Jan. 2, 1962 H. G. ROGERS 3,015,561

NOVEL PHOTOGRAPHIC COLOR PROCESSES AND PRODUCTS

Filed March 15, 1957

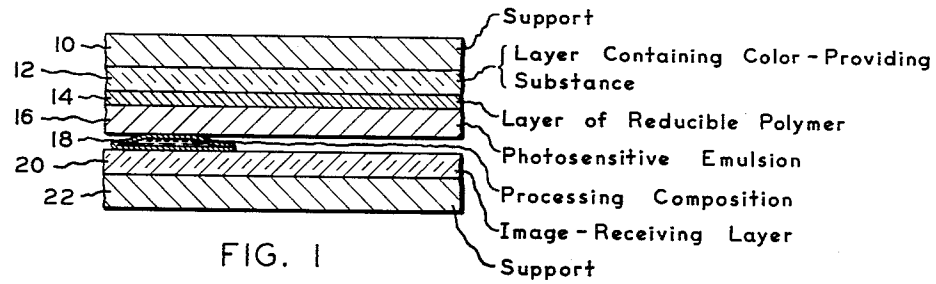


FIG. 1

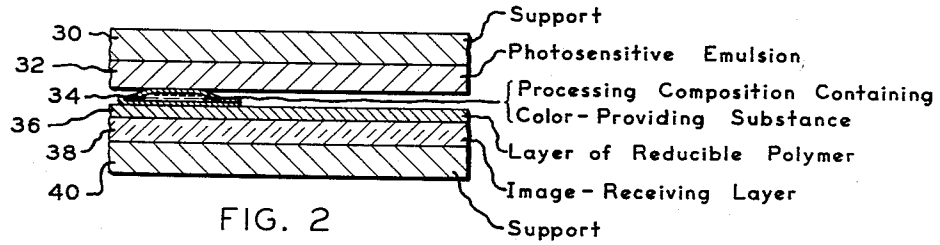


FIG. 2

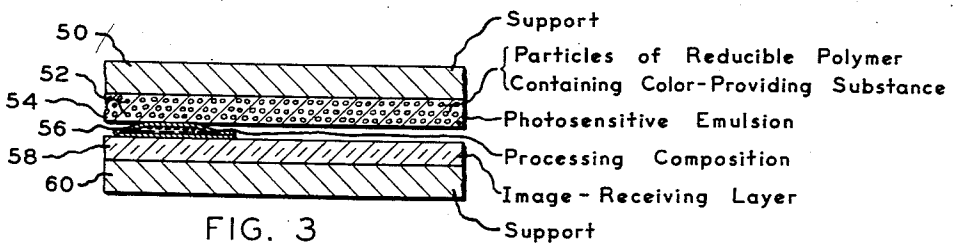


FIG. 3

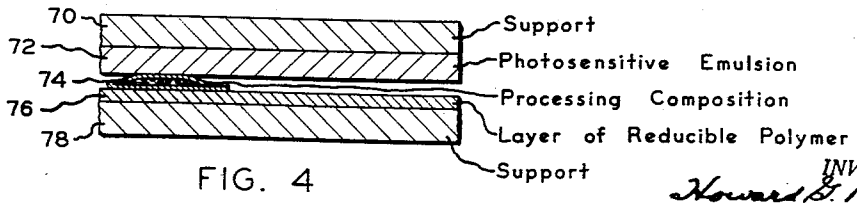


FIG. 4

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NOVEL PHOTOGRAPHIC COLOR PROCESSES AND PRODUCTS

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Filed Mar. 15, 1957, Ser. No. 646,384
5 Claims. (Cl. 96—29)

This invention relates to the art of photography and, more particularly, to novel processes for the formation of color images and to photographic products for use with such processes.

It has previously been proposed, as for example in U.S. Patent No. 2,647,049, issued to Edwin H. Land on July 28, 1953, to form color photographs by a diffusion-transfer reversal process. In such a process, a photosensitive layer containing a latent color record image is processed to develop said latent image and to form a positive color record in an image-receiving element.

The present invention is concerned with improvements in the formation of color images by diffusion-transfer reversal processes and particularly with providing novel processes utilizing, as the means of controlling the diffusibility of a color-providing substance, a substance reducible by unreacted developing agent.

A primary object of this invention, therefore, is to provide novel color processes wherein the formation of an imagewise distribution of color-providing substance is effected by the reducing action of unoxidized or unexhausted developing agent on a reducible substance, and more particularly, a reducible polymeric substance.

A further object of this invention is to provide improved diffusion-transfer reversal processes for the formation of color images, preferably positive color images, wherein the creation of a visible image is effected by the action of unexhausted developing agent on a reducible polymeric substance.

Another object of this invention is to provide novel diffusion-transfer reversal processes for the formation of color images, wherein the color-providing substance is nondiffusible until a reducible substance is acted upon by unexhausted developing agent, and wherein said color-providing substance is an organic compound.

Another object of this invention is to provide novel diffusion-transfer reversal processes for the formation of color images wherein the color-providing substance is a complete dye.

