May 25, 1965 H. G. ROGERS 3,185,567

PHOTOGRAPHIC COLOR PROCESS AND PRODUCT

Filed July 6, 1959

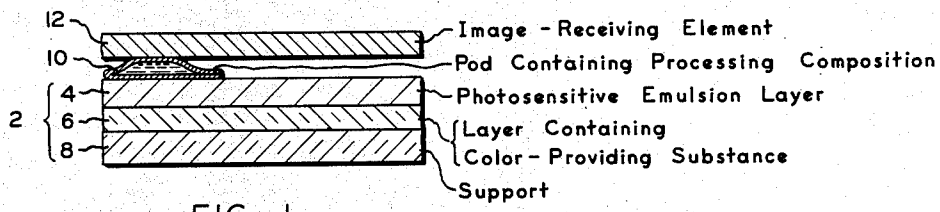


FIG. 1

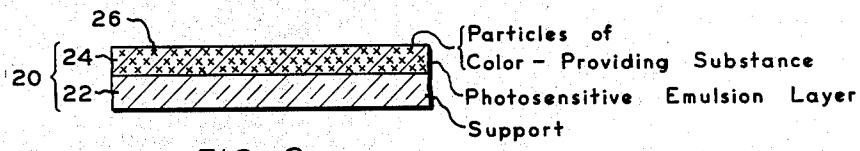


FIG. 2

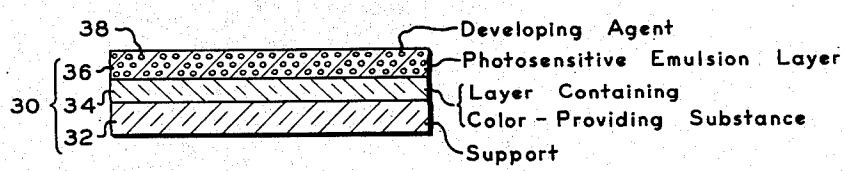


FIG. 3

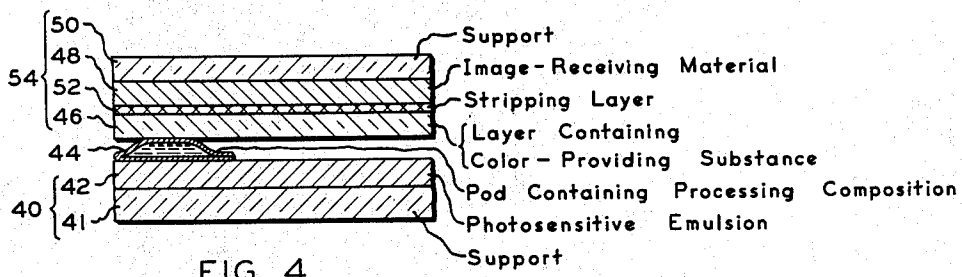


FIG. 4

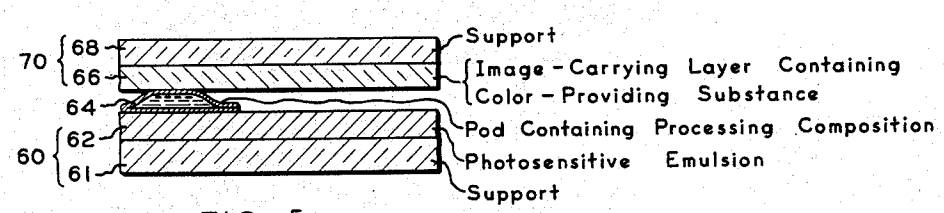


FIG. 5

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PHOTOGRAPHIC COLOR PROCESS AND PRODUCT

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Filed July 6, 1959, Ser. No. 825,359
30 Claims. (Cl. 96—3)

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 color-providing substance for the positive color record, a substance reducible by unreacted developing agent.

A primary object of this invention, therefore, is to provide novel color processes wherein an initially immobile or nondiffusible color-providing substance is rendered mobile or diffusible by the reducing action of unoxidized or unexhausted developing agent.

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 availability for diffusion of a color-providing substance is controlled by the developing agent, and the color-providing substance is nondiffusible until acted upon by unexhausted developing agent.

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 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 suitable for use in the process of this invention;

FIG. 3 is a diagrammatic cross-sectional view of another embodiment of a photosensitive element in accordance with this invention;

FIG. 4 is a diagrammatic cross-sectional view of a further modification of a photosensitive element suitable for obtaining a positive image in accordance with this invention; and

FIG. 5 is a diagrammatic cross-sectional view of a modification of a photosensitive element suitable for obtaining a negative image by the process of this invention.

In diffusion-transfer reversal processes of the type herein contemplated, an exposed photosensitive silver halide emulsion layer containing a latent color record 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 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 positive dye image utilizing the diffusble color components.

Another diffusion-transfer reversal color process, as disclosed and claimed in the copending application of Howard G. Rogers, Serial No. 748,421, filed July 14, 1958 (now U.S. Patent No. 2,983,606, issued May 9, 1961), as a continuation-in-part of Serial No. 415,073, filed March 9, 1954 (now abandoned), proposes to utilized 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 the copending ap-

plication of Howard G. Rogers, Serial No. 613,691, filed October 3, 1956 (now U.S. Patent No. 3,087,817, issued April 30, 1963), as a continuation-in-part of Serial No. 358,012, filed May 28, 1953, now 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 "immobilizing" mechanisms, that is, the color-providing components must be trapped, that is, immobilized, in the exposed portions of the photosensitive layer.

The novel diffusion-transfer 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 employ initially immobile or nondiffusible color-providing substances, which substances are rendered diffusible in unexposed areas of the photosensitive layer by the reducing action of unreacted or unexhausted silver halide developing agent. In the simplest embodiment of this invention, a color-providing substance is employed which is immobile until subjected to the reducing action of unexhausted silver halide developing agent, and which, when so acted upon by the unexhausted developing agent, is rendered diffusible or mobile.

By way of recapitulation, the novel processes of this invention depend upon the action of unexhausted developing agent to initially render a color-providing substance mobile. Thus, the color-providing substance is solubilized imagewise by the reducing action of unexhausted developing agent.

It will, therefore, be readily apparent that the novel diffusion-transfer 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 mobile in a processing liquid as a function of the reducing action of unoxidized silver halide developing agent. 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 they 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 which possess a functional group adapted to be reduced by unexhausted silver halide developing agent and, when so reduced, of being dissolvable in a processing liquid. It is also contemplated to use a color-providing substance which in its reduced 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 immobile color-providing 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 immobile or reducible color-providing substances and in unexposed areas will react with the reducible color-providing substance substantially to the exclusion of unexposed silver halide. It should be noted that, where a color-providing substance does not ordinarily possess a suitable oxidation potential, it is contemplated to adjust such potential to render it useful herein.

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 photosensitive element includes an immobile reducible color-providing substance capable of being reduced by unexhausted silver halide developer. 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, now U.S. Patent No. 3,087,816, issued April 30, 1963. 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 above-mentioned imagewise distribution of unexhausted silver halide developing agent present in the unexposed areas of the photosensitive element reduces a reducible color-providing substance uniformly distributed in the photosensitive element. The reduction product of the immobile color-providing substance is dissolvable in the liquid processing composition and is therefore mobile in the photosensitive element. An imagewise distribution of mobile or diffusible color-providing substance is thus created as a result of the reducing action of the unexhausted developing agent present in the unexposed areas. At least part of this imagewise distribution of mobile color-providing substance is transferred, by imbibition, to a superposed image-receiving layer or element, said transfer substantially excluding unreduced, immobile color-providing substance. 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, or a derivative thereof, which, in its initial condition, is not appreciably dissolvable in the liquid processing composition, at least during the period of imbibition. The immobile color-providing substance contains a functional group which is reducible by a silver halide developing agent to give a color-providing substance which is dissolvable in said liquid processing composition. The term "mobile color-providing substance" therefore refers to a color-providing substance rendered dissolvable in a liquid processing composition, and therefore mobile and diffusible, as the result of the reducing action of unexhausted silver halide developing agent.

As examples of suitable reducible color-providing substances which may be utilized in the processes of this invention, mention may be made of indophenol dyes which are initially immobile but are reducible by a silver halide

developing agent, e.g., toluhydroquinone, to the leuco indophenol form which is soluble in aqueous alkaline liquid processing compositions. Additional useful color-providing substances include substances containing a reducible quinone group, which substances are insoluble in aqueous alkaline processing compositions in the oxidized or quinone state but soluble therein in the reduced or hydroquinone state. In a similar manner one may use a reducible color-providing substance which is composed of a plurality of dye molecules joined together by a reducible grouping, for example, a disulfide (—S—S—) and which may be a dimer or a polymer. It is also within the scope of this invention to employ a color-providing substance associated with a reducible mordant and thus rendered immobile, and which is rendered soluble by the reducing action of the unexhausted silver halide developing agent.

