboxymethyl cellulose ______4 Blackline developer 203½ sold by the Boston Blueprint Company and manufactured by Frederick Post Co., Chicago _______8

Example 26

The process of Example 24 can also be carried out with a processing agent comprising:

5
0
8
3
(

Example 27

Either of the compositions of Examples 25 and 26 can also be used in connection with a diazonium photosensitive material formed by dipping

Watercc_	500
Pontacyl Green Blue (C. I. 666)g_	.2
Naphthosol Fast Blue Salt B. (C. I. 499)g	10

By employing a film-forming material which is transparent and having sheet material 16 transparent, a transparency is obtained. By including a suitable pigment in the processing agent so that a white, opaque film is obtained when the layer of liquid 20 is solidified, a positive print may be formed in layer 20 by the processes of any of Examples 1 through 7 in which the image is visible from the side of the solid film adjacent sheet material 10. When layer 20 contains a white pigment and there is provided on the surface of layer 16 a precipitating stratum 16b in accordance with the process of Examples 10 and 11, a silver image is formed in said stratum 16b and is visible against the white, opaque film obtained by the solidification of layer 20. By using a sheet 16 which is transparent, it becomes unnecessary to strip sheet material 16 from sheet material 10, the image being visible through said sheet material 16.

In the event that the processing agent is a nonalkaline solution, such other film-forming materials as starch, sodium alginate, and gelatin may be employed. Examples of suitable starches are Merck's starch, Argo starch, Maine potato starch, and Brazilian starch. In general, sodium alginate is used in approximately the same proportions as 45 the sodium carboxymethyl cellulose of the foregoing examples, and starches are preferably used in a concentration approximately twice that of the sodium carboxymethyl cellulose.

Although water alone is the solvent for the 50 viscous processing agent in many of the foregoing examples, other solvents may be used, for example acetone and methanol, in mixture with water.

agent solidifies as the liquid of the processing agent is absorbed or evaporated from the layer thereof, but the solidification is not necessarily complete at the time of separation of the two sheet materials after processing. The coating of 60 the film-forming material after separation of the sheet materials may contain an appreciable quantity of liquid which is thereafter removed either by evaporation or by being absorbed into the sheet material to which said coating adheres.

An important function of the viscous filmforming processing agent in the transfer processes is that it may allow small time lags in relating portions of the negative-producing cycle to portions of the positive-producing cycle because 70 of the separation which it maintains between the sheet materials. It also makes possible the postponement of action of ingredients located in one sheet upon the other sheet until the ini-

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. The method of forming an image in a pre-10 determined area of a photosensitive layer of a photographic, photosensitive sheet material, said photosensitive layer having as its photosensitive substance at least one compound from the class consisting of the photosensitive silver halides and a sheet of baryta paper in a bath consisting of: $_{15}$ diazonium compounds, which method comprises locating a viscous liquid processing agent adjacent one edge of said area at least in sufficient quantity to provide all the liquid required for a transformation of an image formed in said photo-20 sensitive layer by photoexposure, said processing agent being located on one side only of said photo-sensitive sheet material and containing a solid film-forming high molecular weight polymer in sufficient quantity to impart to said proc-25 essing agent a viscosity in excess of 1000 centipoises at 24° C., forming a layer of said processing agent between said photosensitive sheet material and another sheet material by applying pressure to the outer surfaces of said sheet materials, the portions of said outer surfaces subjected to said pressure remaining dry during said pressure application, liquid from said processing agent being absorbed by said photosensitive sheet material and, during absorption, distributing, throughout said area of said photosensitive layer, a photographic reagent capable of carrying out the desired image transformation, said photographic reagent being different from the solvent of said processing agent and being provided by one of (a) said sheet materials and (b) said processing agent, the absorption of said liquid from said layer of processing agent increasing the concentration of said polymer in said liquid to produce a coating containing said polymer between said sheet materials which maintains the latter in spaced laminated relationship during the processing.

