March 8, 1966 H. G. ROGERS ETAL 3,239,336

PHOTOGRAPHIC PROCESSES

Filed April 26, 1962

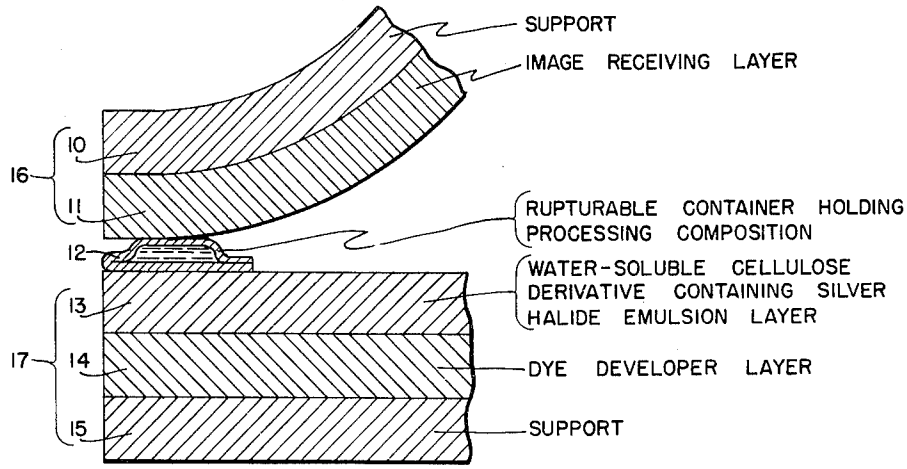



FIG. 1

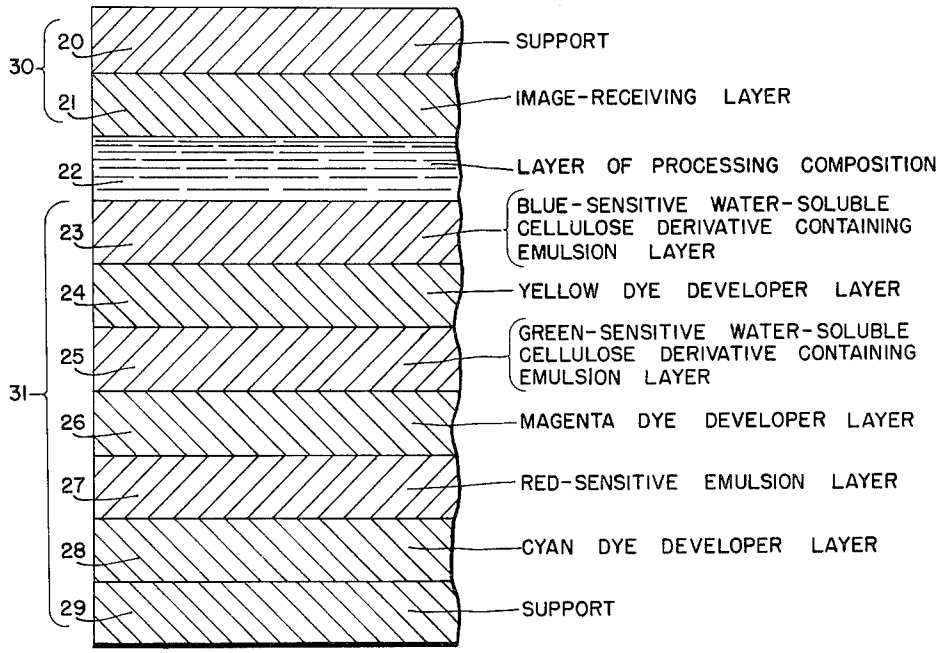



FIG. 2

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# PHOTOGRAPHIC PROCESSES

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1 Claim. (Cl. 96—3)

This application is a continuation-in-part of our copending U.S. application Serial No. 831,363, filed August 3, 1959 (now abandoned).

This invention relates to photography and more particularly to improvements in photographic diffusion-transfer processes for obtaining color images.