In addition to the above-mentioned types of color-providing substances which are in the general nature of complete dyes or dye intermediates, it is also contemplated to employ a color coupler which contains a reducible group and which is immobile in the oxidized state but mobile in the reduced state. In a preferred embodiment such a reduced coupler may couple with the oxidation product of the silver halide developing agent to form a soluble or mobile dye which is transferable to the image-receiving material.

A further example of a suitable reducible color-providing substance utilizable in the processes of this invention is a heavy metal salt of a dye, which salt is less soluble in the alkaline liquid processing composition than is the oxide of said metal, for example, a silver salt of a dye, which salt is less soluble than silver oxide. The heavy metal salt should be one which is reducible by a silver halide developer but which is less readily reduced than is exposed silver halide and more readily reduced than unexposed silver halide.

Metallic complexes, or chelates, of dyes are also contemplated as reducible color-providing substances. Suitable metallic dye complexes are those which are stable to alkali, insoluble in alkali and which are reducible by silver halide developing agents to give a dye which is soluble in the alkaline processing composition. A particular advantage in the use of such metallic complexes lies in the fact that one atom of metal may complex with more than one molecule of dye. Thus, reduction by one unit of unexhausted developing agent may release more than one unit of dye, thereby providing a means of obtaining increased density and contrast.

Metallic complexes of dyes may be prepared by the oxidation of the metal ion in the presence of a suitable metallizable dye, as is well known in the dye art. Metals which have been found to give reducible metallic complexes include manganese and copper, i.e., manganic and cupric complexes of dyes. As illustrations of complexes contemplated, mention may be made of cupric complexes with o,o'-dihydroxy azo dyes and manganic complexes with β-diketone and β-ketonitrile dyes.

In a further embodiment of this invention, it is contemplated to utilize a reducible color-providing substance which is substantially colorless in the reducible or oxidized, immobile state, and which is colored and exhibits the properties of a dye in the reduced or mobile state. An example of such a colorless, reducible color-providing substance is a triazolium compound, such as that used hereinafter in Example 7. Such colorless, reducible color-providing substances may be advantageously incorporated in the silver halide emulsions, since they would not reduce the film speed by undesirable light absorption.

In addition to colorless, reducible color-providing substances, it is within the scope of this invention to utilize reducible color-providing substances which undergo a color change as a result of reduction or of a change in pH. Thus, the reducible color-providing substance will exhibit an absorption maximum, in the oxidized or immobile state, at a substantially lower wavelength than is exhibited after transfer to the image-receiving material. As an illustration of this technique, the reducible color-providing substance may be one which undergoes a color change at very low pH values, for example, pH 1 to 2. When incorporated in the photosensitive element under conditions imparting such a low pH, the reducible color-providing substance will exhibit an absorption maximum at a relatively low wavelength. Upon application of the alkaline liquid processing composition, the absorption maximum of the color-providing substance will be shifted to a higher wavelength imparting the desired color for the positive color record image.

It is further contemplated to utilize the reducible color-providing substances in the form of crystals which may be dispersed throughout the emulsion. In a preferred use of such crystals, it is contemplated to utilize polarizing crystals of the reducible color-providing substance. The use of polarizing crystals effectively reduces light absorption by the colored material and effectively increases the amount of light reaching the inner portions of that emulsion or of an emulsion located behind that emulsion. The size of the crystals is selected to provide the optimum, i.e., minimum, low covering power consistent with high resolution. The greatest increases in light transmission are obtained with fully oriented, needle-shaped crystals, but significant and advantageous increases in light transmission may be obtained by the use of unoriented polarizing crystals of any shape. The use of polarizing crystals of color-providing substances is disclosed and claimed in the copending application of Edwin H. Land, Serial No. 607,820, filed September 4, 1956, now U.S. Patent No. 2,997,390, issued August 22, 1961.

Whether the color-providing substance is utilized in the form of simple particles or of polarizing crystals, it is desirable that the light striking the emulsion not be scattered in the course of transmission. Thus, the particle or crystal should approximately match the index of refraction of the medium of the photosensitive emulsion, for example gelatin.

In a further embodiment of this invention, it is contemplated to control the availability for diffusion of a color-providing substance by the action of unexhausted developing agent on a portion of that color-providing substance. Thus, an ordinarily diffusible color-providing substance may be formed into particles or crystals, and the surface of said particle or crystal converted into a nondiffusible, reducible color-providing substance. The reducible surface or skin controls the diffusibility of all of the color-providing substance contained in the particle or crystal. Reduction of this skin of reducible color-providing substance renders all the color-providing substance diffusible, and offers a method of increasing density by release of more than one unit of color-providing substance per unit of unexhausted developer. Suitable skins of reducible color-providing substances may be formed by treating particles or crystals of suitable color-providing substances with oxidizing agents which affect only the surface of said particle or crystal. Similarly, one may form a reducible metallic complex with only the surface portion of the particle or crystal.

In addition to utilizing particles or crystals of a reducible color-providing substance, it is contemplated to employ the reducible color-providing substance in the form of particles comprising a skin of such color-providing substance around a core or nucleus of an inert, nonreducible material. This embodiment provides a greater surface area of reducible color-providing substance and renders it more readily available for reaction with unexhausted developing agent. The nucleus or core comprises a transparent material having an index of refraction such that no significant loss in light transmission occurs and may comprise a material such as aluminum hydroxide, suitable silicates and fluorides, or a suitable plastic material, such as cellulose acetate. Another advantage of this embodiment is that it offers a method of obtaining

uniform size particles of color-providing substances by starting with uniform size particles for the core or nucleus. By using a diffusible color-providing substance as the material forming the core or nucleus, one may increase the density of the positive image or modify its color.

As previously indicated, the reducible color-providing 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 solubility as between the initial, oxidized condition and its reduced condition in the liquid processing composition. While the color-providing substance in its oxidized or reducible state should be substantially insoluble in the liquid processing composition and thus immobile, it is desirable that the reduced or mobile color-providing substance have a high rate of diffusion in order to provide a high density in a minimum imbibition time.

The silver halide developing agent which is employed in conjunction with a reducible color-providing substance should exhibit a reduction potential such that in exposed areas it will develop exposed silver halide substantially to the exclusion of reaction with immobile or reducible color-providing substance and in unexposed areas will react with the reducible color-providing 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 the image-rceiving 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 reaction with, and release of, a color-providing substance to cause 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.

As examples of suitable silver halide developing agents, mention may be made of hydroquinone, toluhydroquinone, acetamidophenyl hydroquinone, p-anilino-hydroquinone, naphthylazohydroquinone, 2,4-diamino-phenol hydrochloride (Amidol), 2-octyl-hydroquinone, trimethyl-hydroquinone, and 4'-methylphenyl-hydroquinone. These developing agents may be used in combination with other developers e.g., 1-phenyl-3-pyrazolidone (Phenidone).

The physical embodiments of the present invention, as shown in FIGS. 1–3, generally involve photosensitive elements including a reducible color-providing substance and have associated therewith a liquid-carrying container, said container being so positioned that its liquid composition can be released and permeate the photosensitive emulsion. The liquid composition is preferably viscous and includes at least a solvent for the silver halide developing agent and also a solvent for the reduced or mobile color-providing substance.

The embodiment shown in FIG. 1 depicts a photosensitive element **2** which includes a support layer **8** carrying a layer **6** containing a reducible, immobile color-providing substance. A layer **10** of a photosensitive emulsion is cast over the layer **6** containing the immobile color-providing substance. A rupturable container or pod **10** carrying a liquid processing composition, which composition includes a silver halide developing agent and a solvent for the reduced color-providing substance, is associated with the photosensitive element **2** and is adapted to release the processing composition for spreading between said photosensitive element **2** and a superposed image-receiving element **12**.

FIG. 2 illustrates a photosensitive element **20** comprising a support layer **22** carrying a photosensitive emulsion layer **24** having dispersed therein particles **26** of a reducible color-providing substance. Associated with said photosensitive element **20** is a rupturable container or pod, not shown, containing a liquid processing composition, which composition includes a silver halide developing agent and a solvent for the reduced or mobile color-providing substance. It is further contemplated that the silver halide developing agent also may be present in the emulsion layer **24**, suitable precautions being taken to avoid interaction prior to processing after exposure, e.g., by incorporating each in droplets of mutually exclusive solvents. In such an embodiment, the silver halide developing agent may be omitted from the processing composition, or said composition may contain a portion of the required developing agent.

A further embodiment of this invention is shown in FIG. 3 wherein a photosensitive element **30** includes a support layer **32** and a layer **34** containing a reducible color-providing substance on one surface of said support layer **32**. A photosensitive emulsion layer **36** containing particles **38** of a silver halide developing agent dispersed therein is carried by said layer **34** of color-providing substance. Associated with said photosensitive element **30** is a rupturable pod or container, not shown, carrying a liquid processing composition, which composition includes at least a solvent for said dispersed developing agent and also a solvent for said reduced or mobile color-providing substance.

It will be apparent that, while the liquid processing composition has been described as including a solvent for the reduced or mobile color-providing substance, such solvent and such liquid processing composition as a whole should be a nonsolvent for the unreduced portions of the reducible color-providing substance.

