Dec. 18, 1956 H. G. ROGERS 2,774,668

PROCESS AND PRODUCT FOR FORMING COLOR IMAGES FROM COMPLETE DYES

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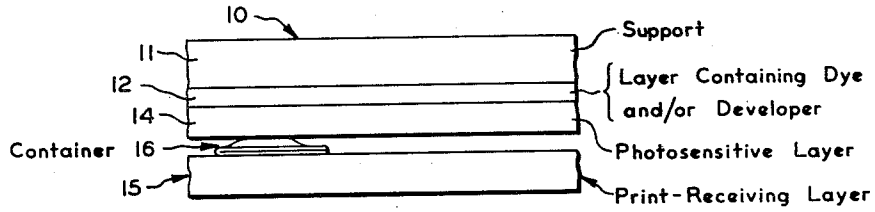



FIG. 1

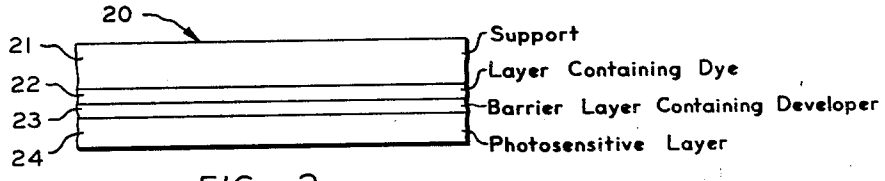



FIG. 2

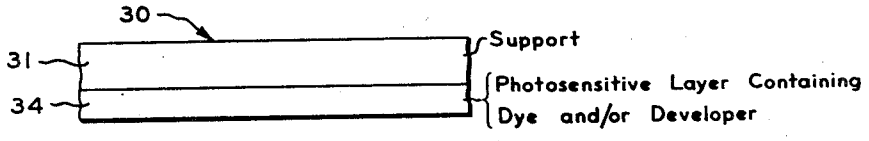



FIG. 3

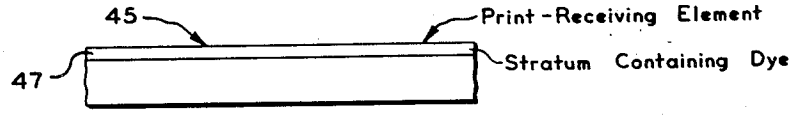



FIG. 4

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2,774,668

# PROCESS AND PRODUCT FOR FORMING COLOR IMAGES FROM COMPLETE DYES

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Application May 28, 1953, Serial No. 358,012

8 Claims. (Cl. 96—29)

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

Objects of this invention are to provide processes for forming color images from complete dyes and involving the steps of providing, in a silver halide layer of a photosensitive element having a latent image therein, a solution of a dye and a silver halide developer of a character which has at least one oxidation product capable of at least assisting in preventing dye in the photosensitive element from transferring from said photosensitive element and comprising a substance reactable with said dye to provide a reaction product having less mobility in the photosensitive element than the dye, developing the latent image with said developer and acting upon dye in the exposed regions of the photosensitive layer with developer which is in oxidized condition whereby to substantially prevent the transfer of dye from the photosensitive element in proportion to the development of silver while providing as a further result of silver development in the photosensitive layer an imagewise distribution comprising mobile dye and unreacted developer, and transferring at least part of said dye from said imagewise distribution to a print-receiving element located in superposed relation to the photosensitive element and depositing the transferred dye upon the print-receiving element and providing an image in terms of said dye; and also to provide processes such as those described which include the step of separating the photosensitive element and the print-receiving element by stripping said elements apart following the deposition of transferred dye on the print-receiving element.

Further objects of the invention are to provide processes of the character set forth wherein dye in solution in the photosensitive element is trapped or retained at least adjacent the exposed regions of a silver halide layer of said element by the reaction therewith of an oxidation product of a silver halide developer of a character capable of providing, upon the reduction of latent silver halide to silver, a substance which is reactable with said dye to provide a substantially immobile reaction product in the photosensitive element, or wherein said dye is trapped or retained in the photosensitive element by the use of a silver halide developer of the type of bis-benzene-sulfonyl hydrazide, that is to say, by a developer which has as one oxidation product thereof a substance reactable with said dye to provide a reaction product having less mobility in the photosensitive element than the dye and which has as a second oxidation product a gas used to form a barrier of bubbles in the photosensitive element for assisting in preventing the transfer of dye from the exposed regions of the photosensitive element.

Still other objects of the invention are to provide processes of the nature described for forming color images from complete dyes wherein dye and unreacted developer from unexposed and less than completely exposed regions of a photosensitive element are transferred to a print-receiving element, as well as where the transfer of dye is effected, substantially to the exclusion of unreacted developer, to the print-receiving element; to provide processes utilizing procedures for keeping developer out of the print-receiving element and including the employment in the photosensitive element of a nondiffusing developer of the type having a large molecule whereby the developer is relatively immobile; to provide processes wherein dye which is reacted in the photosensitive element with the oxidation product of the developer is derived from a stratum of dye carried by the print-receiving element and in this regard especially to employ practices wherein a nondiffusing developer is incorporated in the photosensitive element; and to provide processes of this general character which utilize a developer having an oxidation product reactable with dye to provide a substance having substantially the same color characteristics as said dye or a substance having color characteristics of a desired nature.



Yet other objects of the invention are to provide photographic products comprising a photosensitive element having a liquid-permeable portion including a silver halide layer, a print-receiving element positionable in superposed relation to the photosensitive element for receiving a transfer image, a container holding at least a liquid positioned for releasing its liquid between two layers of said product, and photographic processing materials, rendered effective by the release of liquid from the container, positioned in the product and including a dye which is soluble in said liquid and when dissolved therein is mobile in said photographic product, and also including a silver halide developer which is soluble in said liquid and is characterized by providing, upon the development of latent silver halide to silver, at least one oxidation product which is effective to at least assist in preventing dye present in exposed regions of the photosensitive layer from transferring to the print-receiving element and which comprises a substance reactable with said dye to provide a reaction product which is less mobile in the photographic product than said dye.

Further objects of the invention are to provide photographic products of the character described having a developer characterized by providing an oxidation product reactable with said dye to provide as a reaction product a substance which is substantially immobile in said photosensitive element, as well as a developer having as a first oxidation product a substance reactable with dye to provide a reaction product which is less mobile in the photosensitive element than the dye and as a second oxidation product a gas which is generated in proportion to silver development and provides bubbles in the photosensitive layer in the form of a barrier at least able to assist in preventing the transfer of dye from exposed regions of the photosensitive layer.

Still further objects of the invention are to provide photographic products of the character set forth which employ means for retaining the developer in the photosensitive element or for keeping the developer out of the print-receiving element and including the incorporation in the photosensitive element of a developer having a large molecule of a size sufficient to immobilize the developer in the photosensitive element, as well as to products wherein both the developer and the dye are transportable to the print-receiving element, and especially in this latter regard to products having a developer which provides an oxidation product reactable with dye to provide a substance having substantially the same color characteristics as the dye; and to provide photographic products such as those described which contain a dye mordant or an oxidizing agent in the print-receiving element and also such products wherein the dye is contained in the print-receiving element.

Yet further objects of the invention are to provide photosensitive elements having a support, at least one liquid-permeable layer on the support, silver halide distributed in a permeable layer of the element, a dye distributed in a permeable layer of the element and a silver halide developer distributed in a permeable layer of the element and wherein the dye is soluble in liquid and the developer is soluble in liquid and provides upon silver development at least one oxidation product effective so as to at least assist in preventing dye present in exposed regions of the photosensitive layer from transferring from said element and comprising as said oxidation product a substance reactable with said dye to form a reaction product less mobile in said element than said dye; and to provide photosensitive elements of the nature described wherein dye and developer of the kind set forth are contained in the same permeable layer or in individual permeable layers of said element including the permeable layer containing silver halide.

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

The invention accordingly comprises 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 description taken in connection with the accompanying drawing wherein:

Figure 1 is a diagrammatic side elevation of one embodiment of a film unit forming the subject of this invention and illustrates a product comprising a photosensitive element, a rupturable container and a print-receiving element;

Fig. 2 is a diagrammatic elevation of another embodiment of a photosensitive element forming the subject of this invention;

Fig. 3 is a diagrammatic elevation of still another embodiment of a photosensitive element forming the subject of this invention; and

Fig. 4 is a diagrammatic elevation of a further embodiment of a print-receiving element usable in carrying out the invention.

