April 24, 1973 H. C. HAAS 3,729,314

NOVEL PHOTOGRAPHIC PROCESSES AND PRODUCTS

Filed Dec. 18, 1969

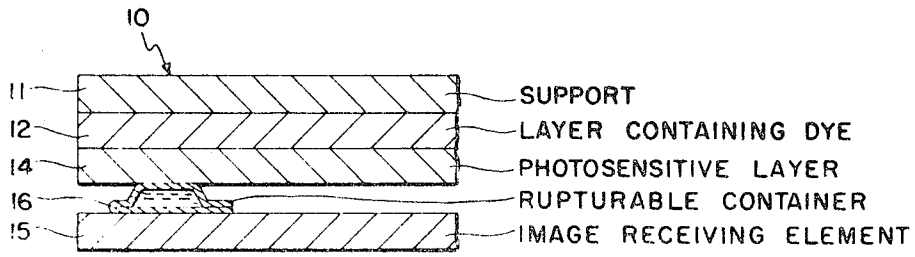


FIG. 1

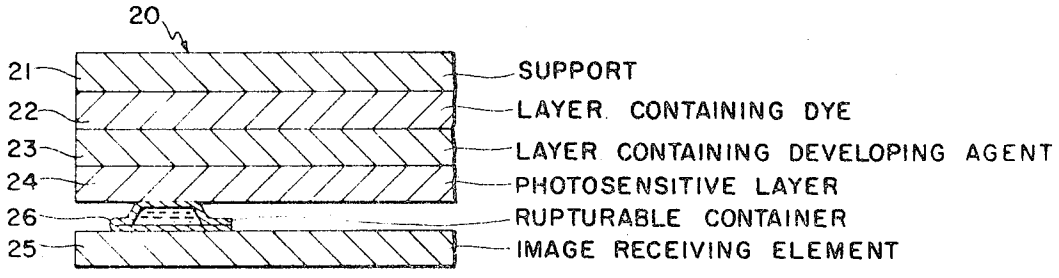


FIG. 2

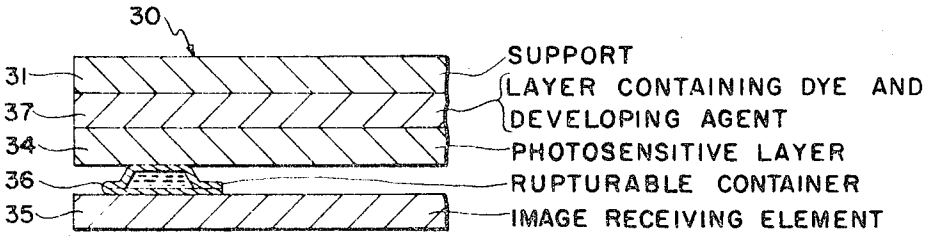


FIG. 3

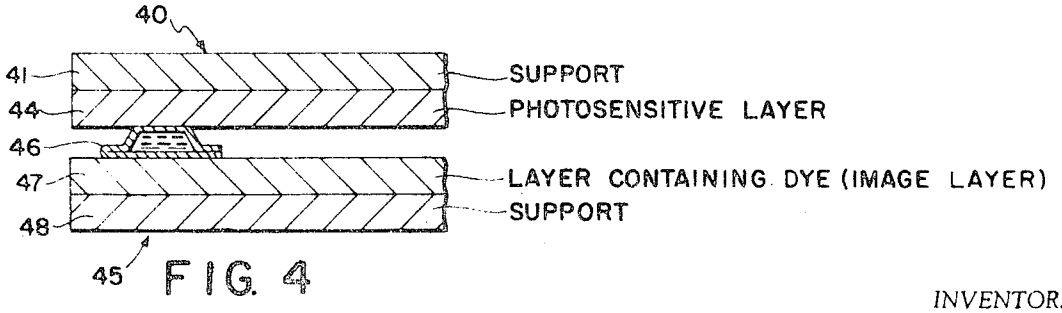


FIG. 4

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3,729,314

NOVEL PHOTOGRAPHIC PROCESSES AND PRODUCTS

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Continuation-in-part of application Ser. No. 740,965, June 28, 1968. This application Dec. 18, 1969, Ser. No. 886,305

Int. Cl. G03c 11/12

U.S. Cl. 96—29 D 10 Claims

ABSTRACT OF THE DISCLOSURE

A novel image forming system comprising forming an imagewise distribution of a mordant in the developed areas of an exposed photosensitive layer, mordanting dye in said areas, and forming a reverse image in terms of dye transferred by diffusion from undeveloped areas of the photosensitive layer to an image-receiving layer.

This application is a continuation-in-part of U.S. application Ser. No. 740,965, filed June 28, 1968, now abandoned.

This invention relates to photography and more particularly to products, compositions and processes for obtaining color images.

Many systems are known for preparing color images by diffusion transfer. In such prior systems, for example, a photosensitive element containing at least one light-sensitive silver halide emulsion, an associated layer of color-providing material, e.g., a complete dye or a color coupler, is exposed and then developed to provide, as a function of development, an imagewise distribution of color-providing material which is transferred, by imbibition, to a superposed image-receiving element, e.g., a dye-able sheet material, to provide thereon a monochromatic or multicolor image of the original subject matter. Many of these prior systems rely for color transfer image formation upon mechanisms for providing, as a function of development, a differential in mobility or diffusibility in the processing fluid of the color-providing material.

One such system is the one described in U.S. Pat. No. 2,983,606, issued to Howard G. Rogers, which utilizes a compound called a dye developer which in its oxidized state is less mobile than in its unoxidized state.