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

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

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed disclosure taken in connection with the accompanying drawing wherein:

FIGURE 1 is a diagrammatic cross-sectional view of one embodiment of a photosensitive element, suitable for use in the process of this invention, in association with an image-receiving element and a rupturable container holding a liquid processing composition;

FIG. 2 is a diagrammatic cross-sectional view of a further embodiment of a photosensitive element, image-receiving element and rupturable container suitable for use in the process of this invention;

FIG. 3 is a diagrammatic cross-sectional view of another embodiment of a photosensitive element, image-receiving element and rupturable container in accordance with this invention; and

FIG. 4 is a diagrammatic cross-sectional view of still another embodiment of a photosensitive element, image-receiving element and rupturable container suitable for use in one embodiment of this invention.

In diffusion-transfer reversal processes of the type herein contemplated, an exposed photosensitive silver halide emulsion layer containing a latent image is processed by a liquid processing composition to obtain an imagewise distribution of diffusible color-providing substances. A positive color image may be obtained by the transfer of at least part of such imagewise distribution of diffusible color-providing substances by imbibition from the developed photosensitive layer to a superposed image-receiving material. The desired positive color image is revealed by separating or stripping the image-receiving material from the developed photosensitive layer after a suitable imbibition period.

Diffusion-transfer reversal color processes hitherto proposed have employed various color-producing mechanisms, both for providing the imagewise distribution of diffusible color-providing substances in the developed photosensitive layer and for imparting the desired positive color image to an image-receiving material. Thus, the previously mentioned U.S. Patent No. 2,647,049 proposes to employ color couplers and color developers of a nature common in conventional color processes. In utilizing such color couplers and color developers, the desired imagewise distribution of color coupler and color developer is dependent upon the immobilization of at least the oxidized color developer in the photosensitive layer as a result of the development of a latent image. In such processes, unreacted color developer and color coupler are transferred to an image-receiving material and there reacted to produce the desired dye image. It will be noted that such processes require a series of reactions to provide the diffusible imagewise distribution and to produce the desired dye image utilizing the diffusible color components.

Another diffusion-transfer reversal color process, as disclosed and claimed in the copending application of Howard G. Rogers, Serial No. 415,073, filed March 9, 1954, now abandoned in favor of a continuation-in-part thereof, Serial No. 748,421, filed July 14, 1958 (now U.S. Patent No. 2,983,606, issued May 9, 1961), proposes to utilize dye developers, that is, complete dyes which have a silver halide developing function. Utilization of dye developers as contemplated therein has the advantage of reducing the number of reactions necessary to provide the positive dye image since the dye developer is a complete dye and no coupling reactions are required in the photosensitive layer or to impart the desired dye image to the image-receiving material.

It has also been proposed to employ complete dyes in diffusion-transfer reversal color processes by utilizing an oxidation product of the silver halide developer to immobilize the dye in exposed areas and thus provide the desired imagewise distribution of diffusible dye. Processes of this type are disclosed and claimed in my U.S. Patent No. 2,774,668, issued December 18, 1956.

It will, therefore, be seen that diffusion-transfer reversal color processes heretofore proposed have relied upon the utilization of an oxidation product of a silver halide developer to immobilize or trap, in the exposed areas of the photosensitive layer, the substances necessary to impart a positive dye image to the image-receiving material whereby an imagewise distribution of diffusible, color-providing substances is also formed. This common characteristic may be described as the use of an "immobilizing" mechanism, that is, the color-providing com-

ponents must be trapped, that is, immobilized, in the exposed portions of the photosensitive layer.

The novel diffusion-transfer reversal color processes of this invention may be readily distinguished from such previously proposed processes by the fact that a "mobilizing" mechanism is employed to provide the desired imagewise distribution of diffusible color-providing substances. Thus, the processes of this invention control the availability for transfer of color-providing substances associated with unexposed areas of the photosensitive layer by the reaction of unreacted or unexhausted silver halide developing agent upon a reducible substance, and more particularly, a reducible polymeric substance.

By way of recapitulation, the novel processes of this invention depend upon the action of unexhausted developing agent to control the availability for transfer of a color-providing substance. Thus, the color-providing substance is rendered transferable imagewise by the reducing action of unexhausted developing agent on a reducible polymeric substance.

It will, therefore, be readily apparent that the novel diffusion-transfer reversal color processes of this invention provide novel methods of creating the desired imagewise distribution of mobile color-providing substances.

The expression "color-providing substances" as used herein is intended to include all types of reagents which may be utilized to produce a color image and which are capable of being rendered soluble in a processing liquid. Such reagents are organic in nature and may initially possess a chromophoric system imparting the desired color in the state in which they are diffusible, or the reagents may undergo reaction after transfer to form such a chromophoric system, as by oxidation and/or coupling. In a preferred embodiment the color-providing substances are complete dyes. It is also contemplated to use a color-providing substance which in its diffusible form is a leuco dye but which is oxidized after imbibition to provide the desired positive dye image. The nature of these and other color-providing substances will be referred to in more detail hereinafter.

The oxidation potential of the reducible polymeric substance should be intermediate between that of exposed silver halide and unexposed silver halide, whereas the reduction potential of the silver halide developing agent should be such that in exposed areas it will develop exposed silver halide substantially to the exclusion of reaction with the reducible polymeric substance and in unexposed areas will react with the reducible polymeric substance substantially to the exclusion of unexposed silver halide.