In general, the photographic processes and products disclosed herein, as in Patent No. 2,559,643, issued on July 10, 1951, to Edwin H. Land for Photographic Product and Process, are concerned with the treatment of a latent negative image in a photosensitive silver halide layer whereby to provide a dye positive image in or on another layer which comprises a print-receiving element.

In the just-mentioned Patent No. 2,559,643, there is disclosed a process adapted to be effected with a negative material in the form of a photosensitive element which includes a photosensitive silver halide layer and which has a conventional photographic coupler, for example a phenol, naphthol, pyrazolone or acetanilide type of coupler, and a silver halide secondary color-forming developer preferably incorporated in some permeable layer of the element. Para-phenylenediamine and derivatives thereof are classic examples of such developers. Other examples include aminophenol types of developers. A positive dye image of a latent image contained in the emulsion layer of the negative element is provided by spreading an alkaline liquid in contact with and between the photosensitive element and a permeable print-receiving element.

The spread liquid permeates into the negative element and developer dissolved in liquid within the element reduces the exposed silver halide of the latent image to metallic silver. Portions of the developer, which are oxidized as a result of silver development, react with the coupler in solution and form a dye image which is co-



extensive with the silver image. The unreacted developer and coupler in the remaining solution provide positive image-forming components which are transferred, by diffusion, from the photosensitive element to the print-receiving element and form thereon an imagewise distribution of unreacted developer and unreacted coupler which, upon oxidation of the unreacted developer, effect the formation of the desired dye positive. Oxidation of the unreacted developer to cause coupling may be effected by an oxidizing agent incorporated in the print-receiving element or the coupling may be allowed to take place by aerial oxidation of the developer after formation on the print-receiving element of the imagewise distribution of the unreacted developer and unreacted coupler material.

Other related applications which disclose the formation of dye images by coupling development and in a manner generally similar to that heretofore described are the copending applications of Edwin H. Land, Serial No. 702,039, filed October 8, 1946, now Patent No. 2,661,293, for Photographic Product and Process; Serial No. 94,647, filed May 21, 1949, now Patent No. 2,698,798, for Color Photographic Process and Product; and Serial No. 176,961, filed August 1, 1950 (now abandoned and replaced by application Serial No. 448,441, filed August 9, 1954) for Multicolor One-Step Photographic Process and Photographic Product for Carrying Out the Same; and also the copending application of Howard G. Rogers, Serial No. 358,011, filed May 28, 1953 (now abandoned and replaced by application Serial No. 577,711, filed April 12, 1956) for Multicolor Photosensitive Film and Process of Making the Same.

Color development making use of conventional couplers and developers of a secondary color-forming type is subject to certain disadvantages. For example, many conventional couplers have different coupling rates. This difference in coupling rates makes it difficult to keep negative image-forming reactions separate in each light-sensitive elemental portion of a photosensitive element utilized in carrying out a one-step multicolor process. Additionally, most dyes formed by coupling, especially so formed magenta and cyan dyes, have objectionable absorption characteristics and hence do not produce as accurate color renditions as desired. Furthermore, dyes formed by ordinary color development are, in general, sensitive to acid, and hence images comprised of these dyes may, in time, fade or change color when subjected to acid gases present in the atmosphere.

The present invention is concerned with improvements in procedures and products utilized in the aforementioned applications and patent for the formation of dye images and especially for the formation of dye images by one-step photographic transfer processing. Accordingly, the invention will be described in connection with such transfer processes and products useful for carrying out the same, although, as will appear, the invention is not limited thereto.

The improvements herein are effected by the employment of complete dyes of a character soluble at least in alkaline solution and by the utilization of procedures and materials wherein dye which is substantially uniformly distributed in a photosensitive silver halide layer having a latent image therein will be immobilized or trapped or retained in exposed portions of the photosensitive layer upon development of the latent image to silver. As a result of development, there will be formed in the photosensitive layer a silver image and an image in terms of the material trapped or immobilized in the exposed regions of the photosensitive layer, while dye which is present in those regions of the photosensitive layer where no exposure or incomplete exposure and silver development have occurred is free for removal therefrom, as for example by transfer, at least in alkaline solution. Silver halide color developers which are soluble in alkaline solu-

tion are utilized with complete dyes in the carrying out of this invention. By this practice, use is made of some product resulting from the oxidation of a color developer by the development of a latent image in a silver halide layer to immobilize dye in the exposed and developed regions of the photosensitive layer.

Many dyes of the character with which this invention is concerned are reactable, as by coupling or other reaction, with an oxidation product of a color developer to provide a reaction product or substance which possesses less mobility in a photosensitive element than the original dye. Reactions of this nature occur when a para-phenylenediamine type of color developer which is employed in the development of a silver halide layer is utilized in conjunction with a complete dye. Similar reactions take place with aminophenol type developers.

It has been discovered, although such a discovery is not a part of this invention, that bis-benzene-sulfonyl hydrazide is a good silver halide developer of black and white images. I have discovered, and utilize my discovery in this invention, that a developer of the bis-benzene-sulfonyl hydrazide type produces, as one product of oxidation, a substance which will react with many of the complete dyes named herein, as by a coupling or other reaction, to form a compound or substance possessing less mobility in a photosensitive element than the original dye.

Additionally, I have found that a substance of the type of bis-benzene-sulfonyl hydrazide, when used in the development of a latent image, gives off a gas in the exposed regions of the photosensitive layer as it becomes oxidized in the development of the latent image to silver. In the case of bis-benzene-sulfonyl hydrazide, the gas is nitrogen. Gas which is produced during the development of a latent image will form bubbles in the photosensitive layer. Where the exposure and development is greatest, bubbles are formed in the greatest concentration. These bubbles are utilized to provide a screen or barrier for dye in the exposed regions of the photosensitive layer whereby to at least assist in immobilizing such dye by preventing its transfer in solution through these exposed regions.

The invention also intends to make use of dyes which, while reacting with an oxidation product of a developer, provide a reaction substance which lacks the desired degree of immobility. For example, the reaction product or substance so formed may be only slightly less soluble than the original dye. When bis-benzene-sulfonyl hydrazide is employed as a developer, use may be made of the bubbles formed by the gas which is emitted upon the oxidation thereof to assist in preventing the transfer of the mobile reaction product.

In instances where the substance produced by the reaction of a complete dye with an oxidation product of a conventional color developer lacks the desired immobility, a nondiffusing developer is employed which has a large molecule whereby the developer when incorporated in the photosensitive element remains substantially immobile therein. 4-amino-3-n-butoxydiethylaniline is an example of nondiffusing color developer which has a long chain on its molecule. Another example is para-aminophenol to which a long carbon chain has been added. In nondiffusing developers of this type, the long chain will be retained on the developer molecule upon oxidation of the developer so that the product remaining after oxidation will still retain its immobility. Since the complete dye enters into a reaction with this product having the long chain on its molecule, the substance resulting from the reaction will also be retained in the photosensitive element.

Several mechanisms are thus presented by which a complete dye, which is at least soluble in alkaline solution, may be immobilized or retained in exposed regions of a photosensitive element while dye in unexposed regions of the element may be removed in solution, as for example by transfer. By way of recapitulation, by one mechanism an oxidation product of the developer reacts with the complete dye to form a substance which is less mobile in a permeable layer of the photosensitive element than the unreacted dye. By a second mechanism a gas given off upon the oxidation of the developer is utilized for immobilizing dye image components in the exposed regions of the photosensitive element by providing a barrier or screen which substantially bars their transfer. In the case of a bis-benzene-sulfonyl hydrazide type of developer, the immobilizing mechanism by which bubbles are produced is available. As a modification of the first-mentioned mechanism, a nondiffusing developer having a molecule sufficiently large so that the developer is retained in the photosensitive element is utilized for immobilizing dye image components in the exposed regions of a photosensitive layer.

Common to these mechanisms is the fact that the color developer provides at least one substance upon its oxidation in the development of a latent image to silver which is capable of acting as an agent for immobilizing dye so as to prevent its transfer from a photosensitive element. It may be here noted that experimental data leads to the belief that immobilization of dye image components in situ with the silver image developed by the developer is carried out primarily by one or more of the mechanisms just described and that any hardening of the carrier material of the photosensitive layer by reaction with the developer or some oxidation product thereof is a negligible factor in trapping and control of the dye.