Color coupling mechanism processes for providing a color image are set forth in U.S. Pats. Nos. 2,661,293 and 2,698,798 issued to Edwin H. Land. In these patents, the principle involved concerning the immobilization of dye in the exposed areas of the photosensitive element is the reaction by "coupling" between oxidized developing agent with a separate complete dye. That is, the developing agent, as it reduces the silver halide to silver is oxidized and this oxidation product reacts with the coupling dye to form a product which is substantially less soluble than the dye itself, such that it will precipitate out in situ in the photosensitive layer, or the reaction product can comprise a molecule of such a size that it is substantially immobile and thus remains in the photosensitive layer. An illustrative reaction is that between an aminophenol developing agent and a dye, which oxidized aminophenol will form an indophenol with the dye, said indophenol dye being a large bulky molecule.

In the present invention, a separate complete dye is mordanted by a mordant function that comprises a part of the silver halide developing molecule. Thus it is seen that whereas in U.S. Pat. No. 3,087,817, the complete dye was capable of reacting only with developing agent that had been oxidized and could not react with developing agent that had not been oxidized, such is not the situation here. In the instant invention, as soon as the dye and the developing agent bearing a mordanting site are

solubilized by the processing composition, the dye is capable of association with the mordant site of the developing agent. In the areas of development, associated dye will become mordanted, i.e., immobilized, in the photosensitive layer since the developing function of the mordanting developer is of a nature such that in its oxidized state upon the reduction of silver halide to silver, it will interact with the polymeric matrix of the silver halide layer and become localized, i.e., immobilized, thereby forming an imagewise distribution of mordanted dye. In the undeveloped areas, dye is free to transfer to the image-receiving layer since it does not comprise immobilized, imagewise distributed mordant. The image-receiving layer preferably comprises a polymeric mordant for the dye being transferred.

Accordingly, a primary object of this invention is to provide novel processes, products and compositions for preparing color images.

Another object is to provide novel products and processes useful for obtaining color images by diffusion transfer.

Still another object is to provide novel systems for obtaining as a function of development of an exposed silver halide layer, an imagewise distribution of dye in the exposed areas of said silver halide layer by the reaction of a dye with a mordant site present as a substituent on a silver halide developing agent, which agent is rendered immobile and becomes localized by the reaction of oxidized developing radicals with certain moieties present in the photosensitive layer upon the reduction of silver halide to silver in said areas.

Yet another object is to provide novel systems for obtaining both positive and negative dye images by the use of a silver halide developing agent characterized by forming upon the development of exposed silver halide to silver, at least one oxidation product which is effective in preventing dye present in exposed regions of the photosensitive layer from transferring to an image-receiving layer and which developing agent comprises a substance reactable with said dye to provide a reaction product which when the developing agent is oxidized, is a substantially non-diffusible mordanted dye localized in the photosensitive layer by interaction of the oxidized developing agent with the matrix material of the photosensitive layer.

Other objects of the present 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 product 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 drawings wherein:

The term "nondiffusing" used herein has the meaning commonly applied to the term in color photography and denotes materials which for all practical purposes do not migrate or wander through organic colloid layers, such as gelatin, in the presence of aqueous alkaline processing solution. The same meaning is to be attached to the term "immobile." The term "diffusible" as applied has the converse meaning and denotes materials having the property of diffusing effectively through the colloid layers of the sensitive elements in the presence of aqueous alkaline processing solution. "Mobile" has the same meaning.

The term "mordant(ed)" as used herein has the meaning commonly applied to the term in color photography

and denotes a substance capable of (the act of) uniting with certain dyes to form insoluble colored compounds fixed in place.

As used herein, the expression "developer" is intended to refer to silver halide developing agents which, as is well known in the art, are compounds which develop a latent image contained in an exposed silver halide emulsion.

The term "dye association reaction" refers to the reaction of the dye with the mordant sites. Since this reaction can take place in solution such that the dye is not fixed in place or immobilized, this term is utilized since *mordanted* refers to dye reacted with mordant sites which are fixed in place. As will be seen from the discussion, when the mordant sites associated with dye become localized, the dye will be said to be then mordanted.

The term "complete dye" is meant to include compounds containing only a chromophore and requisite solubilizing group(s).

FIG. 1 is a diagrammatic cross-section 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 cross-section of another embodiment of a film unit wherein the dye and developing agent are in separate layers of the photosensitive element;

FIG. 3 is a diagrammatic cross-section of a film unit comprising another embodiment of a photosensitive element; and

FIG. 4 is a diagrammatic cross-section of yet another embodiment of a film unit forming the subject matter of this invention.

The present invention is concerned with novel procedures and products 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 processes of this invention are effected by the employment of complete dyes of a character soluble at lease 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 dye 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 developing agents which are soluble in alkaline solution are utilized with complete dyes in the carrying out of this invention. In practice, use is made of a product resulting from the reaction of the oxidized developing agent with the matrix material of the silver halide layer, whereby oxidized developing agent in the areas of development becomes localized and rendered incapable of migration to the image-receiving stratum. Since the developing agent utilized is one that bears a substituent capable of mordanting the complete dye utilized, dye in the developed areas will become associated and localized, thereby forming an imagewise distribution of mordanted dye in the photosensitive layer. In the unexposed areas of the photosensitive layer, since substantially no mordanting sites will be bound in place, dye will be free to diffuse through the photosensitive layer to the image-receiving stratum.

Developing agents suitable for use in the processes of this invention have to perform several functions. The developing agent must of course be able to develop a latent silver halide image. Secondly, in the areas of the photosensitive layer where exposure and development have taken place such that developing agent so situated has been oxidized, this oxidized developing agent must interact with the matrix material of the photosensitive layer to become substantially immobilized in situ. Thirdly, the developing agent must contain a substituent capable of mordanting the dye being utilized.