In carrying out the process of this invention a photosensitive element containing a silver halide emulsion is exposed and wetted with a liquid processing composition, for example by immersing, coating, spraying, flowing, etc. in the dark and the photosensitive element superposed prior to, during or after wetting on a sheetlike support element, which element may be utilized as an image-receiving material. The lamination comprising the processing composition, the image-receiving element and the photosensitive element includes a color-providing substance. In a preferred embodiment, the liquid processing composition is applied to the photosensitive element in a uniform layer as the photosensitive element is brought into superposed relationship with an image-receiving element. It is also within the scope of this invention to apply the liquid processing composition prior to exposure in accordance with the disclosure in the copending application of Edwin H. Land, Serial No. 498,672, filed April 1, 1955. The liquid processing composition permeates the emulsion to provide a substantially uniform distribution of the silver halide developing agent therein. The silver halide developing agent may be initially contained in the liquid processing composition or it may be initially disposed in the photosensitive element.

As the latent image is developed by the silver halide developing agent, an imagewise distribution of unreacted or unexhausted silver halide developing agent is formed. This imagewise distribution of unexhausted silver halide developing agent is formed as a function of the point-to-point degree of exposure creating the latent image. The amount of unexhausted developing agent is thus inversely related to the quantity of silver halide developed, and the quantity of color-providing substance available for transfer will vary directly with the amount of unexhausted developing agent.

The above-mentioned imagewise distribution of unexhausted silver halide developing agent present in the unexposed areas of the photosensitive element reduces a reducible polymeric substance so located in this lamination as to normally prevent the color-providing substance from having access to the image-receiving material. The reduced form of the reducible polymeric substance is permeable to the liquid processing composition. As a result of the change in permeability of such reduced portions of the reducible polymeric substance, an imagewise distribution of diffusible color-providing substance is created. At least part of this imagewise distribution of mobile color-providing substance is transferred, by imbibition, to a superposed image-receiving layer or element. Under certain circumstances, the layer of liquid processing composition may be utilized as the image-receiving material. The latter element receives a depthwise diffusion from the photosensitive element of mobile color-providing substance, without appreciably disturbing the imagewise distribution thereof, to provide a reversed or positive image of the developed image. The desired positive image is revealed by stripping the image-receiving material from the photosensitive element at the end of the imbibition period.

By the expression "immobile color-providing substance," as used herein, is meant a color-providing substance which is incapable of transferring to an image-receiving material because of a reducible polymeric substance, at least during the period of imbibition. The term "mobile color-providing substance" refers to a color-providing substance rendered transferable as the result of the reducing action of unexhausted silver halide developing agent on a reducible polymeric substance.

The reducible polymeric substances employed in the processes of this invention are substantially impermeable in the unreduced state to the processing composition, at least during the imbibition period. Reduction by unexhausted developing agent renders the reduced portions of polymeric substance permeable to the processing composition. Thus, the unreduced polymeric substance is substantially non-swellable by alkali, and the reduced portions thereof are swellable by alkali. The polymers should be free of excessive water-solubilizing groups, such as sulfonic acid groups, so that it will not be water-swellable in the unreduced state.

The desired permeability characteristics of the reducible polymeric substance result from the fact that the polymer is so constituted that its permeability is dependent upon the state of the reactive groups present. These reactive groups are so chosen as to be insoluble in alkali until reduced, in accordance with well-known chemical principles that the reduced forms are more soluble. The permeability, for example, may result from the ability of the reactive groups to form alkali metal salts in the reduced form but not in the oxidized form.

As examples of reducible polymeric substances, mention may be made of polymers containing reducible functional groupings, for example, indophenol or quinone groups. The reducible polymers preferably should be soluble in organic solvents to facilitate their use in preparing the photosensitive products.

Polymers containing indophenol groups may be prepared by oxidative coupling of p-phenylene diamine type compounds with so-called polymeric color couplers. Polymeric color couplers are well-known in the photo-

graphic art and are polymers, for example, polyvinyl alcohol, containing substituents capable of coupling with the oxidation product of color developers. Such substituents may comprise phenolic or naphtholic groups having a coupling position available para to the hydroxyl group, and the term "indophenol" is intended to refer to the grouping which results from such coupling. Thus, one may react polyvinyl alcohol with salicylaldehyde in an acetal synthesis to obtain the polymeric coupler polyvinyl salicylal.

Another suitable type of reducible polymer comprises polymers having reducible metal complex groups. As examples of suitable polymers, mention may be made of polymers having β-ketone or β-ketonitrile substituents capable of forming reducible manganic complexes.

Additional reducible polymers comprise polymers containing reducible disulfide linkages or heavy metal salts, for example silver salts, of polymers containing mercapto groupings.

Where the impermeable characteristics make operations such as coating difficult, it is contemplated to introduce the polymeric substance in a coatable state and convert it to the impermeable state in situ. Thus, where the reducible polymer is to be used in the form of a coating, it is contemplated to first apply a coating of the permeable form or of an intermediate and thereafter convert it to the reducible, impermeable form by suitable treatment. Thus a coating of a polymeric coupler, e.g., polyvinyl salicylal, may be applied and then treated under oxidizing conditions with a para-phenylene diamine type compound to form the impermeable indophenol polymer.