U.S. Patents Nos. 2,647,049, issued July 28, 1953; 2,661,293, issued December 1, 1953; 2,698,244, issued December 28, 1954; 2,698,798, issued January 4, 1955; and 2,802,735, issued August 13, 1957; all to Edwin H. Land disclose and claim diffusion-transfer processes wherein color coupling techniques are utilized which comprise, at least in part, reacting one or more color developing agents and one or more color formers to provide a positive color image to a superposed image-receiving layer. U.S. Patent No. 3,019,124, issued January 30, 1962, discloses the manufacture of photographic color screen elements; and U.S. Patents Nos. 2,983,606, issued May 9, 1961, and 2,968,554, issued January 17, 1961, disclose and claim diffusion-transfer processes wherein a color screen element is utilized to provide a multicolor positive image to a superposed image-receiving layer. U.S. Patent No. 2,774,668, issued December 18, 1956, the copending U.S. application of Edwin H. Land and Howard G. Rogers, Serial No. 565,135, filed February 13, 1956, and the previously cited U.S. Patent No. 2,983,606 disclose and claim diffusion-transfer processes wherein complete dyes are utilized to provide a positive color image on a superposed image-receiving layer.

It is a primary object of the present invention to provide novel photographic diffusion-transfer processes.

A further object of the present invention is to provide novel photographic processes whereby improved control of the transfer of color image-forming components to a superposed image-receiving layer may be obtained.

A still further object of the present invention is to provide novel photographic processes whereby the quality of the positive image, particularly the highlights and light steps obtained in diffusion-transfer processes, may be improved.

A still further object of the present invention is to provide novel photographic processes whereby increased density and improved contrast may be obtained in color diffusion-transfer processes.

A still further object of the present invention is to provide photographic multicolor diffusion-transfer processes whereby improved color rendition may be obtained.

A still further object of the present invention is to provide increased dye transfer rate in color diffusion-transfer processes, thereby reducing the required imbibition time interval necessary to provide a positive dye image to a superposed image-receiving element.

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 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 cross-sectional view of one embodiment of a photographic product, for use in obtaining monochromatic images comprising a photosensitive element, an image-receiving element and a rupturable container holding a liquid processing composition; and

FIG. 2 is a diagrammatic cross-sectional view of one embodiment of the present invention, for use in obtaining multichromatic images during processing, and comprising a multilayer photosensitive element, an image-receiving element and a processing composition.

A preferred embodiment of the present invention comprises forming color images by diffusion-transfer processes utilizing complete dyes, that is, dyes which contain in the same molecular structure a silver halide developing function. The following description is couched in terms of such processes which, however, is not intended to restrict the application thereof, but is intended to be illustrative only.

The previously cited U.S. Patent No. 2,983,606 discloses diffusion-transfer processes wherein dye developers are utilized in development of the latent image present in an exposed photosensitive emulsion and a positive color image is imparted to a superposed image-receiving layer by diffusion of unreacted dye developer originating from unexposed areas of the exposed photosensitive emulsion. The dye developers of this process are dyes which contain, in the same molecule, a silver halide developing function and a chromophoric system of a dye. A particularly useful class of dye developers are those containing a hydroquinonyl developing function. In the previously cited copending application, Serial No. 565,135, there is disclosed the use of dye developers to form multicolor transfer images utilizing an integral multilayer photosensitive element and a single image-receiving layer.

The processes of the type just mentioned employ dye developers which are initially mobile and diffusible and depend upon the immobilization of the dye developer in exposed areas of the photosensitive emulsion to prevent transfer thereof to a superposed image-receiving layer.

The dye developers, as noted above, are compounds which contain, in the same molecule, both the chromophoric system of a dye and also a silver halide developing function. By "a silver halide developing function" is meant a grouping adapted to develop exposed silver halide. As previously noted, a preferred silver halide development function comprises a hydroquinonyl group. Other suitable developing functions include ortho-dihydroxyphenyl and ortho- and para-amino-substituted hydroxyphenyl groups. In general, the development function includes a benzenoid developing function, that is, an aromatic developing group which forms quinonoid or quinone substances when oxidized. Preferred chromophoric systems comprise azo, indophenol, indoaniline, azomethine, and anthraquinone systems. Examples of representative dye developers are given in the previously cited U.S. Patent No. 2,983,606.