2. The method of producing a visible record of a latent image contained in a predetermined area of a silver halide layer of a photosensitive sheet material, which method comprises locating a viscous liquid processing agent on one side only of said photosensitive sheet material adjacent one edge of said area at least in sufficient quantity to provide all the liquid The film-forming material in the processing 55 for the development of said latent image, which processing agent contains an organic high molecular weight film-forming polymer, spreading said processing agent in a layer between said photosensitive sheet material and another sheet material by applying pressure to the outer surfaces of said sheet materials, the portions of said outer surfaces subjected to said pressure remaining dry during said pressure application, liquid from said processing agent being absorbed by said photosensitive sheet material and, during absorption, distributing, throughout said area of said photosensitive layer, photographic material, including a silver halide developer, capable of developing a latent image in said photosensitive layer and of producing an imagewise distribution throughout the liquid of a material for forming a transfer print of said latent image. at least part of said photographic material being dissolved from one of said sheet materials, tiation of a desired reaction in said other sheet. 75 the absorption of said liquid from said layer of

processing agent producing a coating of said film-forming polymer between said sheet materials which maintains the latter in spaced, laminated relationship during the processing, retaining said sheet materials in their superposed condition until there is transported from the photosensitive layer a quantity of said imageforming material sufficient to form said visible record in a stratum of the lamination comprising said coating and said other sheet material, 10 and stripping said lamination from said photosensitive sheet material.

3. The method of producing a visible positive image of the subject matter of a latent image contained in a predetermined area of a silver 15 halide layer of a photosensitive sheet material, which method comprises locating a viscous liquid processing agent on one side only of said photosensitive sheet material adjacent one edge of said area at least in sufficient quantity to 20 material. provide all the liquid for the development of said latent image, which processing agent contains a film-forming high molecular weight polymer, spreading said processing agent in a layer between said photosensitive sheet material and 25 another sheet material by applying pressure to the outer surfaces of said sheet materials, the portions of said outer surfaces subjected to said pressure remaining dry during said pressure application, liquid from said processing agent be- 30 ing absorbed by said photosensitive sheet material and, during absorption, distributing, throughout said area of said photosensitive layer, photographic material including a developer for the silver halide and a silver halide solvent 35 capable of forming a soluble silver complex with the undeveloped silver halide, said photographic material being provided by at least one of (a)said sheet materials and (b) said processing agent, the development of said latent image pro- $_{40}$ ducing an imagewise distribution of said soluble silver complex throughout the liquid of said processing agent, the absorption of said liquid from said layer of processing agent producing a coating of said film-forming polymer between said sheet materials which maintains the latter in 45 spaced, laminated relationship during the processing, and retaining said sheet materials in their superposed condition until there is transported from the photosensitive layer a quantity said positive image in a stratum of the lamination comprising said coating and said other sheet material.

4. The method of producing a visible positive contained in a predetermined area of a silver halide layer of a photosensitive sheet material. which method comprises locating a viscous liquid processing agent on one side only of said photosensitive sheet material adjacent one edge 60 parency is obtained. of said area at least in sufficient quantity to provide all the liquid for the development of said latent image, which processing agent contains a film-forming high molecular weight polymer, spreading said processing agent in a layer be- 65 tween said photosensitive sheet material and another sheet material by applying pressure to the outer surfaces of said sheet materials, liquid from said processing agent being absorbed by said photosensitive sheet material and, during ab- 70 sorption, distributing, throughout said area of said photosensitive layer, photographic material including a developer for the silver halide and a silver halide solvent capable of forming a solu-

halide, said photographic material being provided by at least one of (a) said sheet materials and (b) said processing agent, the development of said latent image producing an imagewise distribution of said soluble silver complex throughout the liquid of said processing agent, the absorption of said liquid from said layer of processing agent producing a coating of said filmforming polymer between said sheet materials which maintains the latter in spaced, laminated relationship during the processing, retaining said sheet materials in their superposed condition until there is transported from the photosensitive layer a quantity of said soluble complex sufficient to form said positive image, at least a part of said complex being precipitated in said coating, and stripping said other sheet material, with the coating of film-forming polymer attached thereto, from said photosensitive sheet