The reducible polymeric substance may be colored or colorless, so long as the color thereof does not interfere with effective use thereof. In certain instances, it may be desirable to employ a colored reducible polymer to obtain an image in terms of two colors, that is, an image in one color on a background of another color. Where the reducible polymeric substance is to be contained in the photosensitive element and is itself colored, it is preferably employed behind the emulsion to avoid undesirable light absorption. The reducible polymeric substance is preferably colorless if it is to be used as a component of the image-receiving element and is to remain there. Where it is desired to utilize colored reducible polymeric substances in the form of particles in the emulsion, undesired light absorption may be reduced by using particles of such size as to have low covering power. In multilayer embodiments, only the reducible polymeric substances associated with the top two emulsions need be in the form of particles for this purpose, and the reducible polymeric substance associated with the innermost emulsion layer may be used as a layer behind said innermost emulsion. Sould the color-providing substance present in such particles be itself colored, it may be present in the form of polarizing crystals in accordance with the disclosure of the copending application of Edwin H. Land, Serial No. 607,820, filed September 4, 1956, and a layer of reducible polymer provided around such crystals. In all instances where particles are employed, it is desirable that light striking the emulsion not be scattered in the course of transmission. Thus, the particles should approximately match the index of refraction of the medium of the photosensitive emulsion, e.g., gelatin.

Suitable color-providing substances for use in the processes of this invention include all types of complete dyes as well as dye intermediates, such as color couplers. The color-providing substances are preferably water-soluble, or at least alkali-soluble. Where the color-providing substance is a color coupler, coupling of the color coupler rendered transferable by the action of unexhausted developing agent may be effected, after transfer to the image-receiving material, with a substance, e.g., a diazonium salt or an oxidized color developer, initially present therein or introduced after the transfer is completed. When the developing agent utilized to reduce the reducible polymeric substance has an oxidation product capable of coupling with the coupler to form a diffusible dye, the desired image may be formed in this manner. The color-providing substances are preferably photographically unreactive and thus do not interfere with processing.

In certain instances, as where a color-providing substance is to be incorporated in the reducible polymeric substance, and especially in particles thereof, the color-providing substance should be water-insoluble but soluble in alkali and organic solvents. Such solubility characteristics facilitate the use of the color-providing substance in the reducible polymeric substance.

The use of color-providing substances which are water-soluble is advantageous in the preparation of additional transfer prints by superposing the developed and stripped photosensitive element with additional image-receiving layers in the presence of a solubilizing composition. In such an embodiment, it may be desirable to neutralize the developed negative to prevent aerial oxidation of the reduced portions of the reducible polymeric substance. This would preclude the use in this embodiment of color-providing substances requiring the presence of alkali for diffusibility. The color-providing substance may then be transferred using a non-alkaline solvent, including organic solvents.

As previously indicated, the reducible polymeric substance employed is one which has an oxidation potential intermediate that of exposed silver halide and unexposed silver halide and which exhibits a relatively large change in permeability to the processing composition as between the initial, oxidized condition and its reduced condition.

The silver halide developing agents which may be employed in conjunction with a reducible polymeric substance should exhibit a reduction potential such that in exposed areas it will develop exposed silver halide substantially to the exclusion of reaction with the reducible polymeric substance, and in unexposed areas it will react with the reducible polymeric substance, substantially to the exclusion of unexposed silver halide. Preferably, the oxidation product of the silver halide developer should be relatively insoluble to insure absence of transfer thereof to the image-receiving material where it might cause stain. Use of a silver halide developing agent having a relatively highly insoluble oxidation product also avoids the possibility of an equilibrium condition and insures completeness of reaction.

The silver halide developing agent is preferably employed in a concentration such that it will be completely reacted or exhausted in photosensitive areas which have been completely exposed, thus preventing stain in the highlights. The amount of exhausted developer is thus a direct function of the degree of exposure on a point-to-point basis of the photosensitive emulsion and the amount of unexhausted developer is an inverse function of the amount of such exposure. The quantity of alkali employed is preferably so limited as to be sufficiently exhausted in exposed areas by the development reaction as to be incapable of releasing the color-providing substance in said exposed areas.

As examples of suitable silver halide developing agents, mention may be made of hydroquinone, toluhydroquinone, acetamidophenyl hydroquinone, p-anilinohydroquinone, naphthylazohydroquinone, Amidol (2,4-diamino-phenol hydrochloride), and Phenidone (1-phenyl-3-pyrazolidone).

Illustrative physical embodiments of the present invention, as shown in FIGS. 1 through 4, generally involve photosensitive elements which have associated therewith a liquid-carrying container, said container being positioned so that its liquid compositon can be released so as to permit the permeation of the photosensitive emulsion by the liquid composition. A color-providing substance is present in the processing composition or in the photosensitive element. The liquid composition is preferably

viscous and includes at least a solvent for the silver halide developing agent and also a solvent for the color-providing substance.

The embodiment shown in FIG. 1 depicts a photosensitive element which includes a support layer **10** carrying a layer **12** containing a color-providing substance. Between this layer and a layer **16** of a photosensitive emulsion is a layer **14** of a reducible polymer. A rupturable container or pod **18** carrying a liquid processing composition, which composition includes a silver halide developing agent and a solvent for the color-providing substance, is associated with the photosensitive element and is adapted to release the processing composition for spreading between said photosensitive element and a superposed image-receiving element comprising a support **22** carrying a layer **20** of a dyeable, image-receiving material. In the course of processing unexhausted developing agent present in unexposed areas of the emulsion reduces the portions of the reducible polymer layer **14** associated with such unexposed areas, and renders such portions permeable to the processing composition. Permeation of the processing composition through such reduced portions of the reducible polymer layer **14** solubilizes the color-providing substance present in the layer **12** behind the reducible polymer, and the thus-formed imagewise distribution of solubilized color-providing substance is transferred to the layer **20** of image-receiving material.