As previously stated, it has been proposed to form color images by diffusion-transfer processes utilizing dye developers. In processes of this type, a photosensitive element containing a dye developer and a silver halide emulsion is exposed and wetted by a liquid processing composition, for example, by immersing, coating, spraying, flowing, etc., in the dark and the exposed photosensitive element is superposed prior to, during, or after wetting, on a sheet-like support element which may be utilized as an image-receiving element. In a preferred embodiment, the liquid processing composition is supplied to the photosensitive element in a substantially uniform layer as the photosensitive element is brought into superposed relationship with an image-receiving element. The liquid processing composition permeates the emulsion to initiate development of the latent image contained therein. The

dye developer is immobilized or precipitated in exposed areas as a consequence of the development of the latent image. This immobilization is apparently, at least in part, due to a change in the solubility characteristics of the dye developer upon oxidation and especially as regards its solubility in alakaline solutions. It may also be due, in part, to a tanning effect on the emulsion by oxidized developing agent and to localized exhaustion of alkali due to development. In unexposed and partially exposed areas of the emulsion, the dye developer is unreacted and diffusible, and thus provides an imagewise distribution of unoxidized dye developer, dissolved in the liquid processing composition, as a function of the point-to-point degree of exposure of the silver halide emulsion. At least part of this imagewise distribution of unoxidized dye developer is transferred, by imbibition, to a superposed image-receiving layer or element, said transfer substantially excluding oxidized dye developer. Under certain conditions, the layer of the liquid processing composition may be utilized as the image-receiving layer. The image-receiving element receives a depthwise diffusion, from the developed emulsion, of unoxidized dye developer without appreciably distrubing the imagewise distribution thereof to provide a reversed or positive color image of the developed image. The image-receiving element may contain agents adapted to mordant or otherwise fix diffused, unoxidized dye developer. If the color of the transferred dye developer is effected by changes in the pH of the image-receiving element, this pH may be adjusted in accordance with well-known techniques to provide a pH affording a desired color. The desired positive image is revealed by stripping the image-receiving element from the photosensitive element at the end of a suitable imbibition period.

It has now been discovered that the aforementioned diffusion-transfer processes may be substantially improved by the employment of a photosensitive silver halide emulsion, the colloid binder of which comprises in whole or in part a soluble cellulose derivative.

The soluble cellulose derivatives comprise cellulose esters selected from the group consisting of cellulose acetate hydrogen phthalate and the alkali metal, ammonium and quaternary ammonium salts thereof.

The preferred soluble cellulose derivative within the last-mentioned group comprises the sodium salt of cellulose acetate hydrogen phthalate.

The ratio of cellulose ester to gelatin colloid binder of a preferred photosensitive gelatino silver halide emulsion may be varied, where desired, over a substantial range to suit the requirements of the operator.

It is to be understood that the addition of the soluble cellulose derivative to a photosensitive silver halide emulsion may be carried out according to the many and varied procedures well known to the emulsion manufacturing art for the inclusion of additives in silver halide emulsions. It is further understood that, where desired, the soluble cellulose derivative may comprise substantially the entire colloid binder for the photosensitive silver halide.

Cellulose acetate hydrogen phthalate is soluble in aqueous alkaline solutions, such as, aqueous alkaline photographic processing compositions, and the above-identified salts thereof are soluble in both aqueous and aqueous alkaline solutions.

The admixture of a soluble cellulose derivative to a photosensitive gelatino silver halide emulsion utilized in multi-chromatic diffusion-transfer processes provides positive image formation exhibiting increased density, improved color rendition, as well as a decrease in emulsion reticulation.

In addition to the preferred gelatino silver halide emulsions previously mentioned, the soluble cellulose derivatives may be used with emulsions employing gelatin derivatives and gelatin substitute. As sample of the many classes of known gelatin substitutes, mention may be made of the following:

water-permeable polyamides such as the salts of N-carboxyalkoxymethyl polyamides and polyamide ethers;

water-permeable hydrolyzed or partially hydrolyzed vinyl ester polymers and interpolymers such as partially hydrolyzed polyvinyl acetate, polyvinyl alcohol and the acetals thereof;

water-permeable cellulose derivatives such as partially hydrolyzed cellulose acetate;

water-permeable polymers and interpolymers of acrylic acid and acrylamide; etc.

As previously stated, in accordance with this invention, it is contemplated to utilize at least one of the photosensitive emulsions required in multicolor diffusion-transfer processes in the form of a soluble cellulose derivative-containing photosensitive emulsion. Sgnificant improvements result from the use of even one soluble cellulose derivative-containing photosensitive emulsion in multicolor processes. It is also contemplated to employ a plurality of soluble cellulose derivative-containing photosensitive emulsions.