5. The method of producing a visible image of a latent image contained in a predetermined area of a silver halide layer of a photosensitive sheet material, which method comprises locating a viscous liquid processing agent on one side only of said photosensitive sheet material adjacent one edge of said area at least in sufficient quantity to provide all the liquid for the development of said latent image, which processing agent contains a film-forming high molecular weight polymer, spreading said processing agent in a layer between said photosensitive sheet material and another sheet material by applying pressure to the outer surfaces of said sheet materials, liquid from said processing agent being absorbed by said photosensitive sheet material and, during absorption, distributing, throughout said area of said photosensitive layer, photographic material capable of developing a latent image in said photosensitive layer and of producing an imagewise distribution throughout the liquid of a material for forming a transfer print of said latent image, said photographic material being provided by at least one of (a) said sheet materials and (b) said processing agent, said other sheet material comprising an image-receiving stratum adjacent the surface thereof for said image-forming material, retaining said sheet materials in their superposed condition until there is transported from the photoof said soluble silver complex sufficient to form 50 sensitive layer through said layer of film-forming polymer a quantity of said image-forming material sufficient to form in said image-receiving stratum a visible image of the subject matter of said latent image, and stripping said photoimage of the subject matter of a latent image 55 sensitive layer, with the layer of film-forming polymer attached thereto, from said other sheet material.

6. The method of claim 5 wherein the other sheet material is transparent so that a trans-

7. The method of claim 5 wherein the other sheet material is opaque so that a reflection print is obtained.

8. The method of producing a visible positive image of a latent image contained in a predetermined area of a silver halide layer of a photosensitive sheet material, which method comprises locating a viscous liquid processing agent on one side only of said photosensitive sheet material adjacent one edge of said area at least in sufficient quantity to provide all the liquid for the development of said latent image, which processing agent contains an organic film-forming high molecular weight polymer, spreading said ble silver complex with the undeveloped silver 75 processing agent in a layer between said photo-

sensitive sheet material and another sheet material by applying pressure to the outer surfaces of said sheet materials, the portions of said outer surfaces of said sheet materials subjected to said pressure remaining dry during said pressure application, the surface of said other sheet material in contact with said liquid layer having coated thereon a film having a lesser affinity for said film-forming polymer in its solid state than the solid organic film-forming poly- 10 mer has for the surface of the photosensitive sheet material, liquid of said processing agent being absorbed by said photosensitive sheet material and, during absorption, transporting, to said area of said photosensitive layer, photo- 15 graphic material including a developing agent for the silver halide and a silver halide solvent capable of forming a soluble silver complex with the undeveloped silver halide, said photographic material being provided by at least one of (a) said sheet materials and (b) said processing agent, the development of said latent image producing an imagewise distribution of said soluble silver complex throughout the liquid of said processing agent, said other sheet material comprising an image-receiving stratum adjacent the surface thereof containing nuclei for aggregating and precipitating the silver of a soluble silver complex, retaining said sheet materials in their superposed condition until the absorption of said liquid from said layer of processing agent produces a continuous solid phase of said organic film-forming polymer between said sheet materials and there is transported from the photosensitive layer through said film-forming polymer a quantity of said soluble silver complex sufficient to form in said image-receiving stratum a visible positive image of the subject matter of said latent image, and stripping said photosensitive sheet material, with the layer of film-forming polymer attached thereto, from said other sheet material and the image formed therein. 9. The method of producing a visible positive

image of a latent image contained in a predetermined area of a silver halide layer of a photosensitive sheet material, which method comprises 45 locating a viscous or liquid processing agent on one side only of said photosensitive sheet material adjacent one edge of said area at least in sufficient quantity to provide all the liquid for the development of said latent image, which 50 processing agent contains an organic film-forming high molecular weight polymer, spreading said processing agent in a layer between said photosensitive sheet material and another sheet material by applying pressure to the outer surfaces 55 of said sheet materials, the portions of said outer surfaces of said sheet materials subjected to said pressure remaining dry during said pressure application, the surface of said photosensitive sheet material in contact with said liquid layer having coated thereon a solid film of said organic filmforming polymer and the surface of said other sheet material in contact with said liquid layer having coated thereon a solid film having a lesser affinity for said organic film-forming polymer in 65 its solid state than said film-forming polymer has for the coated surface of the photosensitive sheet material, liquid of said processing agent being absorbed by said photosensitive sheet material and, during absorption, transporting, to said area of said photosensitive layer, photographic material including a developing agent for the silver halide and a silver halide solvent capable of forming a soluble silver complex with the undeveloped silver halide, said photographic ma- 75