The substance formed by the reaction of a complete dye and an oxidation product of the developer may possess color characteristics which are substantially the same as the unreacted dye or which are different from the unreacted dye. As will presently more fully appear, it is possible in carrying out a transfer process to form the transfer image either by the use of transferred dye which remains in unreacted condition or by the use of the product formed upon the reaction of the transferred dye with an oxidation product of the developer. The color of a substance formed by the reaction of an oxidation product of the developer and a complete dye becomes immaterial in instances where the complete dye is used for transfer image formation.

Uniquely, a developer of the bis-benzene-sulfonyl hydrazide type provides an oxidation product which reacts with a complete dye to provide a substance having substantially the same color characteristics as the unreacted dye. On the other hand, the reaction product of a dye and an oxidation product of a standard color developer is a substance which, while it may possess the desired immobility, usually has color characteristics different from the unreacted dye.

For example, 1,5 dihydroxy naphthalene-4-azo benzene is a magenta dye which is reactable with the oxidation product of a developer and which, in unreacted condition, is of a color suitable for use in the formation of a subtractive dye image. When 1,5 dihydroxy naphthalene-4-azo benzene is reacted with oxidized developer of the type of bis-benzene-sulfonyl hydrazide, the substance formed as a reaction product possesses substantially the same magenta color characteristics as the unreacted dye. On the other hand, if 1,5 dihydroxy naphthalene-4-azo benzene is reacted with an oxidation product of a standard developer of the para-phenylenediamine type, the reaction product formed is a substance which is grayish. Due to the previously pointed out ability of the invention to utilize the unreacted dye or the reacted dye for the purposes of image formation, it is possible to employ either of the types of developers just mentioned.

An advantage in the use of bis-benzene-sulfonyl hydrazide as a developer resides in the fact that it is immaterial if bis-benzene-sulfonyl hydrazide which has been transferred to a print-receiving element becomes oxidized and reacts with unreacted dye which has also been transferred since the reaction product formed will have sub-

stantially the same color characteristics as the unreacted dye.

A large number of complete dyes are available for the practice of this invention. Because of the wide choice of classes from which dyes may be selected as compared to the few available classes of couplers, as well as the ability of the invention to utilize a reacted dye molecule or an unreacted dye molecule, it is possible to form images of dyes having more highly accurate absorption characteristics, as well as images of dyes which are substantially stable. Additionally, in cases where a conventional type of color developer is to be immobilized in the photosensitive element, it is possible to achieve rates of development which are higher than those obtained with the para-phenylenediamine developers by the use of stronger color developers such as ring-substituted para-aminophenols as by one example wherein the ring substitution may be in the form of carbon chains. Furthermore, it is possible, because of the numerous usable dye classes and almost limitless number of dyes in them, to select dyes to carry out a multicolor process wherein the reaction rates of the different dyes will be similar in instances which utilize the reaction of an oxidation product of the developer and a complete dye for the purposes of immobilization.

Among the classes from which suitable dyes are available, mention may be made of the monoazo, disazo, triphenyl methane, xanthene, thiazine and anthraquinone dyes. The field of dye materials is further extended by the employment of dye substances of the type which react with oxidized developer and which, in unreacted form, may be colorless in a particular environment, for example an acid environment, but upon change in the environment, for example to an alkaline environment, take on a color change. Dye substances of this type include indicator dyes, leuco dyes and carbinols of basic dyes.

Complete dyes of the character with which this invention is concerned are employable in a photosensitive element in the same manner as the conventional couplers previously mentioned, i. e., they are preferably incorporated in a permeable layer or stratum of the photosensitive element which may or may not contain other materials used in the photographic process, as for example silver halide and/or the developer. Dyes of the characteristics described and/or their reaction products should also be stable to light and to photographic solutions.

Dyes which are particularly suited for reaction with an oxidation product of a color developer, including bis-benzene-sulfonyl hydrazide, are found in those dyes having an open position on a ring, which position is para to a hydroxyl or an amino group, or those dyes having a reactive methylene group. Many suitable dyes coming within this classification are found among the azo, pyrazolone and triphenyl methane dyes, specific examples of which comprise the following water- and alkali-soluble dyes such as Fast Crimson 6BL (C. I. 57) for magneta; Fast Wool Yellow (C. I. 636) for yellow; Alphazorine 2G (C. I. 712) and Pontacyl Green SX Extra (C. I. 737) for cyan; and Polychrome Blue-Black (C. I. 201) and Rayon Black GSP (which is commercially available from E. I. du Pont de Nemours & Company, Inc., Organic Chemicals Department) for black; as well as water-insoluble but alkali-soluble dyes, such as 1,5 dihydroxy naphthalene-4-azo benzene, for magenta; and Benzene Azo Resorcinol (C. I. 23) for yellow.

The substance formed by the reaction of a complete dye of the character described with the oxidation product of a standard type of color developer will usually possess color characteristics which are undesirably different from those of the unreacted dye as, for example, the grayish substance formed when the magenta dye, 1,5 dihydroxy naphthalene-4-azo benzene, is reacted with the oxidation product of a para-phenylenediamine type of developer. It therefore becomes necessary to utilize the unreacted dye molecule for image formation in transfer processing under circumstances wherein a reaction product of a color developer and a dye possesses an undesired color. However, it should be recognized that it is possible to use the reaction product for transfer image formation in instances where the oxidized developer reacts with the dye to give a reaction product which possesses a desired color, although such color may be different from that of the unreacted dye molecule.

Use of the unreacted dye molecule for image formation is made possible, when employing a para-phenylenediamine or other standard type of color developer, by preventing the reaction, on the print-receiving element, of dye and developer which have been transferred thereto. In this regard, a number of varied practices are available.

By one practice for accomplishing this purpose, there is incorporated in the photosensitive element a developer which possesses a very low solubility in alkali but has good solubility in a high-boiling-point organic solvent. An example of such a developer is 4-amino-di-n-butyl-aniline. Procedures for carrying out this practice are known to the art and are set forth in Patent No. 2,478,400, as well as in the previously mentioned application Serial No. 176,961. Due to the fact that the developer is of low solubility in alkaline solution, its mobility will be substantially restricted to the negative or photosensitive element.

Briefly stated, practices for incorporating a developer which is difficultly soluble in alkali in a photosensitive layer are carried out by dissolving the free base of a standard developer in a high-boiling-point solvent such as tricresyl phosphate. The solution thus formed is then emulsified in a dilute gelatin solution containing an emulsifying agent, as for example alkyl lauryl sulfate, and an appropriate amount of the emulsified product is added to a suitable quantity of a silver halide emulsion and is thoroughly mixed therewith. This procedure is also available for incorporating a dye in a silver halide emulsion which, along with the free base of the developer, may be dissolved in the aforementioned high-boiling-point solvent. However, since the dye is also soluble in alkali, it may be transferred in alkaline solution from the photosensitive element.

Alternatively, a relatively immobile or nondiffusing color developer, of the character previously mentioned, may be incorporated in the negative element as, for example, a developer having a long chain on its molecule such as 4-amino-3-n-butoxydiethylaniline. As a further alternative, the print-receiving element may include, as an image-receptive material, a plastic layer which is of a character displaying a greater affinity for dye than for developer or a preference for the penetration thereof by the dye over its penetration by developer. As an example of a receiving sheet material and a dye of these characteristics, mention may be made of partially hydrolyzed polyvinyl acetate and the previously mentioned magenta dye, 1,5-dihydroxy naphthalene-4-azo benzene. As a still further means for controlling reaction of the dye in the print-receiving element, a strong reducing agent such as hydroquinone may be incorporated in the positive print-receiving element to prevent oxidation of any transferred developer and consequent coupling reaction. These and similar practices are useful individually or in various combinations for the purpose of preventing the reaction of a transferred dye molecule with developer.

A further understanding of the invention will be gained from a consideration of products useful for carrying it into effect. In this regard, there is schematically shown in Fig. 1 a film unit making use of a negative sheet material or photosensitive element **10** comprising a support **11** of paper or film base material upon which there is mounted, in the order named, a layer **12** comprising a silver halide developer and a dye which is reactable with the oxidation product of the developer and a conventional

photosensitive layer 14 of silver halide. The film unit of Fig. 1 also employs a positive sheet material or print-receiving element 15 comprising 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, for example, paper. However, the positive element 15 may comprise a support upon which at least one liquid-permeable and dyeable layer is mounted.