FIG. 2 illustrates a photosensitive element comprising a support layer **30** carrying a photosensitive emulsion layer **32**. Associated with said photosensitive element is a rupturable container **34** containing a liquid processing composition, which composition includes a silver halide developing agent and a color-providing substance. An image-receiving element comprises a support **40**, a layer **38** of image-receiving material and an outer layer **36** of a reducible polymer. Development of the silver halide emulsion layer **32** results in an imagewise distribution of unexhausted developing agent. The unexhausted developing agent reduces the reducible polymer rendering it permeable to the processing composition. The color-providing substance present in the processing composition is thus free to transfer imagewise to the image-receiving layer **38**. Where the reducible polymer is colored or has an undesired color, it may be removed by adhering to the photosensitive element upon stripping by providing a suitable stripping layer between the layers of image-receiving material and reducible polymer.

A further embodiment of this invention is shown in FIG. 3 wherein a photosensitive element includes a support layer **50** and a photosensitive emulsion layer **54** containing particles **52** of a reducible polymer dispersed therein. The particles **52** contain a color-providing substance. Thus, particles **52** comprise a color-providing substance controlled by an outer layer or surface of a reducible polymer. Associated with said photosensitive element is a rupturable container **56** carrying a liquid processing composition, which composition includes at least a solvent for said color-providing substance. The imagewise distribution of unexhausted developing agent formed during processing reduces the reducible polymer present, in the form of particles, in the unexposed areas of the emulsion. Such reduction renders the particles permeable to the processing composition which solubilizes the color-providing substance contained in such reduced particles. The solubilized color-providing substance is transferred to the image-receiving layer to provide the desired positive image.

While the silver halide developing agent may be initially present in the liquid processing composition or in the photosensitive element, it is also within the scope of this invention to dispose a portion of the total silver halide developing agent in the liquid processing composition and a portion in the photosensitive element. Such an embodiment would facilitate the formation of a uniform distribution of the silver halide developing agent in the photosensitive emulsion layer during development.

This invention has been illustrated with reference to processes for the formation of positive color transfer images, wherein a color-providing substance is transferred to the image-receiving element. It is also contemplated to initially dispose a color-providing substance in the image-receiving element and cause it to be removed from said element by the action of unexhausted developing agent on a reducible polymer controlling such color-providing substance. In such an embodiment, one may obtain a negative image.

In lieu of releasing a color-providing substance associated with the image-receiving element, a visible image may be created as a result of a change in color of the portions of the reducible polymer reduced by unexhausted developer, followed by stabilization of the polymer layer. Thus a polymeric coupler which has been coupled to give, for example, an indophenol dye, will be rendered colorless in reduced areas. The polymer may be stabilized in its reduced and unreduced forms by an acidic treatment, such for example, as with boric acid. A positive image may be obtained by using a white or colorless reducible polymer, e.g., a polymer containing triazolium groups, the reduced portions of which will be colored.

FIG. 4 is illustrative of the last-mentioned embodiment and shows a photographic product wherein a support layer **70** carries a photosensitive layer **72**. Associated therewith is a rupturable container **74** holding a processing composition and an image-carrying element comprising a support **78** carrying a layer **76** of a reducible polymer. Rupture of the container **74** releases the processing composition which permeates the photosensitive emulsion layer **72** and initiates development thereof. As the latent image is developed, an imagewise distribution of unexhausted developing agent is transferred to the layer **76** of reducible polymer. Where the reducible polymer is initially colored, e.g., an indophenol polymer, the reduced portions may be rendered colorless to give a negative image. Where the reducible polymer is initially colorless or white, the reduced areas may be rendered colored to give a positive image.

As indicated above, it is within the scope of this invention to utilize color-providing substances which are oxidized after transfer to the image-receiving material. An example of such a color-providing substance is an indophenol dye, which is transferred in the reduced or leuco state, wherein it is colorless or less colored, and which must be oxidized to give the desired color. Such oxidation may be effected by aerial oxidation or by the use of suitable oxidizing agents which may be incorporated in the image-receiving element or applied thereto after separating apart from the photosensitive element.

The incorporation of an oxidizing agent in the image-receiving element is described in U.S. Patent No. 2,559,643, issued to Edwin H. Land. As examples of suitable oxidizing agents, mention may be made of peroxy compounds such as sodium or potassium perborate, and compounds having polyvalent metallic elements in higher valent form, such as copper, iron or cerium, wherein the metallic element is in higher valent form. Examples of these latter-mentioned agents are cupric salts such as cupric sulfate. Another suitable oxidizing agent is benzoyl peroxide. Other suitable oxidizing agents include quinones, such as benzoquinone. A preferred quinone is 2,3-dicyanobenzoquinone, since the corresponding hydroquinone is too weak a reducing agent to interfere in development of the latent image.

The following examples are intended to illustrate methods by which a negative transfer image may be obtained using a reducible polymeric material, and are not intended to be interpreted in a limiting sense.