FIGURE 1 of the accompanying drawing illustrates one method of processing a silver halide emulsion to obtain a monochromatic transfer image. A photosensitive element **17** comprises a support **10**, a layer **14** containing at least one dye developer and a soluble cellulose derivative-containing photosensitive silver halide emulsion layer **13**. As shown in the particular embodiment depicted in FIGURE 1, the photosensitive element **17** is shown in a spread-apart relationship (as, for example, during exposure) with an image-receiving element **16** having mounted thereon a rupturable container **12** holding a liquid processing composition. The image-receiving element **16** comprises a support **10** and an image-receiving layer **11**. After exposure, the image-receiving element **16** is brought into superposed relationship with photosensitive element **17** and the rupturable container **12** is ruptured by application of suitable pressure, for example, by advancing between a pair of suitably gapped rollers (not shown), and a layer of the liquid processing composition is spread between the superposed elements. The processing composition permeates the soluble cellulose derivative-containing photosensitive silver halide emulsion layer **13** and the layer **14** containing at least one dye developer. In exposed areas of the photosensitive element **17** the dye developer, at least to some extent, exhibits decreased alkali solubility in contradistinction to unexposed areas. Thus in unexposed areas, a portion of the imagewise distribuon of soluble dye developer transfers, at least in part by imbibition, to superimposed image-receiving element **16** to form thereon a positive image. The image-receiving element **16** is separated from its superposed relationship with the photosensitive element **17** after at least a portion of the dye developer has been transferred.

It is also contemplated to utilize, in the preparation of monochromatic images, a film structure wherein the silver halide emulsion is coated over the image-receiving layer and the processing composition must permeate through the emulsion before reaching the image-receiving layer. A structure of this type is described, for example, in the previously noted U.S. Patent No. 2,661,293, and particularly with respect to FIG. 7 of said patent.

Multicolor images may be obtained using dye developers and diffusion-transfer processes by several techniques. One such technique contemplates the use of a photosensitive silver halide stratum comprising at least two sets of selectively sensitized minute photosensitive elements arranged in the form of a photosensitive screen. Transfer processes of this type are disclosed in the aforementioned U.S. Patents Nos. 2,983,606 and 2,968,554. In such an embodiment, each of the minute photosensitive elements has associated therewith an appropriate dye developer in or behind the silver halide emulsion portion. In general, a suitable photosensitive screen, prepared in accordance with the disclosures of the last-mentioned

patents, comprises minute red-sensitized emulsion elements, minute green-sensitized emulsion elements and minute blue-sensitized emulsion elements arranged in side-by-side relationship in a screen pattern and having associated therewith, respectively, a cyan dye developer, a magenta dye developer and a yellow dye developer.

Another process for obtaining multicolor transfer images utilizing dye developers employs an integral multilayer photosensitive element such as disclosed and claimed in the previously-mentioned copending application, Serial No. 565,135, wherein at least two selectively sensitized photosensitive strata are superposed on a single support and are processed, simultaneously and without separation, with a single, common image-receiving layer. A suitable arrangement of this type comprises a support carrying a red-sensitive silver halide emulsion stratum, a green-sensitive silver halide emulsion stratum and a blue-sensitive silver halide emulsion stratum, said emulsions having associated therewith, respectively, a cyan dye developer, a magenta dye developer and a yellow dye developer. The dye developer may be utilized in the silver halide emulsion layer, for example, in the form of particles, or it may be employed as a layer behind the appropriate silver halide emulsion strata. In an especially useful mode of disposing the dye developers in the photosensitive element, the dye developer is dissolved in a water-imiscible solvent and then dispersed in a gelatin coating solution. Each set of silver halide emulsion and associated dye developer strata may be separated from the other sets by suitable inter-layers, such as spacer and/or barrier layers, for example, by a layer or layers of gelatin and/or polyvinyl alcohol.