As illustrated in the above-described FIGS. 1–3, the immobile color-providing substance may be initially present in a layer behind a photosensitive emulsion or it may be dispersed in the photosensitive emulsion. It is also contemplated that the immobile color-providing substance may be initially present together with a portion of the photosensitive silver halide in the form of a globule or clump in the photosensitive stratum.

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 the immobile, reducible color-providing substance is initially in the photosensitive element. It is also contemplated to initially dispose the immobile, reducible color-providing substance outside the photosensitive element, i.e., the element containing the photosensitive emulsion, for example in the image-receiving element. In such embodiments, as will be hereinafter described, one may obtain either a positive or negative image by rendering immobile color-providing substances diffusible by the reducing action of unexhausted developer.

A suitable means of carrying out this modification of the invention is illustrated in FIG. 4, wherein is shown a photosensitive element **40** comprising a support **41** carrying a photosensitive emulsion layer **42**, associated with a rupturable container or pod **44** containing a liquid processing composition. Superposed in processing relationship on said photosensitive element is an image-receiving element **54** comprising image-receiving layer **48** on a support **50** and having, on the face nearest the emulsion layer **42**, a stripping layer **52** and a layer **46** of a reducible color-providing substance. After exposure, the process-

ing composition contained in the rupturable pod **44** is spread evenly between the superposed elements. Development of the latent image present in the exposed emulsion layer **42** results in the formation of an imagewise distribution of unexhausted developing agent. This imagewise distribution of unexhausted developing agent diffuses to, and reduces, imagewise, the immobile color-providing substance present in a layer on the surface of the image-receiving element. The reduced color-providing substance is thus rendered mobile and diffuses to the layer **48** of image-receiving material to provide a positive image. After a suitable imbibition period, the photosensitive element is stripped apart from the image-receiving element. The layer of color-providing substance containing the unreduced color-providing substance, as well as the stripping layer, adhere to, and remain with, the photosensitive element on stripping.

A further embodiment of the invention, whereby a negative image may be formed, is shown in FIG. 5. A photosensitive element **60** comprises a support **61** carrying a photosensitive emulsion layer **62**. An image-receiving element **70** comprises a support **68** and an image-carrying layer **66** containing a uniform distribution of reducible, immobile color-providing substance. The photosensitive element is exposed and then processed, in superposed relationship with the image-receiving element, by the processing composition contained in a rupturable pod **64** and which is spread in a uniform layer between the superposed elements. The imagewise distribution of unexhausted developing agent reduces the immobile color-providing substance contained in the image-carrying layer and renders it mobile, whereby it diffuses out of that layer, thus providing a negative image. It will be apparent that the immobile color-providing substance should possess the desired color in the oxidized state, or be capable of being converted to such color, as by a change in the pH. The color-providing substance should be less substantive to the image-carrying material in the reduced state than in the oxidized state.

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 reducible 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.

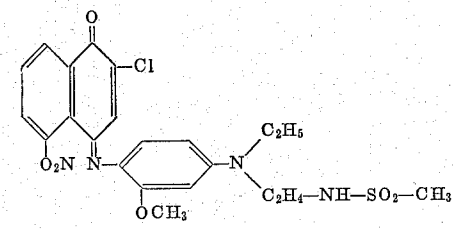
The following examples are intended to illustrate methods by which a positive color image may be obtained using a reducible color-providing substance, and are not intended to be interpreted in a limiting sense.

It should be noted that, except where so indicated, it is not necessary for the transferred, mobile color-providing substance to undergo a reaction in order to impart the desired color image.

Example 1

A photosensitive element similar to that illustrated in FIG. 1 is prepared by coating a subcoated cellulose acetate film base with a composition comprising 6% of an indophenol dye of the structure:

(I)



(prepared by oxidative coupling of 2,4-dichloro-5-nitro-1-naphthol and 4-N-ethyl-N-β-methylsulfonamidoethyl-2-methoxy-aniline) in a solution of 4% cellulose acetate hydrogen phthalate in a 50:50 mixture, by volume, of acetone and tetrahydrofuran, followed by a layer of a silver halide emulsion. 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 an image-receiving element, as said elements are brought into superposed relationship. The image-receiving element is prepared by coating a cellulose acetate coated, baryta paper with a solution comprising 4% N-methoxymethyl polyhexamethylene adipamide (a nylon) in 80% aqueous isopropanol. After an imbibition period of approximately two minutes, the image-receiving element and the photosensitive element are stripped apart. The image-receiving element is swabbed with a 5% aqueous ferricyanide solution to oxidize the transferred, reduced or leuco indophenol, giving a cyan positive image.

Example 2

A photosensitive element similar to that illustrated in FIG. 2 is prepared by coating a gelatin coated, cellulose acetate film base with a silver halide emulsion having dispersed therein the indophenol dye of Formula I. This silver halide emulsion is prepared by passing a mixture of 0.5 g. of the indophenol dye of Formula I, 2.5 cc. of ethyl acetate and 2.5 cc. of tritolylphosphate with 10 cc. of 2% gelatin containing a small amount of an emulsifying agent through an emulsifier five times. The resulting emulsion is mixed with 20 cc. of a silver halide emulsion, 5 cc. of water and a small amount of a wetting agent. After exposure, the photosensitive element is processed by the application of an aqueous liquid processing composition comprising:

	Percent
Sodium carboxymethyl cellulose	4.5
Sodium hydroxide	1.5
Potassium bromide	0.5
Sodium sulfite	0.5
Toluhydroquinone	0.5

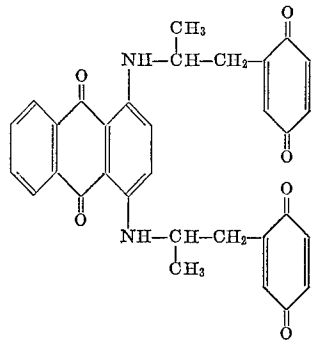
spread between the exposed photosensitive element and an image-receiving element as said elements are brought into superposed relationship. The image-receiving element is prepared in a manner similar to that employed in Example 1 and, after stripping, has a cyan positive image. In this example, the transferred leuco indophenol is oxidized by aerial oxidation.

Example 3

A photosensitive element similar to that described in Example 1, using a coating composition comprising 4%

of 1,4-bis-[α-methyl-β-(2',5'-dioxyphenyl)-ethylamino]-anthraquinone, of the formula:

(II)



in a solution of 4% cellulose acetate hydrogen phthalate in a 50:50 mixture, by volume, of acetone and tetrahydrofuran. After exposure, the photosensitive element is developed with an aqueous liquid processing composition comprising:

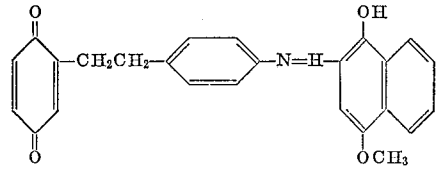
	Percent
Sodium carboxymethyl cellulose	4.5
Sodium hydroxide	2.0
Potassium bromide	0.5
Sodium sulfite	0.5
Toluhydroquinone	1.0

in contact with an image-receiving 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 cyan, positive dye image.

Example 4

The procedure described in Example 3 is repeated, using a coating solution comprising 3% of 2-(p-2',5'-dioxyphenethyl)-phenylazo-4-methoxy-1-naphthol of the formula:

(III)



in a solution of 4% cellulose acetate hydrogen phthalate in a 50:50 mixture, by volume, of acetone and tetrahydrofuran. Development of the exposed photosensitive element 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

yields, after an imbibition period of approximately two minutes, a magenta, positive dye image on the image-receiving sheet.

Example 5

A cyan, positive dye image is obtained when Example 1 is repeated, utilizing an aqueous liquid processing composition comprising:

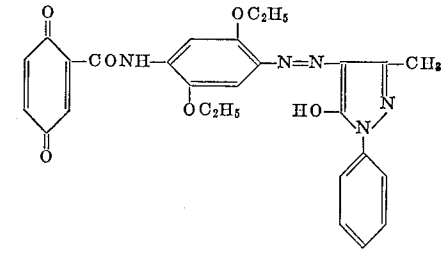
	Percent
Sodium carboxymethyl cellulose	4.5
Potassium bromide	0.5
Sodium hydroxide	2.0
Sodium sulfite	0.5
p-Anilino-hydroquinone hydrochloride	1.0

The transferred, leuco indophenol is oxidized by aerial oxidation.

Example 6

A photosensitive element is prepared in a manner similar to that described in Example 1, using a composition comprising 3% of 1-phenyl-3-methyl-4-[2',5'-diethoxy-4'-(2'',5''-dioxybenzamido)]-phenylazo-5-pyrazolone of the formula:

(IV)



in a solution of 4% cellulose acetate hydrogen phthalate in a 50:50 mixture, by volume, of acetone and tetrahydrofuran. The exposed photosensitive element is processed using an aqueous alkaline solution comprising:

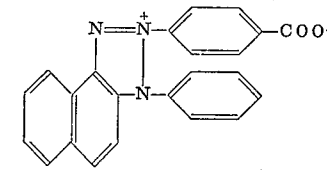
	Percent
Sodium carboxymethyl cellulose	4.5
Toluhydroquinone	0.5
Sodium hydroxide	2.0
Potassium bromide	0.5
Sodium sulfite	0.5

After an imbibition period of approximately two minutes, a pink positive image is obtained using an image-receiving element similar to that described in Example 1.