As shown in Fig. 1, the photosensitive element 10 and the print-receiving element 15, for the purpose of positive image formation, are adapted to be placed in superposed relation and are arranged so that the photosensitive layer or stratum 14 is next to the print-receiving element 15.

Also, in the film unit of Fig. 1 a rupturable container 16, adapted to carry an alkaline solution or liquid composition, is shown as positioned transversely of and adhered to the print-receiving element 15. If desired, the container 16 may be adhered to the photosensitive layer. Container 16 is of a length approximating the width of the film unit and is constructed to carry sufficient liquid to effect negative image formation in an exposed image area of the photosensitive layer 14 and positive image formation in the corresponding image area of the print-receiving element 15. In use, the container 16 is adapted to be positioned between the print-receiving element and the photosensitive element so that it will lie adjacent the edges of the corresponding image areas of these elements which are to be processed by the liquid contents of the container. When the film unit is of the roll film type, a plurality of containers are employed, one for each corresponding pair of successive image areas in the photosensitive and print-receiving elements. Details of such containers may be found in Patent No. 2,634,886, issued April 14, 1953, to Edwin H. Land for Collapsible Fluid Containers.

In one embodiment, the layer 12 comprises a liquid-permeable carrier material in which is incorporated a dye of the character with which this invention is concerned and preferably a silver halide developer. The carrier material with the dye and/or developer therein is coated onto the support 11 to a thickness of about .0001 or .0002 inch. By another embodiment, the layer 12 may be formed of dye and developer dissolved in a volatile solvent or solvent mixture which is coated directly onto the support 11. The thickness of the layer 12 when formed in the last described manner will, of course, be infinitesimal. In any event, the layer 12 is penetrable by the liquid processing composition employed so that dye and/or developer contained therein may be placed in solution.

As will presently be pointed out, it is possible in this embodiment of the invention to locate the developer in the photosensitive layer 14 and, in certain instances, in solution in the liquid in the container 16. Also in this embodiment, the dye distributed in the layer 12 is preferably one of the water-insoluble but alkali-soluble dyes heretofore mentioned.

A suitable carrier material when layer 12 comprises a carrier in which dye and developer are distributed is one which will swell in hydroxide or alkaline liquids sufficiently to release dye and developer contained therein. Examples of carriers comprise gelatin, zein, polymethacrylic acid, shellac and cellulose acetate hydrogen phthalate, of which the latter may be named as preferred for most general purposes.

Where layer 12 comprises a carrier material in which dye and developer are distributed, one example of a composition for forming the layer is as follows:

1 gram 1,5 dihydroxy naphthalene-4-azo benzene
1 gram 4-amino-3-n-butoxydiethylaniline
4 grams cellulose acetate hydrogen phthalate
80 cc. acetone
20 cc. methanol
1 cc. ethyl Cellosolve

In preparing this composition, the dye, developer and cellulose acetate hydrogen phthalate (the carrier material) are mixed together and dissolved in the solvent mixture provided by the acetone, methanol and ethyl Cellosolve. The composition so prepared is then coated onto the support 11.

The foregoing composition illustrates the use of a color developer which on oxidation will provide a reaction product of a color undesired for transfer image formation so that the dye in unreacted condition is intended to be employed to provide the transfer image. As may be noted, the developer in the foregoing composition is of the nondiffusing type so that it is substantially kept out of the print-receiving element. Additionally, a receiving sheet material such as partially hydrolyzed polyvinyl acetate may be used in the print-receiving element. Other practices such as those of the nature heretofore described are available for controlling developer transfer in instances where the reaction product of the oxidized developer and the dye is of an undesired color.

When the layer 12 is provided from a solution of dye and developer in a volatile solvent, one example of a suitable composition for forming the layer is as follows:

1 gram 1,5 dihydroxy naphthalene-4-azo benzene
4 grams bis-benzene-sulfonyl hydrazide
100 cc. acetone

The just-described composition is prepared by mixing the dye and developer together and dissolving the mixture in the acetone, following which the composition is coated onto the support 11.

Other dyes, for example of the same color or of a different color, such as a cyan or a yellow or a black dye, or combinations of differently colored dyes, may be substituted for the particular magenta dye of the foregoing formulas.

The photosensitive silver halide layers used herein are provided by silver halide emulsions of conventional character which are coated onto the layer 12 after the latter has dried. The particular sensitivity range of each photosensitive layer, such as the layer 12, will be chosen to meet the particular requirement of use to which the photosensitive element will be put. These emulsions are conventionally coated onto the layer 14 or otherwise applied thereto to a thickness of from about .0002 to .0005 inch.

As heretofore mentioned, the image-receiving material of the positive element 15 includes any material dyeable from alkaline liquid. The positive element 15 may, as shown, comprises a single sheet of permeable material or it may comprise a support which carries a layer or a stratum of a permeable image-receiving material. An example of such is imbibition paper or baryta paper or conventional film base material upon which a permeable stratum is coated. As a further example, the print-receiving element may comprise a paper support subcoated with a substantially water-impermeable material such as a cellulose ester, i. e., cellulose nitrate, cellulose acetate and the like, and having a stratum of a permeable and dyeable material coated over the subcoat.

Image-receiving materials of a dyeable nature, in addition to those already named, include regenerated cellulose; polyvinyl alcohol; partially hydrolyzed polyvinyl acetate; sodium alginate; cellulose ethers, such as methyl cellulose or other cellulose derivatives such as sodium carboxymethyl cellulose or hydroxyethyl cellulose; papers; proteins, such as glue; carboxydrates, such as gums and starch; and mixtures of such materials where they are compatible. Polyvinyl alcohol may be named as a preferred image-receiving material for use with water-soluble dyes, especially with water-soluble dyes having sulfonate groups on the dye molecule. For water-insoluble dyes, a preferred image-receiving material is partially hydrolyzed polyvinyl acetate.

The liquid processing composition employed in carrying out the invention comprises at least an aqueous alka-

line liquid of sufficient alkalinity to permit the developer to perform its developing function and, in certain instances, may also have the developer dissolved therein. A viscosity-increasing compound constituting a film-forming material of the type which, when spread over a water-absorbent base, will form a relatively firm, dimensionally stable film, is preferably included in the liquid processing composition to assist in carrying out the uniform spreading of the composition between the layers of the film unit. A suitable film-forming material is a high molecular weight polymer as, for example, a polymeric, water-soluble ether, inert to an alkaline solution, such as hydroxyethyl cellulose or sodium carboxymethyl cellulose. Liquid processing compositions of this nature are described in the previously mentioned applications and in Patent No. 2,559,643. A suitable liquid processing composition comprises a mixture of 5 grams of sodium carboxymethyl cellulose, 3 grams of sodium hydroxide and 100 cc. of water. It is here pointed out that while sodium hydroxide is in general the preferred alkali used in the processing liquid, other alkaline materials may be employed, for example potassium or lithium hydroxide, sodium or potassium carbonate and diethylamine.

The incorporation of an oxidizing agent in the print-receiving element for the purpose of oxidizing unreacted developer permeated therein is disclosed in certain of the previously mentioned applications and in Patent No. 2,559,643. While the present invention will generally be practiced without the use of an oxidizing agent, it may be desirable in certain instances to utilize one. For example, it may be preferred to form a transfer image of the reaction product of the complete dye and the oxidation product of a conventional color developer in instances where the reaction product has a suitable color. In such a case, or in instances where deepening of hue of the transfer image is desired, such as for black, it would be desirable to include an oxidizing agent in the print-receiving element for the purpose of speeding up positive image formation.

As specific examples of suitable oxidizing agents, mention may be made of peroxy compounds such as sodium or potassium perborate, certain dichromates such as ammonium dichromate, and compounds having polyvalent metallic elements in higher valent form such as copper, antimony, uranium, manganese, iron and cerium, wherein the metallic element is in higher valent form. Examples of these last-mentioned agents are cupric salts such as cupric sulfate. Another suitable oxidizing agent is benzoyl peroxide.