terial being provided by at least one of (a) said sheet materials and (b) said processing agent, the development of said latent image producing an imagewise distribution of said soluble silver complex throughout the liquid of said processing agent, said other sheet material comprising an image-receiving stratum adjacent the surface thereof containing nuclei for aggregating and precipitating the silver of a soluble silver complex, retaining said sheet materials in their superposed condition until the absorption of said liquid from said layer of processing agent produces a continuous solid phase of said film-forming polymer between said sheet materials and there is transported from the photosensitive layer through said film-forming polymer a quantity of said soluble silver complex sufficient to form in said image-receiving stratum a visible positive image of the subject matter of said latent image, and stripping said photosensitive sheet material with the layer of film-forming polymer attached thereto, from said other sheet material and the image formed therein.

10. The method of producing a visible image of a latent image contained in a predetermined area of a silver halide layer of a photosensitive sheet material, which method comprises locating a viscous liquid processing agent on one side only of said photosensitive sheet material adjacent one edge of said area at least in sufficient quantity to provide all the liquid for the development of said latent image, which processing agent contains an organic film-forming high molecular weight polymer, spreading said processing agent in a layer between said photosensitive sheet material and another sheet material by applying pressure to the outer surfaces of said sheet materials, the surface of said other sheet material in contact with said liquid layer having a lesser affinity for the solidified film-forming polymer than the latter has for the surface of the photosensitive sheet material, liquid from said processing agent being absorbed by said photosensitive sheet material and, during absorption, distributing, throughout said area of said photosensitive layer, photographic material capable of developing a latent image in said photosensitive layer and of producing an imagewise distribution throughout the liquid of a material for forming a transfer print of said latent image, said photographic material being provided by at least one of (a) said sheet materials and (b) said processing agent, said other sheet material comprising an image-receiving stratum adjacent the surface thereof for receiving said image-forming material, retaining said sheet materials in their superposed condition until the absorption of said liquid from said layer of processing agent at least partly solidifies said film-forming polymer and there is transported from the photosensitive layer through said filmforming polymer a quantity of said image-forming material sufficient to form in said image-receiving stratum a visible image of the subject matter of said latent image, and stripping said photosensitive sheet material, with the layer of film-forming polymer attached thereto, from said other sheet material.

11. The method of producing a visible positive image of a latent image contained in a predetermined area of a silver halide layer of a photosensitive sheet material, which method comprises locating a viscous liquid processing agent on one side only of said photosensitive sheet material adjacent one edge of said area at least in sufficient quantity to provide all the liquid for the development of said latent image, which processing agent

comprises (1) a developer for silver halide, (2) a silver halide solvent for forming a soluble complex with silver halide and (3) sodium carboxymethyl cellulose, spreading said processing agent in a layer between said photosensitive sheet material and another sheet material by applying pressure to the outer surfaces of said sheet materials, the portions of said outer surfaces subjected to said pressure remaining dry during said pressure application, liquid of said processing 10 agent being absorbed by said photosensitive sheet material and, during absorption, transporting said developing agent and said silver halide solvent to said area of said photosensitive layer, and retaining said sheet materials in their superposed 15 condition until the absorption of said liquid from said layer of processing agent produces a continuous solid phase of said sodium carboxymethyl cellulose between said sheet materials and there is transported from the photosensitive layer a quantity of said soluble silver complex sufficient to form said visible positive image of the subject matter of said latent image in a stratum of the lamination comprising said two sheet materials and said layer of processing agent, said stratum $_{25}$ being other than said photosensitive layer.