Example 7

A silver halide emulsion is prepared by mixing 25 cc. of a silver iodobromide emulsion with approximately 3 cc. of 10% acetic acid containing, as the reducible color-providing substance, 0.3 g. of the triazolium inner salt of the formula:

(V)

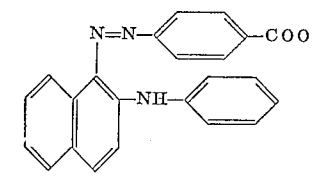


(Beil. 26, 74). This silver halide emulsion is coated on a gelatin coated, cellulose acetate film base and the resulting photosensitive emulsion exposed. An image-receiving element is prepared by casting a layer of polyvinyl alcohol on a cellulose acetate coated, baryta paper support using a 6% aqueous polyvinyl alcohol solution. An aqueous liquid processing composition comprising:

	Percent
Sodium carboxymethyl cellulose	4.5
Sodium hydroxide	5.0
Sodium sulfite	0.5
Potassium bromide	0.5
Toluhydroquinone	0.5

is spread between the exposed photosensitive element and the image-receiving element as said elements are brought into superposed relationship. After an imbibition period of approximately three minutes, the image-receiving element is separated and is found to contain a salmon, positive dye image. The reduced dye, as the free acid, has the formula:

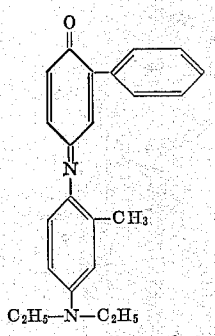
(VI)



Example 8

A photosensitive element is prepared in a manner similar to that described in Example 1, using a coating composition comprising 4% of the indophenol dye of the formula:

(VII)



(prepared by oxidative coupling of o-phenylphenol and 2-amino-5-diethylamino-toluene) in a solution of 4% cellulose acetate hydrogen phthalate in a 50:50 mixture, by volume, of acetone and tetrahydrofuran. After exposure, the photosensitive element is processed with an aqueous composition comprising:

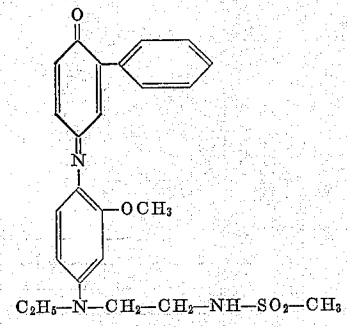
	Percent
Sodium hydroxide	3.0
Potassium bromide	1.0
Sodium sulfite	1.0
Toluhydroquinone	1.0
Sodium carboxymethyl cellulose	4.5

while in superposed relationship with an image-receiving element as described in Example 1, except that 0.6% of benzoyl peroxide is included in the solution of nylon to provide an oxidizing agent. After an imbibition period of approximately two minutes, the image-receiving element is separated and contains a cyan positive image.

Example 9

The procedure described in Example 8 is repeated, using a coating composition comprising 6% of an indophenol dye of the formula:

(VIII)



(prepared by oxidative coupling of o-phenylphenol and 4-amino - N - ethyl - N - (β - methylsulfonamidoethyl) - m-phenetidine oxalate) in a solution of 4% cellulose acetate hydrogen phthalate in a 50:50 mixture, by volume, of acetone and tetrahydrofuran. The photosensitive element is processed, after exposure, with an aqueous composition comprising:

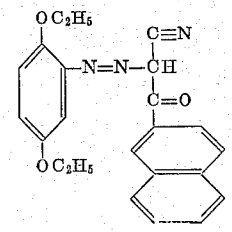
	Percent
Sodium carboxymethyl cellulose	4.5
Sodium hydroxide	2.0
Potassium bromide	0.5
Potassium sulfite	0.5
Toluhydroqinone	0.5

while in superposed relationship with an image-receiving element prepared as described in Example 8. Upon stripping after an imbibition period of approximately two minutes, the image-receiving element is found to contain a cyan positive image.

Example 10

A manganic complex of diethoxyphenylazo-2-naphthoylacetonitrile of the formula:

(IX)



is prepared by the oxidation of manganous acetate in the presence of the dye and phosphoric acid at a pH of 4.5–5 by permanganate (one-fourth molar equivalent of the manganous acetate) in 80% aqueous methyl Cellosolve at room temperature. The manganic complex is obtained as a phosphate salt. A photosensitive element is prepared by grinding 0.7 g. of the thus-prepared manganic complex in 2 cc. of water, adding 20 cc. of a silver halide emulsion to this dispersion, and coating the thoroughly stirred emulsion on a subcoated cellulose acetate film base. After exposure, the photosensitive element is processed with an aqueous composition comprising:

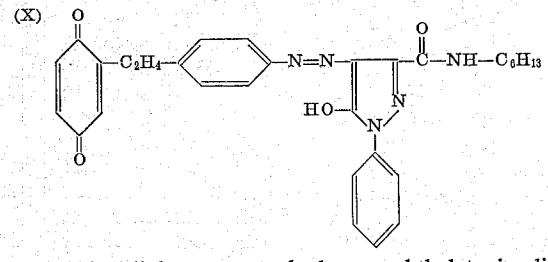
	Percent
Sodium carboxymethyl cellulose	4.5
Sodium hydroxide	2.0
Toluhydroquinone	0.5

while in superposed relationship with an image-receiving element prepared as described in Example 1. After an imbibition period of approximately three minutes, the image-receiving element is separated and contains a yellow, positive image.

Example 11

A subcoated cellulose acetate film base is coated with a solution comprising 3.0% of 1-phenyl-3-n-hexylcarboxamido-4-(p-2',5'-dioxyphenethyl)-phenylazo-5-pyrazolone of the formula:

(X)



and 2% cellulose acetate hydrogen phthalate in dimethoxyethane. After this coating had dried, a blue-sensitive silver iodobromide emulsion is applied. The resulting negative is exposed and then processed with an aqueous solution comprising:

	Percent
Sodium hydroxide	3.0
Sodium carboxymethyl cellulose	5.0
1-phenyl-3-pyrazolidone	1.2
2,5-bis-ethylenimino-hydroquinone	0.9
5-nitrobenzimidazole	0.18

This solution is spread between the exposed negative and a superposed image-receiving element prepared as described in Example 1. After an imbibition period of approximately one minute, the image-receiving element is stripped off and contains a yellow positive dye image.

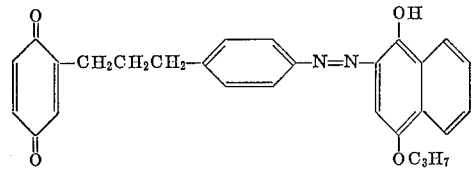
Another processing composition which is effective in the procedure described in Example 11 is an aqueous solution comprising:

	Percent
Sodium hydroxide	3.0
Sodium carboxymethyl cellulose	5.0
2,5-bis-ethylenimino-hydroquinone	0.9
5-nitrobenzimidazole	0.12

Example 12

The procedure of Example 11 is repeated, using, as the coating solution, a tetrahydrofuran solution containing 2% of cellulose acetate hydrogen phthalate and 3% of 2-(p-2',5'-dioxyphenylpropyl)-phenylazo-4-n-propoxy-1-naphthol of the formula:

(XI)



and green-sensitive silver iodobromide emulsion. After an imbibition period of approximately one minute, the image-receiving element is separated and contains a magenta positive image.

The processes disclosed herein are useful also in the formation of multicolor images. One such multicolor embodiment involves the use of a multilayer photosensitive element, as illustrated by the following example.

Example 13

A two-color photosensitive element is prepared as follows: a gelatin-coated film base is coated with an acetone-tetrahydrofuran (50:50 by volume) solution containing 4% of cellulose acetate hydrogen phthalate and 3% of 1,4-bis-[α-methyl-β-(2',5'-dihydroxyphenyl)-ethylamino]-anthraquinone. This coating is allowed to dry and then treated three times with a solution of 8% p-benzoquinone in aqueous methanol (80%) to oxidize the cyan dye to the quinone form. The sheet is then washed three times with aqueous methanol (80%) and five times with water to remove unreacted p-benzoquinone, unoxidized cyan dye and other soluble materials. A red-sensitive silver halide emulsion is then applied. An acetone solution containing 2% cellulose acetate hydrogen phthalate and 2% cellulose acetate is then applied, following by a coating of polyvinyl alcohol (Elvanol 71–30). A layer of yellow reducible dye is then applied using a dimethoxyethane solution of 2% cellulose acetate hydrogen phthalate and 3% 1-phenyl-3-n-hexylcarboxamido-4-(p-2',5'-dioxyphenethyl)-phenylazo-5-pyrazolone (Formula X), followed by a layer of blue-sensitive silver halide emulsion. After exposure, this photosensitive element is processed with an aqueous processing composition comprising:

	Percent
Sodium hydroxide	2.0
Sodium carboxymethyl cellulose	4.5
1-phenyl-3-pyrazolidone	1.8
Xylohydroquinone	0.6
5-nitrobenzimidazole	0.24

while in superposed relationship with an image-receiving element prepared as described in Example 1. After an imbibition period of approximately three minutes, the image-receiving element was stripped apart from the photosensitive element and contained a two-color, positive image.