To build up greater density of image dye in the positive element, it may be preferable to have an efficient dye-precipitating mechanism included in the image-receiving sheet material. Consequently, it is desirable to have a mordant included in the image-receiving sheet, as well as utilizing a print-receiving element having a layer or stratum which has an affinity for dye, such as a suitable plastic stratum. For this purpose, the print-receiving element itself may be formed of a conventional dye-transfer paper which contains a mordant. A suitable dye-transfer paper is commercially available from Eastman Kodak Company under the name of "Dye Transfer Double Weight F." As other examples, a print-receiving element may be provided with a gelatin layer containing a mordant such as nickelous sulfate or aluminum sulfate. Such a material may be used as the image-receiving stratum of the print-receiving element and is easily coated upon a support for the element. The use of a mordant in the print-receiving element is disclosed in the aforesaid Patent No. 2,559,643.

As another practice for providing a dye-precipitating mechanism in the print-recciving element, dyes may be chosen which form lakes with metal salts. Dyes of this character and metal salts usable for this purpose are well known to the art. Where procedure of this type is utilized, metal salts such as chromium and/or barium salts are distributed throughout a permeable stratum of the print-receiving element in which the transfer image is provided.

In all products employed in the practice of the invention, it is preferable to expose the negative material or photosensitive element **10** from the emulsion side. It is therefore desirable to hold the photosensitive element **10** and positive sheet material **15** together at one end thereof by fastening means, not shown but comprising hinges, staples, or the like, in such manner that the photosensitive element **10** and the positive element **15** may be spread apart from their positions illustrated in Fig. 1. When the film unit is of the roll film type, the photosensitive element **10** and the positive sheet **15** 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 95 or similar camera structure, such for example as the camera forming the subject matter of Patent No. 2,435,717, issued February 10, 1948, to Edwin H. Land for Developing Camera Utilizing a Film, Another Sheet Material, and a Fluid Processing Agent. Camera apparatus of this character permits successive exposure of individual frames of the photosensitive element **10** from the emulsion side thereof, as well as individual processing of an exposed frame by bringing the exposed portion of the photosensitive element **10** is superposed relation with a portion of the print-receiving element **15** while drawing these portions of the film assembly between a pair of pressure rolls which rupture the container associated therewith and spread processing liquid between and in contact with the photosensitive element and the corresponding registered area of the print-receiving element.

Assuming that the film unit of Fig. 1 utilizes a layer **12** containing a magenta dye and a developer in accordance with one of the preceding formulas, the processing of the unit for transfer image formation, following the exposure of the photosensitive element **10** to a desired subject, proceeds, by rupturing container **16** and spreading the alkaline liquid processing composition between the photosensitive element and the print-receiving element.

The spread processing liquid migrates into the photosensitive layer **14** and the layer **12**. During permeation into the layer **12**, unreacted dye and unreacted developer contained in this layer are dissolved in the processing liquid and are transported in solution into the photosensitive layer **14**.

Where the developer transported to the photosensitive layer **14** reacts with the exposed silver halide, it is oxidized as a function of the amount of silver halide reduced to silver and at least one oxidation product of the developer reacts with the dye adjacent the developing silver grains to form a reaction product. As previously noted, the product of the reaction of dye and the oxidation product of the developer is at least less mobile in the photosensitive element **10** than the dye itself.

For general purposes in cases where the developer is bis-benzene-sulfonyl hydrazide or where the developer is kept out of the print-receiving element, an excess of developer may be utilized in the photographic product. However, in instances where an oxidation product of the developer reacts with dye to provide a substance of desired color, developer is employed in a quantity controlled to avoid highlight stain in the transfer image. By this control, developer is utilized in a unit area of the layer, adapted to have the developer incorporated therein, in a quantity just sufficient to be completely oxidized by a fully developable or completely exposed silver halide portion of similar unit area.

In general, dye present in a dye-containing layer in a unit area thereof similar to that described is preferably of a quantity just sufficient to be entirely reacted by

that amount of developer which is oxidized by the development of a completely exposed unit area of the photosensitive layer. This procedure is likewise for the purpose of avoiding highlight stain in the transfer image. However, if the dye employed in the photosensitive element has a sufficiently low solubility rate, it is possible to use dye in excess of that just specified.

As intimated in the foregoing, processing of the nature described forms a substantially uniform distribution of dye and developer in the photosensitive layer **14** so that, upon development of silver, dye in the area of the highlights of the negative image is substantially exhausted by reason of its reaction with an oxidation product of the developer to provide a product which is at least less mobile in the negative sheet material than the dye itself. When the developer employed is bis-benzene-sulfonyl hydrazide, the gaseous oxidation product thereof provides an additional trapping or immobilizing mechanism by forming a barrier of bubbles adjacent the developed regions of the photosensitive layer whereby to assist in preventing transfer of the reaction product of development out of the photosensitive element.

As a further result of processing, in places in the negative material where unexposed silver halide grains are present or in places where exposure and subsequent development is less than complete, unoxidized or unreacted developer and dye are in an imagewise distribution proportional to silver development. Dye and developer present in this imagewise distribution are both transportable, at least in part, by imbibition to the print-receiving element. However, the unreacted developer may be prevented from entering the print-receiving element by utilization of one of the precautions or practices previously described, such as the use of a non-diffusing developer, for example 4-amino-3-n-butoxydiethylaniline, or by the employment of a developer which is difficultly soluble in alkali, such as 4-amino-di-n-butylaniline. In all instances, the invention intends to transfer at least part of the dye to the print-receiving element to provide an image in terms of unreacted dye which is the reverse image of the latent image in the photosensitive element.

Following the formation on the print-receiving element of a reverse image of the latent image, the photosensitive element and the print-receiving element are separated, as by being stripped apart. In instances where the developer is retained in the photosensitive element **10** and/or is kept out of the print-receiving element **15**, the reverse image on element **15** will comprise dye in unreacted condition. An advantage of this procedure resides in the simplification of processing and film unit construction by doing away with the need for an oxidation agent in the print-receiving element.

This simplification is enhanced when a developer of the bis-benzene-sulfonyl hydrazide type is employed, since such a developer need not be kept out of the print-receiving element. In instances where unoxidized bis-benzene-sulfonyl hydrazide is transferred to the print-receiving element, any subsequent oxidation thereof is immaterial because of the fact that the reaction between dye and an oxidation product of the bis-benzene-sulfonyl hydrazide will provide a substance having substantially the same color characteristics as the dye itself.

As heretofore noted, bis-benzene-sulfonyl hydrazide upon its oxidation gives off a gas. When bis-benzene-sulfonyl hydrazide in unoxidized condition is transferred to the print-receiving element from the imagewise distribution of developer and dye in the photosensitive element, it will eventually become oxidized from aerial oxidation.

However, it is to be kept in mind that the desired dye image is formed independently of the oxidation of a transferred bis-benzene-sulfonyl type of developer. Also, since an oxidizing agent is not employed in the print-receiving element, oxidation of the transferred bis-benzene-sulfonyl hydrazide developer will take place slowly and solely from aerial oxidation. Consequently, the print-receiving element and the photosensitive element may be stripped apart at least at a time when oxidation of the transferred developer is just being initiated. Under these circumstances and because of the stripping of the print-receiving element from the photosensitive element, gas generated by the developer upon its oxidation will be substantially free to escape into the surrounding atmosphere. As a result, the print-receiving element will be substantially free of the bubbles which were used for trapping purposes in the negative sheet material or photosensitive element **10**.

Where the developer is a standard color developer of the usual type such as para-phenylenediamine, an oxidizing agent such as disclosed in said Patent No. 2,559,643 is preferably included in the print-receiving element in instances where the reaction which takes place between the oxidation product of the standard color developer and the transferred dye provides a substance having the desired color characteristics. As pointed out, the use of an oxidizing agent, while not necessary, considerably speeds up reactions of this sort.

In the film unit of Fig. 1, a construction has been detailed wherein the developer and the complete dye are located in a stratum in back of the photosensitive stratum or between the photosensitive stratum and the support of the photosensitive element **10**. This construction is generally preferred in carrying out a transfer process since it facilitates control of the reactants to the end of achieving substantially complete trapping or immobilization of dye and developer utilized in providing the negative image in the photosensitive element with consequent avoidance of highlight color in the positive.