12. The method of producing a visible positive image of a latent image contained in a predetermined area of a silver halide layer of a photosensitive sheet material which method comprises $_{30}$ locating a viscous liquid processing agent on one side only of said photosensitive sheet material adjacent one edge of said area at least in sufficient quantity to provide all the liquid for the development of said latent image, which processing agent comprises (1) a developer for silver halide, (2) a silver halide solvent for forming a soluble complex with silver halide and (3) hydroxyethyl cellulose, spreading said processing agent in a layer between said photosensitive sheet material and another sheet material by applying pressure to the outer surfaces of said sheet materials, the portions of said outer surfaces subjected to said pressure remaining dry during said pressure application, liquid of said processing agent being absorbed by said photosensitive sheet material and, during absorption, transporting said developing agent and said silver halide solvent to said area of said photosensitive layer, and retaining said sheet materials in their superposed condition until the absorption of said liquid from 50 said layer of processing agent produces a continuous solid phase of said hydroxyethyl cellulose between said sheet materials and there is transported from the photosensitive layer a quantity of said soluble silver complex sufficient to form 55 said visible positive image of the subject matter of said latent image in a stratum of the lamination formed by said two sheet materials and said layer of liquid processing agent, said stratum being other than said photosensitive layer.

13. The method of producing a visible positive image of a latent image contained in a predetermined area of a silver halide layer of a photosensitive sheet material, which method comprises only of said photosensitive sheet material adjacent one edge of said area at least in sufficient quantity to provide all the liquid for the development of said latent image, which processing agent is alkaline and comprises hydroquinone, sodium 70 thiosulfate and sodium carboxymethyl cellulose in a sufficient concentration to impart to said processing agent a viscosity at 24° C. in excess of 1000 centipoises, spreading said processing agent in a layer between said photosensitive sheet ma- 75 pressure application, liquid of said processing

terial and another sheet material by applying pressure to the outer surfaces of said sheet materials, the portions of said outer surfaces of said sheet materials subjected to said pressure remaining dry during said pressure application, liquid of said processing agent being absorbed by said photosensitive sheet material and, during absorption, transporting the hydroquinone and the sodium thiosulfate to said area of said photosensitive layer, and retaining said sheet materials in their superposed condition until the absorption of said liquid from said layer of processing agent produces a continuous solid phase of said sodium carboxymethyl cellulose between said sheet materials and there is transported from the photosensitive layer a quantity of said soluble silver complex sufficient to form said visible positive image of the subject matter of said latent image in a stratum of the lamination formed by said two sheet materials and said layer of liquid processing agent, said stratum being other than said photosensitive layer.

14. The method of producing a visible positive image of a latent image contained in a predetermined area of a silver halide gelatin emulsion layer of a photosensitive film, which method comprises locating a liquid processing agent on one side only of said film adjacent one edge of said area at least in sufficient quantity to provide all the liquid for the development of said latent image, said processing agent comprising an alkaline aqueous solution of sodium carboxymethyl cellulose, hydroquinone and sodium thiosulfate and having a viscosity at 24° C. in excess of 1000 centipoises, spreading said processing agent in a layer between said film and a sheet of baryta paper by applying pressure to the outer surfaces of said film and said paper, the portions of said outer surfaces subjected to said pressure remaining dry during said pressure application, liquid of said processing agent being absorbed by said emulsion and, during absorption, transporting the hydroguinone and the sodium thiosulfate thereto, and retaining said film and said paper in their superposed condition until the absorption of said liquid from said layer of processing agent produces a continuous solid phase of sodium carboxymethyl cellulose between said film and said paper and there is transported from the photosensitive layer to the lamination comprising the carboxymethyl cellulose and the paper a quantity of said soluble silver complex sufficient to form in a stratum of said lamination said visible positive image of the subject matter of said latent image.