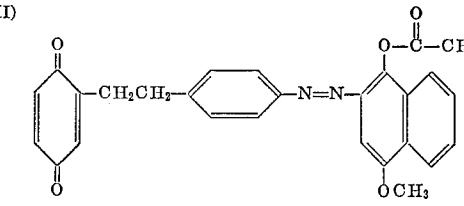
It will be noted that a number of the reducible dyes disclosed herein are quinones of compounds which are useful as dye developers in the processes disclosed and claimed in the previously mentioned, copending application, Serial No. 748,421. These quinones are prepared by selective oxidation of the hydroquinonly radical of such dye developers, e.g., by oxidation with p-benzoquinone. It has been found that the use, as a reducible dye, of the quinone form of the dye developer gives a delay in the availability for diffusion of the dye as compared with the use, as a dye developer, of the same dye in its hydroquinone form. Thus, when the procedure described in Example 11 was repeated under the same conditions except that 2% of 1-phenyl-3-n-hexylcarboxamido-4-(p-2',5'-dihydroxyphenethyl)-phenylazo-5-pyrazolone was used, it was observed that the density build up from the reducible dye was slower by at least several seconds than the density build up using the dye developer. When the transfer density was plotted as a function of imbibition time, the two curves were similar in shape, the density from the reducible dye was initially lower but increased steadily so that the total $D_{max.}$ after a minute was comparable in both instances. The reducible dye process thus provides a delay in the diffusibility of the image dye, and provides a means of preventing premature transfer.

Mention has already been made of the utilization of the reducible color-providing substance in a form which is colorless or which, in the reducible form, exhibits an absorption maximum at a substantially lower wave length than is exhibited after transfer. Another method of effecting a temporary hypsochromatic color shift is to suitably react an auxochrome of the reducible color-providing substance, e.g., by forming an ester of naphtholic hydroxyl group which is ortho to an azo group. The resulting ester may be hydrolyzed during processing to effect a bathochromic color shift to the desired longer wave length. Several methods of accomplishing such color changes are described in the copending application of Howard G. Rogers, Serial No. 789,080, filed January 26, 1959. Use of a color-shifted reducible dye permits incorporation of the dye in the emulsion layer. The following example illustrates the use of a color-shifted, hydrolyzable derivative of a reducible dye.

Example 14

A photosensitive element is prepared by coating a film base with a tetrahydrofuran solution containing 2% of cellulose acetate hydrogen phthalate and 3% of 1-acetoxy-2-(p-2',5'-dioxyphenethyl)-phenazo-4-methoxy-naphthalene of the formula:

(XII)



prepared as described in the copending application of Elbert M. Idelson, Serial No. 788,745, filed January 26, 1959, now U.S. Patent No. 3,086,005, issued April 16, 1963). After this coating has dried, a green-sensitive silver iodobromide emulsion is applied and the photosensitive element is exposed. Processing is effected with an aqueous composition comprising:

	Percent
Sodium carboxymethyl cellulose	5.0
Sodium hydroxide	3.0
1,5-bis-ethylenimino-hydroquinone	0.9
1-phenyl-3-pyrazolidone	1.2
5-nitrobenzimidazole	0.16

while the photosensitive element is maintained in a superposed relation with an image-receiving element prepared as described in Example 1. After an imbibition period of approximately one minute, the image-receiving element was separated and contained a magenta positive image. Examination of the processed photosensitive element showed that the unreduced, reducible dye present in exposed areas was still yellow, indicating that hydrolysis of the acetoxy group had not been effected. This was due to the fact that quinone group had not been reduced and the reducible dye was too insoluble in the quinone form to permit the hydrolysis to occur. It should be noted that the unexposed areas of the photosensitive element were magenta, due to the presence of residual, untransferred reduced dye. A magenta positive on a yellow background was thus obtained in the processed negative element in addition to the positive transfer image.

It should be noted that a negative image may be obtained, in addition to a positive transfer image, by appropriate treatment of the exposed and processed photosensitive element, as illustrated in the following example.

Example 15

The procedure of Example 11 is repeated using, as the coating solution, an acetone-tetrahydrofuran (50:50 by volume) solution containing 2% of cellulose acetate hydrogen phthalate and 3% of 2-(p-2',5'-dioxyphenethyl)-phenylazo-4-n-propoxy-1-naphthol. After an imbibition period of approximately one minute, using an aqueous processing composition comprising:

	Percent
Sodium carboxymethyl cellulose	5.0
Sodium hydroxide	3.0
2,5-bis-ethylenimino-hydroquinone	1.0
5-nitrobenzimidazole	0.12

the image-receiving element is separated and contains a magenta positive image having a $D_{max.}$ of 0.99. The negative was bleached and fixed out, and the emulsion layer stripped off. A negative magnenta image having a $D_{min.}$ of 0.08 was present in the dye layer. The presence of the negative image in the dye layer illustrates the nondiffusibility of the unreduced, reducible dye.

Example 14 has demonstrated that the unreduced portions of the hydrolyzable reducible dye do not undergo hydrolysis. It is also contemplated to locate the hydrolyzable linkage between the dye portion and the reducible group or portion of the hydrolyzable reducible dye. In unexposed areas, unexhausted developing agent will reduce the reducible group to render the dye soluble, at which point hydrolysis will occur. This will release a smaller, nonreactive dye for transfer to the image-receiving layer. If the reduced form of the reducible group which is split off by hydrolysis is itself a reducing agent, it may reduce another molecule of reducible dye (and this cycle may continue in chain-like fashion), thus effecting the transfer of more than one unit of image dye per unit of unexhausted developer.

In integral multilayer negatives for forming multicolor images, it is desirable to localize the action of the imagewise distribution of unexhausted developer which is formed in each emulsion layer. This may be accomplished by the use of low mobility silver halide developing agents which are initially present in the emulsion layers. Their mobility is such that the developing agent will not diffuse to a reducible dye other than the one which is associated with the emulsion in which the developing agent is located, at least during the imbibition period. Suitable developing agents of this type include hydroquinones which have "ballast groups," e.g., long chain alkyl substituents. Another method of controlling or localizing the action of the silver halide developing agent is to provide a barrier layer between each set of emulsion and its associated reducible color-providing substance. This barrier layer contains an oxidizing agent which is effective to oxidize any developing agent which diffuses between emulsion layers. The silver halide developing agent is incorporated in each emulsion layer or in an adjacent layer. If necessary, interlayers, e.g., of gelatin, may be provided to further separate the reacting materials and avoid diffusion to the wrong reducible dye.

Illustration has already been made of the use of indophenol (or more precisely, indoaniline) dyes as reducible dyes. It is also contemplated to form reducible dyes of all colors by attaching indophenol groups to the appropriate dyes. Upon reduction in unexposed areas, the reducible dye is transferred in the leuco form. The leuco indophenol groups of the transferred dyes are split (to prevent oxidation back to the colored indophenol form) by an acid contained in the image-receiving layer or by swabbing with a suitable acid. Appropriate precautions should be taken to prevent aerial oxidation of the leuco indophenol group prior to the acid treatment.

Mention has been made above of the use of color couplers containing reducible groups. As an example of such color couplers, mention may be made of phenolic, anilino, and activated methylene color couplers having an available coupling position and also having a reducible substituent, which couplers are nondiffusible in the unreduced state. In exposed areas, the developing agent is oxidized and is unavailable to reduce the reducible coupler, although if it is a color developer, its oxidation product may couple to form an insoluble dye. In unexposed areas, the unexhausted developing agent reduces the reducible coupler and renders it available for image formation. If the unexhausted silver halide developing agent used to reduce the reducible coupler forms an oxidation product capable of coupling with the coupler, a diffusible dye may be formed by such coupling. If the developing agent is not of this type, the reduced, reducible coupler which is transferred may be coupled with the oxidation product of a color developer or with a diazonium salt. Suitable precautions should be taken to prevent reduction of the diazonium salt by the reduced coupler or by unexhausted developing agent.

In still another embodiment of this invention, the reducible color-providing substance contains a substituent which is specific to making the reduced form thereof soluble in an organic solvent. In this embodiment, it is preferable to use an image-receiving layer which is specific to said organic solubilizing group. This is very useful in monochrome processes, and particularly in the formation of black dye images, as transfer image stain from other reagents is eliminated by the specific dyeability of the image-receiving material.