However, the preferred construction is subject to considerable variation. For example, a layer or stratum containing the developer and/or unreacted dye may be located in front of the photosensitive layer. Also, the developer and the unreacted dye may be incorporated in individual strata of the photosensitive element, including the incorporation of one of these photographic materials in the photosensitive layer itself. Furthermore, in certain instances it is possible to omit the developer and/or dye from the photosensitive element and to include either or both in the alkaline liquid used for processing purposes. Also, the dye may be distributed in a stratum located on the side of the print-receiving element which is adapted to face the photosensitive element in instances where a nondiffusing type of developer is incorporated in the photosensitive element.

It has been previously pointed out that the photosensitive element **10** is designed preferably for use with a water-insoluble but alkali-soluble dye. In general, many dyes will exert a desensitizing action on a silver halide emulsion if they become intimately mixed therewith, as for example by being imbibed into the emulsion from a solution of the dye. Desensitization may be of chemical or physical character whereby the sensitivity of the silver halide is lowered. Also, desensitization may be of an optical nature, that is to say, dye which is intimately mixed with a silver halide emulsion will absorb actinic light intended for the exposure of the emulsion.

In forming the photosensitive element **10**, the silver halide emulsion providing the layer **14** is coated onto the layer **12** after the latter has dried. It is possible for water or moisture in the wet emulsion to penetrate into the layer **12** although the carrier material for layer **12** is difficultly penetrable by water but is readily penetrated by alkaline solutions. If dye incorporated in the layer **12** is of a water-soluble nature, there is some likelihood of its entering into solution in water from the wet emulsion with subsequent migration into the photosensitive layer. In the photosensitive element **10**, this possibility is avoided by utilizing a water-insoluble but alkali-soluble dye, for

example, a dye such as the previously mentioned 1,5 dihydroxy naphthalene-4-azo benzene.

In instances where a dye which is soluble in water, as well as in alkali, is employed, a somewhat different type of photosensitive element is utilized. Such an element is shown in Fig. 2 and comprises a support **21** upon which is coated a layer **22** adapted to contain a water-soluble dye which is incorporated in a carrier material of the character previously described, for example, cellulose acetate hydrogen phthalate or gelatin. Coated upon the dye layer **22** is a barrier layer **23**, comprising a carrier, such as cellulose acetate hydrogen phthalate, in which the developer is incorporated.

One composition suitable for forming a layer **22** comprises:

1 gram Fast Crimson 6BL (water-soluble dye)
2 grams gelatin
100 cc. water

An example of a composition suitable for providing the barrier layer **23** comprises:

4 grams cellulose acetate hydrogen phthalate
4 grams bis-benzene-sulfonyl hydrazide
80 cc. acetone
20 cc. methanol
1 cc. ethyl Cellosolve

After formation and drying of the layer **22**, the layer **23** is applied thereon and, following the drying of the layer **23**, the silver halide photosensitive layer **24** is coated on the layer **23**. While water from the wet silver halide emulsion forming the photosensitive layer **24** may penetrate into the barrier layer **23**, the barrier layer **23** may be made sufficiently thick so as to substantially prevent penetration of moisture from the wet emulsion of layer **24** into the layer **22** which contains the water-soluble dye. The photosensitive element **20** of Fig. 2 is susceptible to modification without change in its structural arrangement of layers. For example, the developer may be omitted from the layer **23** and included in the layer **22** or even in the photosensitive layer **24**.

In instances where the reaction product of the dye and the oxidized developer are of an undesired color, transfer of the unreacted developer to the print-receiving element may be controlled or restrained by any of the procedures heretofore noted. For example, an appropriate amount of a nondiffusing developer, such as 4-amino-3-n-butoxydiethylaniline may be used in the last-disclosed formula, or any of the other practices described are available.

The invention includes within its concept the incorporation of both the dye and the developer in layer **22** of the photosensitive element **20**. In this instance, the barrier layer **23** will consist substantially only of the material which forms it.

The photosensitive element **20** is formed in a manner similar to the photosensitive element **10** and utilizes substantially similar materials for the purposes of construction. Likewise, the photosensitive element **20** is adapted to be used with a print-receiving element **15** of the nature disclosed in Fig. 1 and in a similar manner for providing, in the print-receiving element, a dye image which is the reverse image of a latent silver halide image formed in the photosensitive element **20** upon exposure thereof.

It has been further mentioned as an object of this invention to provide film units making use of a photosensitive element comprising a support having a photosensitive layer thereon in which both the dye and the developer are incorporated. Such a photosensitive element **30** is disclosed in Fig. 3 as comprising a support **31** having thereon a photosensitive layer **34** which incorporates silver halide, unreacted dye and a silver halide developer in a suitable carrier material, for example gelatin.

Practices for incorporating dye and a developer in a silver halide emulsion are similar to those well understood to the art for incorporating a coupler and a developer therein.

A developer such as bis-benzene-sulfonyl hydrazide may be incorporated in a silver halide emulsion by dissolving 1 gram of bis-benzene-sulfonyl hydrazide in 30 cc. of acetone and stirring the solution thus formed into 70 cc. of an appropriate silver halide emulsion.

Where the developer employed is of the type which provides a substance of an undesired color upon the reaction of its oxidation product with dye, the invention may be carried out with a nondiffusing developer or by utilization of other practices of the character heretofore mentioned for controlling the transfer of the developer to the receiving sheet. In this regard, one nondiffusing developer for use with the photosensitive element **30** of Fig. 3 is the previously mentioned nondiffusing developer, 4-amino-3-n-butoxydiethylaniline. A composition comprising silver halide and 4-amino-3-n-butoxydiethylaniline of a nature suitable for providing the photosensitive layer **34** may be formed by dissolving the hydrochloride of the developer in water to which an approximately equal amount of phosphoric acid has been added. The solution thus formed is added directly to the silver halide emulsion and the mixture is spread upon the support **31** to provide the photosensitive layer **34**.

As previously set forth, there is a tendency among many dyes to effect emulsion desensitization when the dye is incorporated in a silver halide emulsion. Preferably, the invention utilizes a dye of a nature which exerts a minimum chemical and/or physical desensitizing action on a silver halide emulsion. Preferably, also, the dye employed is of a water-insoluble nature whereby to limit its intimate mixture with a silver halide emulsion to the end of avoiding possible optical desensitization. An example of a water-insoluble dye is the previously mentioned 1,5 dihydroxy naphthalene-4-azo benzene which may be mixed with a silver halide emulsion from a solution of the previously described character, namely, a solution of dye in acetone and methanol.

Furthermore, desensitization by dye in the emulsion may be avoided by encasing the dye in particles comprised of hardened gelatin and by distributing the dye-containing particles throughout the silver halide emulsion. These dye-containing particles may be formed by procedures similar to those taught in U. S. Patent No. 2,618,553. In place of hardened gelatin, the dye may be incorporated in particles of a material which is difficultly penetrable by water but is readily penetrated by alkaline solutions such, for example, as the cellulose acetate hydrogen phthalate, already mentioned, or similar materials. Colored dye materials which are incorporated in a photosensitive layer preferably have a particle size which is greater than the particle size of the silver halide grains whereby to lower the covering power of the dye to permit photographic exposure of the photosensitive layer to its full thickness.

Mention has been made of compounds in the nature of dyes which are substantially colorless in a particular environment but become colored when this environment is changed. Such compounds include indicator dyes, leuco dyes and carbinols of basic dyes. Dye substances of this nature should possess the properties heretofore enumerated as requisites for carrying out the purposes of this invention and, in addition, should preferably be colorless or yellow or slightly so in a neutral or acid environment. For example, indicator dyes such as 2,5-dinitrophenol, quinaldine red and quinoline blue have, respectively, a yellow, a red and a blue color at a relatively high pH but are substantially colorless in a neutral or acid environment.

Such dye substances as those capable of assuming a color change are especially adapted for use with a photosensitive element having a layer of silver halide in which the dye and the developer are incorporated as, for example, the photosensitive element **30** of Fig. 3. Since

dye substances of this nature are utilized in a photosensitive element in their colorless form, it is possible to increase the concentration of the dye substances in the element without having any effect upon the satisfactory exposure of the photosensitive layer. Preferably, the dye of this nature is colorless at a pH of about 7. To provide an acid environment in the photosensitive layer, a suitable acid such as an appropriate amount of phosphoric acid may be added to the photosensitive emulsion. Alkali contained in the processing liquid will, in general, supply the alkaline environment needed for creating the desired color change in the dye substance. If dye substances of the nature under discussion exert a desensitizing effect upon the silver halide, practices such as those described may be utilized to restrain desensitization.