A multilayer photosensitive element of the type just described is illustrated in FIG. 2 of the accompanying drawing and is depicted during processing. An exposed photosensitive element **31** comprises: a support **29**; a layer **28** containing a cyan dye developer; a layer **27** of a red-sensitive silver halide emulsion; a layer **26** of a magenta dye developer; a layer **25** of a green-sensitive soluble cellulose derivative-containing silver halide emulsion; a layer **24** containing a yellow dye developer; and an outermost layer **23** of a blue-sensitive soluble cellulose derivative-containing silver halide emulsion. As previously mentioned, each set of silver halide emulsion and associated dye developer strata may be separated from the other sets thereof by suitable spacer and/or barrier strata, for example, by the aforementioned layer or layers of gelatin and/or polyvinyl alcohol. In certain instances, it may be desirable to incorporate a yellow filter in front of the green-sensitive emulsion layer and such yellow filter may be incorporated in the respective spacer layer. Where the yellow dye developer is of appropriate absorption characteristics and present in a state capable of functioning as a yellow filter, a separate yellow filter may be omitted.

Referring again to FIG. 2, a multilayer phototsensitive element **31** is shown in processing relationship with an image-receiving element **30** and a layer **22** of a processing composition. The image-receiving element **30** comprises a support **20** and an image-receiving layer **21**. As noted in connection with FIGURE 1, the liquid processing composition is effective to initiate development of the latent image in the respective exposed silver halide strata. After a suitable imbibition period during which at least a portion of the dye developer associated with unexposed areas of each of said emulsions is transferred to superposed image-receiving element **30**, the latter element is separated to reveal the postive multi-color image.

The present invention will be illustrated in greater detail in conjunction with the following procedures which set out representative embodiments and photographic utilization of the novel photosensitive emulsions of this invention, which, however, are not limited to the details therein set forth and are intended to be illustrative only.

A photosensitive element similar to that shown in FIG. 2 may be prepared by coating in succession, on a suitable film base, the following compositions:

(1) 1,4-bis-(β-[2′,5′-dihydroxyphenyl]-α-methyl-ethylamino)-anthraquinone dissolved in a 1:1 mixtures of acetone and tetrahydrofuran containing 2% cellulose acetate hydrogen phthalate;

(2) 20 cc. of a red-sensitive silver halide gelatin emulsion, 13 cc. of water and 8 drops of 1% potassium chrome alum;

(3) 2 - (p - [2′,5′ - dihydroxyphenethyl] - phenylazo)-4-n-propoxy-1-naphthol dissolved in a 1:1 mixture of acetone and tetrahydrofuran containing 2% cellulose acetate hydrogen phthalate;

(4) 5 cc. of a green-sensitive silver halide gelatin emulsion, 15 cc. of 2% sodium cellulose acetate hydrogen phthalate and 3 drops of 1% potassium chrome alum;

(5) 4 - p - [2′,5′, - dihydroxyphenethyl] - phenylazo)-3-(N-n-hexylcarboxamido)-1-phenyl - 3 - pyrazolone dissolved in a 1:1 mixture of acetone and tetrahydrofuran containing 2% cellulose acetate hydrogen phthalate; and

(6) 5 cc. of a blue-sensitive silver halide gelatin emulsion, 15 cc. of 2% sodium cellulose acetate hydrogen phthalate and 2 drops of 1% potassium chrome alum.

Photosensitive elements prepared according to the procedures set forth above may be exposed and processed by spreading an aqueous liquid processing composition comprising:

| | Percent |
|---|---|
| Sodium hydroxide | 3.0 |
| 1-phenyl-3-pyrazolidone | 1.2 |
| 2,5-bis-ethyleneiminohydroquinone | 0.9 |
| 6-nitrobenzimidazole | 0.12 |
| Sodium carboxymethyl cellulose | 5.0 |

between a photosensitive element and an image-receiving element as said elements are brought into superposed relationship. The image-receiving element comprises a cellulose acetate-coated baryta paper which has been coated with a solution comprising 10% N-methoxymethyl polyhexamethylene adipamide in 80% aqueous isopropanol. After an imbibition period of approximately 3 minutes, the image-receiving element is separated from superposed relationship with the photosensitive element and contains a multicolor positive image.

As mentioned previously, the salts of cellulose acetate hydrogen phthalate, which are particularly useful in the photosensitive elements of this invention, are the ammonium, quaternary ammonium and those of the alkali metals.