It is also contemplated to use basic dyes as color-providing substances in the processes of this invention. Particularly suitable basic dyes are those which will form salts, e.g., quaternary salts, in the oxidized form but do not form salts in the reduced form. The oxidized basic dye is rendered nondiffusible by forming a salt with a sulfonated compound, e.g., a sulfonated dye or a sulfonated polymer. In either situation, reduction of the basic dye by unexhausted developing agent results in the splitting of the salt. If the salt is with a sulfonated dye, either the basic or sulfonated dyes may be transferred. Transfer of both the basic dye and the sulfonated dye released by the splitting of the salt results in the transfer of two units of dye per unit of unexhausted developing agent and thus facilitates high transfer densities.

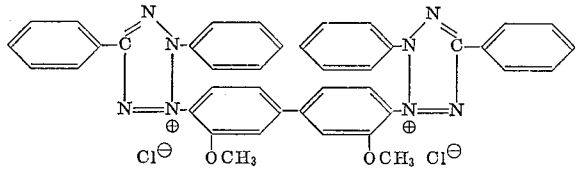
Example 7 illustrated the use of triazolium salts as reducible dyes. The triazolium salt of Formula V is an inner salt, and the formazan formed upon reduction is soluble. It is also contemplated to use reducible quaternary salts, e.g., triazolium and tetrazolium outer salts whose solubility in aqueous media is derived from the quaternary charge, and which form salts with other substances. These quaternary compounds are capable of forming salts with acids as a result of the quaternary charge, but reduction eliminates the quaternary charge as a result of which the ability to form a salt which will hold the dye is lost. These compounds may thus be characterized as reducible mordants whose mordanting ability is destroyed by reduction. These reducible quaternary salts may be used to immobilize acid dyes by the formation of salts, in which event a transfer image is obtained in terms of acid dye released by reduction of the tetrazolium or triazolium ring. In another embodiment, nontransfer, direct positive images may be obtained in terms of the formazan formed upon reduction, by forming a salt of the tetrazolium or triazolium compound with a long chain organic acid, e.g., the alkylnaphthalene sodium sulfonate available under the trade name Alkanol B (E. I. du Pont de Nemours & Co., Wilmington, Delaware). Direct positive multicolor images may be ob-

tained by bleaching to remove silver and removing unreduced tetrazolium salts. If the latent image is developed to give a low covering power negative image, bleaching may be omitted if a rapidly formed image is desired.

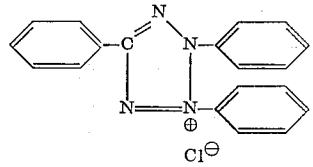
Many of the salts so formed have been found to be alkali-insoluble, even though one or both of the dye and quaternary compounds may have been soluble in alkali.

The following compounds are examples of tetrazolium and triazolium compounds which form reducible salts with acids, e.g., acid dyes:

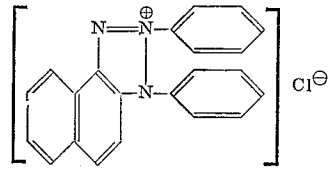
Tetrazolium Blue: [1]



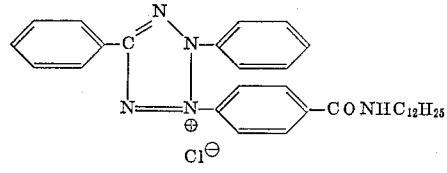
Tetrazolium Triphenyl: [1]



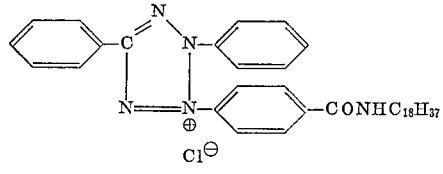
2,3-diphenyl-naphthotriazolium chloride:



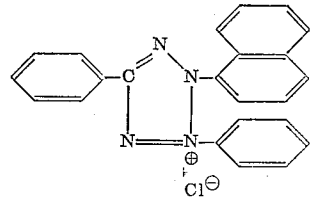
2-(4'-N-dodecyl-carboxamido)-phenyl-3,5-diphenyl-tetrazolium chloride:



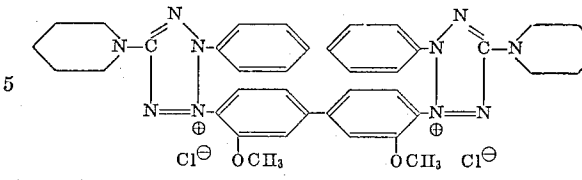
2-(4'-N-octadecyl-carboxamido)-phenyl-3,5-diphenyl-tetrazolium chloride:



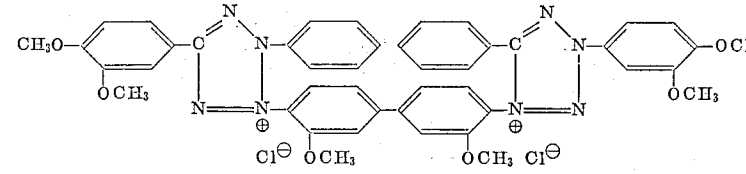
Tetrazolium α-naphthyl: [1]



Piperonyl Tetrazolium Blue: [1]

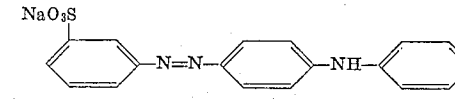


Veratryl Tetrazolium Blue: [1]

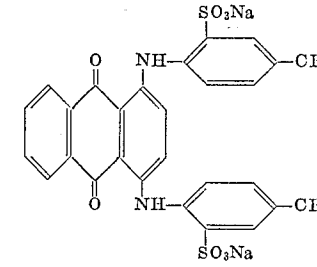


The following dyes are given as examples of acid dyes which have been used to from reducible tetrazolium or triazolium dye salts (reference is to the Colour Index, 2nd edition, 1956):

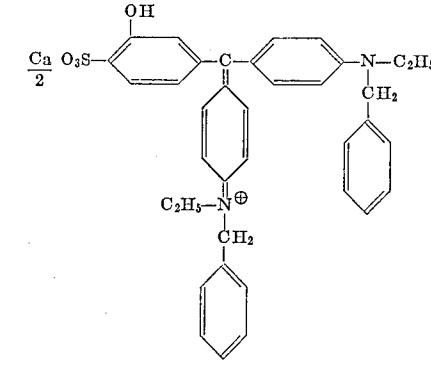
C.I. 13065 (C.I. Acid Yellow No. 36):



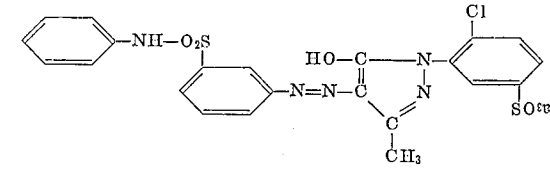
C.I. 61570 (C.I. Acid Green No. 25):



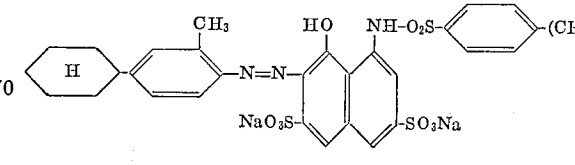
C.I. 42052 (C.I. Acid Blue No. 5):



C.I. 18900 (C.I. Acid Yellow No. 29):

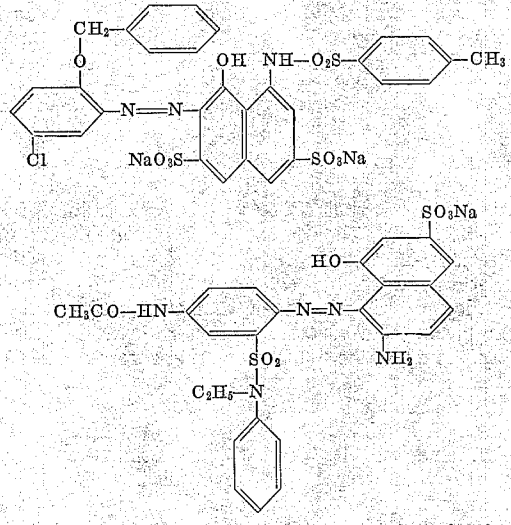


C.I. 18130 (C.I. Acid Red No. 155):



[1] Commercially available from The Synthetical Laboratories, 5556 Ardmore Avenue, Chicago, Illinois.

C.I. 18135 (C.I. Acid Red No. 172):



The formation of direct positive, nontransfer images using reducible quaternary salts is illustrated by the following example.

Example 16

Alkanol B is dissolved in 30 cc. of 10% gelatin, which had been warmed, to give a 6% solution. Tetrazolium Blue is dissolved in 20 cc. of methanol to give a 2% solution. The Tetrazolium Blue solution is warmed and added to the warm gelatin-Alkanol B solution. The solutions are mixed and then chilled, noodled and washed 7.5 cc. of the resulting dispersion of the white Tetrazolium Blue-Alkanol B salt are added to 7.5 cc. of water and 10 cc. of green-sensitive gelatino silver halide emulsion, mixed, and then coated on a film base. After exposure the photosensitive element is processed with an aqueous composition comprising:

	Percent
Sodium hydroxide	3.0
Sodium carboxymethyl cellulose	5.0
2-octyl-hydroquinone	1.0
5-nitrobenzimidazole	0.06

while in superposed relationship with an image-receiving element prepared as described in Example 1. After approximately one minute, the photo-sensitive element was separated and contained a positive blue-purple image. Substantially no loss in film speed or sensitivity was obtained.