Example 1

A photosensitive element similar to that illustrated in

FIG. 4 is prepared by coating a subcoated cellulose acetate film base with a silver halide emulsion. An image-carrying element is prepared by coating a cellulose acetate-coated baryta paper with a composition comprising 4% Nylon Type F8 (trade name of E. I. du Pont de Nemours & Co., Wilmington, Delaware, for N-methoxymethyl polyhexamethylene adipamide) in 80% aqueous isopropanol. After this coating has dried, a coating of polyvinyl salicylal is applied using a 4% solution of polyvinyl salicylal in acetone. The polyvinyl salicylal is coupled by treatment with 0.5% of 2-amino-5-diethylaminotoluene in 1% sodium hydroxide followed by treating with 5% aqueous ferricyanide. After rinsing twice with water, the image-carrying element is ready for use. The photosensitive element is exposed and an aqueous liquid processing composition comprising:

	Percent
Sodium carboxymethyl cellulose	4.5
Sodium hydroxide	2.0
Potassium bromide	0.5
Sodium sulfite	0.5
Toluhydroquinone	0.5

is applied by spreading between said photosensitive element and said image-carrying element, as said elements are brought into superposed relationship. After an imbibition period of approximately two minutes, the image-carrying element is stripped apart to reveal a cyan negative image and is swabbed with 2% boric acid.

Example 2

An image-carrying element similar to that used in Example 1 is prepared by treating the layer of polyvinyl salicylal with a solution of 0.5% of N,2,6-trichloro-p-quinoneimine in 1% sodium hydroxide to effect coupling, after which the image-carrying element is rinsed with water. After exposure, a photosensitive element is processed by the application of an aqueous liquid processing composition comprising:

	Percent
Sodium carboxymethyl cellulose	4.5
Sodium hydroxide	2.0
Potassium bromide	0.5
Sodium sulfite	2.0
Toluhydroquinone	0.5

spread between the exposed photosensitive element and the image-carrying element as said elements are brought into superposed relationship. The stripped image-carrying element has a cyan negative image and is swabbed with 2% boric acid.

The following example illustrates the embodiment described in connection with FIG. 2 using a colored reducible polymer.

Example 3

A photosensitive element is exposed and then developed with an aqueous liquid processing composition comprising:

	Percent
Sodium carboxymethyl cellulose	4.5
Sodium hydroxide	2.0
Potassium bromide	0.5
Sodium sulfite	0.5
Toluhydroquinone	0.5
Azorubine (C.I. 179)	2.0

in contact with an image-carrying element similar to that described in Example 1. After an imbibition period of approximately two minutes, the image-receiving element is separated and contains a two-color image in terms of a red positive image on a cyan background. The stripped image-receiving element is swabbed with 2% boric acid.

It is also contemplated to utilize the color-providing substance in particles of a reducible material which is not a polymer but which is alkali-impermeable until reduced by unexhausted developing agent. The color-providing substance is so selected or modified as to have more solubility in the reducible solvent or plasticizer than in alkali, until said solvent is reduced. Upon reduction of at least a portion of the reducible solvent comprising the particle, the color-providing substance is rendered diffusible. Suitable reducible solvents may comprise mixtures of quinones or indophenols, with a small proportion of an inert material, such as a high boiling, alkali-immiscible liquid, if necessary to keep such solvent in liquid form.

In all products employed in the practice of this invention, it is preferable to expose the photosensitive element from the emulsion side. It is, therefore, desirable to hold said photosensitive element and the image-receiving element together at one end thereof by fastening means not shown but comprising hinges, staples, or the like in such manner that the photosensitive element and the image-receiving element may be spread apart from their processing positions illustrated in FIG. 1. Where the film unit is of the roll film type, said photosensitive element and image-receiving element are wound into separate rolls and the free ends of said rolls are connected together in the manner described. A camera apparatus suitable for processing roll film of the type just mentioned is providde by the Polaroid Land Camera Model 95A, sold by Polaroid Corporation, Cambridge, Massachusetts, or similar camera structure such, for example, as the camera forming the subject matter of U.S. Patent No. 2,435,717. Camera apparatus of this type permits successive exposure of individual frames of the photosensitive element from the emulsion side thereof as well as individual processing of an exposed frame by bringing said exposed frame into superposed relation with a predetermined portion of the image-receiving element while drawing these portions of the film assembly between a pair of pressure rollers which rupture a container associated therewith and effect the spreading of the processing liquid released by rupture of said container, between and in contact with the exposed photosensitive frame and the predetermined, registered area of the image-receiving element.

The nature and construction of rupturable containers, such as container 18 of FIG. 1, is well understood in the art; see, for example, U.S. Patent No. 2,543,181, issued to Edwin H. Land on February 27, 1951, and U.S. Patent No. 2,634,886, issued to Edwin H. Land on April 14, 1953.