Such developing agents comprise compounds of the general formula:

DEV—MORD

wherein DEV is a silver halide developing radical whose oxidation product is capable of interacting with the polymeric matrix of the photosensitive layer; and MORD is a radical capable of mordanting a dye.

Silver halide developing agents whose oxidation products are capable of such matrix interaction, include but are not limited to the so-called tanning developers. These are developing agents which interact with gelatin with the result that the gelatin is hardened in those areas of interaction. Further discussion about the tanning developers will be found at page 304 of The Theory of the Photographic Process, third edition, by Mees and James.

Well-known among the tanning developers are those of the dihydroxyphenyl series which in their oxidized form will interact with gelatin. While applicant is not certain of the nature of the interaction between the oxidized form of the developing agent and the gelatin, it is believed that amine groups found in the gelatin attack the quinone ring.

The hydroquinone developers, i.e., the hydroquinone developing radicals, are the preferred developing agents since it is known that they will interact not only with gelatin, but also with other polymeric materials utilized as the matrix of the photosensitive layer.

It can be concluded therefore, that the choice of developing radical is dependent upon the choice of the emulsion binder or matrix. The ultimate choice lies within the skill of the art.

While the hydroquinonly developing agents are the preferred developing agents, aminophenol silver halide developing compounds can be utilized in a similar manner.

The silver halide developing moiety of the mordanting developing agent alternatively may be a diaminophenyl group, as is common in color developing agents. Such diaminophenyl developing agents may be immobilized in developed areas by a coupling reaction between the quinoneimine group, formed upon oxidation, with an immobile coupling radical, e.g., a nondiffusible color coupler or a silver halide binder having color coupler substituents, e.g., a modified polyvinyl alcohol wherein positions on its chain have been substituted with phenol or naphthol and wherein the substituted phenols or naphthols have open positions for coupling which are para to hydroxyl groups. Another example occurs where the polyvinyl alcohol has been substituted with a compound containing a reactive methylene group which is available for coupling. The incorporation of lightsensitive silver halide in polymers of the character mentioned is understood by the art, an example thereof being disclosed in U.S. Pat. No. 2,397,864.

In a further embodiment, it is contemplated to employ developing agents, the main mordanting function of which is insulated from the developing system of said molecule. By "insulated" it is meant that the mordanting function is separated from the developing system by a linkage which prevents any system of conjugation or resonance from extending from the mordanting function to the developing function of the molecule. Dyes mordanted to such compounds would be immobilized in developed areas in the manner described.

As an illustration of an insulated mordanting developer, mention may be made of compounds of the general formula:

DEV—LINK—MORD

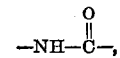
wherein DEV is a silver halide developing radical capable of interacting with the polymeric matrix of the photosensitive layer; LINK is a linking or connecting radical between DEV and MORD; and MORD is a radical capable of mordanting a dye.

The silver halide developing substituents and the divalent linking groups referred to above may be selected from those heretofore well-known in the art.

As examples of useful dihydroxyphenyl silver halide developing substituents, mention may be made of ortho-dihydroxyphenyl, para-dihydroyphenyl and nuclear-substituted derivatives thereof, e.g., chloro, methyl, phenyl, and/or methoxy-substituted derivatives thereof, particularly nuclear-substituted p-dihydroxyphenyls such as methylhydroquinonyl, p-methylphenylhydroquinonyl, chlorohydroquinonyl, methoxyhydroquinonyl, 2,6 - dimethylhydroquinonyl, 2,6 - dimethoxy - hydroquinonyl, 2-methoxy - 6 - methyl-hydroquinonyl, 2,3 - dimethyl-hydroquinonyl, 2,5,6-trimethyl-hydroquinonyl, etc.

As examples of useful nitrogen containing silver halide developing radicals, mention can be made of any of the above-mentioned dihydroxyaryl radicals wherein one or both of the hydroxyl groups is replaced by an $—NH_2$ group. The precursors for such nitrogen containing developing radicals are those radicals which contain either two $—NO_2$ groups or one $—NO_2$ group and one hydroxyl precursor group in an ortho or para relationship to each other.

As examples of useful divalent linking groups, for the preferred embodiment, to join the dihydroxyphenyl moiety to the designated group capable of mordanting the dye, mention can be made of



aminophenalkylthio, aminoalkylamino, aminophenalkyl, alkylthio, aminophenyl, acyl, aminophenoxy, lower alkylene, as well as other linking groups known from the art as linking groups.

A mordant as is generally known in the art is a chemical that is used to fix a chromophore to a substrate, usually by adsorption. Mordants and the act of mordanting are both well known and further explanatory discussion is unnecessary.

For use in the present invention, the mordant for the dye comprises a compound of the formula:

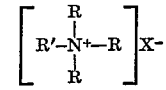
DEV—$LINK_n$—MORD

wherein DEV is a radical as previously defined, LINK is a radical as previously defined, n is 0 or 1, and MORD is a radical capable of mordanting a dye.

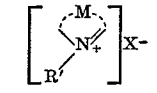
As has been indicated, the choice of the mordant is dependent on the dye utilized. The ultimate selection lies within the skill of the art. Suffice it to say that for use within the environs of the present invention the mordant must be associated with a silver halide developing moiety which in its oxidized state is capable of interacting with the matrix material of the photosensitive layer whereby it is rendered immobile.