The following example illustrates the use of a tetrazolium salt of an acid dye.

Example 17

A dispersion of the Tetrazolium Blue salt of C.I. Acid Red No. 172 is obtained by adding 4% of the C.I. Acid Red No. 172 and 1.93% of Tetrazolium Blue to a methanol-tetrahydrofuran (50:50 by volume) solution containing 4% cellulose acetate hydrogen phthalate. The dye and tetrazolium compound go into solution as the salt is formed, and NaCl precipitates out. The resulting solution is filtered or decanted to remove NaCl and other insoluble materials, and then is coated on a film base. A silver halide emulsion is applied by coating a composition comprising 20 cc. of green-sensitive galatino silver halide emulsion, 10 cc. of water and 5 cc. of a 2-octyl-hydroquinone dispersion (containing 7.5% of 2-octyl-hydroquinone). When exposed and processed in the manner described in Example 16, a positive transfer image in C.I. Acid Red No. 172 is obtained. Examination of the photosensitive element reveals a positive image in terms of the formazan formed upon reduction of the Tetrazolium Blue. The unreduced salt remains in place as it is insoluble in alkali.

Positive transfer images also may be obtained by forming a reducible tetrazolium or triazolium salt of a sulfonated color coupler, the sulfonate being nondisplaceable by the oxidation product of a color developer. In exposed areas, the oxidized color developer couples with the reducible coupler salt but forms a nondiffusible dye. In unexposed areas, the color developer reduces the tetrazolium group, thus splitting the salt, and the oxidized color developer coupled to form a soluble dye which transfers to the image-receiving layer.

Reducible quaternary salts, e.g., of tetrazolium and triazolium compounds, also may be formed with sulfuric acid esters of luco vat dyes.

The above examples have illustrated the formation of images by the reducing action of unexhausted silver halide developing agent on a reducible color-providing substance, which may be a dye or a dye intermediate, or a derivative thereof. The use of a reducible salt or mordant has illustrated how a color-providing substance, which is itself nonreducible, may be modified to provide a reducible color-providing substance useful in the processes of this invention. In addition, the creation of a visible image, e.g., in terms of an imagewise distribution of a diffusible color-providing substance, may be effected by the reducing action of unexhausted developing agent upon a reducible material, e.g., a polymer or a solvent, which controls the diffusibility of the color-providing substance. Processes of this type are described and claimed in my copending application, Serial No. 646,384, filed March 15, 1957 (now U.S. Patent No. 3,015,561, issued January 2, 1962), and are illustrated by Example 3 of that application. In another embodiment, negative transfer images are obtained by the reducing action of unexhausted developing agent upon a colored reducible polymer, e.g., the product obtained by coupling the oxidation product of a color developer with a polymeric color coupler such as polyvinyl salicylal, as illustrated by Examples 1 and 2 of said application, Serial No. 646,384.

The above examples have illustrated the formation of an image by the reducing action of unexhausted silver halide developing agent upon a color-providing substance, as a result of which a color-providing substance is rendered diffusible or is caused to change its color. It is also contemplated to render a reducible color-providing substance nondiffusible as a result of reduction by unexhausted developing agent, and to transfer the unreduced, reducible color-providing substance. An example of such a reducible color-providing substance is a tetrazolium salt, such as one of those referred to above but in the form of the chloride salt, which is soluble in an alkaline processing composition and which forms a nondiffusible formazan upon reduction. In unexposed areas, the unexhausted developing agent will reduce the tetrazolium chloride to the insoluble formazan. In exposed areas, the silver halide developing agent will be exhausted reducing the exposed silver halide, and the thus unreacted tetrazolium chloride will transfer to an image-receiving material, where it may be reduced to the insoluble formazan, e.g., by a nondiffusible reducing agent (which need not be a silver halide developing agent) or by an after-applied reducing agent. The transfer image will be a negative image in terms of the developed latent image.

A number of reducible color-providing substances disclosed herein, e.g., reducible dyes, are mobile or immobile depending upon their oxidation-reduction state. Such dyes include a group, which, when reduced, provides a solubilizing group, so that the dye is transferable, i.e., diffusible in the processing composition, substantially only in the reduced form. An example of such a group is a benzoquinone group, which is reducible to the corresponding dihydroxyphenyl group, which in turn is effective to solubilize the dye. Color-providing substances whose diffusibility or nondiffusibility depend upon the oxidation-reduction state of a diffusion-controlling group may be referred to as "redoluble" color-providing substances. The diffusion-controlling group may be one which is re-

ducible and upon reduction provides solubilizing groups, as illustrated by the reducible dyes containing reducible quinone radicals. Another group of color-providing substances which may be characterized as redoluble color-providing substances constitutes reagents which are rendered nondiffusible by oxidation, e.g., dyes which contain an oxidizable solubilizing group. One such group of oxidizable redoluble dyes is the dye developers of the previously mentioned copending application of Howard G. Rogers, Serial No. 748,421, wherein the solubilizing group is a dihydroxyphenyl group which is oxidizable to the corresponding quinone. The reducible or oxidizable solubilizing group may be referred to as a redoluble group. The reducible color-providing substances of this invention whose solubility is determined by the oxidation-reduction state of a solubilizing group may be referred to as reducible redoluble dyes.

This invention may be practiced with direct reversal emulsions, such as internal latent image emulsions which are processed to obtain positive images by reversal development. In such processes, development occurs in portions of the emulsion corresponding to the unexposed areas. Development is effected in the presence of a reagent capable of fogging the emulsion. Internal latent image emulsions are known in the art, as are fogging agents for effecting development of such internal latent image emulsions to obtain a positive image. As an example of suitable fogging agents, mention may be made of hydrazines.

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 provided 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 wtih 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 **10** 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. 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 technique described in the copending application of Edwin H. Land, Serial No. 498,672, filed April 1, 1955.

The image-receiving element or material 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. 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. 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 therein; 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 **10**, 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 render an immobile color-providing substance diffusible.

It has heretofore been proposed to utilize unexhausted silver halide developing agent in the formation of a positive transfer color image; see, for example, U.S. Patent No. 2,661,293, issued to Edwin H. Land on December 1, 1953. 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 are readily distinguishable from such processes in that the unexhausted silver halide developing agent is utilized to render mobile or diffusible an initially immobile color-providing substance. No similar role is performed by the unexhausted developer in the processes of said patent.

Reducible color-providing substances may be employed to provide one or more of the requisite monochromatic images for multicolor reproduction. By way of illustration, reducible color-providing substances 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.

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 color-providing substance. Use of such low mobility developing agents may avoid or reduce any need for a barrier layer, such as disclosed in the said copending application, Serial No. 565,135. It is to be noted that where reducible color-providing substances are utilized in a multicolor photosensitive element, the reduced or mobile color-providing substance should be substantially unreactive in any differently sensitized emulsion area. Thus, if the mobile form of the color-providing substance is itself capable of developing exposed silver halide, such mobile color-providing substance should be a substantially less effective developing agent than the developing agent employed to develop the latent image of any emulsion layer through which the mobile color-providing substance must diffuse, and should be too weak a reducing agent to reduce any reducible dye with which it may come into contact during diffusion to the image-receiving layer.

The inventive concepts herein set forth are also adaptable for the formation of multicolored images in accordance with the photographic products and processes of U.S. Patent No. 2,647,049, issued July 28, 1953 to Edwin H. Land.

Similarly, the inventive concepts herein disclosed are adaptable for use in photosensitive screen products and processes such as disclosed and claimed in the copending application of Edwin H. Land, Serial No. 448,441, filed August 9, 1954, now U.S. Patent No. 2,968,554, issued January 17, 1961. Such screen negatives comprise a plurality of minute photosensitive portions arranged in a screen manner, and the reducible color-providing substance being located in or behind the various emulsions. Since the unreduced, reducible color-providing substance is nondiffusible until reduced, it may be used in a layer over the emulsion with the developing agent being located in or behind the emulsion. Where the reducible color-providing substance is of the right color, it may act as a filter and be coated over a panchromatic emulsion; alternatively appropriate filters may be used with such an emulsion.

Although the concepts of this invention have been illustrated in one-step, diffusion-transfer reversal processes and possess unique advantages in such processes, it is contemplated that in certain intances these concepts also may be employed in multiple-step processes. In such cases the reducible color-providing substance should be one which is rendered more insoluble or nondiffusible by the action of the developing agent used to develop exposed areas, as by coupling therewith, 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 color-providing substance. In the exposed areas, the color-providing substance remains nondiffusible, although reduced, due to the action of the exhausted developing agent, and the color-providing substance present in unexposed areas is diffused to a superposed image-receiving material. Where the diffused color-providing substance does not possess the desired color, any necessary reaction to obtain such color may be performed concurrently with, or subsequent to, diffusion.