The liquid processing composition utilized to process the exposed photosensitive element comprises at least an aqueous solution, and may contain an alkaline reagent. It is a solvent for the color-providing substance employed. If the liquid processing composition is to be applied to the exposed photosensitive element by being spread thereon, preferably in a relatively thin, uniform layer, it may also include a viscosity-increasing compound constituting a film-forming material of the type which, when said composition is spread and dried, will form a relatively firm and relatively stable film. A preferred film-forming material is a high molecular weight polymer such as a polymeric water-soluble ether which is inert to an alkaline solution as, for example, a hydroxyethyl cellulose or sodium carboxymethyl cellulose. Other film-forming materials or thickening agents, whose ability to increase viscosity is substantially unaffected when left in solution for a long period of time, may also be used. The film-forming material is preferably contained in the processing composition in suitable quantities to impart to said 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. Illustrations of suitable liquid processing compositions may be found in the several patents and copending applications herein mentioned, and also in the examples herein given. Under certain circumstances, it may be desirable to apply the liquid processing composition to the photosensitive element prior to exposure in accordance with the tech-

nique described in the copending application of Edwin H. Land, Serial No. 498,672, filed April 1, 1955.

The image-receiving or image-carrying element comprises an image-receiving layer of opaque or transparent material which is liquid permeable and dyeable from alkaline solutions and which has been illustrated for purposes of simplicity as comprising a single sheet of permeable material, for example paper. This element, however, may comprise a support upon which at least one liquid-permeable and dyeable layer is mounted. In certain instances, it may also carry a layer of a reducible polymer, and such layer may also constitute the image-carrying layer. The support layer may have a water-impermeable subcoat over which the stratum of permeable and dyeable material is applied. In certain instances, the dyeable layer may comprise a layer of liquid processing composition which is adapted to remain adhered to the support layer upon stripping.

A preferred material for the image-receiving layer is a nylon and preferably a nylon such as N-methoxymethyl polyhexamethylene adipamide which is available under the trade name of Nylon Type F8 from E. I. du Pont de Nemours & Co. Other materials suitable for image-receiving layers comprise a partially hydrolyzed polyvinyl acetate such as that commercially available under the trade name of Vinylite MA–28–18 from Bakelite Division, Carbide and Carbon Chemicals Co.; polyvinyl alcohol with or without plasticizers; baryta paper, i.e., a support having a baryta coating thereon; cellulose acetate with filler as, for example, one-half cellulose acetate and one-half oleic acid, and other materials of a similar nature, as is well known in the art.

While a rupturable container **18**, such as has been illustrated with the film unit of FIG. 1, provides a convenient means for spreading a liquid processing composition between layers of a film unit whereby to permit the processing to be carried out within a camera apparatus, the practices of this invention may be otherwise effected. For example, a photosensitive element, after exposure in suitable apparatus and while preventing further exposure thereafter to actinic light, may be removed from such apparatus and permeated with the liquid processing composition as by coating the composition on said photosensitive element or otherwise wetting said element with the composition following which the permeated, exposed, photosensitive element, still without additional exposure to actinic light, is brought into contact with the image-receiving element for image formation in the manner heretofore described.

It is also to be understood that the invention may be successfully practiced without the use of a film-forming material in the liquid processing composition. As an illustration, a nonviscous liquid processing composition is particularly applicable with the processing technique last mentioned above and may be applied to the exposed photosensitive element by imbibition or coating practices and may be similarly applied to the image-receiving element before said elements are brought into superposed relation or contact for carrying out the transfer of mobile, diffusible color-providing substances.

It is recognized that it has been previously proposed in U.S. Patents Nos. 2,661,293, issued December 1, 1953, and 2,698,244, issued December 28, 1954, both in the name of Edwin H. Land, to form a positive image by action of unexhausted developer diffused from unexposed areas of a photosensitive element to a superposed image-receiving element containing a reducible metallic salt, the diffused, unexhausted developer reducing the metallic salt to give a positive image in terms of a metallic pigment. The invention herein set forth is readily distinguished from the above-mentioned disclosure since it is herein contemplated that the unexhausted developer be utilized to react with a reducible organic material, and preferably a reducible polymer.

The processes of this invention may be similarly distinguished from prior proposals to utilize unexhausted silver halide developing agent in the formation of a positive transfer color image, such, for example, as the aforementioned U.S. Patent No. 2,661,293. The processes contemplated in said patent involve the transfer of unexhausted silver halide developing agent to the image-receiving material where it enters into a coupling or dye-forming reaction.

The processes of this invention may be similarly distinguished from the invention disclosed and claimed in my copending application Serial No. 599,122, filed July 20, 1956, now abandoned in favor of a continuation-in-part thereof, Serial No. 825,359, filed July 6, 1959. The processes of that invention utilize unexhausted developing agent to act upon a reducible color-providing substance, the reduced form of which is transferable, as distinguished from the nontransferable reducible substances of this invention.

While this invention has been illustrated by the formation of monochromatic color images, it is to be understood that it may be utilized in the formation of multicolor images. In such embodiments, the use of reducible polymeric materials may be employed to provide one or more of the requisite monochromatic images. The techniques of this invention are particularly useful in multicolor processes since they permit the use of color-providing substances which are photographically unreactive. By way of illustration, reducible polymeric materials such as contemplated herein may be employed in the multilayer delayed transfer processes disclosed and claimed in the copending application of Edwin H. Land and Howard G. Rogers, Serial No. 565,135, filed February 13, 1956, as, for example, to control a color-providing substance associated with the innermost emulsion. In such a multilayer embodiment, it may be desirable to utilize a developing agent having relatively low mobility or diffusibility to restrict the developing agent to its particular environment and associated reducible polymeric material. Use of such low mobility developing agents may avoid or reduce any need for any other barrier layer, such as disclosed in the said copending application, Serial No. 565,135.