The inorganic salts of cellulose acetate hydrogen phthalate for use in this invention may be prepared by the processes such as those disclosed in U.S. Patent No. 2,093,463. The preparation of the quaternary salts, like the others, comprises a simple neutralization of the free acid and the consequent separation of the resulting salt. Cellulose acetate hydrogen phthalates for use in the preparation are readily available commercially. The cellulose acetate hydrogen phthalates available commercially comprise, in general, 30% to 40%, by weight, phthalyl groups and 17% to 22%, by weight, acetyl groups.

The preferred alkali metal salts for use in this invention are those of sodium, potassium and lithium.

As examples of quaternary ammonium salts of cellulose acetate hydrogen phthalate, mention may be made of tetra-alkyl ammonium bases, e.g., tetraethyl ammonium hydroxide and the alkyl-quaternized heterocyclic nitrogen bases, e.g., N-methyl pyridinium hydroxide. The alkyl radicals or heterocyclic rings of the bases used may be unsubstituted or substituted, depending upon the particular form desired. As examples of bases in which the alkyl radicals or the heterocyclic rings are substituted, mention may be made of tetra-β-hydroxyethyl ammonium hydroxide and N-methyl picolinium hydroxide. As further examples of other alkyl-quaternized heterocyclic nitrogen bases contemplated to be useful, mention may be made of those comprising piperidinium, pyrazolium and

imidazolium radicals. Quaternary bases comprising less than nine carbon atoms are preferred; however, when desired, it is contemplated that quaternary ammonium salts comprising nine or more carbon atoms may be used, e.g., surface-active quaternary ammonium salts comprising a hydrophobic radical, e.g., a radical comprising eight or more carbon atoms. An example of such a surface-active quaternary ammonium base is lauryl-triethyl ammonium hydroxide.

In this invention, a mixture of cellulose acetate hydrogen phthalate (free acid) and the salts herein disclosed are used. Ratios of about 1 to 1 of the free acid to the salt may be employed; however, the ratio may be varied to suit particular needs. Cellulose acetate hydrogen phthalates having a portion of the free carboxyl groups neuralized may be used in place of the mixtures.

In addition to the above-mentioned dye developers, additional dye developers useful in the practice of the present invention are set forth in the previously cited U.S. Patent No. 2,983,606.

A further technique for obtaining multicolor images employs a plurality of photosensitive elements associated with appropriate numbers of image-receiving elements and adapted to be treated with one or more liquid processing compositions, the appropriate dye developers being incorporated in the phototsensitive elements. Examples of film structures of this type are disclosed in the previously cited U.S. Patent No. 2,647,049.

The dye developers utilized in the description of the present invention may be incorporated in the photosensitive elements, for example, in, on or behind the respective silver halide emulsion. However, the dye developer is preferably in a coating or layer being the silver halide emulsion and such a layer of dye developer may be applied by the use of a coating solution containing approximately 0.5% to 8% by weight of the dye developer as illustrated above. Thus, in one useful embodiment, the dye is dispersed in a layer of a waterpemeable plastic, for example gelatin, behind the emulsion.

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

The liquid processing composition herein referred to comprises at least an aqueous solution of an alkaline compound, for example, diethylamine, sodium hydroxide or sodium carbonate. If the liquid processing composition is to be applied to the emulsion by being spread thereon, preferably in a relatively thin uniform layer, it might also include a viscosity-increasing compound constituting film-forming material of the type which, when said composition is spread and dried, forms a relatively firm and relatively stable film. A preferred film-forming material is a high molecular weight polymer such as a polymeric, water-soluble ether which is inert to an alkaline solution as, for example, a hydroxyethyl cellulose or sodium carboxymethyl cellulose. Other film-forming materials or thickening agents whose ability to increase viscosity is substantially unaffected if left in solution for a long period of time may also be used. The film-forming material is preferably contained in the processing composition in suitable quantities to impart to said composition a viscosity in excess of 1,000 centipoises at a temperature of approximately 24° C. and preferably of the order of 1,000 to 200,000 centipoises at said temperature. Illustrations of suitable liquid processing compositions may be found in the several patents and co-pending applications herein mentioned and also in examples herein given. Under certain circumstances, it may be desirable to apply a liquid processing composition to the photosensitive element prior to exposure, in accordance with the technique described in the copending application of Edwin H. Land, Serial No. 498,672, filed April 1, 1955.