In a preferred embodiment of the invention, wherein an acid dye is used as the dye, which requires the use of a basic mordant, especially useful results have been obtained through the use of quaternary ammonium compounds. As is known, quaternary ammonium compounds are organic compounds containing a pentavalent nitrogen atom. Generally they can be considered as derivatives of ammonium compounds wherein the four valences usually occupied by the hydrogen atoms are occupied by organic radicals. Generally, the organic radicals are joined directly to the pentavalent nitrogen through a single or double carbon-to-nitrogen bond. The term quaternary ammonium, as used herein, is intended to cover compounds wherein the pentavalent nitrogen is one of the nuclear atoms in a heterocyclic ring as well as those wherein each of the four valences is attached to separate organic radicals, e.g., tetraalkyl quaternary ammonium compounds. As illustrations of quaternary ammonium compounds, mention may be made of those represented by the following formulae:

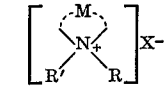
(1)



(2)



(3)



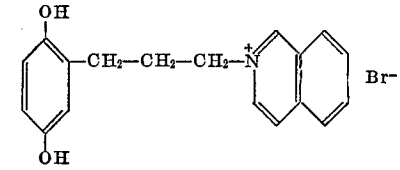
wherein each R is an organic radical, R' comprises the silver halide developing radical DEV, X is an anion, e.g., hydroxyl, bromide, chloride, toluene sulfonate, etc., and M represents the atoms necessary to complete a heterocyclic ring. Where the pentavalent nitrogen atom is joined to the remainder of the MORD radical via a double carbon-to-nitrogen bond [as in (2) supra], care should be taken that no alkyl substituent be present on the alpha or gamma carbon in the MORD moiety in order to preclude enamine formation when the compounds are contacted with alkali. (Enamine formation in compounds so substituted, and color photographic processes based thereon, are described in copending applications Ser. Nos. 741,548 and 741,549, both filed July 1, 1968, in the name of Stanley M. Bloom.)

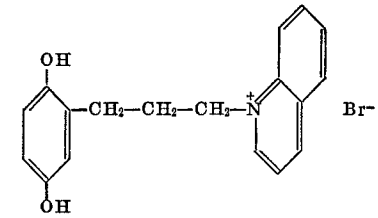
Other useful onium compounds which comprise mordants for the preferred embodiment include but are not limited to the tertiary sulfonium and the quaternary phosphonium compounds.

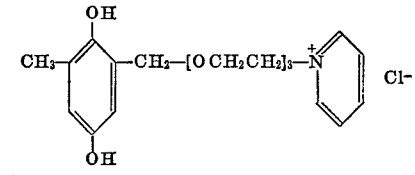
As examples of useful compounds within the scope of formula:

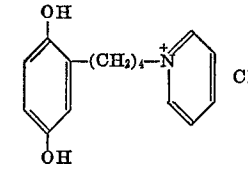
DEV—LINK—MORD

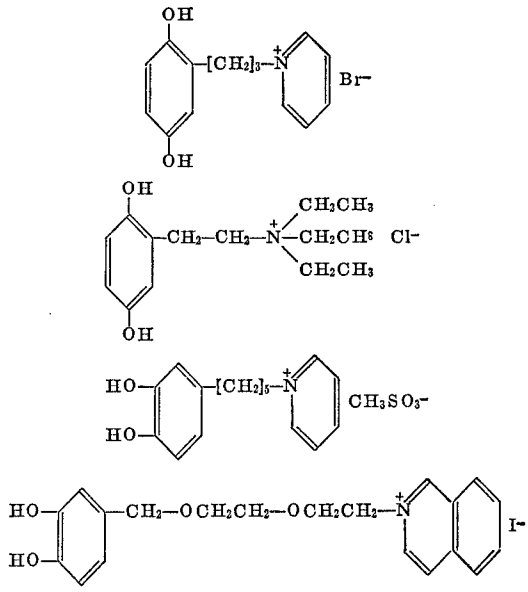
as previously defined, and which are suitable for use in this invention, mention may be made of the following:











Compounds of the structure

DEV—LINK—MORD

can be prepared among other ways by the alkylation of an amine. This mode of preparation of such compounds forms part of the subject matter of a copending application Ser. No. 741,293, filed July 1, 1968, in the name of Stanley M. Bloom.

Example 1 below is reproduced from said Bloom application for convenience.

A large number of dyes are available for the practice of this invention. Because of the wide choice of classes from which the dyes may be selected, it is possible to form images of dyes which have highly accurate absorption characteristics, as well as to form images which are substantially stable.

The only factors to be considered in choosing dyes for use in the instant invention are whether the dye can be mordanted by the particular mordant group present on the developing agent molecule; whether the dye will diffuse sufficienty through the emulsion to the image-receiving layer to form an acceptable image during the time period allocated for processing; and whether dye mordanted in the developed areas of the photosensitive layer will remain substantially immobile during the period of processing.

It is considered to be within the skill of the art to know which dyes can be mordanted by certain mordants and which mordants will mordant certain dyes. Optimization of the process can be achieved by routine experimentation.

Among the classes from which suitable dyes are available, mention may be made of the monoazo, disazo, triphenyl methane, xanthane, thiazine and anthraquinone dyes. The field of dye materials is further extended by the employment of dye substances of the type 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 conventional couplers, 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 the developing agent. Dyes of the characteristics described and/or their reaction products should also be stable to light and to photographic solutions. Further discussion on the employment of dyes subject to environmental change for use in this invention will be found infra.

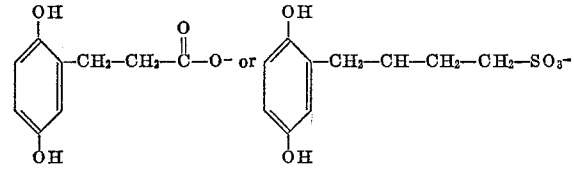
As has been indicated, many classes of dyes are suitable for use in this invention. A preferred type of dye is that commonly referred to as an acid dye. This type includes any dye which in alkaline medium forms a negative charge. Dyes which possess phenolic, imide and carboxyl groups, as well as —SO_2H; —SO_3H; —SO_2NHR; and —C=O—NH—C=O— moieties fall within this category.