The inventive concepts herein set forth are also adaptable for the formation of multicolored images in accordance with the photographic products and processes of the aforementioned U.S. Patent No. 2,647,049.

Similarly, the inventive concepts herein disclosed are adaptable for use in photosensitive screen products and processes wherein the photosensitive screen elements are prepared as disclosed in the said copending application of Howard G. Rogers, Serial No. 415,073, now abandoned, and also in the copending application of Edwin H. Land, Serial No. 448,441, filed August 9, 1954, now U.S. Patent No. 2,968,554.

Although the concepts of this invention have been illustrated in one-step, diffusion-transfer processes and possess unique advantages in such processes, it is contemplated that in certain instances these concepts also may be employed in multiple-step processes. In such cases, the emulsion medium should be one which is rendered more insoluble or impermeable by the action of the developing agent used to develop exposed areas, as by tanning, and is substantially unaffected by unexhausted developing agent in unexposed areas. After development is completed, a stronger developer or other reducing agent may be employed to reduce the reducible polymeric material. In the exposed areas, the stronger developing agent cannot permeate through the emulsion to reduce the reducible polymer, while in unexposed areas, it is capable of reaching and reducing the reducible polymer to release the color-providing substance for transfer.

Throughout the specification and appended claims, the expression "positive image" has been used. This expression should not be interpreted in a restrictive sense since

it is used primarily for purposes of illustration, in that it defines the image produced on the image-carrying layer as being reversed, in the positive-negative sense, with respect to the developed image in the photosensitive element. As an example of an alternative meaning for "positive image," assume that the photosensitive element is exposed to actinic light through a negative transparency. In this case, the latent image in the photosensitive element will be a positive and the image produced on the image-carrying layer will be a negative. The expression "positive image" is intended to cover such an image produced on the image-carrying layer. It is to be understood that certain embodiments of this invention may be used to obtain negative transfer images of the developed image, as hereinbefore set forth.

In preceding portions of the specification, the expression "color" has been frequently used. This expression is intended to include the use of one or more colors to obtain black.

Throughout the specification and claims, the expression "superposing" has been used. This expression is intended to cover the arrangement of two layers in overlying relation to each other either in face-to-face contact or in separated condition and including between them at least one layer or stratum of a material which may be a viscous liquid.

Since certain changes may be made in the above products and processes without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description or shown in the accompanying drawing shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. The process comprising developing an exposed silver halide emulsion with an aqueous alkaline solution containing a silver halide developing agent, said silver halide developing agent being present in such quantity per unit area of silver halide emulsion as to be substantially completely reacted in fully developed areas of said emulsion, forming in undeveloped areas of said emulsion as a result of said development an imagewise distribution of unoxidized silver halide developing agent having a concentration substantially inversely proportional to the degree of development per unit area of said silver halide emulsion, reducing a reducible polymer imagewise with said unoxidized silver halide developing agent, said reducible polymer being the product obtained by coupling the oxidation product of a color developer with a polyvinyl acetal formed from polyvinyl alcohol and an aromatic aldehyde selected from the group consisting of aromatic aldehydes containing benzene and naphthalene nuclei containing a hydroxyl group and having an available coupling position para to said hydroxyl group, the substituent formed by said coupling reaction being reducible by said unoxidized silver halide developing agent less readily than is said exposed silver halide but more readily than is said unexposed silver halide, said reduction of said substituent of said reducible polymer forming the leuco derivative of said substituent.

2. A process as defined in claim 1, wherein said substituent of said reducible polymer is colored, said leuco derivative is substantially colorless, the layer containing said reducible polymer is separated from superposition with said exposed silver halide emulsion after said leuco derivative has been formed, and said separated layer containing said reducible polymer treated with an acidic solution to stabilize the reduced and unreduced forms of said reducible polymer, thereby providing a negative transfer image in said polymer layer of the developed areas of said exposed silver halide emulsion.

3. A process as defined in claim 1, wherein said reducible polymer is the cyan coupling product of polyvinylsalicylal and the oxidation product of 2-amino-5-diethylaminotoluene, and said silver halide developing agent is toluhydroquinone.

4. A process as defined in claim 1, wherein said reducible polymer is the cyan coupling product of polyvinylsalicylal and N,2,6-trichloro-p-quinoneimine, and said silver halide developing agent is toluhydroquinone.

5. A process as defined in claim 1, wherein the portions of said reducible polymer unreduced by said silver halide developing agent are substantially impermeable to said aqueous alkaline solution, and portions of said reducible polymer which are reduced by said unoxidized silver halide developer are permeable to said aqueous alkaline solution, and a dye is diffused into and through said reduced, permeable portions of said reducible polymer to form a positive image of the developed areas of said exposed silver halide emulsion.

References Cited in the file of this patent

UNITED STATES PATENTS

2,538,257	Martin	Jan. 16, 1951
2,614,926	Land	Oct. 21, 1952
2,647,049	Land	July 28, 1953
2,661,293	Land	Dec. 1, 1953
2,698,798	Land	Jan. 4, 1955
2,704,711	Hanson	Mar. 22, 1955
2,774,668	Rogers	Dec. 18, 1956