It will be noted that the liquid processing composition may, and in the above examples does, contain an auxiliary or accelerating developing agent, such as p-methylaminophenol, 2,4-diaminophenol, p-benzylaminophenol, hydroquinone, toluhydroquinone, phenylhydroquinone, 4-methylphenylhydroquinone, etc. A preferred accelerating developing agent is a 3-pyrazolidone developing agent and preferably 1-phenyl-3-pyrazolidone which is available under the trade name "Phenidone" from Ilford Limited. It is also contemplated to employ a plurality of auxiliary or accelerating developing agents, such as a 3-pyrazolidone developing agent and a benzenoid developing agent, as disclosed and claimed in the copending application of Howard G. Rogers and Harriet W. Lutes, Serial No. 654,781, filed April 24, 1957. As examples of suitable combination of auxiliary developing agents, mention may be made of 1-phenyl-3-pyrazolidone in combination with p-benzylaminophenol and 1-phenyl-3-pyrazolidone in combination with 2,5-bis-ethylenimino hydroquinone. Such auxiliary developing agents may be employed in the liquid processing composition or they may be initially incorporated, at least in part, in the silver halide emulsion strata or the strata containing the dye developers. It may be noted that at least a portion of the dye developer oxidized during development may be oxidized and immobilized as a result of a reaction, e.g., an energy-transfer reaction, with the oxidation of an oxidized auxiliary developing agent, the latter developing agent being oxidized by the development of exposed silver halide. Such a reaction of oxidized developing agent with unoxidized dye developer would regenerate the auxiliary developing agent for further reaction with the exposed silver halide.

In addition, development may be effected in the presence of an onium compound, particularly a quaternary ammonium compound, in accordance with the processes disclosed and claimed in the copending U.S. application of Milton Green and Howard G. Rogers, Serial No. 50,851 filed August 22, 1960.

The dye developers are preferably selected for their ability to provide colors that are useful in carrying out substractive color photography, i.e., cyan, magenta and yellow. It should be noted that it is within the scope of this invention to use mixtures of dye developers to obtain a desired color, e.g., black. Thus, it is to be understood that the expression "color" as used herein is intended to include the use of a plurality of colors to obtain black, as well as the use of a single black dye developer.

In all products employed in the practice of this invention, it is preferable to expose from the emulsion side. It is, therefore, desirable to hold the photosensitive element and the image-receiving element together at one end thereof by suitable fastening means in such manner that the photosensitive element and the image-receiving element may be spread apart from their superposed processing position during exposure. A camera apparatus suitable for processing roll film of the type just mentioned is provided by the Polaroid Land Camera, sold by Polaroid Corporation, Cambridge, Massachusetts, or similar camera structure such, for example, as the camera forming the subject matter of U.S. Patent No. 2,435,717. Camera apparatus of this type permits successive exposure of individual frames of the photosensitive element from the emulsion side thereof as well as individual processing of an exposed frame by bringing said exposed frame into superposed relation with a predetermined portion of the image-receiving element while drawing these portions of the film assembly between a pair of pressure rollers which

rupture a container associated therewith and effect the spreading of the processing liquid released by rupture of said container, between and in contact with the exposed photosensitive frame and the predetermined, registered area of the image-receiving element.

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

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

As examples of useful image-receiving materials, mention may be made of nylon such as N-methoxymethyl-polyhexamethylene adipamide; partially hydrolyzed polyvinyl acetate such as that commercially available under the trade name of Vinylite MA–28–18 from Bakelite Division, Carbide and Carbon Chemicals Co.; polyvinyl alcohol with or without plasticizers; baryta paper, i.e., a support having a baryta coating thereof; cellulose acetate with filler as, for example, one-half cellulose acetate and one-half oleic acid; gelatin; and other materials of a similar nature, as is well known in the art. Preferred materials comprise polyvinyl alcohol or gelatin containing a dye mordant such as poly-4-vinylpyridine, as disclosed and claimed in the copending U.S. application of Howard C. Haas, Serial No. 50,848, filed August 22, 1960.