Acid dyes, as is known in the art, are mordantable by compounds bearing a positive charge. For use in the present invention this positive charge must be capable of existing in a highly alkaline environment. Typical positively charged compounds which are suitable as mordants for acid dyes are those compounds bearing onium groups, e.g. quaternary ammonium. The advantage to be gained from the use of acid dyes is the fact that the dyeing process does not depend on the spatial configurations of the dye and the material to be dyed for satisfactory results, but only on the neutralization of opposing charges.

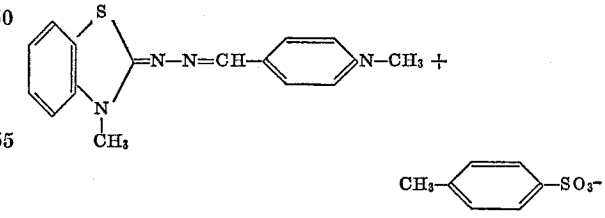
Typical acid dyes include but of course are not limited to the following:

Color index No.:	Color index Name
14645	Mordant Black 11.
16105	Mordant Red 9.
16185	Acid Red 27.
17560	Acid Black 84.
19020	Acid Yellow 18.
43820	Mordant Blue 3.
44100	Mordant Blue 42.
59040	Solvent Green 7.

While the use of acid dyes as the dye with a mordanting developer containing a positive charge has been described as an especially useful preferred embodiment, results of equal quality can be obtained in the situation where the charges are reversed. Such a system would utilize an anionic mordanting developing agent such as:



with a cationic, i.e., basic dye, such as:



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 dye of the character with which this invention is concerned, and a conventional photosensitive layer **14** of silver halide.

Layer **12** is penetrable by the liquid processing composition employed so that dye contained therein may be placed in solution. 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. It is also contemplated that the layer of liquid processing composition may serve as the image-receiving, i.e., dyeable material under certain circumstances.

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.

In the embodiment of FIG. 1, the mordanting developing agent used in this invention comprises a constituent of the liquid processing composition. In other embodiments, the mordanting developing agent may be positioned in a separate and distinct layer of the photosensitive element.

In addition to the alkaline material, the processing composition may include viscosity increasing film-forming reagents such as hydroxyethyl cellulose, sodium carboxymethyl cellulose, etc., additional reagents performing specific desired functions, e.g., antifoggants, etc., it being understood that any of these ingredients may be present initially in the film unit, in which case the processing composition is formed by contacting the film unit with the aqueous alkaline material. In any event, the processing composition may, if desired, be confined in a frangible container or "pod" such as described, for example in U.S. Pats. Nos. 2,543,181 and 2,634,886, issued to Edwin H. Land.

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 the 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.

The photosensitive silver halide layers used herein are provided by any of the conventional silver halide emulsions, e.g., silver chloride, silver bromide, silver bromoiodide, silver chlorobromide or silver chlorobromoiodide. The emulsion layer may also contain the various additives heretofore employed in such layers, e.g., optical sensitizers, antifoggants, hardeners, plasticizers, coating aids, speed-increasing materials, ultraviolet absorbers, etc.

As examples of typical materials which may be employed for the support mention may be made of films of cellulose nitrate, cellulose acetate, polyvinyl acetal, polystyrene, polyethylene terephthalate, polyethylene, polypropylene, etc., paper, glass and others.

The particular sensitivity range of the photosensitive layer will be chosen to meet to the particular requirements necessary for ultimate usage of the product. The silver halide emulsions comprise the photosensitive material and other additives if any preferably in a matrix or binder. It is preferred to utilize gelatin as the hydrophilic colloid or binder material although such material as polyvinyl alcohol and its water-soluble derivatives and copolymers, as well as water-soluble polymers such as polyacrylamide, imidized polyacrylamide, etc., and other water-soluble film-forming materials that form water-permeable coats such as colloidal albumin, water-soluble cellulose derivatives, etc., can be utilized in preparing the present photographic elements. Compatible mixtures of two or more of such colloids can also be utilized.

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 upon the support. Layer **12** may or may not be penetrable by water but it is necessary that it be readily penetrable 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.

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 layer **23**, comprising a carrier, such as cellulose acetate hydrogen phthalate, in which the developing agent is incorporated.

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 layer **23**, the layer **23** may be made sufficiently thick so as to substantially prevent pentration 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. For example, the developer may be omitted from the layer **23** and included in the photosensitive layer **24**.

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 **25** 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 image formed in the photosensitive element **20** upon exposure thereof.

The photosensitive element of FIG. 3 is formed in a similar manner to the elements of FIGS. 1 and 2 and it uses substantially similar materials for the purpose of construction. It too is adapted for use with an image or print-receiving element. In this embodiment of the invention, the

dye and the developing agent are situated in the same layer, **37**.

A suitable carrier material when layer **37** comprises a carrier in which dye and developing agent are distributed is one which will swell when subjected to hydroxyl ion or alkaline liquids sufficiently to release dye and developing agent contained therein. Examples of carriers include gelatin, zein, polymethacrylic acid, shellac and cellulose acetate hydrogen phthalate.

In FIGS. 1, 2 and 3 a construction has been detailed wherein the developing agent and the complete dye are located in strata in back of the photosensitive stratum or between the photosensitive stratum and the support of the photosensitive element. 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 developing agent utilized in providing the negative image in the photosensitive element with consequent avoidance of highlight color in the transfer or positive image.

However, the preferred construction is subject to considerable variation. For example, a layer or stratum containing the developing agent and/or dye may be located in front of the photosensitive layer. Such a situation comprises FIG. 4 wherein the dye is initially placed in a layer **47** of the image-receiving element **45** and the developing agent is contained in rupturable container **46**.