When a dye substance which is colorless in a neutral or acid environment is utilized in a photosensitive element such as the element **30**, the portions of said substance which are employed to provide the positive image are transferred to the print-receiving element in unreacted form. Under these conditions, it is also desirable to utilize one of the practices previously pointed out for restraining reaction of oxidized developer on the print-receiving element with transferred dye. The processing of the photosensitive element **30** is carried out in a manner similar to that heretofore detailed. In the case of some dye substances which change color according to their environment, it may be desirable to incorporate alkali, for example sodium carbonate, in the print-receiving element. Also, in the case of leuco dyes and carbinols of basic dyes, it may also be desirable to include an oxidizing agent in the print-receiving element for the purpose of speeding up the color change. Both of the latter-mentioned practices are included within the scope of the present invention.

The photosensitive element **30** is especially adapted for use with the embodiment of the invention wherein a photosensitive element has a nondiffusing developer incorporated in the photosensitive layer thereof and such an element is utilized with a print-receiving element **45** which carries a stratum **47** of dye coated on the side thereof which is adapted to face the photosensitive element when processed. A dye stratum **47** is provided by incorporating the dye in a volatile solvent, for example 1 gram of dye in 100 cc. of acetone, and by coating the solution onto the surface of the print-receiving element **45**. Print-receiving element **45** comprises any of the embodiments thereof heretofore specifically discussed. As another practice, the dye utilized may be incorporated in a carrier material, such as one of those already described, for coating in a thin layer upon th print-receiving element. In this embodiment, the photosensitive layer is prepared in the manner described from a composition comprising a silver halide emulsion to which has been added a solution of the hydrochloride of the developer in water and phosphoric acid.

In the embodiment of the invention utilizing a print-receiving element **45**, a dye-precipitating mechanism is provided by the oxidation product of the nondiffusing developer incorporated in the photosensitive layer. Liquid spread between the photosensitive element and the print-receiving element is absorbed into both of these elements. In the photosensitive element, developer in solution in the absorbed liquid develops latent image therein and its oxidation product attracts dye placed in solution by the liquid in contact with the print-receiving element to cause liquid containing dye in solution to migrate into the photosensitive element in the exposed regions of the photosensitive layer where it is acted on by the oxidation product of the developer and becomes substantially immobilized or trapped in the photosensitive element. On the other hand, dye which may migrate into the photosensitive element but is not acted upon by the oxidation product of the developer is available in the usual manner for formation, on the print-receiving element, of a dye image which is the reverse of the latent image formed in the photosensitive element.

In cases where a photosensitive element is employed in which dye is incorporated, it is possible to make two or more transfer prints from the photosensitive element. This may be accomplished by utilizing a dye which is slowly soluble in alkaline solution and by employing a quantity of this dye in the photosensitive element which is in excess of that needed to provide a transfer print. Due to the fact that the dye used in this procedure is in excess of that required to provide a transfer print and because of its slow solubility rate, a quantity of this dye at least sufficient for a second transfer print remains in the processed photosensitive element. A second transfer print may be obtained by pressing the photosensitive element against an unused print-receiving element into which has been permeated a solvent for the dye. When sodium hydroxide is the alkali added to the liquid employed for processing the latent image, the dye in the photosensitive element will, in most instances, be converted to its sodium salt when in solution in the liquid. In general, the sodium salts of dyes are water soluble so that water may be employed as the liquid or solvent for effecting the second transfer of dye although, if necessary, an alkaline solution may be utilized.

Additionally, a photosensitive element such as the element **30** is useful in carrying out practices of this invention wherein the dye and/or the developer are included in the processing liquid such, for example, as in a container **16**, although as heretofore pointed out it is usually preferable to incorporate both the dye and the developer in the photosensitive element.

Modifications of the film structure, in addition to those already discussed, are included within the scope of the invention. For example, either the photosensitive element **10** or the photosensitive element **20** is useful for carrying out the invention when the developer is omitted from the element and is included in the processing liquid as in the container **16** shown in Fig. 1. The photosensitive element **10** is also available for practices wherein the developer is incorporated in the layer **12** thereof and dye is in solution in the processing liquid in container **16**. Other modifications of the photosensitive elements are possible. For example, either of the photosensitive elements **10** or **20** may include between the respective bases and the photosensitive layers thereof an additional liquid-permeable layer. In such event, developer may be distributed throughout such an additional layer and dye may be distributed throughout the layer **12** or **22**, or this procedure may be reversed. Also, as has been indicated, both the dye and the developer may be incorporated in the layer **22** of the photosensitive element **20**.

The invention also contemplates the modification of dyes to the end of improving their characteristics for use in the processes described herein. For example, a dye which has good characteristics as to color may not have the preferred characteristics for undergoing immobilization in a photosensitive element. It is possible to suitably modify the dye to improve its overall characteristics. For example, 1,5, dihydroxy naphthalene-4-azo benzene provides much higher contrast images with a conventional color developer than its commercially available form which has sulfonate groups added thereto. Such groups are solubilizing so that if a dye is too soluble and transfers too fast, it can be appropriately modified by omitting these solubilizing groups or by adding carbon chains of suitable lengths to the dye molecule.

Furthermore, a dye may be modified in other ways. For example, if the dye does not couple efficiently with the color developer employed, it may be modified by condensation with a phenol or naphthol preferably having a chloro group or groups para to the OH group of the phenol and in such a way that there is no conjugation between the new coupling function and the original dye, or, if the color of the original dye has changed, this change

is in a desired direction. As a further illustration it may be noted that it is, in general, most convenient if the dye is insoluble in water but is soluble in alkali. To decrease the solubility of such a dye in water, sulfonate groups thereon may be replaced with carboxy or sulfonamido groups. Generally, replacement of the sulfonate groups in this instance is preferred because omission of the sulfonate groups without replacement may deleteriously affect the stability of the dye.

It is particularly pointed out that practice of the invention is not limited to the use of cyan, magenta or yellow images. For example, dye positive images of a color other than those just mentioned are obtainable when several dyes, rather than a single dye, are employed in the photosensitive layer. The result of such an expedient is to give a positive image different from each of the individual dyes that are utilized for image formation. Thus, it is possible to form black and white dye positive images by the use of suitably colored dyes in appropriate quantities which, when added together, give black.

While the present invention is particularly suited for the formation of colored images, it is to be especially observed that practices herein are also utilizable for the formation of black and white positive images by the use of a mixture of dyes as just described or by the use of a single dye which is black such as, for example, any one of the black dyes heretofore mentioned. Additionally, the use of a black dye or a mixture of dyes which together provide black may be utilized for forming a black component in a multicolor picture.

The present invention finds particular utility in the field of color photography and, in addition to providing for the formation of monochromatic images of a single color, is useful in providing multicolor images. For example, the practices set forth herein may be used to provide the light-sensitive elemental portions in a multicolor photosensitive element of the type set forth in the previously mentioned application Serial No. 176,961 and also in my previously mentioned application Serial No. 358,011. Such multicolor photosensitive elements are processed in the manner described in the just-mentioned applications for providing in one step a multicolor image on a print-receiving element.

Additionally, two or more transparent print-receiving layers, each containing an individual color component image of a multicolor image, may be assembled in superposed and registered relation on a common support in a manner well understood by the art whereby to provide the desired multicolor image.

As another example, the invention is adapted for multicolor work carried out with special film units wherein two or more appropriately sensitized photosensitive elements are associated with a like number of print-receiving elements in a manner similar to that set forth in the copending application of Edwin H. Land, Serial No. 730,661, filed February 25, 1947, now Patent No. 2,647,049, for Photographic Element for Color Photography and a Process of Producing Multicolor Pictures. Also, as shown in the last-mentioned application, a plurality of color component images may be formed in the same print-receiving element by successively bringing the print-receiving element into registered contact with individual negative elements, each of which latter contains a negative latent image representative of a positive color component image to be formed in the print-receiving element.

Furthermore, the invention is useful for copying purposes from separation positives with any of the types of film units described. Of course, when the invention is used in the production of photographic originals, the spectral sensitivity of the different emulsion layers must be suitably chosen. For instance, instead of using a blue-sensitive emulsion, a panchromatic or a specially red sensitized emulsion is employed for producing a cyan positive image. However, for copy work from separation positives, this is obviously unnecessary.