While a rupturable container, such as container **14** in FIG. 1, provides a convenient means for spreading a liquid processing composition between layers of a film unit whereby to permit the processing to be carried out within a camera apparatus, the practices of this invention may be otherwise effected. For example a photosensitive element, after exposure in suitable apparatus and while preventing further exposure thereafter to actinic light, may be removed from such apparatus and permeated with the liquid processing composition as by coating the composition on said photosensitive element or otherwise wetting said element with the composition following which the permeated, exposed, photosensitive element, still without additional exposure to actinic light, is brought into contact with the image-receiving element for image formation in the manner heretofore described.

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

In all examples of this specification, percentages of components are given by weight unless otherwise indicated.

Although the illustrative photographic products and processes herein detailed employ dye developers, it will be apparent that the several features comprising the herein disclosed inventive concepts are also applicable to diffusion-transfer processes employing any image dye and/or image dye precursor as color image-forming components to provide the desired positive image formation on an appropriately positioned image-receptive layer. Such color image-forming components may comprise, in whole or in part, for example, coupling dyes, that is, complete dyes which possess a coupling function and react with the oxidation product of a color developer to provide the desired positive image formation according to the processes disclosed in the aforementioned U.S. Patent No. 2,774,668 and the copending U.S. application of Howard G. Rogers, Serial No. 613,691, filed October 3, 1956. In addition, the concepts herein disclosed are equally applicable to diffusion-transfer processes wherein the formation of an imagewise distribution of dye components is controlled by the concentration of alkali present as, for example, the alkali exhaustion transfer processes disclosed in the copending U.S. application of Edwin H. Land, Serial No. 640,821, filed February 18, 1957. As previously stated, processes employing color coupling techniques to provide the desired positive image formation are disclosed in the aforementioned U.S. Patents Nos. 2,647,049; 2,661,293; 2,698,244; 2,698,798; and 2,802,735. In such processes, color formers and color developing agents comprise the color image-forming components.

Throughout the specification and appended claims, the expression "positive image" has been used. This expression should not be interpreted in a restrictive sense since it is used primarily for purposes of illustration, in that it defines the image produced on the image-carrying layer as being reversed, in the positive-negative sense, with respect to the 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 positive and the image produced in the image-carrying layer will be negative. The expression "positive image" is intended to cover such an image produced on the image-carrying layer.

Throughout the specification and claim, the expression "superposed" has been used. This expression is intended to cover the arrangement of two layers in overlying relation to each other either in face-to-face contact or in a separated condition.

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

What is claimed is:

A process of forming multicolor transfer images which comprises the steps of exposing a photosensitive element comprising a plurality of layers including blue-sensitive, green-sensitive and red-sensitive silver halide gelatin emulsion layers mounted on a common support, said blue-sensitive, green-sensitive and red-sensitive silver halide gelatin emulsion layers having positioned contiguous, respectively, yellow, magenta and cyan dye containing layers, each of said yellow, magenta and cyan dyes being a silver halide developing agent, at least one of said blue-sensitive, green-sensitive and red-sensitive silver halide gelatin emulsions including a soluble cellulose ester selected from the group consisting of cellulose acetate hydrogen phthalate and the alkali metal, ammonium and quaternary ammonium salts thereof; permeating said photosensitive element with an aqueous alkaline processing composition to effect development of the latent images contained in said emulsions and solubilization, at least in part, of said cellulose ester; immobilizing said yellow, magenta and cyan dyes in exposed areas, as a result of development; forming thereby an imagewise distribution of mobile yellow magenta and cyan dye, as a function of the point-to-point degree of exposure of said element; and transferring, by imbibition, at least a portion

of each of said imagewise distributions of mobile dye to a superposed image-receiving layer to provide thereto a multicolor positive dye image.

**References Cited by the Examiner**

UNITED STATES PATENTS

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|---|---|---|---|
| 2,127,573 | 8/1938 | Sheppard et al. | 96—113 |
| 2,983,606 | 5/1961 | Rogers | 96—29 |
| 3,043,692 | 7/1962 | Haas et al. | 96—29 |
| 3,044,873 | 7/1962 | Haas | 96—29 |
| 3,061,428 | 10/1962 | Haas | 96—29 |
| 3,069,263 | 12/1962 | Haas | 96—29 |
| 3,077,400 | 2/1963 | Rogers et al. | 96—3 |

OTHER REFERENCES

Malm: Journal of the American Pharmaceutical Assoc., Science Edition, vol. XL, No. 10 (1951), pp. 520–525.



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