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; carbohydrates, 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. Other preferred, especially for phenolic and naphtholic dyes, image-receiving materials are nylons.

A particularly useful image-receiving layer is a mixture of polyvinyl alcohol and poly-4-vinylpyridine. Such receiving layers are disclosed and claimed in U.S. Pat. No. 3,148,061, issued Sept. 8, 1964, to Howard C. Haas.

In the preferred embodiment wherein acid dyes are used, the preferred image-receiving layers comprise either a polymeric amine, such as referred to in the paragraph above or a polymeric quaternary salt such as a trialkylammonium benzaldehyde quaternary salt of the nature disclosed in U.S. Pat. No. 3,239,337, issued Mar. 8, 1966, to Howard C. Haas.

It will be noted that other materials useful in the diffusion transfer processes may be incorporated into the image-receiving layer or one of the other layers of the image-receiving element. As an example of such a material, mention may be made of development restrainers such as 1-phenyl-5-mercaptotetrazole.

It will be apparent that, by appropriate selection of the component strata of the image-reeciving element from among suitable known opaque and transparent materials, it is possible to obtain either a colored positive reflection print or a colored positive transparency.

As heretofore mentioned, the image-receiving material of the positive element **15** includes any material dyeable from alkaline liquid. The positive elements **15**, **25**, and **35** may, as shown, comprise a single sheet of permeable materials or may comprise a support which carries a layer or stratum of a permeable imge-receiving material. An example of such is imibition 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.

When any of the photosensitive elements such as those illustrated in FIGS. 1–4 are exposed and then processed by spreading an aqeuous alkaline processing composition between the thus exposed element and an image-receiving layer or dyeable stratum shown as but not limited to being integrated into the image-receiving elements **15**, **25**, **35** and **45**, a positive colored transfer image is obtained, in addition to the original colored negative image.

Referring to the film unit of FIG. 1 the processing for transfer image formation, following the exposure of the photosensitive element **10**, proceeds by rupturing container **16** and spreading the alkaline liquid processing 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**, dye is dissolved in the processing liquid and transported in solution into the photosenitive layer **14**.

Where the mordanting developing agent transported to the photosensitive layer **14** reacts with the exposed silver halide, it is oxidized as a function of development, i.e., the reduction of silver halide to silver. The oxidized developing function interacts with the matrix of the photosensitive layer and the mordanting function reacts with adjacent dye to form an association product. As previously noted, the dye reacted with, i.e., associated with the mordanting function of the developer, is immobilized in the developed areas to provide imagewise distribution of mordanted dye in the developed areas of the photosensitive layer. Non-mordanted dye remains free to transfer from the undeveloped areas of the photosensitive layer to a dyeable stratum comprising a polymeric mordant for said dye, whereupon the dye will be mordanted in an imagewise distribution.

In the embodiment of the invention set forth in FIGS. 1, 2 and 3 control of dye diffusion to insure immobilization in developed areas due to the formation of an imagewise distribution of mordanted dye and the formation on the image-receiving element of a dye image can be readily achieved by the adjustment of the various factors that influence the chemical reactions taking place. The formation of mordanted dye in the desired areas of the photosensitive element is influenced by the size, the diffusibility rate and the solubility of the dye, as well as the size, diffusibility rate and the solubility of the mordanting agent, as well as the distance of the transfer gap and the overall spatial relationship of the reactants. Control of these factors is considered to be within the skill of the art.

In the embodiment of the invention of FIG. 4 utilizing an image-forming element **45**, a dye-precipitating mechanism is provided by the oxidation product of the developing agent containing mordanting groups. Liquid spread between the photosensitive element **30**, and the image-forming element is absorbed into both of these elements. In the photosensitive element, developing agent in solution in the absorbed liquid develops the latent image and said developing agent's mordant site attracts dye, dissolved from dye layer **47** by the liquid in contact with the image-receiving element, to cause dye in solution to migrate into the photosensitive element in the developed regions of the photosensitive layer where due to interaction between the matrix and the oxidized developing agent, it becomes substantially immobilized or trapped in the photosensitive element. On the other hand, dye which may migrate into the photosensitive element but is not immobilized by oxidized, bound in place developing agent is available in the usual manner for formation, on the image-forming element, of a dye image which is the reverse of the image developed in the photosensitive element. It is to be seen that in an embodiment of this nature that the developing agent can be situated in

several locations, namely in layer **47**, in the processing composition, and above, underneath or in photosensitive layer **44**. It is also to be seen that in this embodiment since all the dye is originally located in the image-forming layer, that in order for part of the dye to migrate into the photosensitive layer, the mordanting substituent on the developing agent, should exert a preferential attraction for the dye.

The photosensitive element and the image-receiving stratum are separated from each other, as by stripping, aftr processing, unless they are separated by an opaque layer, e.g., of titanium dioxide, which effectively masks the negative image.

To recapitulate and further explain, it is seen that the positive image can potentially be derived from two sources: dye that was never associated with mordanting sites, as well as dye which though associated has not been rendered immobile because the developing moiety was not oxidized and subsequently immobilized in the manner heretofore discussed.

As has been indicated, the term "mordanted" refers to dye fixed in place. Thus it is seen that associated dye that is not fixed in place in the photosensitive layer by the mechanism relating to the developing radical can not be said to be mordanted. Therefore, all dye not mordanted is available for image formation and shall be referred to as unmordanted dye.

In regard to positive image formation, unmordanted dye which is not associated will become mordanted to the dyeable stratum comprising the image-receiving layer, which layer comprises a polymeric mordant for said dye. Dye that is associated with mordanting sites, will take part in an interchange reaction with the mordant in the image-receiving layer, which mordant is a preferential mordant for the non-immobilized dye.