While the processes of this invention have been disclosed as being of primary utility in the formation of color images by a diffusion-transfer reversal process, the techniques herein disclosed are also suitable for use in preparing a direct color negative image. Thus, a photosensitive element containing an initially immobile color-providing substance may be processed in accordance with the disclosure therein, the unexhausted silver halide developing agent being utilized to render all of the color-providing substance present in unexposed areas mobile or soluble in the processing composition, thus washing out the color-providing substance in such unexposed areas to leave them clear. The thus developed negative may be subjected to a silver bleach treatment to remove the developed silver from the exposed areas, and silver halide from the unexposed areas may also be removed by means of a suitable fixing bath, in accordance with well-known procedures. The resulting negative contains a negative image in terms of the color-providing substance.

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.

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 viscous liquid.

This application is in part a continuation of my copending application, Serial No. 599,122, filed July 20, 1956 (now abandoned).

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. A photographic process comprising exposing a photosensitive element, said element including a photosensitive silver halide emulsion, developing said exposed silver halide emulsion with a silver halide developing agent, said silver halide developing agent being present in such quantity per unit area of said silver halide emulsion as to be substantially completely exhausted in fully exposed and developed unit areas of said silver halide emulsion, providing, as a function of said development, an imagewise distribution of unoxidized, unexhausted silver halide developing agent in undeveloped areas of said silver halide emulsion, transferring, by diffusion, at least a portion of said imagewise distribution of unoxidized, unexhausted silver halide developing agent to a first superposed layer containing a reducible organic color-providing substance, said reducible organic color-providing substance being substantially nondiffusible and also being reducible by said unoxidized silver halide developing agent and having an oxidation potential less than that of exposed silver halide of said silver halide emulsion and greater than that of unexposed silver halide of said silver halide emulsion, reducing said reducible organic color-providing substance with said transferred, unoxidized silver halide developing agent, said reduction of said reducible organic color-providing substance providing a reduction product more diffusible than said reducible organic color-providing substance, transferring, by diffusion, said more diffusible reduction product to a second superposed layer, and separating said second superposed layer from said first superposed layer after said diffusible reduction product has been transferred.

2. A process as defined in claim 1, wherein said diffusible reduction product is a dye.

3. A process as defined in claim 1, wherein said diffusible reduction product is a color coupler, and including the step of coupling said color coupler to provide a dye.

4. A process as defined in claim 1, wherein said reducible organic color-providing substance is a dye.

5. A process as defined in claim 1, wherein said reducible organic color-providing substance is a reducible salt of a dye.

6. A process as defined in claim 1, wherein the reduction product of said reducible organic color-providing substance has a color different from that of said reducible organic color-providing substance.

7. A process as defined in claim 1, wherein said reducible organic color-providing substance is a reducible mordant.

8. A process as defined in claim 1, wherein said silver halide developing agent is a hydroquinone.

9. A process as defined in claim 1, wherein said reducible organic color-providing substance is an indoaniline dye.

10. A process as defined in claim 9, including the step of oxidizing the leuco indoaniline formed by reduction of said indoaniline dye after said leuco indoaniline has been transferred to said second superposed layer.

11. A process as defined in claim 1, wherein said reducible organic color-providing substance is a triazolium salt.

12. A process as defined in claim 1, wherein said reducible color-providing substance is a tetrazolium salt.

13. A process as defined in claim 1, wherein said reducible color-providing substance is selected from the group consisting of azo and anthraquinone dyes which contain a benzoquinone group reducible by said unoxidized silver halide developing agent.

14. A process as defined in claim 1, wherein said reducible color-providing substance is a metallic complex of a dye.

15. A process as defined in claim 1, wherein said reducible organic color-providing substance includes a quinonyl radical which is reducible by said unoxidized silver halide developing agent.

16. A process as defined in claim 15, including the step of hydrolyzing said reduction product.

17. A process as defined in claim 1, wherein said reducible organic color-providing substance contains a reducible radical which includes a quaternary nitrogen atom.

18. A process as defined in claim 1, wherein said first superposed layer containing said reducible color-providing substance is positioned in said photosensitive element and including the steps of reducing, with said unoxidized silver halide developing agent, substantially all of said reducible organic color-providing substance present in unexposed areas of said exposed silver halide emulsion, removing substantially all of said more diffusible reduction product from said emulsion, removing the silver present in developed areas of said emulsion, and removing the silver halide present in undeveloped areas of said emulsion.

19. In a process of forming a photographic image in color, the steps which comprise exposing a photosensitive element, said element including a photosensitive silver halide emulsion and a nondiffusible reducible organic color-providing substance which is less reducible than exposed silver halide and more reducible than unexposed silver halide, developing a latent image contained in said exposed photosensitive element with a silver halide developing agent to provide in unexposed areas of said emulsion an imagewise distribution of unexhausted silver halide developing agent, reducing said nondiffusible reducible organic color-providing substance present in unexposed areas of said photosensitive element with said unexhausted silver halide developing agent, and transferring, by imbibition, at least a portion of the thus reduced organic color-providing substance to a superposed image-receiving material, substantially to the exclusion of unreduced reducible organic color-providing substance, to impart thereto a positive color image of the developed image.

20. A process as defined in claim 19, wherein said nondiffusible reducible color-providing substance is contained in a layer positioned between the layer containing said photosensitive silver halide emulsion and the support carrying said layers.

21. A process as defined in claim 19 wherein a portion of said silver halide developing agent is disposed prior to exposure in said photosensitive element containing said silver halide emulsion and another portion of said developing agent is contained, prior to exposure, in a liquid processing composition.

22. A process as defined in claim 19, wherein oxidized silver halide developing agent is substantially excluded from transfer to said image-receiving material.

23. A process as defined in claim 19, including the step of separating said image-receiving material and said photosensitive element from their superposed relationship at some stage of said process after said reduced organic color-providing substance has been transferred to said image-receiving material.

24. A process as defined in claim 19 wherein said photosensitive element includes at least two silver halide emulsions each sensitized to different portions of the visible spectrum, each of said emulsions has associated therewith a reducible organic color-providing substance adapted to provide, upon reduction, a diffusible color-providing substance which provides an image dye having a color substantially complementary to the portion of the visible spectrum to which the respective associated silver halide emulsion is sensitized, and said positive color image is composed of at least two colors.

25. A process of forming a negative diffusion transfer image comprising the steps of exposing a photosensitive element, said element including a photosensitive silver halide emulsion, developing said exposed silver halide emulsion by applyng an alkaline processing composition which provides a silver halide developing agent, said silver halide developing agent being present in such quantity per

unit area of said silver halide emulsion as to be substantially completely exhausted in fully exposed and developed unit areas of said silver halide emulsion, said development being effected in the presence of a tetrazolium salt which is soluble in said alkaline processing composition, providing, as a function of said development, an imagewise distribution of unoxidized, unexhausted silver halide developing agent in undeveloped areas of said silver halide emulsion, reacting said unoxidized silver halide developing agent with said tetrazolium salt, thereby reducing said tetrazolium salt to a nondiffusible formazan and thereby providing an imagewise distribution of unreduced tetrazolium salt, transferring, by diffusion, at least part of said imagewise distribuiton of unreduced tetrazolium salt to a superposed layer where said transferred tetrazolium salt is reduced to an insoluble formazan to provide a negative transfer image, said process including the step of separating said superposed layer from said silver halide emulsion after said tetrazolium salt has been transferred thereto.

26. A photographic product comprising a support, a photosensitive silver halide emulsion contained in a layer carried on one side of said support, and a tetrazolium salt contained in a layer on the same side of said support as said silver halide emulsion, said tetrazolium salt being reducible by an unoxidized silver halide developing agent and having an oxidation potential less than that of exposed silver halide of said silver halide emulsion and greater than that of unexposed silver halide of said silver halide emulsion.

27. A photographic product as defined in claim 26, wherein said tetrazolium salt is a salt of a tetrazolium compound and a compound containing a sulfonic acid group.

28. A photographic product as defined in claim 27, wherein said compound containing a sulfonic acid group is a dye.

29. A photographic product comprising a support, a layer carried on said support and containing a photosensitive silver halide emulsion, said layer also containing a silver halide developing agent, and a layer containing a tetrazolium salt, said last-mentioned layer being positioned between said support and said silver halide emulsion layer, said tetrazolium salt being reducible by an unoxidized silver halide developing agent and having an oxidation potential less than that of exposed silver halide of said silver halide emulsion and greater than that of unexposed silver halide of said silver halide emulsion.

30. In a process of forming a positive image in color, the steps comprising exposing a photosensitive element as defined in claim 26, developing said exposed silver halide emulsion with a silver halide developing agent, said silver halide developing agent being present in such quantity per unit area of said silver halide emulsion as to be substantially completely exhausted in fully exposed and developed unit areas of said silver halide emulsion, forming, as a function of said development, an imagewise distribution of unoxidized, unexhausted silver halide developing agent in undeveloped areas of said silver halide emulsion, and reacting said unoxidized silver halide developing agent with said reducible tetrazolium salt to provide a positive color image comprising the formazan formed upon reduction of said reducible tetrazolium salt.

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