Also, as has been intimated, photosensitive elements of this invention are available for color image formation therein, such, for example, as a master negative image. In this regard, a photosensitive element containing a dye and a silver halide developer of the character described is exposed to a suitable subject, and the photosensitive element is then permeated with the usual alkaline liquid. The result of permeation of the alkaline liquid into the photosensitive element is to develop latent image therein to silver and a colored substance which is in situ with the silver image and is less mobile in the element than dye, this colored substance comprising the reaction product of dye in the photosensitive layer and an oxidation product of the developer.

As the result of development there is also provided in the photosensitive element an imagewise distribution of dye and unreacted developer in the unexposed regions of the photosensitive element which is removable, as for example by washing, from the element. Following the removal of dye and developer, there remains in the photosensitive layer a silver image and a color image comprising the relatively immobile colored substance in situ with the silver image. The silver image may then be removed by the use of conventional silver bleaches which will not harm the substance providing the colored image, for example a bleach such as a mixture of a sodium or potassium halide and potassium ferricyanide. Prior or subsequent to bleaching, the photosensitive layer may be fixed in conventional manner. If the developer, because of its low mobility, is difficult to wash out of the photosensitive element, it is possible to effect its deactivation by appropriately acidifying it.

While a liquid container 16, which has been illustrated with the film units of this invention, provides a convenient means for spreading a liquid 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 layer, after exposure in suitable apparatus and while preventing further exposure thereof to actinic light, may be removed from such apparatus and permeated with the liquid processing composition as by coating the composition on the photosensitive layer or otherwise wetting the layer with the composition, following which the permeated layer, still without exposure to actinic light, is brought into contact with a print-receiving element for image formation in the manner heretofore described.

It is also to be kept in mind that the invention may be successfully practiced without the use of a film-forming material in the liquid processing reagent. As an illustration, with this latter expedient, a nonviscous processing composition is particularly applicable and may be applied to the negative material by imbibition or coating practices and may be similarly applied to the print-receiving element before the latter and the negative material are brought into superposed relation or contact for carrying out the transfer of positive image-forming components.

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 process of forming images in color which comprises absorbing a liquid into a photosensitive element including a photosensitive silver halide layer having a latent image therein and providing in solution in said layer a substantially uniform distribution of (1) a dye which possesses a coupling function and which is reactable with oxidized portions of a silver halide developer, said dye being mobile in said photosensitive layer when dissolved in said liquid and (2) a silver halide developer capable of providing, upon the development of said latent

image to silver, a gas which is generated in the exposed regions of said photosensitive layer and which thereby forms bubbles at least in the photosensitive layer and adjacent said exposed regions thereof, developing said latent image to silver with said developer in said photosensitive layer and immobilizing said dye in exposed regions of said photosensitive layer, said immobilization being effected at least in part by the formation of a barrier comprising bubbles of a gas formed in said photosensitive layer as a result of the oxidation of said developer while providing in said photosensitive layer as a further result of development an imagewise distribution comprising mobile dye and unreacted developer and transferring from said photosensitive layer, by imbibition, at least part of said imagewise distribution of mobile dye to a print-receiving element located in superposed relation to said photosensitive element to impart to said print-receiving element an image in terms of said mobile dye.

2. The process of forming images in color as defined in claim 1 wherein said print-receiving element and said photosensitive element are separated from superposed relationship at some stage of said process after the imagewise distribution of dye has been transferred from said photosensitive element to said print-receiving element.

3. The process of forming images in color which comprises spreading a liquid in a layer between and in contact with a photosensitive element comprising a photosensitive silver halide layer having a latent image therein and a print-receiving element comprising an image-receiving layer, absorbing said liquid into said photosensitive element including said photosensitive layer and providing in solution in said layer a substantially uniform distribution of (1) a dye which comprises a coupling function and which is reactable with oxidized portions of a silver halide developer, said dye being mobile in said photosensitive element when dissolved in said liquid and (2) a silver halide developer capable of providing upon the development of said latent image to silver a gas which is generated in the exposed regions of said photosensitive layer and which forms bubbles at least in said photosensitive layer and adjacent said exposed regions thereof, developing said latent image to silver with said developer in said photosensitive layer and immobilizing said dye in said exposed regions, said immobilization of dye in exposed regions being effected at least in part by a barrier comprising bubbles formed in said photosensitive layer by said gas produced by said developer upon development of a latent image, providing as a further result of development an imagewise distribution comprising mobile dye and unreacted developer in said photosensiitve layer and transferring from said photosensitive layer by imbibition at least part of said imagewise distribution of dye to a print-receiving element located with respect to said photosensitive element in superposed relation thereto for receiving a deposition of liquid from said photosensitive layer to deposit said dye contained in said imagewise distribution upon said print-receiving element to impart thereto an image in terms of said dye.

4. A process of forming images in color as defined in claim 1 wherein both the unreacted developer and the dye present in said imagewise distribution in said photosensitive layer are transferred, by imbibition, at least in part to said print-receiving element.

5. A process of forming images in color as defined in claim 1 including the step of mordanting in said print-receiving element dye which is transferred thereto.

6. A process of forming images in color which comprises absorbing a liquid into a photosensitive element including a photosensitive silver halide layer having a latent image therein and providing in solution in said layer a substantailly uniform distribution of (1) a dye which comprises a coupling function and which is reactable with oxidized portions of a silver halide developer, said dye being mobile in said photosensitive element when dissolved in said liquid and (2) bis-benzene-sulfonyl hydrazide, developing said latent image to silver with said bis-benzene-sulfonyl hydrazide and immobilizing said dye in exposed regions of said photosensitive element, said immobilization being effected at least in part by the formation of a barrier comprising bubbles of a gas formed in said photosensitive layer as a result of the oxidation of said bis-benzene-sulfonyl hydrazide while providing as a further result of development an imagewise distribution comprising mobile dye and unreacted bis-benzene-sulfonyl hydrazide and transferring from said photosensitive element, by imbibition, at least part of said imagewise distribution of mobile dye to a print-receiving material located in superposed relation to said photosensitive element to impart thereto an image in terms of said mobile dye.

7. A photographic product comprising a photosensitive element having a liquid permeable portion including a silver halide photosensitive layer, a print-receiving element for receiving a transferred image and a container holding a liquid, said photosensitive element, said print-receiving element, and said container being attached together to permit at least a portion of said print-receiving element and said photosensitive element to be superposed with said container so positioned as to be capable of being ruptured and of releasing its liquid content to at least partially permeate said superposed print-receiving element and photosensitive element including said photosensitive layer, said product having positioned therein (1) a dye which comprises a coupling function and which is reactable with oxidized portions of a silver halide developer, said dye being soluble in said liquid and mobile in said photographic product when in solution in said liquid and (2) a silver halide developer which is also soluble in said liquid and which upon the development of a latent silver halide image to silver provides as an oxidation product a gas which is generated in the exposed regions of said photosensitive layer and forms bubbles at least in said photosensitive layer and adjacent said exposed regions thereof to provide a barrier to at least assist in preventing the transfer of dye from said exposed regions of said photosensitive layer, said developer being bis-benzene-sulfonyl hydrazide, said materials being rendered effective upon the rupture of said container for providing in said photosensitive layer a substantially uniform distribution of said dye and said bis-benzene-sulfonyl hydrazide in solution in said liquid, thereby to develop a latent image in said photosensitive layer and to form said gas and to immobilize said dye in said exposed regions as well as to provide in the photosensitive layer an imagewise distribution comprisnig dye and unreacted bis-benzene-sulfonyl hydrazide, at least said dye in said imagewise distribution being in mobile condition and transportable from said photosensitive element to said print-receiving element for imparting to said print-receiving element a transfer image in terms of said dye.

8. A photosensitive element comprising a support, at least one liquid-permeable layer mounted upon said support, photosensitive silver halide substantially uniformly distributed throughout a permeable layer of said element, a dye comprising a coupling function and which is reactable with oxidized portions of a silver halide developer, said dye being uniformly distributed throughout a liquid-permeable layer of said element, bis-benzene-sulfonyl hydrazide substantially uniformly distributed throughout a permeable layer of said photosensitive element, said dye and said bis-benzene-sulfonyl hydrazide being soluble in a liquid processing composition permeated into said photosensitive element to effect the processing thereof and when so dissolved being mobile in said photosensitive element.

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