The substance formed by the reaction of the complete dye with the image-receiving layer's mordanting sites or with the photosensitive layer's mordanting developing agent may or may not possess color characteristics which are the same as unreacted (unassociated) dye. Techniques to tailor chromophores are within the skill of the art, and may be applied to either the image-receiving layer or the photosensitive layer in accordance with the end use of the images formed in the respective layers.

As has been indicated, the preferred dyes are acid dyes, which are mordantable by groups bearing a positive charge. The preparation of a silver halide developing agent which is capable of interaction with a polymeric matrix such as gelatin and which contains a group bearing a positive charge which will act as a mordant site for an acid dye is illustrated by the following preparation of 2,5-dihydroxyphenyl propyl 3-pyridinium bromide, a compound within the formula:

DEV—LINK—MORD.

This preparation is intended to be illustrative only and should not be interpreted as limiting the applicant to the details therein set forth.

EXAMPLE I

Preparation of N-γ(2′,5′-dihydroxyphenyl)propyl pyridinium bromide.

In a nitrogen atmosphere, 15 g. of lithium aluminum hydride (M.W. 37.95), 0.4 mole, was slurried in 200 cc. of dry ether. 87 g. of 2,5-dimethoxydihydrocinnamic acid, 0.416 mole, in 550 cc. of dry ether was added dropwise. The addition of the ether caused the dihydrocinnamic acid to reflux without the addition of extra heat. Stirring was continued for a period of one hour. Sufficient water was added dropwise, to decompose excess lithium aluminum hydride.

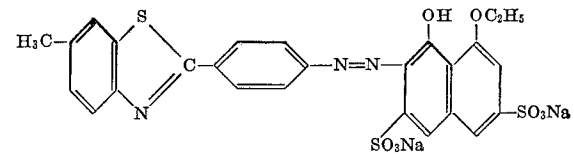
620 cc. of 10% H_2SO_4 were added to the reaction vessel. A two layer system results. The ether layer is separated and washed several times with an aqueous solution of $NaHCO_3$, cautiously, and then with water and dried. The ether was evaporated off having a fluid oil comprising 2,5-dimethoxyphenyl propyl alcohol. 54 g. of the approximately 70 g. of said alcohol were cooled to —10° C. To this was added 40 g. of PBr_3, 0.14 mole, dropwise. The temperature was permitted to reach room temperature and the mixture was stirred for 2 hours and then allowed to stand overnight. It was heated to 80° C. for 0.5 hour and then cooled and poured on to ice mixed with water. The end product which was 2′,5′-dimethoxyphenyl 3-propyl bromide was extracted with ether, washed and dried. 52 g. (0.2 mole) of the bromide and 15.8 g. (0.2 mole) of pyridine in 200 cc. of dioxane were heated for 52 hours, with two layers being formed. The desired product, a yellow viscous oil, was separated and then refluxed overnight in approximately 350 cc. of 48% HBr, while under nitrogen. The nitrogen blanket was maintained until most of the liquid evaporated. The remainder was cooled and acetone was added. The resulting precipitate was washed in acetone, collected and dried under vacuum. Approximately 16 g. of an orange-tan product was obtained. The product was recrystallized from ethanol, melting point 167° C., for analysis. The analysis was in agreement with the assignment of the structure as N-γ(2′, 5′-dihydroxyphenyl) propyl pyridinium bromide.

Analysis.—Calc'd for $C_{14}H_{16}NO_2Br$ (percent): Nitrogen, 4.52. Found (percent): Nitrogen, 4.52.

The invention will be illustrated in greater detail in conjunction with the following specific example which sets forth a representative process and which is not intended to be limiting, but is meant to be illustrative only of the novel image forming process of this invention, and wherein the dye utilized is an acid dye.

EXAMPLE II

A photosensitive element was prepared as follows: 3.75 grams of C.I. 15080 Direct Red 3, Benzo Brilliant Geranine B, of the formula:



was dissolved in 45 cc. of water. This solution was emulsified by means of a high shear mechanical agitator, with 5 g. of an aqueous solution of 10% gelatin to obtain a uniformly blended mixture. 50 cc. of the resulting dye emulsion were mixed with 78 cc. of water and then coated upon a subcoated film base. After this coating dried, a blue-sensitive silver iodobromide emulsion was coated thereupon at a coverage of 317.9 mg. per square foot of silver and allowed to dry. This photosensitive element was exposed and processed by spreading, between the thus exposed photosensitive element and a superposed image-receiving element, an aqueous processing composition comprising:

	G.
Water	90
NaOH	4
Hydroxyethyl cellulose	3

1-(2′,5′-dihydroxyphenyl)propyl-3-pyridinium bromide 3 g. The image-receiving element comprised baryta paper coated with a layer of a 2:1 mixture, by weight, of polyvinyl alcohol and poly-4-vinyl-pyridine. After an imbibition period of approximately one minute, the image-receiving element was separated and contained a red positive image.

g. The image-receiving element comprised baryta paper ing out the invention comprises at least an aqueous alkaline liquid of sufficient alkalinity to permit the developing agent to perform its developing function and, in certain instance, may also have the developing agent dissolved therein. A viscosity-increasing compound constituting a film-forming material of the type which, when spread

over a water-absorbent base and dried will form a relatively grm, 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. 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.

Processing can be effected in the presence of an auxiliary or accelerating silver halide developing agent which is substantially colorless, at least in the unoxidized form. Particularly useful are substituted hydroquinones, such as phenylhydroquinone, 4'-methyl-phenylhydroquinone, tolu-hydroquinone, tertiary-butyl-hydroquinone, and 2,5-triptylcene diol. These hydroquinones may be employed as components of the processing composition or they may be incorporated in one or more layers of the negative.