15. The method of producing a visible positive image of a latent image contained in a predetermined area of a silver halide layer of a photosensitive sheet material, which method comprises locating a viscous liquid processing agent on one side only of said photosensitive sheet material adjacent one edge of said area at least in sufficient quantity to provide all the liquid for the development of said latent image, which processing agent contains a developer for silver halide, a silver locating a liquid processing agent on one side 65 halide solvent for forming a soluble complex with silver halide and a high molecular weight polymer in a sufficient concentration to impart to said processing agent a viscosity at 24° C. in excess of 1000 centipoises, spreading said processing agent in a layer between said photosensitive sheet material and another sheet material by applying pressure to the outer surfaces of said sheet materials, the portions of said outer surfaces subjected to said pressure remaining dry during said agent being absorbed by said photosensitive sheet material and, during absorption, transporting said developing agent and said silver halide solvent to said area of said photosensitive layer, and retaining said sheet materials in their superposed condition until the absorption of said liquid from said layer of processing agent produces a coating of said high molecular weight polymer between said processing.

17. The processing said sheet materials and there is transported from the photosensitive layer a quantity of said soluble silver complex sufficient to form said positive image in a stratum of the lamination comprising said coating and said other sheet material.

16. The method of forming an image in a predetermined area of a photosensitive layer of a la photographic photosensitive sheet material, said photosensitive layer having as its photosensitive substance at least one salt from the class consisting of (a) the photosensitive diazonium salts and (b) the heavy metal salts capable of form- 2 ing a latent image upon photoexposure and capable of development to produce a visible image comprising the metal of said salt, which method comprises locating a viscous liquid processing agent adjacent one edge of said area in sufficient 2 quantity to provide at least part of the liquid required for a transformation of an image formed in said photosensitive layer by photoexposure, said processing agent being located on one side only of said photosensitive sheet material and 3 containing a solid film-forming organic colloid, forming a layer of said processing agent between said photosensitive sheet material and another sheet material by applying pressure to the outer surfaces of said sheet materials, the portions of 3 said outer surfaces subjected to said pressure remaining dry during said pressure application, liquid from said processing agent being absorbed by said photosensitive sheet material and, during absorption, distributing, throughout at least a 4 portion of said area of said photosensitive layer, a photographic reagent capable of carrying out the desired image transformation, said photographic reagent being different from the solvent of said processing agent and being provided by 45 at least one of (a) said sheet materials and (b) said processing agent, the absorption of said liquid from said layer of processing agent increas-

ing the concentration of said colloid in said liquid to produce a coating containing said colloid between said sheet materials which maintains the latter in spaced laminated relationship during said processing.

17. The process of claim 16 wherein the photosensitive layer is a silver halide emulsion and the reagent is a substance from the class consisting of the silver halide developers and the silver halide solvents

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References Cited in the file of this patent UNITED STATES PATENTS

	UNITED STATES PATENTS				
5	Number	Name	Date		
	312,451	Ehret	Feb. 17, 1885		
	935,115	Kelly et al			
	1,170,506	Blondel	Feb. 8, 1916		
	1,939,026	Spencer	Dec. 12, 1933		
09	2,029,922	Heckel et al			
	2,035,650	Gustafson	Mar. 31, 1936		
	2,054,448	Russell			
	2,059,887	Mannes et al			
	2,072,597	Keen	Mar. 2, 1937		
25	2,113,944	Leuch	Apr. 12, 1938		
	2,121,397	Downing			
	2,196,226	Murray	Apr. 9, 1940		
	2,273,677	Wallach	Feb. 17, 1942		
	2,317,750	Fermazin			
30	2,320,108	Tull	May 25, 1943		
	2,323,246	Schneider	June 29, 1943		
	2,328,034	Sease	Aug. 31, 1943		
	2,350,380	White	June 6, 1944		
. ~	2,352,014	Rott	June 20, 1944		
35	2,386,602	Gioseffi	Oct. 9, 1945		
	2,417,713	Stein	Mar. 8, 1947		
		FOREIGN PATENT	rs		
10	Number	Country	Date		
ŧυ	9,248	Great Britain	1905		
	115 221	Switzerland			

Number	Country	Date
9,248	Great Britain	1905
115,331	Switzerland	_ June 16, 1926
141,872	Austria	_ May 25, 1935
879,995	France	_ Dec. 10, 1942

OTHER REFERENCES

Colson Le Developpement Confine Bulletin Societe Française Photographie 1898, pp. 108–111.