Modifications of the film structure, in addition to those already discussed, are included within the scope of the invention.

In instances where the matrix material of the photosensitive layer contains an insufficient amount of the substituents capable of reacting with the oxidized developing agent, additive materials can be mixed into the photosensitive emulsion formulation. Any polymeric material which contains an active hydrogen atom, is compatible with the matrix of the photosensitive layer and is capable of reacting with oxidized developing agent can be used for this purpose. A typical compound is polyethylene imine.

In general, dye present in a dye-containing layer is preferably of a quantity just sufficient to be entirely reacted and immobilized by that amount of developing agent which is oxidized by the development of a completely exposed unit area of the photosensitive layer. This procedure avoids highlight stain in the transfer image. However, if the dye employed in the photosensitive element has a sufficiently low solubility rate or slow diffusibility rate, it is possible to use dye in excess of that just specified.

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 may be desirable to have extra mordant included in the image-receiving sheet.

As another practice for providing a dye-precipitating mechanism in the print-receiving 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 the 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.

Mention may be 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. Such dye systems as those capable of assuming a color change in alkaline solution can be utilized in this invention so long as in an alkali they provide a suitable color. Preferably, the dye of this nature is colorless at a pH of about 7. Alkali contained in the processing liquid will in general supply the alkaline environment needed for creating the desired color change in the desired substances. When such dyes are utilized, the processing of the photosensitive element is carried out in the manner similar to those 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.

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.

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. 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. 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 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.

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 provided 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 a new print-receiving element in the presence of 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.

In all products employed in the practice of the invention, it is preferable to expose the negative material or photosensitive element from the emulsion side. It is therefore desirable to hold the photosensitive element and positive sheet material 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 positive element may be spread apart from their positions illustrated in FIG. 1. When the film unit is of the roll film type, the photosensitive element and the positive sheet are wound into separate rolls and the free ends of said rolls are connected together, in the manner described.

This invention is especially useful in composite film units intended for use in a "Polaroid Land Camera," made by Polaroid Corporation, Cambridge 39, Mass., or a similar camera structure such, for example, as the roll film type camera forming the subject matter of U.S. Pat. No. 2,435,717, issued to Edwin H. Land on Feb. 10, 1948, or the film pack type camera shown in U.S. Pat. No. 2,991,-702, issued to Vaito K. Eloranta on July 11, 1961. In general, such composite film units comprise a photosensitive sheet are wound into separate rolls and the free ends pod containing an aqueous alkaline processing solution, and may take the form of roll film, sheet film or film packs. The elements and pod are so associated with each other that, upon processing, the photosensitive element may be superposed on the image-receiving element and the pod may be ruptured to spread the aqueous alkaline processing solution between the superposed elements. The nature and construction of such pods is well-known to the art. See, for example, U.S. Pats. Nos. 2,543,181 and 2,634,886 issued to Edwin H. Land.

The inventive concepts herein set forth are adaptable for multicolor work by the use of special photographic materials, for example, film material of the type containing two or more photosensitized layers associated with an appropriate number of image-receiving layers and adapted to be treated with one or more liquid processing compositions, appropriate dyes suitable to impart the desired subtractive colors being incorporated into separate alkali permeable layers of the element.

Throughout the specification 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 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 the preceding portions of the specification, the expression "color" has been used. This expression is intended to include the use of a plurality of colors to obtain black, as well as the use of a single black dye.

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

What is claimed is:

1. A process for forming images in color which comprises:

(1) imagewise exposing a photosensitive element comprising a stratum of photosensitive silver halide dispersed in a polymeric matrix, said photosensitive element also including a dye;

(2) developing the exposed photosensitive element with a dye-mordanting silver halide developing agent dissolved in an alkaline solution which solubilizes said dye, said developing agent having a dye-mordanting substituent capable of associating with said solubilized dye and also having a developing group which contains a disubstituted benzene nucleus whose substituents are selected from hydroxyl and/or amino radicals located in the para or ortho positions with respect to each other, said developing group being capable upon oxidation of interacting with the polymeric matrix of said silver halide stratum and becoming immobilized therein;

(3) immobilizing oxidized dye-mordanting silver halide developing agent in developed areas of the photosensitive element and thereby mordanting said dye where said developing agent is immobilized; and

(4) transferring by imbibition remaining unmordanted dye from areas corresponding to undeveloped portions of the photosensitive element to an image-receiving layer in superposed relationship with said photosensitive stratum, thereby imparting to said image-receiving layer a positive dye image of the developed image.

2. A process as defined in claim 1 wherein the developing group of said dye-mordanting developing agent is a hydroquinone and the dye-mordanting substituent is a quaternary ammonium moiety.

3. The process of forming images in color as defined in claim 1 wherein the dye mordanting substituent of said developing agent is insulated from the developing group of said developing agent.

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

5. The process of forming images in color as defined in claim 1 wherein said dye is an acid dye.

6. The process of forming images in color as defined in claim 5 wherein said acid dye is Benzo Brilliant Geranine B.

7. The process of forming images in color as defined in claim 1 wherein said developing agent is N-γ(2',5'-dihydroxyphenyl)propyl-pyridinium bromide.

8. The process of forming images in color as defined in claim 1 including the step of mordanting said dye which is transferred to the image-receiving layer.

9. A process of forming images in color as defined in claim 1 wherein said dye is of a color complementary to the color by which the silver halide is exposable.

10. The process of forming images in color as defined in claim 1 wherein the dye is diffused through the silver halide emulsion after said emulsion has been developed by the dye-mordanting developing agent and said developing agent has been oxidized and immobilized in developed areas by its interaction with the polymeric matrix.

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